

**Vapochromism in Coordination Complexes: Chemical
Sensors for Volatile Organic Compounds**

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Vapochromism in Organometallic and Coordination Complexes: Chemical Sensors for Volatile Organic Compounds

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32 1. Introduction

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34 1.1 Scope of the review

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40 The development of chemical sensors is a subject that continues to fascinate chemists in
41 academic research. Aside from the purely academic interest there is of course the important issue
42 of finding suitable sensors for harmful chemical substances that might be present in the
43 environment or at our workplaces. Consequently, the detection of volatile organic compounds
44 (VOCs) by simple means requiring only a low-cost technology is an attractive research target. In
45 this context vapochromism is a promising phenomenon. A vapochromic substance changes color
46 upon exposure to certain vapors,¹ and therefore the detection of analytes can often occur even by
47 naked eye. In addition, there is the phenomenon of luminescence vapochromism, often called
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3 vapoluminescence, which refers to changes in photoluminescence properties in the course of
4 vapor exposure. The class of compounds in which these two closely related phenomena occur
5
6 most frequently is undoubtedly the area of coordination complexes. This review therefore
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8 focusses on transition metal compounds that change color and/or their emission properties when
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10 exposed to VOCs. Where appropriate, information regarding the detection of other analytes (e.
11
12 g., oxygen, humidity in air, acids or bases) will be included as well. Along the same lines, the
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14 related phenomena of mechanochromism or thermochromism will be discussed briefly where
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16 appropriate and were thematically fitting.
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22 The article is written from the perspective of a coordination chemist with an emphasis on
23 understanding the origin of the vapochromic / vapoluminescent responses of the individual
24 sensor materials. In this sense the current review is less geared towards applications than much
25 of what has been published under the broadly defined label “electronic noses”.²⁻⁶ Nevertheless
26 the present review includes analytical details for the sensors for which such information is
27 available, but many original studies do not report quantitative analytical results and focused
28 themselves on understanding the vapochromism / vapoluminescence phenomenon on a
29 molecular level rather aiming to develop actual sensing devices. A separate section with an
30 comprehensive table summarizes the available analytical information in a compact manner.
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43 Many of the coordination compounds discussed in the current article have been part of other
44 reviews. For example, there exist several recent reviews on chemosensing with platinum(II) and
45 gold(I) complexes.⁷⁻¹⁷ Most recently, a “feature article” on the specific subject of recent
46 advances in the field of vapoluminescence in metal complexes appeared,¹⁸ but the scope of the
47 current review is significantly broader, and it contains substantially more detailed information.
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The optical spectroscopic and photophysical properties of some of the metal complexes relevant

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3 for the current article have been reviewed separately,¹⁹⁻²² and reviews on the related phenomena
4 of thermochromism and mechanochromism also exist.²³⁻²⁷
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8 The two largest families of vapochromic / vapoluminescent substances are platinum(II) and
9 gold(I) containing compounds which are treated in two separate dedicated sections of this
10 review. Sensors devoid of these two elements are discussed in a subsequent section which is
11 divided into subsections according to the transition metals they contain. Until now purely organic
12 vapochromic / vapoluminescent substances are relatively rare and are not considered here. Pt(II)
13 and Au(I) containing vapochromic substances are treated in separate sections not only because
14 by mere number they represent the two most important classes of vapochromic substances, but
15 also because a more or less common mode of operation can be identified for many of these
16 particular substances (sections 1.3 and 6). Briefly, in many of the Pt(II) and Au(I) compounds the
17 vapochromic response is the result of changes in intermolecular interactions (e. g., weak metal-
18 metal interactions, π -stacking, hydrogen-bonding, C-H- π interactions) as a result of analyte
19 uptake into the crystal lattice, while for many (but not all) of the substances presented in section
20 4 direct ligation of an analyte to a metal center is observed.
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41 1.2 Metal-metal interactions in d^8 and d^{10} compounds 42 43 44

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46 Because of the special importance of Pt(II) and Au(I) compounds in the field of vapochromism
47 it is useful to recapitulate a few elementary aspects regarding weakly interacting metals with d^8
48 and d^{10} electron configurations. There exist numerous didactical articles on non-covalent Pt(II)-
49 Pt(II) and aurophilic interactions,^{7, 22, 28-31} hence only the most fundamental aspects needed to
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3 comprehend the photophysical behavior of some of the vapochromic substances discussed in
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5 sections 2 and 3 will be briefly discussed here.
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8 Square planar d^8 and linear d^{10} complexes tend to approach each other in such a way that their
9
10 $5d_{z^2}$ and $6p_z$ orbitals can interact with each other.³² Figure 1 shows the relevant part of the
11
12 molecular orbital diagram for d^8 - d^8 dimers. The interaction of $5d_{z^2}$ and $6p_z$ orbitals leads the
13
14 formation of bonding and anti-bonding dimer orbitals, commonly designated as $d\sigma / d\sigma^*$ ($5d_{z^2}$)
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16 and $p\sigma / p\sigma^*$ ($6p_z$).³¹ In the electronic ground state of d^8 - d^8 and d^{10} - d^{10} dimers the $d\sigma$ and $d\sigma^*$
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18 orbitals are filled whereas the $p\sigma$ and $p\sigma^*$ orbitals are empty. In both cases there is the possibility
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20 of $d\sigma^* \rightarrow p\sigma$ transitions leading to excited-states in which the metal-metal distance is shorter
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22 than in the ground state due to an increase in bond order. However, in many of the cases from
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24 sections 2 and 3 for which intermetallic interactions are relevant the LUMO is a ligand-based
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26 orbital, typically with π or π^* character; π - π interactions between ligands may themselves lead to
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28 “dimer π orbitals”. The HOMO-LUMO transition in these cases is a so-called metal/metal-to-
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30 ligand charge transfer (MMLCT) which distinguishes itself from ordinary metal-to-ligand charge
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32 transfer (MLCT) transitions in that the HOMO is a “dimer orbital” (or “oligomer” / “polymer”
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34 orbital) resulting from intermetallic interactions. Depending on the strength of the metal-metal
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36 interaction the dimer HOMO shifts in energy, and for many sensors this forms the basis for
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38 vapochromism or vapoluminescence. However, there are numerous other mechanisms that may
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40 lead to vapor-induced color and emission changes, and the full breadth of possibilities will
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42 become obvious from the following sections.
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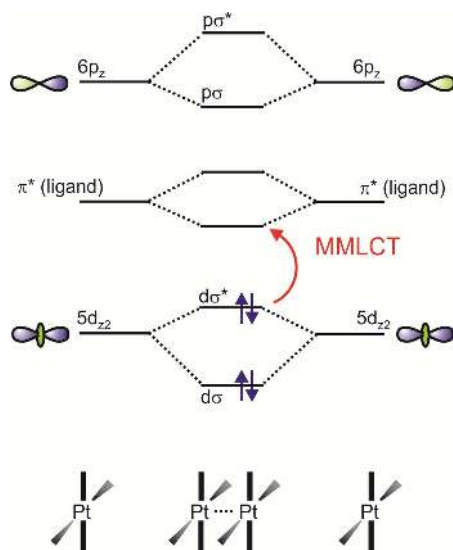


Figure 1. Simplified MO diagram illustrating metal-metal interactions between square planar Pt(II) complexes. MMLCT = metal/metal-to-ligand charge transfer. More elaborate diagrams can be found in the literature.^{33, 34}

1.3 Unifying themes in research on vapochromic substances

The vapochromism of many of the Pt(II) and Au(I) containing substances discussed in sections 2 and 3 is more or less closely related to metallophilic interactions and/or π -stacking. A common theme for many (but not all) of the vapochromic substances presented in section 4 is the occurrence of changes in the first coordination sphere, including both alterations in coordination number and coordination geometry. This is particularly true for several of the vanadium, cobalt, nickel, copper, and metalloporphyrin-based vapochromic substances. One may therefore differentiate between two fundamentally different manners by which vapochromic substances respond to VOCs: Type I of vapochromic substances exhibits more or less subtle structural changes in crystal packing leading to alterations in intermolecular interactions such as for

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3 example metal-metal interactions, π -stacking, hydrogen-bonding, and C-H- π interactions. In type
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6 II vapochromic substances direct ligation of an analyte to a solid-state material occurs. Type I is
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8 of key importance in sections 2 and 3, type II is prominent in section 4 (subsection 4.1) but
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10 several substances from section 4 are type I vapochromic systems (subsection 4.2).

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12 A unifying theme for many vapochromic substances is an exceptionally high complexity of the
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14 solid-state structures. Aside from the intermolecular interactions mentioned above, the presence
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16 of voids plays an important role in many cases. In this context, the size and shape of counterions
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18 can have an important influence. In several cases the vapochromic property is strongly dependent
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20 on the polymorph or solvate which is formed; while one polymorph or solvate may exhibit
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22 spectacular vapochromism, a closely related polymorph or solvate may be completely insensitive
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24 to VOCs. The most important insights to vapochromism therefore come from solid-state
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26 investigations including X-ray crystallography, powder X-ray diffraction, thermogravimetry, and
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28 solid state absorption (or reflectance), and luminescence. Solution studies are usually
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30 considerably less insightful. However, as will be seen from this review, even the simplest
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32 structure-property relationships in many vapochromic materials have remained extremely
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34 elusive. Consequently, it is very difficult to “engineer” vapochromic materials. It is even difficult
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36 to optimize the VOC response behavior of known vapochromic substances because even the
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38 slightest changes can lead to complete disappearance of the vapochromic property. In short,
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40 many challenges are associated with research on vapochromism.
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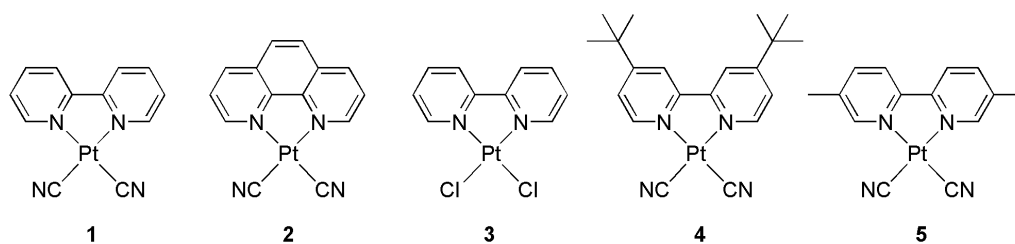
2. Platinum(II) compounds

2.1 Materials with charge-neutral Pt(II) complexes

2.1.1 [Pt(α -diimine)(CN)₂] complexes and their derivatives

One of the earliest reports of vapochromism in a platinum(II) coordination compound dates from 1974.³⁵ Gillard and coworkers found that [Pt(bpy)(CN)₂] (bpy = 2,2'-bipyridine) (**1**) (Scheme 1) changes color from red to yellow when solid samples are exposed to HF, H₂O or H₂S vapors. Similarly, [Pt(phen)(CN)₂] (phen = 1,10-phenanthroline) (**2**) was observed to turn from yellow to red upon exposure to anhydrous organic solvent vapors. At that time the existence of a red and yellow form of [Pt(bpy)Cl₂] (**3**) was already known from the early work by Morgan and Burstall.³⁶ In the Gillard paper the vapor-induced color changes were discussed in terms of protonation of the CN ligands, and it was speculated that covalent addition of H₂O to one of the pyridine rings of bpy might also play a role.

Scheme 1. [Pt(α -diimine)(CN)₂] complexes, part I.



Nearly 20 years later Shih and Herber reported on water sorption by [Pt(^tBu₂bpy)(CN)₂] (^tBu₂bpy = 4,4'-di-*tert.*-butyl-2,2'-bipyridine) (**4**).³⁷ At relative humidities above 40% this material reversibly uptakes 5 water molecules but no color changes occur because all relevant

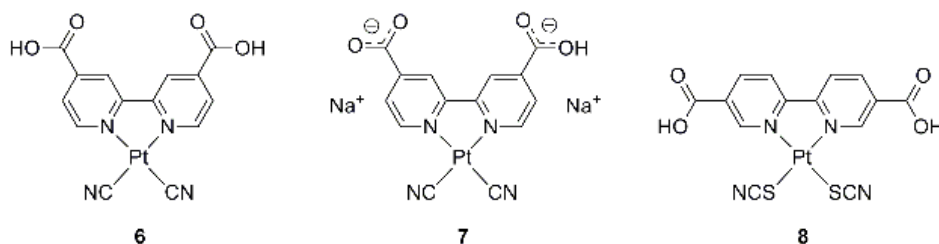
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3 absorptions are in the UV. The compound $[\text{Pt}(5,5'\text{-Me}_2\text{bpy})(\text{CN})_2]$ ($5,5'\text{-Me}_2\text{bpy} = 5,5'\text{-}$
4 dimethyl-2,2'-bipyridine) (**5**) was investigated in the same study and was found to change color
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6 from light yellow to deep orange on hydration.³⁷ Thus, by investigating a series of
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nowadays.

Nearly another 10 years later the Kato group began to publish an entire series of papers on
vapo-chromic $[\text{Pt}(\alpha\text{-diimine})(\text{CN})_2]$ compounds.^{13, 38-42} Initial studies focused on the
 $[\text{Pt}(\text{bpy})(\text{CN})_2]$ material (**1**) investigated already by Gillard and coworkers.³⁸ Based on X-ray
crystallographic investigations it was possible to elucidate the origin of the water-vapor induced
color change. The anhydrous red form of $[\text{Pt}(\text{bpy})(\text{CN})_2]$ was found to contain infinite stacks of
complexes with regular intermolecular Pt(II)-Pt(II) distances of 3.34 Å, while in the yellow
 $[\text{Pt}(\text{bpy})(\text{CN})_2]\cdot\text{H}_2\text{O}$ (**1**·H₂O) material the sorbed water molecule causes a deformation of the
stacking structure and an interruption of the infinite Pt(II)-Pt(II) chain. In the yellow form there
are inclined stacks with alternating short (3.3289(3) Å) and long (4.6814(3) Å) Pt(II)-Pt(II)
distances, and the crystal water connects individual stacks via hydrogen-bonding to the cyanide
ligands. Thus it became clear that vapo-chromism of $[\text{Pt}(\text{bpy})(\text{CN})_2]$ was due to changes in the
Pt(II)-Pt(II) interaction brought about by a structural change upon water sorption. This
conclusion was particularly obvious in light of prior vapo-chromism studies with platinum double
salts by Mann and coworkers (see below), and the fundamental work on the electronic structures
of d⁸-d⁸ dimers,^{43, 44} stacked platinum(II) diimine complexes,⁴⁵⁻⁴⁸ and tetracyanoplatinates.²²

Kato and coworkers noted that the photoluminescence band maximum of $[\text{Pt}(\text{bpy})(\text{CN})_2]$ (**1**) shifts from 602 nm to 566 nm upon exposure to humid air while maintaining similar emission intensity.³⁸ Thus, unlike the yellow form of $[\text{Pt}(\text{bpy})\text{Cl}_2]$ which is a much weaker emitter than its red polymorph,⁴⁹ the yellow form of $[\text{Pt}(\text{bpy})(\text{CN})_2]$ is strongly emissive. Presumably this is because $[\text{Pt}(\text{bpy})(\text{CN})_2]\cdot\text{H}_2\text{O}$ (**1** $\cdot\text{H}_2\text{O}$) contains dimers with short Pt(II)-Pt(II) distances which are able to exhibit ³MMLCT emission while yellow $[\text{Pt}(\text{bpy})\text{Cl}_2]$ (**3**) has no short contacts between Pt(II) centers.⁴⁶

Scheme 2. $[\text{Pt}(\alpha\text{-diimine})(\text{CN})_2]$ complexes, part II.



The complex $[\text{Pt}(4,4'\text{-H}_2\text{dcbpy})(\text{CN})_2]$ ($4,4'\text{-H}_2\text{dcbpy} = 4,4'\text{-dicarboxyl-2,2'-bipyridine}$) (**6**) (Scheme 2) represents a milestone discovery in the area of vapochromic platinum compounds.^{13,}
³⁹ The color of this material is dependent on the pH at which it is recrystallized and can adopt a range of colors from white to yellow, red, blue and purple. The different colors are a manifestation of different polymorphs with variable Pt(II)-Pt(II) interactions and are unusually diverse for linear-chain platinum(II) compounds. The red form was found to have short Pt(II)-Pt(II) contacts of about 3.3 Å and a network structure with relatively large cavities in which water molecules can be included. The cavities form as a result of molecular alignments dictated by Pt(II)-Pt(II) interactions and hydrogen bonds between carboxylic acid and cyano groups. Upon exposure of any of the polymorphs to volatile organic compounds, reversible color

changes can be induced. Because the differently colored forms of $[\text{Pt}(4,4'\text{-H}_2\text{dcbpy})(\text{CN})_2]$ are all emissive, vapor exposure further induces changes in the luminescence properties (Figure 2).

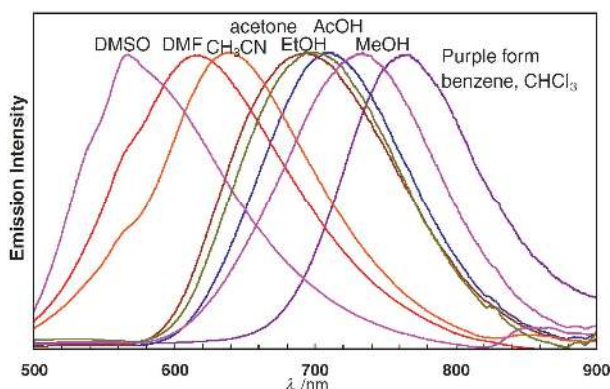


Figure 2. Photoluminescence of $[\text{Pt}(4,4'\text{-H}_2\text{dcbpy})(\text{CN})_2]$ (**6**) after exposure to different VOCs.¹³

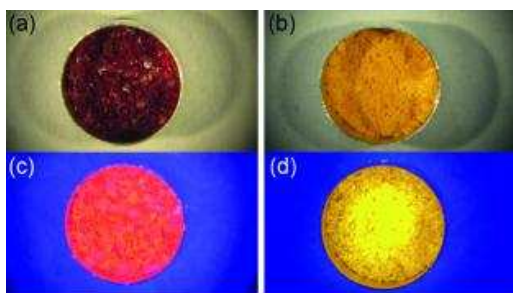
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In this system, there is a reasonably good correlation between the emission band maximum and the dielectric constant of the vapors to which the material is exposed; solvents such as DMSO and DMF cause significantly more blue-shifted emission than substances like benzene or chloroform. The emission originates from a $^3\text{MMLCT}$ state which shifts to lower energy with increasing metal-metal interaction; direct evidence for the correlation between the luminescence band maximum and the Pt(II)-Pt(II) distance comes from the observation of thermochromism in the red form of $[\text{Pt}(\text{dcbpy})(\text{CN})_2]$ and from the observed shortening of the metal-metal distance from 3.28 Å at ambient temperature to 3.22 Å at 100 K.³⁹

When $[\text{Pt}(4,4'\text{-H}_2\text{dcbpy})(\text{CN})_2]$ (**6**) is exposed to sodium methoxide in CH_3OH solution the carboxylic acid groups of the bpy ligand are deprotonated and a material with the stoichiometry $\text{Na}_2[\text{Pt}(4,4'\text{-dcbpy})(\text{CN})_2]\cdot 2\text{H}_2\text{O}$ (**7** $\cdot 2\text{H}_2\text{O}$) is obtained.⁴⁰ The coordination unit in this compound

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3 is formally anionic, but since it contains the deprotonated form of the complex discussed in the
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5 preceding paragraph it appears meaningful to discuss this vapochromic material in the current
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7 section.
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10 $\text{Na}_2[\text{Pt}(4,4'\text{-dcbpy})(\text{CN})_2]\cdot 2\text{H}_2\text{O}$ ($7\cdot 2\text{H}_2\text{O}$) was obtained as a red and amorphous substance
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12 which changes color to yellow in humid air or when exposed to hydrophilic organic vapors such
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14 as those from methanol, acetone or DMF. Powder X-ray experiments reveal that the color change
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16 is accompanied by a structural transformation from an amorphous to a crystalline state, but
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18 inclusion of organic vapors into the solid did not occur. According to single crystal X-ray studies
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20 the yellow form of $7\cdot 2\text{H}_2\text{O}$ has long ($> 4.9 \text{ \AA}$) intermolecular Pt(II)-Pt(II) distances while the red
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22 amorphous polymorph probably has short metal-metal contacts, hence the difference in color.
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24 The most interesting aspect of this material is certainly the fact that it exhibits structural changes
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26 upon exposure to hydrophilic VOCs without actually adsorbing anything. Unfortunately these
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28 structural transformations seem to be irreversible, limiting the application potential of the
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30 respective material severely. Both forms of $7\cdot 2\text{H}_2\text{O}$ are luminescent when irradiated with UV
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32 light, and thus vapor exposure can be monitored both in absorption and emission (Figure 3).
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51 **Figure 3.** Photographs of $7\cdot 2\text{H}_2\text{O}$ before (a) and after (b) exposure to MeOH vapor. Panels (c) and
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53 (d) show the emission of the same compound before and after MeOH exposure. (A. Kobayashi,
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55 T. Yonemura, M. Kato: Vapor-Induced Amorphous-Crystalline Transformation of a
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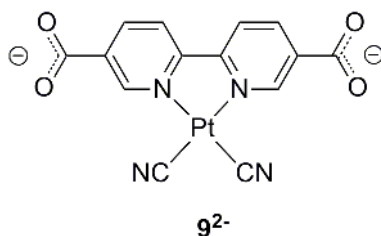
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3 Luminescent Platinum(II)-Diimine Complex. *Eur. J. Inorg. Chem.*, 2010, 2465-2470. Copyright
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5 Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
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11 When the cyano ligands of $[\text{Pt}(4,4'\text{-H}_2\text{dcbpy})(\text{CN})_2]$ are replaced by SCN^- an unusual
12 vapochromic material results.⁵⁰ By synthesizing the $[\text{Pt}(4,4'\text{-H}_2\text{dcbpy})(\text{SCN})_2]$ complex (**8**) at 0
13 °C it was possible to obtain the S-bound linkage isomer of this material, which, by analogy to the
14 thiocyanato complex $[\text{Pt}(\text{bpy})(\text{SCN})_2]$ is presumably the kinetically (but not thermodynamically)
15 favored product. The $[\text{Pt}(4,4'\text{-H}_2\text{dcbpy})(\text{SCN})_2]$ complex is an orange non-luminescent material
16 which crystallizes as a monohydrate (**8**·H₂O). Exposure to DMF vapor induces a change in color
17 to red, and the material becomes emissive ($\lambda_{\text{max}} = 660 \text{ nm}$, $\tau = 16 \text{ ns}$), presumably from a
18 ³MMLCT excited state indicative of Pt(II)-Pt(II) interactions. The CN stretching frequency red-
19 shifts from 2128 cm^{-1} to 2115 cm^{-1} in the course of DMF uptake, and the three ¹H NMR
20 resonances from the bpy backbone undergo high-field shifts. These two observations are
21 consistent with a linkage isomerization reaction from S-bound thiocyanate to N-bound
22 isothiocyanate. According to thermogravimetric studies the DMF adduct contains 3 molecules of
23 DMF per formula unit (**8**·3DMF). By crystallization from DMF solution it was possible to obtain
24 single-crystals of the formulation **8**·4DMF in which the SCN^- ligand is clearly nitrogen bound,
25 but there are no short intermetallic contacts in this specific material. Some of the DMF molecules
26 form hydrogen-bonds to the carboxyl groups and indeed, the CO stretching frequency of DMF in
27 **8**·3DMF is lowered by 22 cm^{-1} compared to liquid DMF, suggesting that in the material with
28 only 3 molecules of DMF, hydrogen-bonding between DMF and carboxyl groups of the H₂dcbpy
29 ligand occurs as well. Thus, hydrogen-bonding seems to play an important role in the vapor-
30 induced linkage isomerization. This interpretation is supported by the finding that solvents with a
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3 Gutmann donor number above 26 induce the isomerization reaction for both SCN^- ligands of a
4 given complex (DMSO, DMF, dimethylacetamide), whereas solvents with donor numbers
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6 between 10 and 26 (methanol, ethanol, acetone, acetonitrile) induce S-to-N isomerization of only
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8 one of the two ligands.⁵⁰ Presumably, the explanation for this behavior is that the initial S-bound
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10 form is stabilized by hydrogen-bonding between the terminal (more electronegative) N-atoms of
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12 the thiocyanato-ligands and the carboxyl-groups of neighboring complexes; upon sorption of a
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14 good hydrogen-bond donor these existing hydrogen-bonds are disrupted, making the
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16 thiocyanato-ligation thermodynamically unstable. Even though the crystal structure of **8**·4DMF
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18 fails to provide direct evidence for intermetallic interactions it is easy to see why such
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20 interactions are more likely to occur in **8**·3DMF than in **8**·H₂O: S-coordinated thiocyanate has a
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22 bent structure which can be directed up or down from the coordination plane, whereas N-
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24 coordinated isothiocyanate is expected to lead to essentially planar complexes, hence close
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26 Pt(II)-Pt(II) contacts become more readily possible.
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34 Building on their own prior work Kato and Kobayashi recently reported on a series of
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36 coordination polymers containing $[\text{Pt}(\text{bpy})(\text{CN})_2]$ units. Specifically, their work focused on
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38 $[\text{Pt}(5,5'\text{-dcbpy})(\text{CN})_2]^{2-}$ complexes (5,5'-H₂dcbpy = 5,5'-dicarboxyl-2,2'-bipyridine) (**9**²⁻)
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40 bridged by Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} or Zn^{2+} cations (Scheme 3).^{41, 42} Respective systems with
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42 formally anionic platinum complexes are discussed in this chapter because of their chemical and
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44 functional kinship to the materials discussed above.
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51 **Scheme 3.** $[\text{Pt}(\alpha\text{-diimine})(\text{CN})_2]$ complexes, part III.
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In the zinc compound the $[\text{Pt}(5,5'\text{-dcbpy})(\text{CN})_2]^{2-}$ units act as bridges between individual Zn^{2+} ions to form an infinite chain.⁴¹ The platinum complexes themselves are stacked perpendicularly to these chains with an intermetallic distance of 3.309(1) Å which is responsible for the orange color as well as the $^3\text{MMLCT}$ emission (at 614 nm) exhibited by the $\text{Zn}[\text{Pt}(5,5'\text{-dcbpy})(\text{CN})_2]\cdot 4\text{H}_2\text{O}$ material at room temperature. Three of the four water molecules from this formula unit are coordinated to $\text{Zn}(\text{II})$ (along with two carboxylate oxygens), while the fourth water molecule is only hydrogen-bonded to a cyano group. When heating to 100°C all four water molecules can be driven off, thereby inducing a color change from orange to red and finally purple. The anhydrous purple form is vapochromic; when exposed to humid air at room temperature it readily re-converts to the initial orange tetrahydrate form. Thus, water adsorption/desorption occurs predominantly at the $\text{Zn}(\text{II})$ site, but this influences the stacking of the chromophoric and emitting platinum complexes (Figure 4).

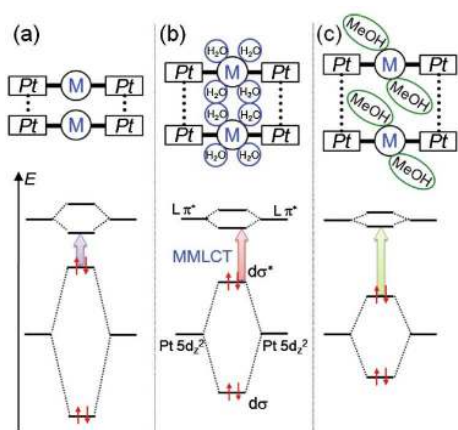


Figure 4. Illustration how solvent uptake at the Zn(II) sites in the $M[\text{Pt}(5,5'\text{-dcbpy})(\text{CN})_2]$ coordination polymers affects the Pt(II)-Pt(II) distance (upper part) and the energy level structure (MO diagrams in lower part). Reprinted with permission from ref. ⁴². Copyright 2011 The Royal Society of Chemistry.

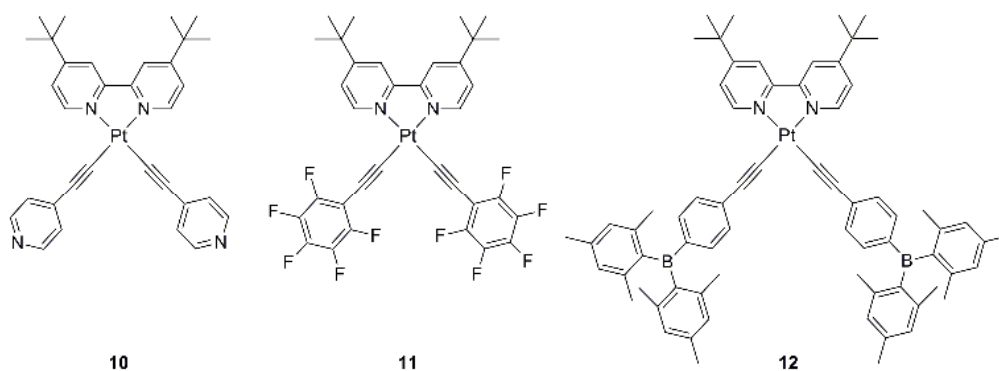
When replacing Zn(II) by other dications it becomes possible to alter the intermolecular Pt(II)-Pt(II) distances in the $M[\text{Pt}(5,5'\text{-dcbpy})(\text{CN})_2] \cdot n\text{H}_2\text{O}$ coordination polymers;⁴² in a way this is similar to cation exchange in tetracyanoplatينات although the accessible Pt(II)-Pt(II) distance range is more narrow for the newly explored coordination polymers.²² Compounds with $M^{2+} = \text{Mg}^{2+}$, Ca^{2+} , Sr^{2+} , and Ba^{2+} are thought to be isomorphous with $\text{Zn}[\text{Pt}(5,5'\text{-dcbpy})(\text{CN})_2] \cdot 4\text{H}_2\text{O}$, and hence it appears plausible that the alkaline earth metals act as water adsorbing sites similar to the Zn(II) ion in the parent compound, but this is not known for sure. By analogy to the zinc compound discussed above, heating to 100°C drives off all four water molecules in all compounds, and the resulting anhydrous forms readily re-adsorb water vapor at ambient temperature. In the case of the compounds with Mg^{2+} and Ca^{2+} this is accompanied by significant chromic shifts both in absorption and emission, hence these two materials may be considered vapochromic substances. Contrary to the zinc compound, the alkaline earth metal based

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3 coordination polymers can all adsorb methanol vapor, and this alters their luminescence with
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5 respect to the anhydrous forms. It is thought that the methanol molecules simply occupy the
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7 adsorption sites filled with water in the $M[\text{Pt}(5,5'\text{-dcbpy})(\text{CN})_2]\cdot n\text{H}_2\text{O}$ forms.

12 13 2.1.2 $[\text{Pt}(\alpha\text{-diimine})(\text{acetylide})_2]$ complexes

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18 The search for phosphorescent metal complexes which can be used as triplet harvesters in
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20 organic light emitting diodes (OLEDs) has lead, inter alia, to platinum(II) complexes with
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22 acetylide ligands.^{16, 51-55} When combining acetylide ligands with α -diimines or cyclometalating
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24 chelating agents very strong ligand fields can be exerted on coordinated Pt(II) centers,^{56, 57} and
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26 this is beneficial for the luminescence properties due to suppression of multiphonon relaxation
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28 from metal-localized (d-d) excited states.⁵⁸ In the course of research on such complexes a few
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30 vapochromic materials have been discovered.
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37 **Scheme 4.** $[\text{Pt}(\alpha\text{-diimine})(\text{acetylide})_2]$ complexes, part I.



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Che, Wong, and coworkers report on a series of $[\text{Pt}(\textit{t}\text{Bu}_2\text{bpy})(\text{arylacetylide})_2]$ complexes two of which are vapoluminescent (Scheme 4).⁵⁹ Thin films of the complex in which the arylacetylide is 4-ethynylpyridine exhibit greatly enhanced green luminescence upon sorption of CH_2Cl_2 or CHCl_3 vapor; the detection limits are around 25 and 450 ppm, respectively, while polar VOCs such as methanol produce no response. In crystals of $[\text{Pt}(\textit{t}\text{Bu}_2\text{bpy})(4\text{-ethynylpyridine})_2]\cdot\text{CH}_2\text{Cl}_2$ (**10** $\cdot\text{CH}_2\text{Cl}_2$) there are interactions between the relatively acidic protons of CH_2Cl_2 and the 4-ethynylpyridine $\text{C}\equiv\text{C}$ bonds.⁵⁹ As a consequence, an infinite chain of CH_2Cl_2 molecules forms within a hydrophobic channel between the platinum complexes; C-H–N interactions between the $\textit{t}\text{Bu}_2\text{bpy}$ ligands and the pyridyl N atoms complement the network of noncovalent interactions. Presumably, the high selectivity for CH_2Cl_2 in the vapoluminescent response of neat $[\text{Pt}(\textit{t}\text{Bu}_2\text{bpy})(4\text{-ethynylpyridine})_2]$ (**10**) is at least partly due to the hydrogen bonding interactions which have been observed in crystals of the CH_2Cl_2 adduct. Acetonitrile has less acidic protons hence hydrogen bonding to the 4-ethynylpyridine $\text{C}\equiv\text{C}$ bonds is weaker and no vapoluminescence is observed; alcoholic vapors presumably cannot intrude into the hydrophobic environment produced by the *tert.*-butyl substituents. The emission spectrum of the crystalline CH_2Cl_2 adduct is similar to that obtained when dissolving the complex **10** in CH_2Cl_2 and has been interpreted in terms of ³MLCT emission from discrete molecules; there are no short Pt(II)-Pt(II) contacts in the crystalline form.

When the arylacetylide is ethynylpentafluorophenyl another vapoluminescent material is obtained.⁵⁹ When crystallized from benzene solution $[\text{Pt}(\textit{t}\text{Bu}_2\text{bpy})(\text{ethynylpentafluorophenyl})_2]$ (**11**) forms orange crystals which exhibit an intense structureless emission with $\lambda_{\text{max}} = 595$ nm. Upon exposure to CH_2Cl_2 vapor, the orange emission gradually changes to green ($\lambda_{\text{max}} = 500$ nm). While the orange photoluminescence is thought to be excimeric emission originating from

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3 electronically interacting complexes the green luminescence was attributed to $^3\text{MLCT}$ emission
4 from isolated complexes. The dichloromethane adduct of this material could not be crystallized
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6 but it was possible to investigate $\mathbf{11}\cdot\text{CH}_3\text{CN}$ by X-ray crystallography. The shortest Pt(II)-Pt(II)
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8 contact in the acetonitrile adduct is at 9.957 Å, while in the solvent-free compound the shortest
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10 metal-metal distance is 5.172 Å. In the latter, the distances between neighboring luminophore
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12 layers are between 3.3 Å and 3.6 Å which is indicative of π -stacking between pentafluorophenyl-
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14 rings and $^t\text{Bu}_2\text{bpy}$. The excimeric orange emission of solvent-free $\mathbf{11}$ may have its origin in these
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16 weak intermolecular interactions.
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22 Wang and coworkers recently reported on a structurally related platinum(II) material
23 exhibiting vapochromism that relies on an entirely different concept which has nothing to do
24 with metal-metal distances or π -stacking.⁶⁰ Instead, the vapochromism of complex $\mathbf{12}$ appears to
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26 be due to changes in the excited-state structure resulting from direct interactions between the
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28 complex and adsorbed molecules. Complex $\mathbf{12}$ contains two triarylboron groups, similar to those
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30 investigated in the context of fluoride sensors or electron-deficient materials.⁶¹⁻⁶³ Neat $\mathbf{12}$ shows
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32 yellow $^3\text{MLCT}$ emission ($\lambda_{\text{max}} = 559 \text{ nm}$) following UV irradiation (Figure 5). Exposure to *n*-
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34 hexane, toluene or methanol vapors quenches the luminescence, while exposure to benzene or
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36 cyclohexane induces a change in emission color from yellow to red ($\lambda_{\text{max}} = 580 - 620 \text{ nm}$). By
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38 contrast, when the same complex is exposed to vapors of CH_2Cl_2 , CHCl_3 , CH_3CN , acetone, THF,
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40 or ethanol, the emission color shifts from yellow to green ($\lambda_{\text{max}} = 490 - 500 \text{ nm}$). Thus, complex
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49 $\mathbf{12}$ exhibits unusual behavior in that different groups of solvent vapors induce emission color
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51 shifts to either shorter or longer wavelengths.
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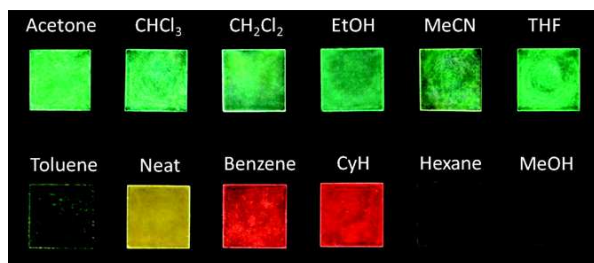


Figure 5. Photoluminescence of complex **12** after exposure to different VOCs. Reprinted with permission from ref. ⁶⁰. Copyright 2011 American Chemical Society.

This phenomenon has been explained in terms of solvent-induced switching in the nature of the emissive excited-states: While the yellow luminescence of neat **12** and the red emission after exposure to benzene or cyclohexane are assumed to originate from a ³MLCT state, the green emission following adsorption of more polar vapors is attributed to ligand-centered emission (³LC). This interpretation makes sense in view of the fact that many Pt(II) complexes exhibit negative solvatochromism, because of their large ground-state dipole moments which are opposite to the direction of the MLCT.^{64, 65} In complex **12**, solvents of a certain threshold polarity shift the ³MLCT state energetically above the ³LC level which is then largely insensitive to further polarity changes (left part of Figure 6); this explains why solvents ranging in polarity from CH₂Cl₂ to CH₃CN all lead to essentially the same green emission.⁶⁰ Conversely, nonpolar solvents decrease the energy of the ³MLCT state, resulting either in red luminescence (benzene, cyclohexane) or, in the extreme case (*n*-hexane), to emission quenching.

Single-crystal X-ray diffraction of **12**·4CH₂Cl₂ reveals that the shortest intermolecular Pt(II)-Pt(II) separation is above 12 Å and the shortest distance between aromatic planes is ~5.7 Å.⁶⁰ Powder X-ray studies show that CH₂Cl₂, benzene, and hexane adducts are structurally very similar to neat **12**. This finding is corroborated by solid state NMR studies monitoring the ¹H,

^{13}C , and ^{195}Pt nuclei. ^{11}B NMR spectroscopy shows that the boron center is unaltered by adsorption of CH_2Cl_2 or benzene. On the basis of these observations Wang and coworkers postulated that interactions between the bpy ligands and the adsorbed molecules are responsible for the energetic changes in the emissive $^3\text{MLCT}$ state.⁶⁰

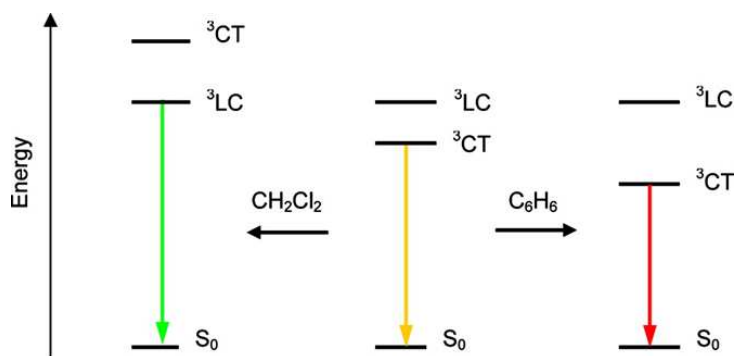


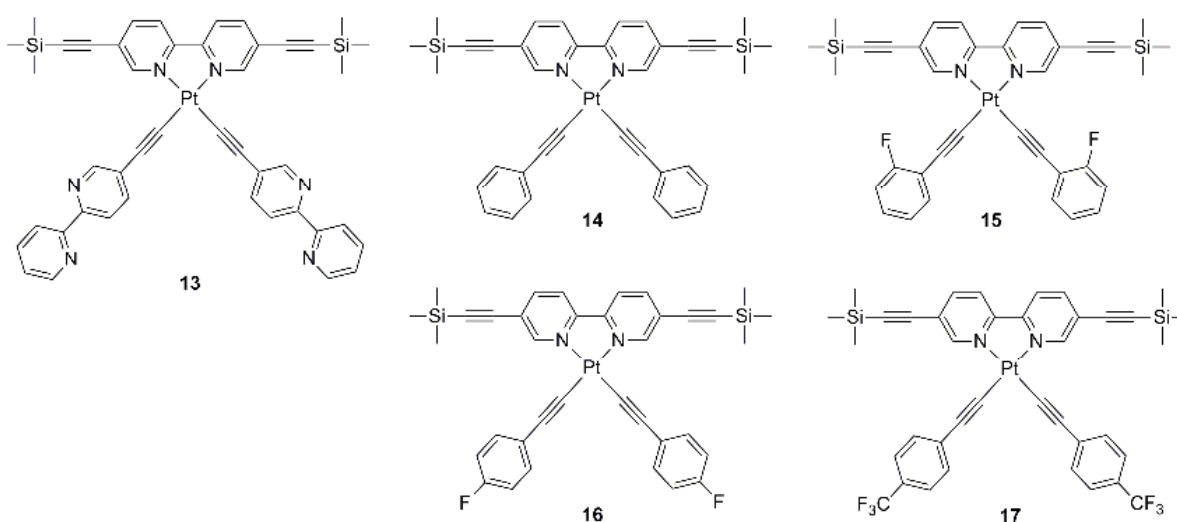
Figure 6. Changes of the excited-state structure in complex **12** as a function of VOC exposure.

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Chen and coworkers report on a vapoluminescent platinum(II) bis(acetylide) complex (**13**) with a bpy ligand substituted at its 5- and 5'-positions with trimethylsilyl-protected ethynyl groups,⁶⁶ its acetylide ligands are two 5-ethynyl-2,2'-bipyridine molecules (Scheme 5). The luminescence of **13** is strongly sensitive to a variety of VOCs. When exposed to acetone, structured luminescence with a band maximum at 562 nm is observed while exposure to THF leads to unstructured emission with λ_{max} at 747 nm. For other solvent vapors, emission band maxima between these two extremes are detected. Structural investigations of different solvent adducts of **13** reveal that there is a correlation between the shortest Pt(II)-Pt(II) distance ($d_{\text{Pt-Pt}}$) with the solvent-induced shift of the emission band maximum: While for the acetone and *n*-hexane adducts $d_{\text{Pt-Pt}} = 4.8406(15) \text{ \AA}$ and $4.3091(9) \text{ \AA}$, respectively, chloroform and THF adducts

exhibit short Pt(II)-Pt(II) contacts of 3.2363(15) Å and 3.2195(5) Å. Thus, it appears plausible that the emissive state changes from $^3\text{MLCT}$ to $^3\text{MMLCT}$ for VOCs such as acetone, CH_2Cl_2 , and *n*-hexane. In the CH_2Cl_2 adduct, intermolecular π - π stacking as well as C-H / π (C \equiv C) interactions may play a role as well.⁶⁶

Scheme 5. [Pt(α -diimine)(acetylide)₂] complexes, part II.



Chen and coworkers further reported on a Pt(II) complex with 5,5'-bis(trimethylsilylethynyl)-2,2'-bipyridine and phenylacetylene ligands (**14**) exhibiting selective vapoluminescence response to volatile halohydrocarbons with only one carbon atom and molecular masses below 150 g/mol.⁶⁷ The crystal structure of neat **14** as well as those of solvent adducts with 1,2-dichloroethane and toluene exhibit no Pt(II)-Pt(II) distances shorter than 4.7 Å. By contrast, in the structure of the CHCl_3 adduct there is a short intermetallic distance of 3.302(1) Å between pairs of complexes. The structural changes following CHCl_3 uptake are accompanied by a change from orange ($\lambda_{\text{max}} = 561$ nm and 603 nm) to red emission ($\lambda_{\text{max}} = 761$ nm), which has

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been explained by a changeover from $^3\text{MLCT}$ emission with some admixed $^3\text{LLCT}$ character ($\tau = 2.12 \mu\text{s}$) to $^3\text{MMLCT}$ emission. Computational studies support this interpretation and hint to an admixture of $^3\text{LLCT}$ character even to the $^3\text{MMLCT}$ luminescence. Neat **14** was exposed to a variety of different solvent vapors including those from diethyl ether, ethyl acetate, methyl acetate, acetone, methanol, ethanol, acetonitrile, pyridine, dibromomethane, bromoform, carbon tetrachloride, 1,2-dichloroethane, 1,2-dibromoethane, 1,1,2-trichloroethane, and toluene. However, a vapoluminescence response was only obtained with CH_2Cl_2 , CHCl_3 , and CH_3I . The vapochromic response to CH_2Cl_2 is illustrated by Figure 7.

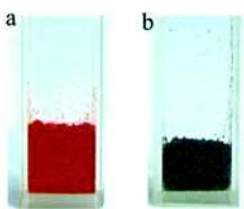
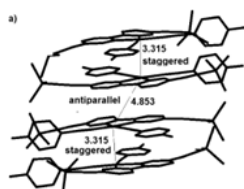


Figure 7. Photograph of crystalline samples of **14** (a) and **14**· CH_2Cl_2 (b). Reprinted with permission from ref. ⁶⁶. Copyright 2009 American Chemical Society.

Complexes **15** and **16** differ from **14** only by the fluoro-substituents at the phenylacetylene ligands yet exhibit substantially different vapoluminescence behavior.⁶⁸ Complex **15** is specifically selective to CHCl_3 vapors, while complex **16** responds to both CHCl_3 and CH_2Cl_2 . Unlike **14**, neither **15** nor **16** are sensitive to CH_3I , but the effect of chloroform and/or dichloromethane exposure is the same in all three complexes, namely the change from orange $^3\text{MLCT}/^3\text{LLCT}$ to red $^3\text{MMLCT}/^3\text{LLCT}$ emission mentioned above for **14**. The structure of the adduct between **15** and 1,2-dichloroethane, as well as the structures of **16**· $0.5\text{CH}_2\text{Cl}_2$,

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3 **16**·CH₂ClCH₂Cl, and **16**·CH₂BrCH₂Br were determined by single crystal X-ray diffraction
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5 (Figure 8). Individual complexes are either stacked in staggered or anti-parallel fashion in these
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7 structures. The staggered mode permits formation of Pt(II)-Pt(II) contacts shorter than 3.4 Å,
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9 whereas in the anti-parallel mode individual complexes are forced to slide away from each other
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11 so as to enforce intermetallic distances longer than 3.5 Å. Both stacking modes appear in the
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13 structure of **16**·0.5CH₂Cl₂ as there are pairs of complexes with short (3.315(9) Å) and long
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15 (4.853(10) Å) metal-metal distances (Figure 8). The structures of **15**·CH₂ClCH₂Cl and
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17 **15**·CH₂ClCH₂Cl exhibit relatively short intermetallic contacts (3.514(16) Å and 3.513(5) Å) as
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19 well, but there is no significant vapoluminescence response of **15** or **16** to 1,2-dichloroethane. A
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21 notable feature of several of the abovementioned crystal structures is the presence of C-
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23 H/ π (C \equiv C) interactions between the halocarbon adsorbents and the fluorophenylacetylides. The
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25 reversible structural changes following the conversion of **16**·CH₂BrCH₂Br to **16**·CH₂Cl₂ were
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27 studied by monitoring X-ray diffraction (XRD) patterns after different times following exposure
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29 to CH₂Cl₂ or 1,2-dibromoethane vapors. Given the reversibility of the structural transformations
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31 the observation of fully reversible vapoluminescence responses by **15** and **16** is not particularly
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33 surprising. Several solvent adducts of **15** and **16** were found to exhibit mechanochromic
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35 luminescence.^{23, 68}
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3 **Figure 8.** Molecular packing in single crystals of **16**·0.5CH₂Cl₂. (J. Ni, X. Zhang, Y.-H. Wu, L.-
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5 Y. Zhang, Z.-N. Chen. *Chem. Eur. J.*, 2011, 17, 1171-1183. Copyright Wiley-VCH Verlag
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7 GmbH & Co. KGaA. Reproduced with permission.)
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14 A closely related Pt(II) complex has two 4-trifluoromethylphenylacetylide ligands (**17**) and is
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16 selectively sensitive to vapors from cyclic ethers such as THF, dioxane, or tetrahydropyran
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18 (THP) (Figure 9).⁶⁹ As in the case of **13** – **16**, the vapoluminescence response of **17** is triggered
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20 by changes in intermetallic distances causing a red-shift in luminescence due to the changeover
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22 from ³MLCT/³LLCT to ³MMLCT emission. In **17**·THF there is a short (3.255(8) Å) Pt(II)-Pt(II)
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24 distance between staggered complexes, and the overall crystal structure appears to be stabilized
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26 by host-guest interactions through hydrogen-bonding between C-H groups of the complex and
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28 the oxygen atom of THF, as well as between C-H groups of THF and the trifluoromethyl group
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30 of the phenylacetylide ligands. It is possible that this is the origin of the selective
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32 vapoluminescence response to certain O-heterocyclic compounds (Figure 9). XRD studies reveal
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34 that the structural conversion between **17**·CH₂ClCH₂Cl and **17**·THF is fully reversible. Exposure
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36 to vapors of methanol, ethanol, acetone, furan, diethyl ether, ethyl acetate, hexane, toluene,
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38 pyridine, and various halohydrocarbons produces no significant vapoluminescence changes. The
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40 initial motivation for introducing the electron-withdrawing trifluoromethyl group at the
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42 phenylacetylide ligands was to increase the HOMO-LUMO energy gap, and the expected
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44 emission blue-shift could indeed be observed (λ_{max} of **17** in CH₂Cl₂ solution: 568 nm; λ_{max} of **14**
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46 in CH₂Cl₂: 616 nm). However, the selective vapoluminescence response of **17** is most likely an
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60 accidental result.

Similar to **15** and **16**, neat **17** and some of its solvent adducts exhibit mechanochromic properties and luminescence thermochromism.^{23, 69}

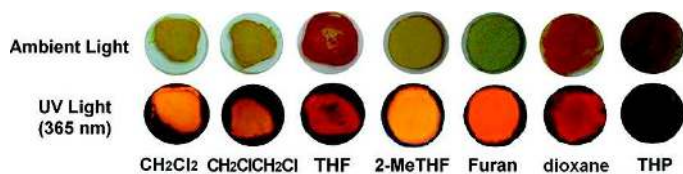


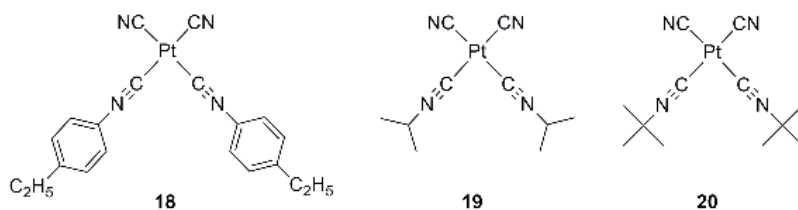
Figure 9. Vapochromic and vapoluminescent response of complex **17** to selected VOCs.

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2.1.3 [Pt(isocyanide)₂(CN)₂] complexes

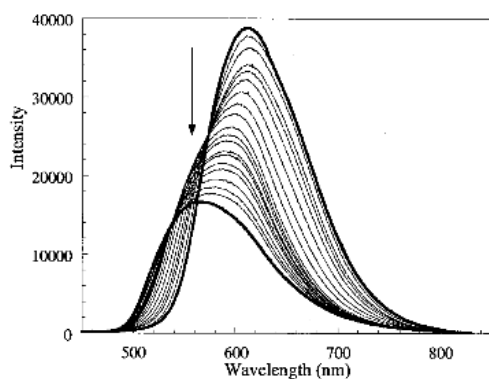
When heating double salt compounds of the stoichiometry [Pt(CNR)₄][Pt(CN)₄] (see next chapter) to their melting point in absence of solvent, ligand rearrangement occurs and isomeric charge-neutral [Pt(CNR)₂(CN)₂] complexes are formed.⁷⁰ Starting from the respective double salt, Mann and coworkers prepared [Pt(CN-C₆H₄-C₂H₅)₂(CN)₂] (**18**) at 201 °C (Scheme 6).

Scheme 6. Vapochromic [Pt(isocyanide)₂(CN)₂] complexes.



Subsequent re-crystallization of the raw product gives either an orange or a purple form of the same product: Slow crystallization from CH₂Cl₂ yields the orange form, while the purple isomer

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4 is obtained via rapid addition of hexanes to the CH_2Cl_2 solution. Of specific interest here is the
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6 orange form because it exhibits vapoluminescence, whereas the purple isomer does not appear to
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8 respond to VOCs. Orange **18** is the *cis*-isomer of **18** (*cis*-**18**) and exhibits luminescence from a
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10 $d\sigma^* \rightarrow p\sigma$ excited state similar to tetracyanoplatinates. When exposed to vapors of toluene,
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12 benzene, chlorobenzene, *p*-xylene, mesitylene, or ethanol in an N_2 stream at 296 K, the
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14 maximum of the broad emission band of *cis*-**18** shifts from 611 nm to shorter wavelengths by up
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16 to 46 nm (Figure 10). In the case of toluene a VOC mole fraction of 0.0337 in the N_2 stream is
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18 necessary to induce this blue-shift while in the case of mesitylene only a mole fraction of 0.0028
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20 is required to induce the same effect. Analysis of the luminescence data suggests that toluene
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22 sorption occurs in two steps, involving adducts with the stoichiometry *cis*-**18** $\cdot 0.25\text{C}_6\text{H}_5\text{CH}_3$ and
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24 *cis*-**18** $\cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$. Gravimetric studies, however, indicate that *cis*-**18** rapidly sorbs 0.5
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26 equivalents of toluene while prolonged exposure produces an adduct with 0.9 equivalents of
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28 toluene. Subsequent partial removal of toluene by continued purging with N_2 occurs readily, but
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30 the last 0.25 equivalents are held with tenacity and neat *cis*-**18** can only be recovered with
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32 simultaneous heating.
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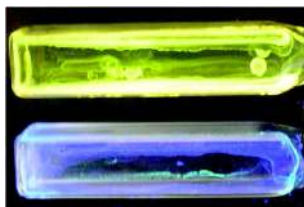
55 **Figure 10.** Emission spectral changes of *cis*-**18** in the course of toluene vapor uptake. Reprinted
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57 with permission from ref. ⁷⁰. Copyright 2002 American Chemical Society.
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6 The structures of *cis*-**18**·0.5C₆H₅CH₃ and *cis*-**18**·x(hexanes) were determined by X-ray
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8 analysis.⁷⁰ The packing arrangements in both structures are nearly identical, there are infinite
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10 stacks of *cis*-[Pt(CN-C₆H₄-C₂H₅)₂(CN)₂] molecules with chains of Pt(II) atoms along the c-axis.
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12 The in-chain Pt(II)-Pt(II) separation in the toluene adduct is alternating between 3.281 Å and
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14 3.300 Å, but the chain is slightly zigzagged with Pt-Pt-Pt angles of 175.5°. The *cis*-
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16 **18**·0.5C₆H₅CH₃ adduct incorporates 4 toluene molecules per unit cell, thereby the volume of the
17
18 latter increases by 160 Å³ or 43% of the estimated volume of 4 toluene molecules (372 Å³).
19
20 Uptake of toluene vapor increases the packing efficiency by 10%, which is significantly greater
21
22 to what is commonly observed for the vapochromic Pt(II) double salts discussed in the next
23
24 section (6%). Toluene sorption increases the length of the unit cell along the c-axis by 0.35 Å,
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26 resulting in an increase of the Pt(II)-Pt(II) distance by about 0.09 Å. However, among the VOCs
27
28 investigated, no obvious correlation between the magnitude of the vapochromic luminescence
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30 band shift and any one VOC molecular parameter was found, and it was cautiously suggested
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32 that the molecular shape of the VOC guest plays an important role.
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39 When the [Pt(CNR)₄][Pt(CN)₄] double salt with R = C₆H₄-C₂H₅ is heated to reflux in
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41 chloroform, the purple *trans*-isomer of compound **18** is obtained.⁷¹ Expectedly, *trans*-**18** differs
42
43 from *cis*-**18** not only in color (purple vs. orange) but by an ensemble of physical properties, e. g.,
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45 different cyanide stretching frequencies, different chemical shifts for the ¹⁹⁵Pt NMR signals, and
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47 molecular packing in single crystals. The Pt(II)-Pt(II) separation (3.1253(8) Å) in *trans*-**18** is one
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49 of the shortest in the entire class of Pt(II) double salts. Furthermore, there are intermolecular π-π
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51 interactions between isocyanide ligands of different stacks leading to a relatively close-packed
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53 structure in two of the three dimensions. As noted by Mann and coworkers, it is possible that the
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compact two-dimensional packing motif is responsible for the absence of vapochromism or vapoluminescence of *trans*-**18**.⁷¹

This *cis*-isomer of $[\text{Pt}(\text{CN-}^i\text{C}_3\text{H}_7)_2(\text{CN})_2]$ (*cis*-**19**) was synthesized from the respective double salt like *cis*-**18**.⁷² Individual Pt(II) complexes in *cis*-**19** are slip-stacked in staggered fashion along the c-axis with an intermetallic distance of 3.256 Å, the color of the material is yellow. When exposed to benzene vapors, the structure changes to an eclipsed orientation of Pt(II) complexes with an intermetallic separation that has increased to 3.485 Å, and the color of this compound (*cis*-**19**·0.5C₆H₆) is blue. The structural change including a 20% expansion in unit cell volume is further accompanied by a change in luminescence properties (Figure 11). Modeling of the spectral changes observed in the course of exposure to benzene leads to the conclusion that benzene uptake is a consecutive two-step reaction (A → B → C) with an intermediate B of unknown structure. Interestingly, *cis*-**19** does not respond to vapors of substituted derivatives of benzene such as toluene, *p*-xylene, *m*-xylene, *o*-xylene, mesitylene, chloroform, and hexafluorobenzene. Presumably the selectivity of *cis*-**19** for benzene has its origin in the absence of a stable solvate phase for adducts such as *cis*-**19**·*n*(C₆H₅CH₃). Unfortunately, the reversibility of the benzene uptake is poor due to crystalline degradation. The slow kinetics for benzene sorption additionally limits the usefulness of *cis*-**19** as a benzene sensor for practical purposes.



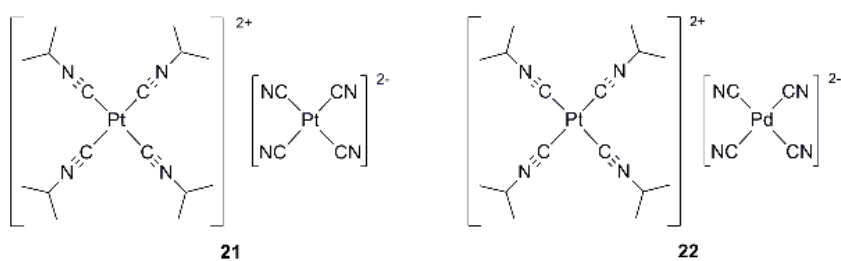
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3 **Figure 11.** Photoluminescence of cuvettes filled with crystalline films of *cis*-**19** before (top) and
4 after (bottom) exposure to benzene vapor. Reprinted with permission from ref. ⁷². Copyright
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8 2009 American Chemical Society.
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13 Using the compound [Pt(CN-^tBu)₂(CN)₂] (**20**) it has been possible to fabricate vapor-
14 responsive microwires.⁷³ For this purpose, **20** was dissolved in methanol and deposited onto
15 insulating SiO₂ substrates bearing two pre-installed small gold electrodes on the surface. The
16 microwires were typically longer than 10 μm and hence they were able to cross over two
17 neighboring electrodes. When slowly evaporating solvent over a time period of 6 days the
18 diameter of the microwires was typically on the order of 1.2 μm. The electrical conductivity of
19 an operating electrode-microwire-electrode device at a bias of 5 Volts was determined to be 6.86
20 μA. The conductivity is perturbed upon VOC exposure, but only toluene, acetonitrile, and
21 methanol produce a significant response. Vapors of THF, acetone, ethyl acetate, diethyl ether,
22 petroleum ether, hexane, nitromethane, ammonia, chlorobenzene, cyclohexane, dichloromethane,
23 chloroform, and hydrazine lead to a comparatively small change in conductivity. It has been
24 suggested that changes in the Pt(II)-Pt(II) interactions are responsible for the vapor-induced
25 variations in conductivity.⁷³ X-ray diffraction indicates that upon acetonitrile uptake the Pt(II)-
26 Pt(II) distance remains almost unchanged (3.354(1) Å vs. 3.3525(2) Å), but the coordination
27 bond angles around the Pt(II) center are altered.⁷⁴ Consequently, CH₃CN exposure is associated
28 with a relatively small change in luminescence properties and the 5dσ*←6pσ emission simply
29 decreases in intensity but does not change color (λ_{max} stays at 534 nm).
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2.2 Platinum(II) / palladium(II) double salts

When stirring an acetonitrile solution of $\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2$ and $[(n\text{-Bu})_4\text{N}]_2[\text{M}(\text{CN})_4]$ ($\text{M} = \text{Pt}$, Pd) in presence of isopropylisocyanide one obtains two compounds which are reminiscent of the Magnus Green Salt (MGS, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$), namely $[\text{Pt}(\text{CN-}^i\text{C}_3\text{H}_7)_4][\text{Pt}(\text{CN})_4]$ (**21**) and $[\text{Pt}(\text{CN-}^i\text{C}_3\text{H}_7)_4][\text{Pd}(\text{CN})_4]$ (**22**) (Scheme 7).⁷⁵

Scheme 7. Vapochromic d^8 - d^8 double salts, part I.



Bulk samples of **21** are red with a green metallic reflectance whereas **22** is yellow. From aqueous solution **21** crystallizes as a hexahydrate adduct with alternating cation-anion stacking similar to MGS (Figure 12), and the water molecules connect individual stacks through hydrogen-bonding to the cyanide ligands of the anion. Gravimetric investigations demonstrated that dry **21** readily uptakes either 12 molecules of H_2O , 8 molecules of methanol, 6 molecules of chloroform, or 4 molecules of trifluoroethanol when exposed to the corresponding vapors.

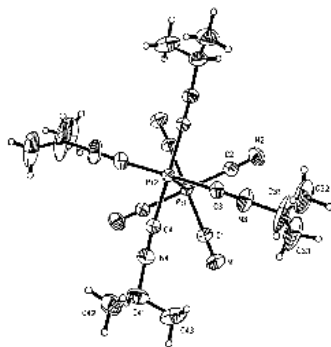
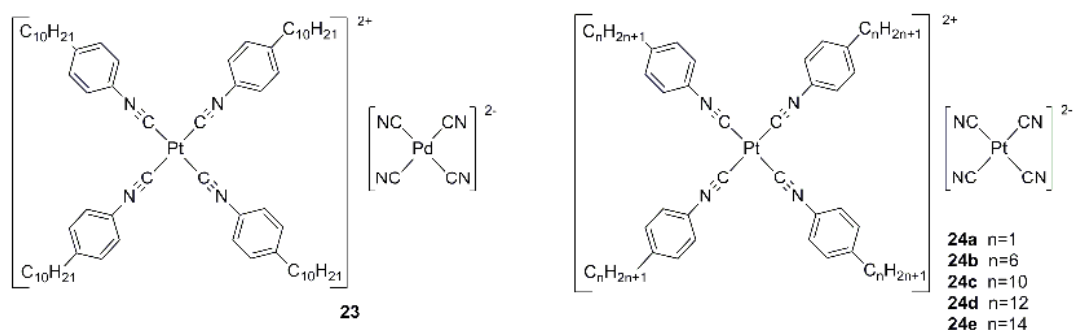


Figure 12. A cation-anion pair in compound **21**. Reprinted with permission from ref. ⁷⁵. Copyright 1998 American Chemical Society.

Interestingly, none of these sorption processes influences the Pt(II)-Pt(II) distance much, the unit cell parameter in the stacking direction (*c*-axis) varies in the narrow range from 6.303(2) Å to 6.337(2) Å. As a consequence, the absorption maximum of the lowest-energetic absorption varies only from 573 nm to 603 nm and vapochromism is not particularly spectacular. However, the vapor-sorption induced changes in the distance between individual Pt(II)-Pt(II) stacks in the *ab* plane are all the more noteworthy; the respective distance varies between 10.416 Å(1) (in dry **21**) to 18.271(4) Å (in **21**·12 H₂O). Large unit cell volume expansions reflecting the size of the guest vapor are observed: For H₂O the cell volume expands by 54%, for methanol 60%, for trifluoroethanol 73%, and for chloroform 94% relative to the volume of dry **21**. Thus, it is clearly the size of the guest, and not the size of any preexisting pores in the host material which determines the magnitude of the lattice expansion. Principally these changes in the plane perpendicular to the Pt(II)-Pt(II) stacking direction are thought to be responsible for the weak vapochromism of **21**, but how exactly this occurs is not known.⁷⁵

Scheme 8. Vapochromic d⁸-d⁸ double salts, part II.



A variety of different isonitrile ligands can be used for obtaining vapochromic double salts similar to **21** or **22**, an early example is $[\text{Pt}(\text{CN}-\text{C}_6\text{H}_4-\text{C}_{10}\text{H}_{21})][\text{Pd}(\text{CN})_4]$ (**23**) (Scheme 8).⁷⁶ Analogous compounds with isonitriles containing n C_6 , C_{12} , and C_{14} chains were investigated as well, but the C_{10} compound has the highest responsivity to solvent vapors. Thin films of **23** change color from pink to blue with a response time ($t_{1/2}$) of ~ 350 ms when exposed to CHCl_3 -saturated air at room temperature. The associated shift of the visible absorption band from 548 nm to 578 nm is reversible thanks to a minimal disruption of crystallinity upon vapor sorption. It has been suggested that this is possible due to the rather large size mismatch between Pt(II) dications and Pd(II) dianions, producing a relatively large free volume through which CHCl_3 can easily move in and out of the material. IR spectroscopy suggests that the CHCl_3 guest interacts predominantly with the $[\text{Pd}(\text{CN})_4]^{2-}$ anion because the CN vibration in pure **23** exhibits a single band at 2125 cm^{-1} while in the CHCl_3 adduct a splitting into two bands (at 2127 and 2132 cm^{-1}) is observed; the CN stretching frequency of the isonitrile ligands of the cation are invariant to CHCl_3 uptake.

Bailey and Hupp reported on chemoresponsive diffraction gratings which make use of the vapochromic ($[\text{Pt}(\text{CN}-\text{C}_6\text{H}_4-\text{C}_{10}\text{H}_{21})_4][\text{Pd}(\text{CN})_4]$ material (**23**)).⁷⁷ A film of compound **23** was cast onto a patterned poly(dimethylsiloxane) stamp having $5 \times 5\ \mu\text{m}^2$ wells arranged periodically, and

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3 the stamp was subsequently brought into contact with a transparent microscope slide. The lattice
4 periodicity of 10 μm is nicely observable by AFM and permits the diffraction of visible light.
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6 The uptake of chloroform vapor by the vapochromic layer results in an increase of the refractive
7 index of the diffraction grating because voids (or initially present water molecules) in the
8 vapochromic material are replaced by an organic substance. The increase in refractive index
9 difference between grating and surrounding medium in turn causes an increase in diffraction
10 efficiency. This effect is particularly strong when using light of a wavelength at which the
11 diffraction lattice absorbs: Using 632.8 nm as an irradiation wavelength the loss-corrected
12 diffraction efficiency is ~ 3000 times larger than when irradiating at a wavelength where the
13 lattice does not absorb. Because the magnitude and the direction of the vapor-induced absorption
14 band shifts in compound **23** depends on the VOC, the resonance effect observed in diffraction
15 efficiency at a given irradiation wavelength is dependent on analyte, i. e., the effect shows
16 certain solvent selectivity. Based on uptake isotherms a detection limit of a few mg/m^3 was
17 estimated for CHCl_3 vapor.
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21 Analogous double salts with tetracyanoplatinate(II) instead of tetracyanopalladate(II) anions
22 exhibit vapochromism as well. On the cations, arylisocyanide ligands ($p\text{-CN-C}_6\text{H}_4\text{-C}_n\text{H}_{2n+1}$) with
23 $n = 1, 6, 10, 12, 14$ were explored, and it was found that compounds with $n = 1, 6$ (**24a**, **24b**)
24 respond better to polar VOCs whereas compounds with $n > 6$ are more sensitive to nonpolar
25 VOCs (**24c**, **24d**, **24e**) with compound **24c** ($n = 10$) being the most responsive.⁷⁸ Despite the
26 change from a 4d to a 5d metal in the dianion, there is still a significant size mismatch between
27 counterions which is important for the reversible vapochromism of this family of compounds
28 (Figure 13).
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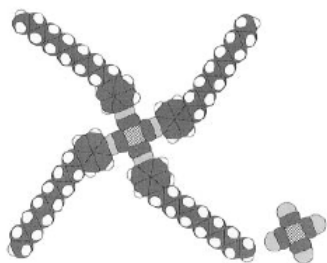
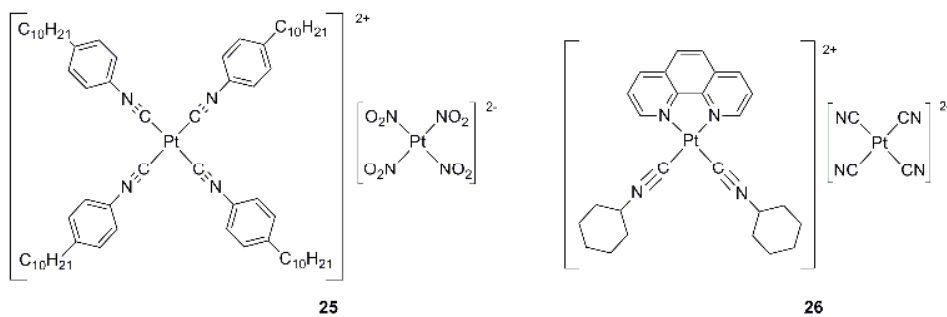


Figure 13. Space-filling model of double salt **24d**. Reprinted with permission from ref. ⁷⁸.
Copyright 1998 American Chemical Society.

These Pt(II)-Pt(II) double salts are mostly insoluble solids with a blue color, caused by a $d\sigma^* \rightarrow p\sigma$ transition arising from $5d_{z^2}-5d_{z^2}$ and $6p_z-6p_z$ orbital overlaps between neighboring Pt(II) atoms in linear stacks of alternating cations and anions (Figure 2). In neat **24c** the maximum of the respective absorption is at 746 nm, and upon exposure of a thin film of **24c** to CHCl_3 λ_{max} shifts to 837 nm. Methanol, ethanol, 2-propanol, diethyl ether, acetonitrile, hexanes, acetone, benzene, and dichloromethane produce vapochromic shifts as well, but to a smaller extent than chloroform (11 – 65 nm). The luminescence of **24c** is affected by vapor sorption, too, but the emission band maximum of neat **24c** is already outside the visible spectral range (944 nm) and further moves into the NIR upon vapor sorption (e. g., to 1018 nm for CHCl_3). The timescale of the vapochromic response is ~ 500 ms ($t_{1/2}$). IR spectroscopy monitoring the CN stretching vibrations of the cyanide and arylisonitrile ligands indicates that solvents capable of forming hydrogen bonds mostly interact with the $[\text{Pt}(\text{CN})_4]^{2-}$ anion, whereas apolar VOCs (e. g., benzene) cause very small shifts in $\nu(\text{CN})$ but produce a significant change in the NIR portion of the optical absorption spectrum. From these observations it was concluded that the vapochromic response of this family of compounds is governed by a complicated interplay of hydrogen-bonding, lipophilic, and dipole-dipole interactions.

In-depth IR studies of **24c** revealed a correlation between the cyanide stretching frequency and the hydrogen-bonding ability of the adsorbed VOC,⁷⁹ as expressed by Abraham's α parameter.⁸⁰ The vapor-induced $\nu(\text{CN})$ shifts are between 1 and 17 cm^{-1} . The only solvent which does not at all fit into the correlation between $\nu(\text{CN})$ and α is water, due to its inability to pass the hydrophobic barriers imposed by the long alkyl chains of the dicationic.

Scheme 9. Vapochromic d^8-d^8 double salts, part III.

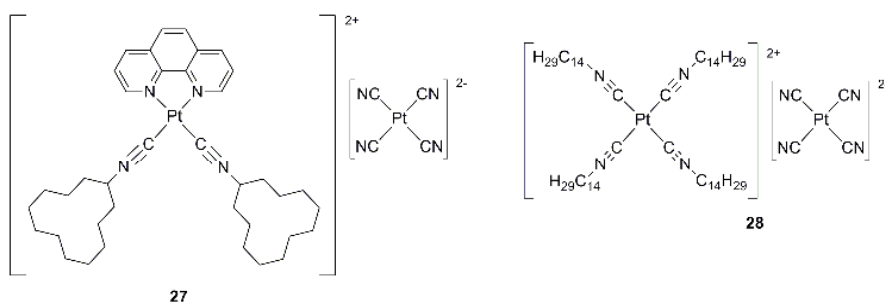


Based on the double salt family of vapochromic compounds several molecular devices were constructed. The first to be mentioned here is that of a vapochromic light-emitting diode (LED).⁸¹ For this purpose, a 700-nm layer of tris-(4-(2-thienyl)phenylamine) was deposited on an ITO coated glass and oligomerized anodically to produce a hole transport layer. This was followed by casting a 200-nm film of compound **25** (Scheme 9) on top. Finally, vapor deposition was used to deposit a 700-nm film of aluminum on top of everything. Application of an external voltage then resulted in electron flow from aluminum through the two molecular layers to ITO, inducing electroluminescence with a photon/electron efficiency of about 0.01%. The electroluminescence was clearly due to compound **25** and exhibited a similar response to acetone vapor as the photoluminescence spectrum of **25**, namely a shift of λ_{max} from 540 to 575 nm. The

motivation for using **25** with its tetranitroplatinate(II) anion instead of the analogous tetracyanoplatinate(II) salt (**24c**) was mainly the experience that **25** forms better films.

A device containing the same components but with somewhat different film thicknesses was used as a vapochromic photodiode.⁸² Rectification of the current favoring electron flow from aluminum through the two molecular layers was observed, the rectification ratio at 5 Volts was ~100. Under application of 2 Volts of reverse bias it is possible to induce a photocurrent using the visible light output of a 450 W Xenon lamp. When blowing acetone vapor into the device, the photocurrent increased more than 10 times within 2 minutes. It was noted that this photodiode acts like vapochromic absorption sensor without the need for a separate detector.

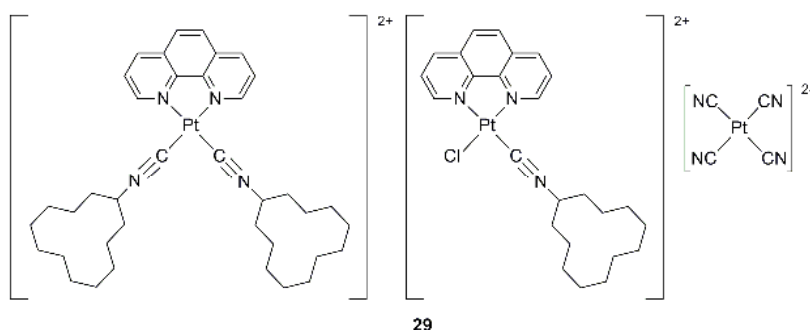
Scheme 10. Vapochromic d⁸-d⁸ double salts, part IV.



In addition to the vapochromic LED and the vapochromic photodiode Mann and coworkers reported on electronic nose devices based on vapoluminescent Pt(II)-Pt(II) double salts.^{83, 84} The principle of electronic noses is to use an array of chemical substances which respond differently when exposed to different vapors such that one obtains a response pattern from which one is able to discriminate between various odors.^{2, 85} Using a combination of compounds **27**, **28** and **26** (Scheme 10), deposited in submilligram quantities onto inert support disks made from platinum or carbon fibers, it was possible to construct a device which is able to differentiate chloroform,

water, methanol, and dichloromethane from a broad variety of other solvent vapors. Interestingly, the device is able to differentiate between two the isomeric forms of propanol, but *n*-hexane and cyclohexane are not well resolved from each other.⁸³ The discrimination ability of this device relies on the fact that compounds **27** and **26** give differently pronounced gradual vapor-induced luminescence shifts, whereas compound **28** acts essentially as a binary sensor with only two distinct responses. Principal component analysis of the overall luminescence spectra after vapor exposure then permits distinction between different vapors.

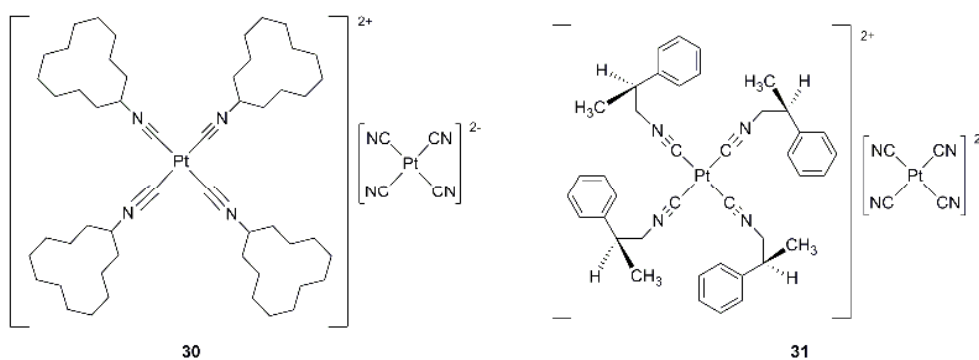
Scheme 11. Vapochromic d⁸-d⁸ double salts, part V.



In subsequent electronic nose studies, compound **28** was replaced by the more temperature-resistant compound **29**, a mixed cation platinum(II) double salt which can be formulated as [dication]₂[monocation]₂[Pt(CN)₄]₃ (Scheme 11).⁸⁴ This was necessary because heating and cooling cycles of the array elements while purging with N₂ gas between solvent vapor exposures turned out to be the most effective way to increase the reversibility and reproducibility of the device response. In addition, elevated operating temperatures (typically 50°C) did at least partially eliminate the problem of undesired devices responses to air humidity. Using principal component analysis of vapor-induced luminescence changes the electronic nose constructed from

compounds **27**, **26** and **29** was able to differentiate between 10 different solvents. The detection limit for acetone was at 12% saturation (75 g/m^3), for methanol an even lower detection limit of 3% (6 g/m^3) was determined.⁸⁴

Scheme 12. Vapochromic d^8-d^8 double salts, part VI.



Unusually direct insight into the phenomenon of vapo-chromism in Pt(II)-Pt(II) double salts was obtained from investigation of compound **30** using a quartz crystal microbalance on which mass changes and spectral changes as a function of water uptake from air humidity could be detected simultaneously (Scheme 12).⁸⁶ The employed experimental setup revealed a type of behavior which was not previously known for this class of compounds, namely a strongly nonlinear response behavior to varying concentrations of water vapor. At low water vapor concentrations compound **30** sorbs 0.5 water molecules per formula unit, followed by a sudden uptake of 2.5 water molecules per formula unit when the water vapor concentration increases to ~25% relative humidity. This phenomenon is accompanied by a stepwise change of the reflectance spectrum of compound **30** on the quartz crystal microbalance, i. e., optical spectroscopic and sorptive properties of thin films of **30** changed in a correlated fashion. CH_2Cl_2 and CHCl_3 vapors produce reflectance changes as well, but as their concentrations are increased

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3 the step-like response behavior is much less pronounced than for water vapor. Benzene, toluene,
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5 and *p*-xylene induce a gradual vapochromic response. It thus appears that vapors capable of
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7 hydrogen-bonding produce fundamentally different optical species in **30** than non-hydrogen-
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9 bonding VOCs.
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12 Starting from enantiomerically pure isocyanide ligands, Drew, Mann and coworkers recently
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14 synthesized and explored a double salt which is capable of enantiomerically selective
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16 vapoluminescence sensing.⁸⁷ Compound **31** with chiral β -methylphenethylisocyanide ligands on
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18 the cation can be obtained in pure *R*- and *S*-forms, and the two enantiomers are able to
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20 differentiate between vapors of *R*-2-butanol and *S*-2-butanol. The enantiomeric selectivity cannot
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22 be pinned down to one specific effect but was rather considered as resulting from a combination
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24 of three possible effects: (i) differential selective hydrogen-bonding between the chiral 2-butanol
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26 guest and the cyanide ligands, (ii) selective solvation at the chiral host sites, and (iii) selective
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28 permeation of the chiral guest into the interstitial voids of the chiral host. Compound **31** suffers
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30 from water sensitivity and stability issues which need to be resolved before efficient
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32 vapochromic devices with enantiomeric selectivity can be envisaged; however, the proof of
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34 concept has clearly been provided.
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43 2.3 Cationic Pt(II) complexes with tridentate N[^]N[^]N ligands

44 2.3.1 Terpyridine complexes

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50 Electrostatic repulsion is a significant obstacle to obtaining stacks of cationic Pt(II) complexes
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52 with short metallophilic contacts. In view of this problem, many researchers have turned their
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attention to 2,2':6',2''-terpyridine ligands because they have strong σ -donating and π -accepting character, because these properties are beneficial for Pt(II)-Pt(II) stacking.

Scheme 13. Pt(II) terpyridine complexes, part I.

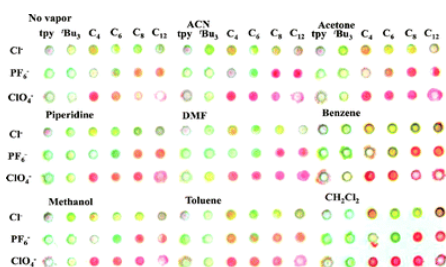
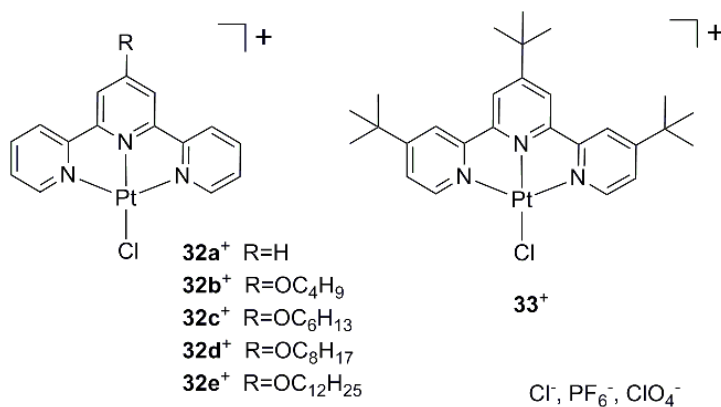
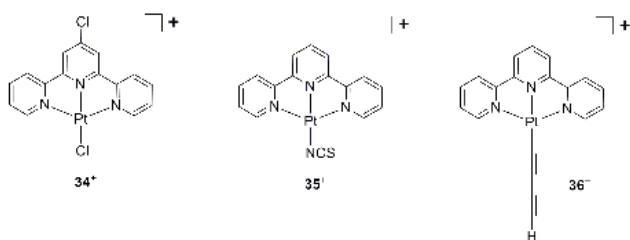


Figure 14. Vapochromic response of microarrays with complexes $32a-e^+ - 33^+$. Reprinted with permission from ref. ⁸⁸. Copyright 2008 The Royal Society of Chemistry.

Among the structurally most simple Pt(II) terpyridine complexes that have been investigated in the context of vapochromism and vapoluminescence are the cations $32a-e^+ - 33^+$ which were each isolated as a chloride, hexafluorophosphate, and perchlorate salt, resulting in a total of 18 compounds (Scheme 13).⁸⁸ 4 nmol portions of these substances were put into 6×3 microarrays from which the vapor-induced color and luminescence changes could be detected using a flatbed

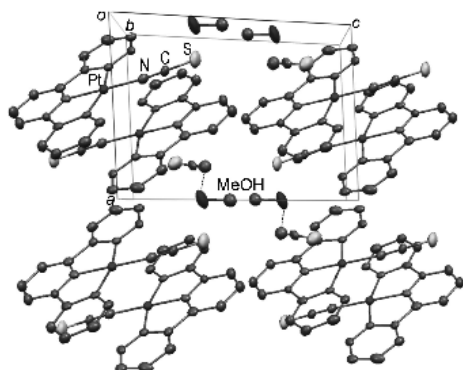
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3 scanner (Figure 14). Alkoxy-substituents on terpyridine were used because they have previously
4 been demonstrated to favor π -stacking,⁸⁹ whereas the *tert*-butyl groups are likely to lead to
5 longer metal-metal contacts. Variation of the counterion affects packing of the Pt(II) terpyridine
6 cations in the crystals.⁴⁸ Making these simple chemical variations on the
7 chloro(terpyridine)platinum(II) backbone, it was hoped that exposure to different VOCs would
8 produce distinct colorimetric / luminometric patterns and that the microarrays would be able to
9 qualitatively mimic the olfactory system.⁸⁸ Indeed, the individual Pt(II) salts respond
10 distinctively to different analytes, but research on microarrays with these salts did not go far
11 beyond providing the proof of concept. Anyhow, it was demonstrated that VOCs with lone pairs
12 such as acetonitrile, piperidine and DMF produce the greatest vapochromic and vapoluminescent
13 changes in the salts of complexes **32a-e**⁺ – **33**⁺.
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32 **Scheme 14.** Pt(II) terpyridine complexes, part II.
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Despite its chemical simplicity the chloride salt of the (4-chloro(terpyridine)platinum(II) complex **34**⁺ is a highly selective vapoluminescent sensing material (Scheme 14).⁹⁰ It responds only to methanol vapor whereas all other tested VOCs, including halogenated solvents (CH₂Cl₂, CHCl₃, CCl₄), aromatic substances (benzene, toluene, *p*-xylene, pyridine), amines (triethylamine, diethylamine, diisopropyl amine), other alcohols (ethanol, isopropanol, *n*-butanol, *t*-butanol),

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3 THF, diethyl ether, acetone, ethyl acetate and alkanes elicit no response. Methanol uptake is
4 accompanied by a color change from red to yellow, and the emission band maximum undergoes
5 a blue-shift from 665 nm to 615 nm. Even though no crystallographic data is available it is
6 reasonable to assume that the red form contains short Pt(II)-Pt(II) contacts which make a
7 $^3\text{MMLCT}$ state the energetically lowest and emissive excited state, whereas the yellow color of
8 the methanol-exposed material signals the absence of significant metallophilic interactions.
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10 Consequently, the vapoluminescence response most likely relies on the disruption metal-metal
11 contacts and changeover from $^3\text{MMLCT}$ to $^3\text{MLCT}$ emission. In addition to the unusual
12 selectivity, the high reversibility of the vapoluminescence response is an attractive feature of
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25 **34Cl**.



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43 **Figure 15.** Packing diagram for **35SCN·MeOH**. Reprinted with permission from ref. ⁹¹.
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45 Copyright 2009 The Chemical Society of Japan.

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50 After the chloro(terpyridine)platinum(II) complexes the chemically next simple Pt(II)
51 terpyridine exhibiting vapochromism is the thiocyanato complex **35⁺**. When exposing the
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53 rhodanide salt of this complex (**35SCN**) to methanol vapor, an unusual stepwise vapochromism
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3 response is detected.⁹¹ Initially, the **35**SCN compound is red but upon methanol exposure there is
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5 first a color change to dark red before the material turns yellow. The structure of the yellow
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7 compound was determined by X-ray diffraction on single crystals grown from methanol solution
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9 and was found to consist of dimers of cations with an intermetallic distance of 3.4567(3) Å
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11 (Figure 15). Between individual dimers there are no metal-metal contacts shorter than 6 Å.
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13 Methanol solvate molecules are hydrogen-bonded to the N atoms of the NCS⁻ anions, forming
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15 one-dimensional channels along the crystallographic b-axis. In air, the yellow crystals rapidly
16
17 change to red due to facile methanol loss. On the basis of combined diffuse reflectance and
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19 powder X-ray diffraction studies, a two-step structural transformation from the initial red
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21 methanol-free form to an intermediate dark red form containing some methanol to finally a
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23 yellow fully adsorbed form was postulated. The color changes were explained by an increase of
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25 π - π stacking and/or Pt(II)-Pt(II) interactions when the first methanol molecules enter the
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27 structure of neat **35**SCN, followed by a decrease of the respective interactions in the course of
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29 further methanol uptake. In other words, methanol sorption is accompanied by shrinking and
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31 elongation processes resembling a breathing motion of the crystalline lattice.⁹¹
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39 The hexafluoroantimonate salt of **35**⁺ was found to exhibit vapochromic behavior which is
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41 selective and reversible for vapors of acetonitrile, DMF, and pyridine.⁹² Using ¹⁵N NMR
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43 spectroscopy it was demonstrated that in solution 95% of the complexes have nitrogen-bound
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45 NCS ligands while only 5% are sulfur-bound, and this was explained by the electron-
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47 withdrawing nature of the terpyridine ligand making the Pt(II) center relatively hard. The crystal
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49 structure of the acetonitrile solvate **35**SbF₆·CH₃CN contains dimers of cations with Pt(II)-Pt(II)
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51 distances of 3.293(1) Å, the shortest intermetallic distance between individual dimers is 4.246(1)
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53 Å. The crystal structure of **35**SbF₆ without CH₃CN is not known, but it is assumed that the Pt(II)-
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Pt(II) interactions within dimers are retained when acetonitrile is removed and that intact cation dimers can slide into new positions such that an infinite linear chain structure with extensive Pt(II)- Pt(II) interactions is adopted. This structural transformation would explain the maroon color and the observation of $^3\text{MMLCT}$ emission of neat 35SbF_6 . Upon exposure to acetonitrile, DMF or pyridine the maroon color rapidly changes to yellow, and thermogravimetric studies demonstrated that 1 equivalent of CH_3CN or 0.5 equivalents of DMF or pyridine are adsorbed. The solvates can be converted back to the neat material upon gentle heating.

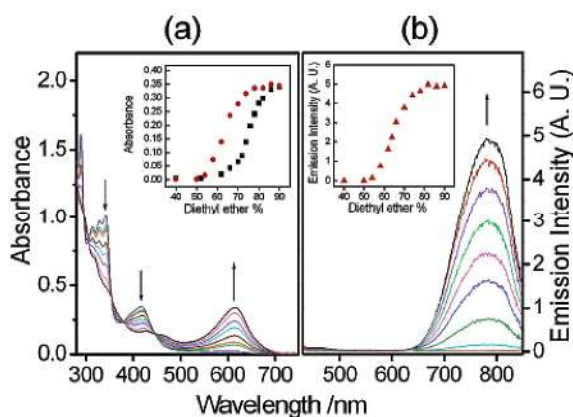
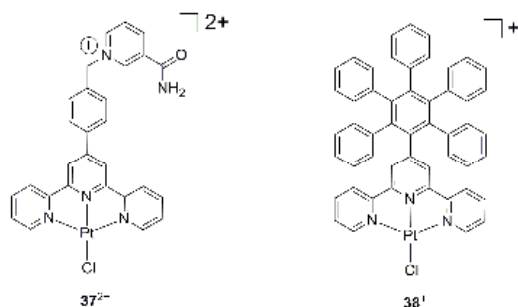


Figure 16. (a) Absorption and (b) emission changes as a function of diethyl ether addition to acetonitrile solutions of compound **36**. Reprinted with permission from ref. ⁶⁴. Copyright 2002 American Chemical Society.

A Pt(II) terpyridine diynyl complex was found to exhibit strong solvatochromism but no vapochromism and will therefore be treated only very briefly here.⁶⁴ $[\text{Pt}(\text{tpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$ (**36**) crystallizes in a dark green form with platinum atoms arranged in a linear chain with intermetallic contacts of 3.388 Å, and a red form exhibiting a dimeric structure with zigzag arrangement and alternating short (3.394 Å) and long (3.648 Å) Pt(II)-Pt(II) distances. When

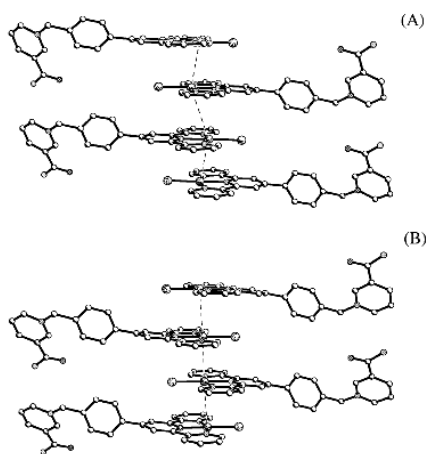
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3 dissolved at $\sim 10^{-4}$ M concentration in CH_3CN the color of the resulting solution is yellow but
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5 upon addition of increasing amounts of diethyl ether the color changes first to green and finally
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7 to blue (Figure 16). This phenomenon has been explained by solvent-induced aggregation of
8
9 individual Pt complexes to dimer, trimer, or even oligomer structures. Moreover, ether addition
10
11 induces a dramatic enhancement of the luminescence emitted by these solutions; the emission
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13 has been assigned to a $^3\text{MMLCT}$ state.
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20 **Scheme 15.** Pt(II) terpyridine complexes, part III.
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37 A study of a Pt(II) terpyridine-nicotinamide complex (37^{2+}) (Scheme 15) provided unusually
38
39 direct insight into the phenomenon of vapochromism because it was possible to structurally
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41 characterize both the neat form of $37(\text{PF}_6)_2$ as well as its CH_3OH adduct using *the same* single
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43 crystal before and after methanol vapor exposure.⁹³ This is remarkable because such single-
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45 crystal transformations involving the loss or gain of solvent molecules while at the same time
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47 retaining the integrity of the crystal lattice are rare. Both the red solvent-free form and the orange
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49 methanol adduct contain dimers of cations which are doubly hydrogen-bonded through their
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51 nicotinamide groups.⁹³ There are three important differences in cation packing between the two
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53 forms: (i) the Pt-Pt-Pt arrangement is significantly more linear in the red form (Pt-Pt-Pt angle of
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3 171.9°) than in the orange form (126.7°) (Figure 17); (ii) the separation between the planes of
4 individual tpy ligands alternates between 3.453 Å and 3.660 Å in the red form (distance between
5 N-atoms of central pyridine ring), but increases to alternating distances of 3.692 Å and 3.763 Å
6 in the orange form; (iii) the Pt(II)-Pt(II) distances increase from 3.301 Å / 3.336 Å in the red
7 form to 3.622 Å / 3.964 Å in the orange form. These structural changes clearly help to promote
8 π - π stacking and Pt(II)-Pt(II) interactions between neighboring complexes in the solvent-free red
9 form, while such interactions are essentially absent in the orange methanol adduct. Accordingly,
10 the emission of red **37**(PF₆)₂ is assigned to a ³MMLCT state (λ_{max} = 660 nm) while the
11 luminescence of **37**(PF₆)₂·CH₃OH (λ_{max} = 630 nm) is attributed to ³MLCT emission of isolated
12 chromophores. Thus, compound **37**(PF₆)₂ is not only vapochromic but also vapoluminescent. It
13 exhibits a selective and reversible vapochromic response when exposed to methanol, acetonitrile,
14 or pyridine.⁹³



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Figure 17. Stacking of complexes in (a) **37**(PF₆)₂·CH₃OH (orange form) and (b) **37**(PF₆)₂ (red form). Reprinted with permission from ref. ⁹³. Copyright 2004 American Chemical Society.

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3 A platinum(II) complex with a pentaphenyl-benzene moiety linked to a terpyridine chelating
4 agent (**38Cl**) has been reported to exhibit unusually large vapor-induced luminescence band
5 shifts from the red to the green spectral range upon exposure to VOCs (Figure 18).⁹⁴ This
6 vapoluminescence response is relatively selective and occurs only for CH₂Cl₂, ethanol, CH₃CN,
7 and ethyl acetate although the response time is by far the shortest for CH₂Cl₂. The initial red
8 form of **38Cl** is a methanol adduct and contains Pt(II) cations which are stacked in a spiral
9 fashion with each complex rotated by ca. 120° along the stacking direction. There are four
10 independent nearest-neighbor Pt(II)-Pt(II) distances in this helix, two of which (3.30 Å and 3.34
11 Å) are indicative of metallophilic interactions. Therefore it has been concluded that the red
12 emission ($\lambda_{\text{max}} = 654 \text{ nm}$) of this form originates from a ³MMLCT state. Crystals of the green
13 form of **38Cl** were grown from dichloromethane solution and contain one molecule of CH₂Cl₂
14 (instead of CH₃OH) per formula unit. This entails a dramatic change in cation packing and leads
15 to a zigzag arrangement of neighboring Pt(II) complexes which are now found to be in head-to-
16 tail orientation with Pt(II)-Pt(II) distances (3.9092(9) Å and 4.5483(11) Å). Both of these
17 distances are both significantly beyond what can be considered a metallophilic contact.
18 Consequently, the green emission ($\lambda_{\text{max}} = 514 \text{ nm}$) of this form was attributed to ³MLCT
19 luminescence from isolated Pt(II) terpyridine chromophores. Clearly the disruption of Pt(II)-Pt(II)
20 interactions is responsible for the strong vapochromic and vapoluminescence response of
21 compound **38Cl**.
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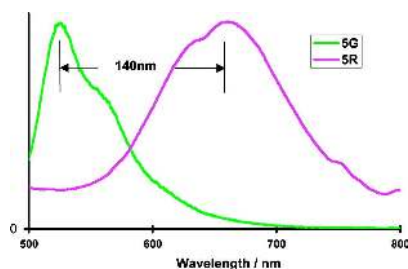
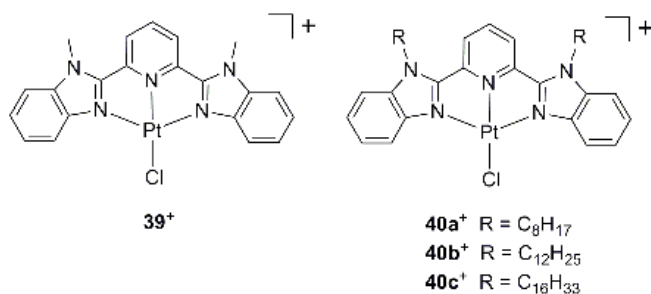


Figure 18. Photoluminescence of the green (5G) and red (5R) form of **38Cl**. Reprinted with permission from ref. ⁹⁴. Copyright 2008 American Chemical Society.

An interesting aspect is the absence of thermochromism of the red form of **38Cl**.⁹⁴ This is noteworthy because linear-chain compounds with stacked Pt(II) complexes exhibiting ³MMLCT luminescence often show a pronounced red-shift of the emission with decreasing temperature due to contraction of the crystal lattice and a shortening of Pt(II)-Pt(II) distances, resulting in a smaller HOMO/LUMO energy gap.^{13, 46} The absence of thermochromism in red **38Cl** is presumably due to the bulky nature of the pentaphenyl-benzene unit and its propeller-shaped nature which impedes tighter stacking of individual Pt(II) complexes at lower temperatures.

2.3.2 Complexes with 2,6-bis(*N*-alkylbenzimidazol-2'-yl)pyridine

Scheme 16. Vapochromic 2,6-bis(*N*-alkylbenzimidazol-2'-yl)pyridine complexes.



Complex **39**⁺ (Scheme 16) forms vapochromic salts with chloride and hexafluorophosphate anions.⁹⁵ **39**Cl changes color from yellow-orange to red when exposed to methanol, ethanol, chloroform, or acetonitrile (Figure 19). A color change from yellow to violet is detected upon exposure of **39**PF₆ to acetonitrile, but many other solvents (including water, methanol, ethanol, 2-propanol, diethyl ether, CH₂Cl₂, CHCl₃, CCl₄, acetone, hexanes, and benzene) produce no response. Gravimetric studies indicate that **39**Cl sorbs up to two molecules of CH₃OH per formula unit whereas **39**PF₆ can only sorb one equivalent of CH₃CN. Unlike for some of the Pt(II) terpyridine materials from the prior section in which VOC uptake results in the disruption of metallophilic contacts, the yellow-to-red color change observed for **39**Cl and **39**PF₆ rather suggests that Pt(II)-Pt(II) interactions strengthen in the course of methanol and acetonitrile sorption. Indeed, 2,6-bis(*N*-alkylbenzimidazol-2'-yl)pyridine complexes of Pt(II) are known to have a strong tendency to aggregate in solution.^{47, 96}

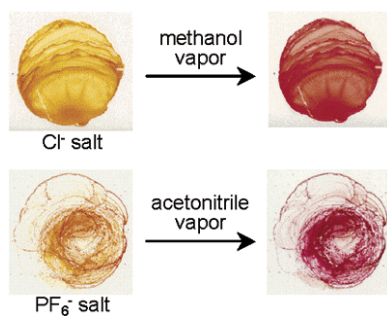


Figure 19. Vapochromic response of **39**Cl and **39**PF₆. Reprinted with permission from ref. ⁹⁵.

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3 In the crystal structure of **39**PF₆·DMF Pt(II) complexes are oriented in zigzag head-to-tail
4 arrangement with long intermolecular contacts (4.336(2) Å and 4.565(2) Å) but comparatively
5 short distances between the ligand planes (3.35 Å and 3.39 Å).⁹⁷ Chloride anions and DMF
6 solvent molecules fill the voids between the columns of cations. Exposure of single crystals of
7 **39**PF₆·DMF to acetonitrile vapor induced a color change from orange to violet as noted above for
8 powder samples of solvent-free **39**PF₆, but subsequent X-ray diffraction yielded only powder
9 rings. Thus, the precise structure of the acetonitrile adduct remains unknown, but an interesting
10 hypothesis has been put forward: The slippage of Pt(II) complexes by 1.35 Å along vectors lying
11 parallel to the plane of each complex to give cation dimers with Pt(II)-Pt(II) distances of ~3.39 Å
12 is conceivable since this represents the simplest imaginable deformation upon CH₃CN uptake.
13 This structural rearrangement would be in line the yellow-to-violet color change and the high
14 reversibility of the vapochromism.
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31 An unrelated but noteworthy observation is that orange powder samples of **39**PF₆ quickly sorb
32 1 equivalent of DMF and turn violet, but the **39**PF₆·DMF single crystals grown from mixed
33 CH₃CN/DMF solution are orange and unresponsive to DMF vapor. These observations suggest
34 that there is both an orange and a violet polymorph of the DMF adduct.
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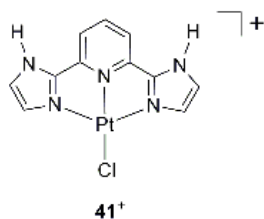
41 When complex **39**Cl is incorporated into a zirconium phosphate (ZrP) framework, a different
42 type of vapochromic behavior is observed.⁹⁸ First of all, different colors than in neat **39**Cl are
43 obtained with certain VOCs. Secondly, despite the lower concentration of the platinum(II)
44 complexes in ZrP compared to neat **39**Cl, the color response is equally strong or even stronger in
45 the inorganic framework. The Pt:ZrP ratio was typically between 1:5 and 1:30, yet the
46 vapochromic response upon exposure to water, MeOH, CH₃CN, CH₂Cl₂, THF, benzene, and *n*-
47 hexane occurs within minutes. Interestingly, the vapochromic response patterns of the ZrP-
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3 incorporated complex are different than those of neat **39Cl** or **39PF₆**. Fast and reversible
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5 (³MMLCT) vapoluminescence responses were detected.
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8 An entire series of 2,6-bis(*N*-alkylbenzimidazol-2'-yl)pyridine complexes of Pt(II) with
9
10 various alkyl-substituents (R) and counterions was found to exhibit vapochromic behavior
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12 similar to that of **39Cl** and **39PF₆**.⁹⁹ This includes the chloride salts of complexes with R = C₈H₁₇
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14 (**40a**), C₁₂H₂₅ (**40b**), C₁₆H₃₃ (**40c**), as well as the hexafluorophosphate, perchlorate,
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16 tetrafluoroborate, triflate, and acetate salts of the complex with R = C₁₆H₃₃ (**40c**). Both the alkyl
17
18 chain length and the size of the anion affect the vapochromic response because these factors
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20 influence the molecular stacking pattern. However, no clear systematic trends could be
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22 recognized. When constructing an array from all these vapochromic substances it becomes
23
24 possible to distinguish between different VOCs, i. e., to some extent the array can function as an
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26 electronic nose. The solvents to which these arrays were exposed are acetone, acetonitrile,
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28 methanol, ethanol, dichloromethane, chloroform, ethyl acetate and benzene. The majority of the
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30 vapochromic responses involve a transition from lighter to darker color (typically from yellow-
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32 orange to red or violet), similar to what has been observed for **39Cl** and **39PF₆**, suggesting that
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34 Pt(II)-Pt(II) interactions are strengthened upon VOC uptake. Two notable exceptions are the
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36 chloride and triflate salts of **40c** which change from deep orange to yellow. In these two salts
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38 solvent uptake seems to reduce Pt(II)-Pt(II) and/or π - π interactions.
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48 2.3.3 Complexes with 2,6-bis-(1*H*-imidazol-2-yl)pyridine 49 50 51 52

53 **Scheme 17.** A vapochromic Pt(II) 2,6-bis-(1*H*-imidazol-2-yl)pyridine complex.
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Complex **41**⁺ was synthesized along with a few other related complexes with a view to obtaining a quasi-2D framework made of planar Pt(II) complexes.¹⁰⁰ The idea was to exploit Pt(II)-Pt(II) interactions and π - π stacking to induce ordering of individual complexes along one direction while at the same time making use of hydrogen-bonding interactions to induce ordering along a second direction. In the course of these studies it was discovered that **41**Cl is a vapoluminescent substance. Solvent-free **41**Cl exhibits emission with λ_{max} at 525 nm, the occurrence of vibrational fine structure with $\sim 1500\text{ cm}^{-1}$ intervals between individual progression members suggests that the emission contains significant intraligand π - π^* character. When brought in contact with vapors from CH_2Cl_2 , CH_3CN , CH_3OH or acetone, the emission red-shifts to $\lambda_{\text{max}} = 630\text{ nm}$ and becomes broad and unstructured. The red emission has been tentatively attributed to the presence of close Pt(II)-Pt(II) contacts or π - π interactions between ligands. Support for this hypothesis comes from the X-ray crystal structure of **41**Cl \cdot DMSO \cdot 2H₂O which exhibits intermolecular π - π distances of 3.370 Å and 3.395 Å, but in this specific solvate structure the shortest Pt(II)-Pt(II) distance is 4.33 Å.

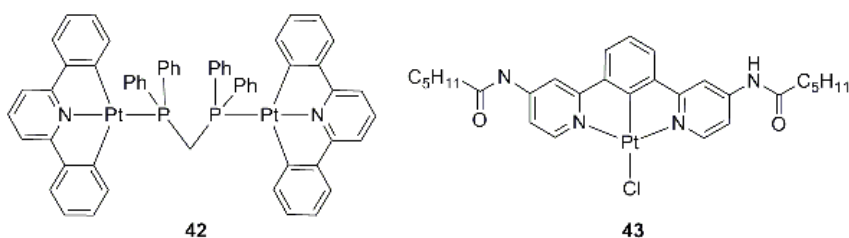
An electron mobility value of $0.4\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ has been determined for solvent-free **41**Cl which is a low value compared to that measured for a related 2,6-bis(1*H*-pyrazol-3-yl)pyridine complex of Pt(II) ($20\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).¹⁰⁰ Cofacial π - π and Pt(II)-Pt(II) interactions are thought to be responsible for the high electron mobility in the pyrazolyl-complex. It has been noted that if such

interactions could be induced by vapor (e. g., in **41Cl** or related other materials), transistor-based sensors and other multi-functionalized optoelectronic devices could be created based on Pt(II) complexes.

2.4 Cyclometalated Pt(II) complexes

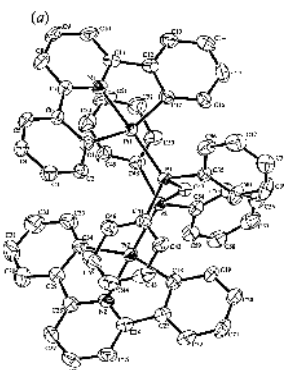
2.4.1 Complexes with 2,6-diphenylpyridine (N[^]C[^]N) ligands

Scheme 18. Vapochromic cyclometalated Pt(II) complexes, part I.



The bis(diphenylphosphino)methane (dppm) bridged dinuclear Pt(II) complex **42** (Scheme 18) is a vapochromic substance functioning on the basis of intramolecular π - π stacking rather than inter- or intramolecular Pt(II)-Pt(II) interactions.¹⁰¹ Both a solvent-free yellow form and an orange chloroform adduct of this charge-neutral complex were characterized crystallographically, and it was found that the yellow form exhibits weak π - π interactions between one of the Pt(N[^]C[^]N) planes and a phenyl ring of the dppm ligand with interplanar separations ranging from 3.38 Å to 3.67 Å. In the orange chloroform adduct each Pt(N[^]C[^]N) plane makes a π - π interaction with a phenyl ring from different P-atoms of the dppm ligand, and the interplanar distances are in the range of 3.12 Å to 3.29 Å (Figure 20), i. e., noticeably shorter than in the yellow form. A variety of different VOCs (CH₂Cl₂, CH₃OH, acetone, benzene,

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3 pentane) induce a change in color from yellow to orange, and given the structural information
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5 from above it appears plausible to conclude that each of these solvents induces a strengthening of
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7 intramolecular π - π interactions when sorbed by the yellow form of **42**.
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26 **Figure 20.** Crystal structure of **42**. Reprinted with permission from ref. ¹⁰¹. Copyright 2001
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28 American Chemical Society.
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34 The amide-decorated [Pt(2,6-diphenylpyridine)Cl] complex **43** exhibits an interesting
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36 combination of mechanochromism and vapochromism.¹⁰² When crystallizing from DMF, one
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38 obtains green emitting **43**·DMF. This material exhibits sharp diffraction peaks in powder X-ray
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40 analysis. When **43**·DMF is ground in a ceramic mortar one obtains an orange luminescent
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42 powder which does not give clear X-ray diffraction. Subsequent exposure of this amorphous
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44 substance to methanol vapors leads to **43**·CH₃OH, a yellow emitter which exhibits sharp X-ray
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46 diffraction peaks again. This two-step conversion from crystalline **43**·DMF to amorphous **43** and
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48 finally crystalline **43**·CH₃OH is a highly unusual phenomenon. X-ray diffraction studies on
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50 single crystals reveal long Pt(II)-Pt(II) contacts of 4.854 Å between nearest neighbors in the
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52 DMF adduct, whereas in **43**·CH₃OH the shortest intermetallic separation is only 3.385 Å. The
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54 observation of metal-metal distance shrinking may explain the change from green to red
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luminescence accompanying the two-step transformation from **43**·DMF to **43**·CH₃OH. The hydrogen-bonding ability of the dangling amide groups is suspected to play an important role for the mechano- and vapochromism of **43** because the hexanoylamide groups form hydrogen-bonds to the DMF and methanol guest molecules in crystals of **43**·DMF and **43**·CH₃OH. Heating crystals of **43**·DMF to 150 °C induces release of the DMF molecule and produces the same luminescence change as grinding, suggesting that the amorphous orange-luminescent powder is a solvent-free form of **43**. Along with complex **43** two closely related Pt(II) complexes with shorter alkanoylamide groups were investigated, but these substances did not show any mechano- or vapoluminescence properties, demonstrating once again how subtle the search for materials with such properties has to be.¹⁰²

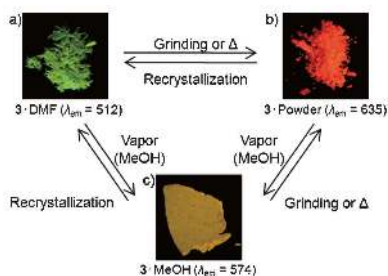
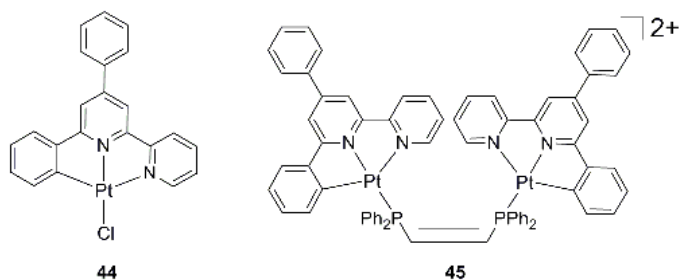


Figure 21. Mechano- and vapoluminescent properties of **43**. Copyright 2012 The Chemical Society of Japan.

2.4.2 Complexes with 6-phenyl-2,2'-bipyridine (C^NN) ligands

Scheme 19. Vapochromic Pt(II) complexes with C^NN ligands.



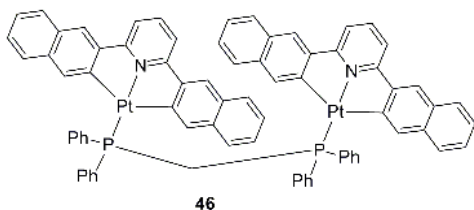
The luminescent complex **44** (Scheme 19) was reacted with amino-decorated silica gel in order to immobilize a luminescent probe on the surface of a supporting matrix.¹⁰³ It was envisioned that host-guest interactions between the surface-bound complexes and VOC analytes would affect metal-metal and/or ligand-ligand interactions to the extent that a vapochromic or vapoluminescent response would result. Indeed this turned out to be possible when using MCM-41 and MCM-48 silica gel supports which were first reacted with (3-aminopropyl)triethoxysilane and then loaded with 2.8 wt% of platinum in the form of complex **44**. The resulting material displays red emission at 662 nm (λ_{max}) at room temperature. When placing the Pt-decorated silica gel samples into an air-tight tank containing a saturated atmosphere of pentane, benzene, chloroform, or dichloromethane for ~10 minutes, the emission shifted to substantially shorter wavelength ($\lambda_{\text{max}} = 548$ nm). Drying in air for 3 days then restores the initial red luminescence. Presumably the red emission is due to ³MMLCT states resulting from tightly interacting Pt(II) complexes whereas the yellow luminescence comes from ³MLCT excited states of isolated complexes. The disruption of metal-metal and/or π - π interactions following the uptake of nonpolar solvents may potentially be explained by the high sorption capacity of silica for such substances.

Complex **45**²⁺ contains two Pt(C[^]N[^]N) units which are linked by a rigid *cis*-1,2-bis(diphenylphosphino)ethylene ligand. This dinuclear complex responds to vapors of

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3 heteroatom-containing VOCs such as acetonitrile, ethanol, diethyl ether, THF, ethyl acetate,
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6 CH_2Cl_2 , CHCl_3 by a change in color from yellow to deep red.¹⁰⁴ Since no structural information
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8 is available for compound **45** (ClO_4)₂ an explanation for its vapochromism cannot be provided. It
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10 is clear, however, that *intramolecular* stacking leading to closer Pt(II)-Pt(II) contacts after
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12 solvent exposure (as observed for the dppm-bridged dinuclear Pt(II) complex **42**) is impossible
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14 for complex **45**²⁺ due to the rigidity of the *cis*-1,2-bis(diphenylphosphino)ethylene bridging
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16 ligand.
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22 2.4.3 Complexes with 2,6-di(2'-naphthyl)pyridine (C^NC) ligands

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27 **Scheme 20.** A vapochromic dinuclear complex with C^NC ligands.



Building on the prior observation of weak vapochromism in the dinuclear dppm-bridged Pt(N^CN) complex **42** a series of dinuclear Pt(C^NC) complexes was investigated with a view to obtaining new vapochromic or vapoluminescent materials.¹⁰⁵ It was anticipated that the large π-system of 2,6-di(2'-naphthyl)pyridine would be beneficial for π-π and C-H-π interactions between this ligand and VOCs, and that the disruption of such weak non-covalent interactions would potentially entail a significant vapochromic response. In one out of four investigated complexes of this type (**46**) (Scheme 20) this turned out to be the case.¹⁰⁴ The solvent-free form

of complex **46** is a weak emitter, but exposure to a variety of different VOCs produces an enhancement of its orange-yellow luminescence ($\lambda_{\text{max}} = 602 \text{ nm}$) (Figure 22).

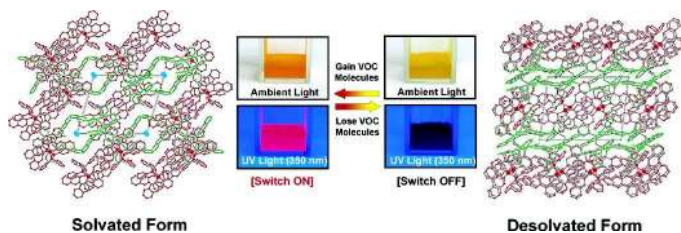


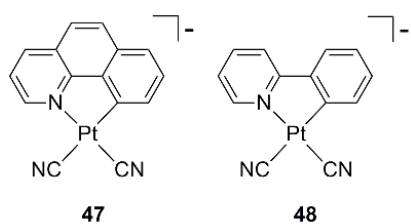
Figure 22. Changes in crystal structure, color, and photoluminescence upon vapor uptake / release by compound **46**. Reprinted with permission from ref. ¹⁰⁵. Copyright 2006 American Chemical Society.

Halogenated vapors (CH_2Cl_2 , CH_2Br_2 , CHCl_3 , 1,2-dichloroethane, 1,2-dibromoethane, CH_3I but not CCl_4) lead to particularly strong luminescence enhancements, but small polar VOCs such as acetone, diethyl ether, THF, ethyl acetate also produce a significant response. X-ray diffraction studies on $\mathbf{46} \cdot 6\text{CHCl}_3 \cdot \text{C}_5\text{H}_{12}$ reveal that both the *syn*- and *anti*-conformations of **46** are present in the combined chloroform/pentane adduct. The most notable feature of this crystal structure is the presence of continuous solvent channels with an aperture size of ca. $6.5 \text{ \AA} \times 4.3 \text{ \AA}$ along the *c*-axis (Figure 22). Such large channels are absent in the crystal structures of three analogous dinuclear complexes bearing aromatic substituents at the 4-position of the central pyridine ring of the $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ ligand, and this may understand why vapoluminescence is observed exclusively for complex **46**.¹⁰⁴ X-ray diffraction of the desolvated form shows that the crystallographic *a*-axis decreases substantially upon solvent removal, resulting in a reduction of the unit cell volume from 7374 \AA^3 to 6188 \AA^3 . The intramolecular Pt(II)-Pt(II) distance increases from $3.29(3) \text{ \AA}$ to $3.40(3) \text{ \AA}$ in the *syn* form, whereas in the *anti*-conformer there is an increase

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2
3 from 5.68(2) Å to 5.40(3) Å. In the desolvated form, individual molecules are held in place by
4
5 intermolecular π - π interactions (the relevant interplanar separations range from 3.20 Å to 3.47
6
7 Å) and by C-H- π interactions. Aggregation of the *syn*- and *anti*-forms in solvent-free **46** is tighter
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9 than in **46**·6CHCl₃·C₅H₁₂, and it has been proposed that this is the origin of the luminescence
10
11 quenching in dry **46**. In other words, the molecular conformations (*syn* or *anti*) do not appear to
12
13 play a decisive role for the vapoluminescence. Temperature-dependent luminescence studies
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15 indicate that there can be emission from a ³ $\pi\pi^*$ state of isolated complexes and excimeric ³ $\pi\pi^*$
16
17 luminescence at longer wavelengths resulting from aggregated complexes; the formation of tight
18
19 aggregates in the solvent-free form of **46** can red-shift the excimeric ³ $\pi\pi^*$ states to the extent that
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21 radiative relaxation is no longer competitive with multiphonon relaxation. Sorption of VOCs can
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23 then restore the luminescence by disruption of aggregation. The observation that acetonitrile,
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25 methanol, and ethanol produce no vapoluminescence response was explained by insufficient
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27 hydrophobicity of these solvents, whereas the insensitivity of **46** to benzene, toluene and *n*-
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29 hexane was explained by the size of these VOCs.
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40 2.4.4 Complexes with 7,8-benzoquinolinato and 2-phenylpyridine (C[^]N) ligands

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44 **Scheme 21.** Two anionic vapochromic Pt(II) complexes.



Complexes **47**⁻ and **48**⁻ (Scheme 21) are two rare examples of anionic Pt(II) complexes exhibiting vapochromism. Their optical spectroscopic properties are strongly dependent on the cation: The tetrabutylammonium salts are yellow, whereas the respective potassium salts are obtained as red and purple solids which are to be formulated as monohydrates (**K47**·H₂O and **K48**·H₂O).¹⁰⁶ When heating to 110 °C the crystal water can be removed, and this procedure induces a change in color from red or purple to yellow (Figure 23).

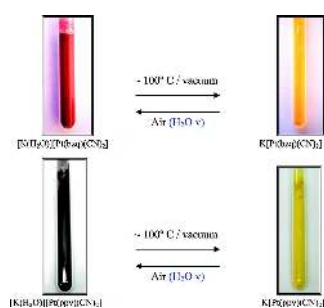


Figure 23. Color changes in **K47**·H₂O and **K48**·H₂O upon water release and uptake. Reprinted with permission from ref. ¹⁰⁶. Copyright 2008 American Chemical Society.

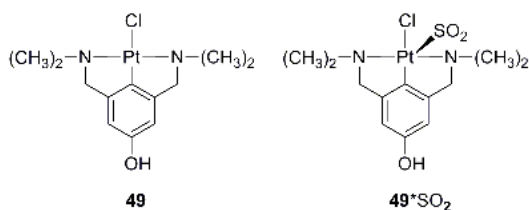
In air, the red and purple forms rapidly regenerate due to spontaneous water uptake. This behavior is opposite to that observed for red [Pt(bpy)(CN)₂] which sorbs water to form yellow [Pt(bpy)(CN)₂]·H₂O.³⁸ Apparently, in **K47**·H₂O and **K48**·H₂O short Pt(II)-Pt(II) contacts lead to MMLCT absorptions which are responsible for the red and purple colors of these forms while in the anhydrous yellow forms intermetallic contacts are largely disrupted.¹⁰⁶ Thin films of **K47**·H₂O are responsive to a variety of anhydrous VOCs with response time increasing in the order of methanol (~5 s), ethanol (~10 s), acetonitrile (~30 s), acetone (~2 min), and THF (~45 min). **K48**·H₂O does not respond to any of these anhydrous solvent vapors, perhaps because the

crystal water molecule is more strongly bound to the lattice than in the case of **K47**·H₂O. This interpretation is in line with thermogravimetric analyses.

2.4.5 Pincer complexes

The complexes presented in this chapter are exceptional vapochromic Pt(II) compounds in that they exhibit vapochromism as a result of direct ligation of the analyte to the metal center. Thus, unlike the vast majority of the other compounds from section 2, the pincer complexes in this chapter are type II vapochromic substances according to the definition used in section 1.3.

Scheme 22. Vapochromic pincer complexes, part I.



Several square-planar Pt(II) complexes with monoanionic N^{^-}C^{^-}N pincer ligands were found to be highly selective sensors for gaseous SO₂. Complex **49** (Scheme 22) self-assembles in the solid state to form a network with intramolecular hydrogen-bonds between the chloro-ligand of one complex and the hydroxyl-group of its neighbor (Figure 24).¹⁰⁷ Exposure of **49** to sulfur dioxide for ~1 minute affords the SO₂ adduct **49**·SO₂ in which a sulfur dioxide molecule is ligating to the Pt(II) center. Remarkably, the crystallinity of compound **49** is retained in the course of this process. Associated with the uptake of SO₂ is a change in coordination geometry from square-planar to pyramidal, and this affects the packing index and the density of the material.

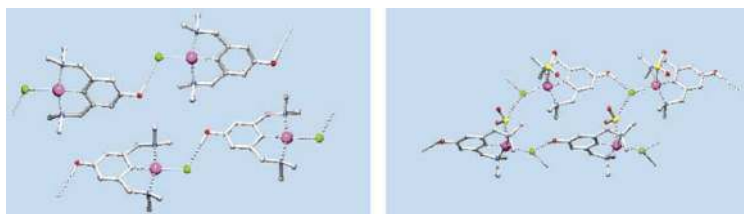
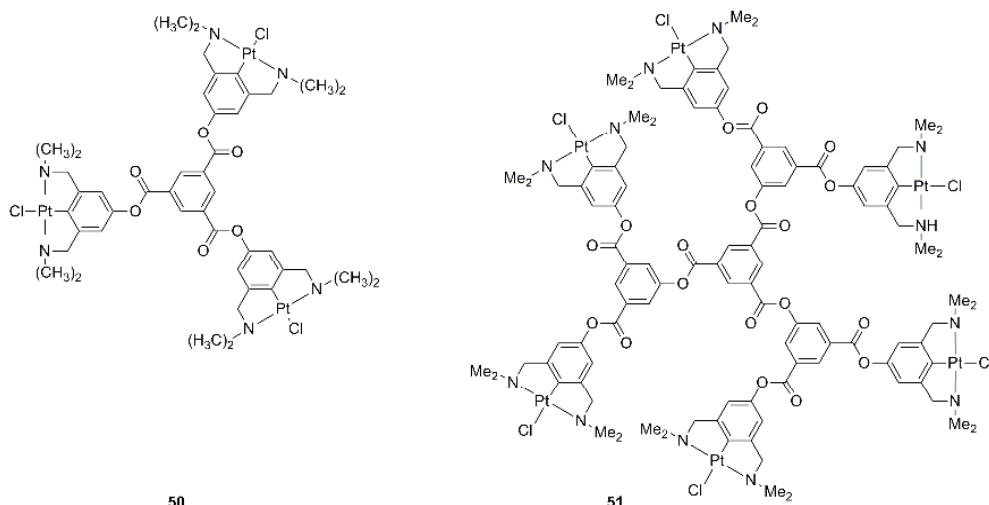


Figure 24. Extracts from the crystal structure of **49** before (left) and after SO₂ uptake (right).

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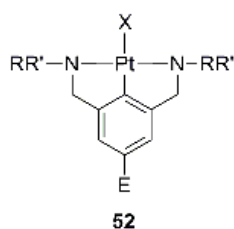
The unit cell volume increases by more than 15% upon SO₂ sorption, whereas the density decreases from 2.1606(6) g/cm³ to 2.1473(6) g/cm³. The pyramidal complex retains the hydrogen bonds between chloro-ligands and hydroxyl-groups of adjacent ligands (the O-Cl distance remains virtually unchanged: 3.126(8) Å before and 3.127(8) Å after SO₂ uptake). In addition there are non-covalent interactions between SO₂ and chloro-ligands of adjacent complexes perpendicularly to the hydrogen-bonding network. **49** is colorless while **49**·SO₂ is deep orange hence the transformation can easily be detected by naked eye. The recovery of **49** from **49**·SO₂ in an atmosphere of air was studied by time-dependent powder X-ray diffraction and infrared spectroscopy (monitoring the SO₂ stretching vibrations at 1072 cm⁻¹ and 1236 cm⁻¹), and it was concluded that SO₂ release follows a zero-order rate law with the absolute rate being strongly dependent on the surface area of the sample. It was assumed that the rate-determining step in SO₂ release is the diffusion-controlled transfer of SO₂ molecules from one complex to the other from the inner part of the crystalline material to its surface.

Scheme 23. Vapochromic pincer complexes, part II.



Immobilization of the pincer complex **49** on a surface is of interest for obtaining a functional SO_2 sensor device. Instead of layering these complexes into a polymer in which they may be less accessible to SO_2 from the atmosphere, functional dendrimers (**50**, **51**) (Scheme 23) with well-defined connectivities were synthesized and explored.¹⁰⁸ According to molecular models, the macromolecular constructs have disk-like structures with diameters of 2.4 nm and 3.4 nm, respectively, and they are found to maintain the high sensitivity for SO_2 observed for the monometallic complex **49**. When coating a cellulose surface with dendritic **50** at a density of 20 nm/mm^2 the detection of SO_2 at a concentration of $8.5 \pm 0.5 \mu\text{g}/\text{cm}^3$ is possible. Even at 190 K, the response (a change from colorless to orange) occurs within 2 ms. Exposure to SO_2 -free air regenerates the initial colorless state within a few minutes. A promising resistance against atmospheric impurities such as water and acids has also been noted.

Scheme 24. Vapochromic pincer complexes, part III.



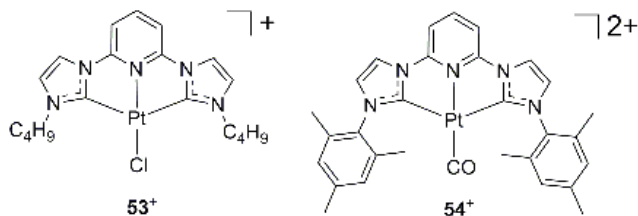
Fundamental studies in which the electronic structure and the steric bulk of mononuclear pincer complexes are varied systematically have been conducted.¹⁰⁹ On the generic structure **52** (Scheme 24) the monodentate ligand *X* was varied from Cl to Br, I, and *p*-tolyl in order to modulate the electron density at the metal center. The substituents R and R' at the nitrogen donor atoms were varied between methyl and ethyl in order to explore the influence of steric constraints on SO₂ binding. Finally, the *para*-substituent E was varied between H, OH, OSiMe₂ and ^tBu in order to tune the electron density in the aromatic system. SO₂ binding is possible irrespective of which of the four monodentate ligands (*X*) is chosen. However, SO₂ binding is suppressed when all four substituents at the N atoms are ethyl groups. At least one of them has to be a methyl-substituent otherwise there is apparently too much steric bulk. Solution titrations show that the nature of the *para*-substituent E has relatively little influence because the equilibrium constants for SO₂-binding of 7 complexes with variable E are all in the range between 8.48±0.34 M⁻¹ and 14.81±0.35 M⁻¹ in benzene. Stopped-flow experiments in benzene solution showed that the reaction of pincer complexes with different *X*, E, and R is complete within 50 μs. In air at room temperature, the complexes lose SO₂ over several weeks, but when heated to 40°C the initial state can be recovered within minutes.

Pt(II) complexes with the anionic N⁻C⁻N⁻ pincer ligand in the generic complex **52** have an enhanced nucleophilicity when compared to other d⁸ metal complexes.¹¹⁰ This explains why they react with the Lewis acid SO₂, yet the selective recognition of sulfur dioxide even in presence of

other acids such as HCl, CO₂ or H₂O is spectacular. Two additional fundamental observations are noteworthy: (i) platinum-bound SO₂ does not undergo subsequent reactions such as insertion into a metal-carbon bond or oxidation to sulfate in air; (ii) in the complexes with X = I there is no SO₂-binding to the iodide, despite the expected competitive behavior of iodide in terms of nucleophilicity.¹¹¹ In-depth mechanistic studies (theoretical and experimental) lead to the conclusion that iodide-bound SO₂ does not even play a role as a reaction intermediate during SO₂ uptake or release.¹¹² Using ¹H NMR spectroscopy the exchange rate of the SO₂ ligand on the complex with X = I, R = CH₃, and E = H was investigated at cryogenic temperatures. When extrapolating to room temperature, one obtains an exchange rate of 1.5·10⁸ s⁻¹, which is close to the rate constants for some of the fastest enzymatic reactions. This underscores the point that these Pt(II) pincer complexes are suitable for on-line monitoring of the SO₂ concentration in air.

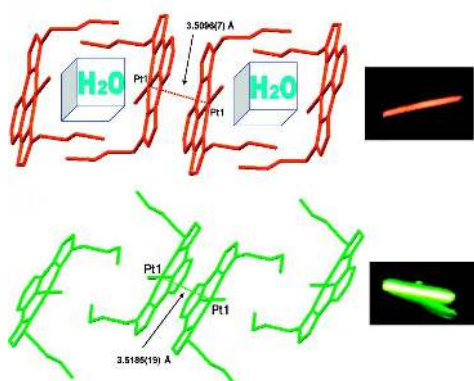
2.4.6 NHC complexes

Scheme 25. Vapochromic Pt(II) complexes with NHC ligands.



Transition-metal complexes with N-heterocyclic carbenes (NHCs) are playing an increasingly important role in organometallic chemistry,¹¹³⁻¹¹⁵ and until now two vapochromic Pt(II) complexes with such ligands have been reported (Scheme 25).^{116, 117} Complex **53**⁺ is synthesized via transmetallation from an Ag(I) precursor complex and crystallizes in two different structures

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3 depending on what solvent is used.¹¹⁶ Recrystallization from methanol/diethyl ether yields a
4 hydrated form with the sum formula $53\text{Cl}\cdot 2.5\text{H}_2\text{O}$, whereas crystallization from CH_2Cl_2 /hexane
5 affords the anhydrate form 53Cl . Both crystal structures contain dimers of head-to-tail oriented
6 complexes with short Pt(II)-Pt(II) contacts (Figure 25). In $53\text{Cl}\cdot 2.5\text{H}_2\text{O}$ the shortest intermetallic
7 distance is 3.5096(7) Å, in 53Cl it is 3.5185(19) Å. The interplanar (π - π) stacking distances are
8 not much different either and vary between 3.342 Å ($53\text{Cl}\cdot 2.5\text{H}_2\text{O}$) and 3.472 Å (53Cl).
9 However, the hydrate exhibits orange luminescence ($\lambda_{\text{max}} = 614 \text{ nm}$) whereas the anhydrate form
10 emits green ($\lambda_{\text{max}} = 555 \text{ nm}$) which is difficult to explain by the observed structural changes. At
11 any rate, when the green-emitting dehydrated form (53Cl) is exposed to moisture, the emission
12 changes to orange and powder X-ray analysis is in line with the formation of $53\text{Cl}\cdot 2.5\text{H}_2\text{O}$.
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43 **Figure 25.** Crystal packing and emission colors of $53\text{Cl}\cdot 2.5\text{H}_2\text{O}$ (top) and 53Cl (bottom).
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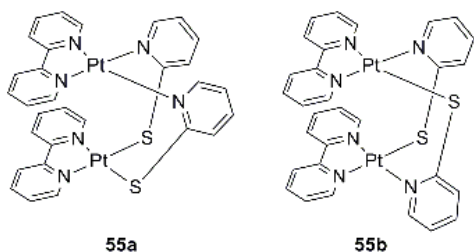
45 Reprinted with permission from ref.¹¹⁶. Copyright 2010 American Chemical Society.
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51 Complex 54^{2+} contains mesityl-substituents instead of *n*-butyl groups and the fourth
52 coordination site is occupied by a carbonyl instead of a chloro-ligand. The bulky mesityls form a
53 small pocket which allows VOCs to enter the crystal structure of $54(\text{PF}_6)_2$ in order to form
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3 solvent adducts with different luminescence properties than the desolvated form.¹¹⁷ The solvent-
4 free form of **54**(PF₆)₂ exhibits structured emission with a band maximum at 462 nm but exposure
5 to vapors of small molecules containing nitrogen or oxygen donor atoms such as methanol,
6 water, THF, diethyl ether, DMF, or pyridine leads to a yellow featureless emission with $\lambda_{\text{max}} =$
7
8 529 nm. Small VOCs without donor atoms such as CH₂Cl₂, CHCl₃, or benzene do not trigger any
9 response. The exact mechanism for the luminescence vapochromism is not clear, but the crystal
10 structure of **54**(PF₆)₂·2(CH₃)₂CO shows signs of solvate/Pt-CO interactions. Specifically, the
11 distance of 2.82 Å between the O-atom of acetone and the C-atom of the carbon monoxide
12 ligand is significantly shorter than what is expected based on the van-der-Waals radii of oxygen
13 and carbon (3.22 Å). Moreover, the CO stretching frequency of the solvated acetone is 10 cm⁻¹
14 lower than that of free acetone, and the CO stretching frequency for the carbon monoxide ligand
15 is 15 cm⁻¹ lower in **54**(PF₆)₂·2(CH₃)₂CO than in desolvated **54**(PF₆)₂.
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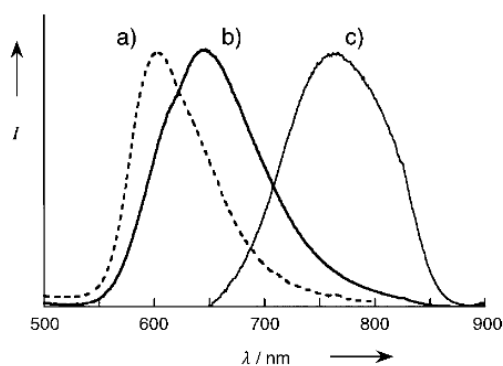
34 2.5 Pt(II) complexes with S-, P-, and As-ligand atoms

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39 **Scheme 26.** *Syn*- and *anti*-isomers of a vapochromic Pt(II) complex with thiolate ligands.



A dinuclear pyridine-2-thiolate bridged Pt(II) bpy complex was obtained both as a *syn*- (**55a**)
and an *anti*-isomer (**55b**) (Scheme 26).¹¹⁸ The *syn*-isomer (**55a**) has one Pt(II) ion in a

1
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3 coordination sphere of four N-atoms (2 from bpy, 2 from pyridine-2-thiolate), and the second
4 metal center is coordinated to the two thiolate functions in addition to bpy. In the *anti*-isomer
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6
7
8 (**55b**) both Pt(II) centers are coordinated to 3 N-atoms and 1 S-atom. Both isomers exhibit
9
10 unusually short (intramolecular) Pt(II)-Pt(II) distances of 2.923(1) Å (*syn*) and 2.997(1) Å (*anti*).
11
12 The *syn* isomer changes color from dark red to lighter red upon standing in air, and this is
13
14 accompanied by changes in the luminescence properties as illustrated in Figure 26. Exposure to
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16 methanol or acetonitrile reverses the color and luminescence changes.
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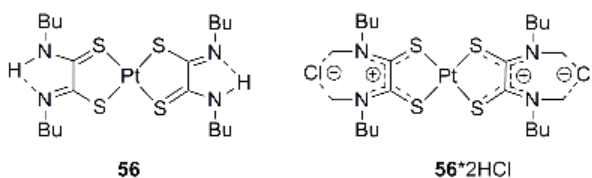


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36 **Figure 26.** Room-temperature photoluminescence spectra of (a) the *anti*-isomer **55b**, (b) the
37 desolvated form of the *syn*-isomer **55a**, (c) the solvated form of *syn*-isomer **55a**. (M. Kato, A.
38 Omura, A. Toshikawa, S. Kishi, Y. Sugimoto: Vapor-Induced Luminescence Switching in
39 Crystals of the *Syn* Isomer of a Dinuclear (Bipyridine)platinum(II) Complex Bridged with
40 Pyridine-2-Thiolate Ions. *Angew. Chem. Int. Ed.*, 2000, *41*, 3183-3185. Copyright Wiley-VCH
41 Verlag GmbH & Co. KGaA. Reproduced with permission.)
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53 The crystal structure of the dark red acetonitrile adduct (**55a**·CH₃CN) exhibits short
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55 *intermolecular* Pt(II)-Pt(II) distances of 3.384(1) Å in addition to the short *intramolecular* Pt(II)-
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57 Pt(II) contacts mentioned above. Thus, there is extensive interaction between metal centers along
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59
60

one dimension, and therefore the strongly red-shifted emission at $\lambda_{\text{max}} = 766 \text{ nm}$ is most likely due to a low-energy $^3\text{MMLCT}$ state. The structure of **55a**·CH₃CN contains channels in which the solvate molecules are located, providing a pathway for them to diffuse in and out of the lattice. The sensitivity of **55a** for VOCs decreases with increasing steric bulk of the solvent vapors, in line with the hypothesis that the adsorbates must be small enough to penetrate these channels. Methanol and acetonitrile produce a rapid response, ethanol and isopropanol lead to slower color and luminescence changes, whereas *t*-butanol triggers no response at all, despite the fact that these five VOCs have similar vapor pressures. The *anti*-isomer (**55b**) is neither vapochromic nor vapoluminescent but emits orange emission ($\lambda_{\text{max}} = 603 \text{ nm}$, $\tau = 240 \text{ ns}$), presumably from a $^3\text{MMLCT}$ state resulting from intramolecular Pt(II)-Pt(II) interactions.

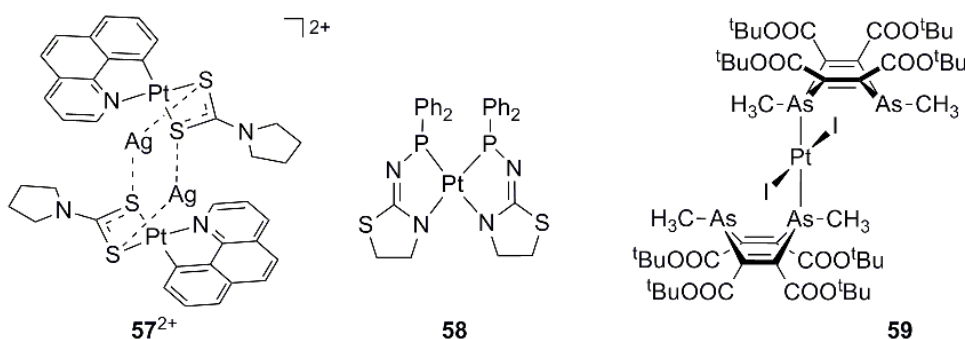
Scheme 27. A vapochromic Pt(II) dithiooxamide complex.



The Pt(II) dithiooxamide complex **56** is sensitive to gaseous HCl (Scheme 27).¹¹⁹ The initial form of this material is orange-red and non-luminescent, but when exposed to HCl it forms an adduct (**56**·2HCl) which is purple-brown and emits in the red spectral range ($\lambda_{\text{max}} \approx 740 \text{ nm}$, $\tau = 28 \text{ ns}$). According to prior studies of the same process in solution the red emission is due to a charge transfer state in which electron density has been transferred from the Pt/S moiety to the dithiooxamide backbone.¹²⁰ In the course of HCl uptake this state shifts to lower energy and begins to emit, whereas in the initial form the CT state is energetically close to other non-

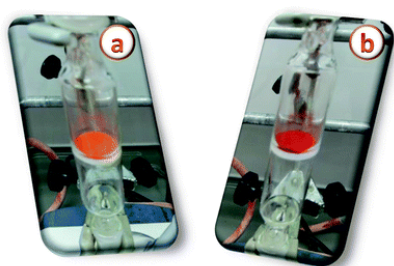
emissive excited states leading to nonradiative energy dissipation. Conversion back from $56 \cdot 2\text{HCl}$ to **56** is possible either by heating to 80 °C or by exposure to NH_3 vapor.¹¹⁹

Scheme 28. Vapochromic Pt(II) complexes with S, P, or As-ligands.



Complex 57^{2+} is a tetranuclear $[\text{Pt}_2\text{Ag}_2]$ cluster made from two Pt(II) benzoquinoline pyrrolidinedithiocarbamate units bridged via the sulfur atoms through two Ag(I) cations (Scheme 28).¹²¹ The separation distance between the two silver ions (3.0394(18) Å) is significantly shorter than the sum of their van der Waals radii (3.44 Å), i. e., they show argentophilic interactions. In the perchlorate salt of complex 57^{2+} the $[\text{Pt}_2\text{Ag}_2]$ clusters form a polymer along the crystallographic *c*-axis with short (3.1390(7) Å) Pt(II)-Pt(II) contacts. Consequently, the red emission of solid $57(\text{ClO}_4)_2$ ($\lambda_{\text{max}} = 610$ nm) is most likely due to $^3\text{MMLCT}$ or excimeric $^3\pi\pi^*$ states. Exposure of solid $57(\text{ClO}_4)_2$ to acetonitrile induces a rapid change in color from orange to garnet red (Figure 27), but several other vapors (including CH_2Cl_2 , methanol, H_2O , acetone, diethyl ether, DMF, DMSO, toluene, *n*-hexane) produce no response. The origin of the selective vapochromism with CH_3CN is not known but it has been noted that acetonitrile may replace the perchlorate anions which are weakly coordinated to the Ag(I) ions. The smaller size of CH_3CN relative to ClO_4 would then allow the individual $[\text{Pt}_2\text{Ag}_2]$ clusters to get closer to each other, and

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3 this may well lead to the observed vapochromism. The selectivity of **57**(ClO₄)₂ to acetonitrile is
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5 quite unusual, but unfortunately the vapochromic response does not appear to be easily
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7 reversible.
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23 **Figure 27.** Sample of **57**(ClO₄)₂ before (a) and after (b) exposure to CH₃CN vapor. Reprinted
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25 with permission from ref. ¹²¹. Copyright 2008 The Royal Society of Chemistry.
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31 The bischelated Pt(II) complex **58** with two identical aminophosphine ligands was obtained in
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33 its *cis*-form and exhibits a vapoluminescence response to small alcohols.¹²² Two crystal
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35 structures of this complex were studied by X-ray diffraction but none of them contains short
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37 Pt(II)-Pt(II) contacts. The shortest intermetallic distances found are 5.9267(2) Å in **58**·C₆H₅CH₃
38
39 and 8.9268(2) Å in **58**·2CH₃OH·CH₃CN. The origin of the emission which turns on after
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41 methanol exposure is unclear, but given the large intermetallic distances participation of
42
43 ³MMLCT states appears highly unlikely. It has been speculated that a rigidochromic effect
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45 induced by hydrogen-bonding could be the reason why methanol-exposed **58** is emissive.
46
47 (Rigidochromism is a change of color occurring as a consequence of changes in the rigidity of
48
49 the surrounding medium). Hydrogen-bond donation from methanol to the aminophosphine
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51 ligands may render the overall complex less flexible, making multiphonon relaxation less
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3 efficient. Aside from methanol, ethanol, and (to a lesser extent) isopropanol cause a
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6 luminescence turn-on, but *t*-butanol produces no significant response.
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8 The organoarsenic complex **59** can be crystallized either in neat form or as adducts of
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10 dichloromethane (**59**·2CH₂Cl₂), acetone (**59**·2acetone) or toluene (**59**·C₆H₅CH₃).¹²³ In the crystal
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12 structure of **59**·2CH₂Cl₂ there are no large cavities and the void volume is only 1.1% of the total
13
14 crystal volume, but in the structure of neat **59** the void volume amounts to 6.0%. Consequently,
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16 when exposing neat **59** to vapors of CH₂Cl₂, acetone, or toluene, these solvent vapors are taken
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18 up and the abovementioned adducts are formed rapidly. Vapor sorption is accompanied by the
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20 appearance of very intense red luminescence ($\lambda_{\max} = 658$ nm) within seconds. This emission turn-
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22 on has been tentatively explained by a conformational fixation of the emissive species due to
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24 tighter crystal packing in the solvent adducts compared to neat **59**.
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32 2.6 MMX chains made from [Pt₂(pop)₄I]⁴⁻ units

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36 The photochemistry of the [Pt₂(pop)₄I]⁴⁻ complex (pop = μ -pyrophosphito) in solution has been
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38 explored extensively.^{124, 125} This diphosphito-bridged d⁸-d⁸ dimer exhibits favorable
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40 photophysical and photochemical properties due its short (2.925(1) Å) intramolecular Pt(II)-
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42 Pt(II) distance.³¹ Halogenides can bind to the [Pt₂(pop)₄I]⁴⁻ core, resulting in so-called MMX
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44 compounds in which M = Pt and X = halogenide. A few of these MMX materials were found to
45
46 exhibit vapochromism.¹²⁶⁻¹²⁸ The compound [NH₃(CH₂)₄NH₃]₂[Pt₂(pop)₄I]·4H₂O (**60**) forms
47
48 linear PtPtI chains along the crystallographic *c*-axis with Pt(II)-Pt(II) distances of 2.837 Å and
49
50 Pt(II)-I distances of 2.722 Å, the counter-cations are in the spaces between individual chains.¹²⁶
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52 At 296 K there is a single Pt-Pt vibration band at 98 cm⁻¹ but upon heating to 340 K the
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respective IR signal splits into two separate bands, indicating that there are two kinds of Pt-Pt units at elevated temperatures. Simultaneously, the color of the compound changes from green to red (Figure 28). These observations were explained in terms of a structural transition from a paramagnetic charge-polarization (CP) state to a diamagnetic charge-density-wave (CDW) state. In the initial CP state the individual molecular components are formally best regarded as $\text{Pt}^{2+}-\text{Pt}^{3+}-\text{I}$ units which are linearly linked through weak interactions from the terminal iodo-ligand of one unit to the Pt^{2+} center of the nearest neighbor ($\text{Pt}^{2+}-\text{Pt}^{3+}-\text{I}\dots\text{Pt}^{2+}-\text{Pt}^{3+}-\text{I}$). In the CDW state, there are two different kinds of Pt_2 units because this structure is formally best described by alternating $\text{Pt}^{2+}-\text{Pt}^{2+}$ and $\text{I}-\text{Pt}^{2+}-\text{Pt}^{3+}-\text{I}$ units ($\text{Pt}^{2+}-\text{Pt}^{2+}\dots\text{I}-\text{Pt}^{2+}-\text{Pt}^{3+}-\text{I}$), resulting in a lower band gap of only 1.12 eV (1110 nm) compared to 2.52 eV (520 nm) in the CP state. In dry atmosphere, the red CDW state remains stable upon cooling from 340 K to room temperature. However, upon exposure of the metastable CDW form to saturated water vapor the CP state is recovered, manifesting itself in a color change from red to green.¹²⁶ The anhydrous red form of **60** can be crystallized directly from methanol solution and X-ray diffraction on single crystals confirms the CDW structure of this modification.¹²⁸ The difference in lattice volume between anhydrous **60** and **60**·4H₂O amounts to 150 Å³ whereas the volume of a water molecule is generally approximated to 30 Å³, suggesting that the total volume of eight H₂O molecules in the unit cell of **60**·4H₂O should be around 240 Å³. This analysis suggests that crystal packing in anhydrous **60** is not as tight as it could be, and this might account for the facile water uptake in humid atmosphere. The X-ray crystal structure of a methanol adduct (**60**·2CH₃OH) has also been reported,¹²⁸ but it is not yet clear whether this material exhibits vapochromism.

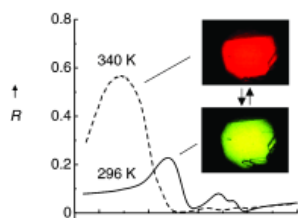


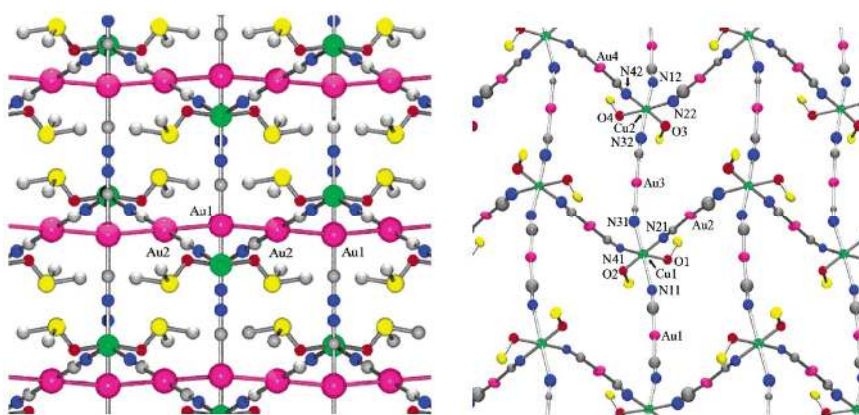
Figure 28. Reflectivity spectra and microscope images of compound **60** at two different temperatures. (Vapochromic Behavior Accompanied by Phase Transition between Charge-Polarization and Charge-Density-Wave States in a Quasi-One-Dimensional Iodine-Bridged Dinuclear Platinum Compound. *Angew. Chem. Int. Ed.*, 2005, 44, 3240-3243. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

When replacing the $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}$ cation of compound **60** by the larger $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{2+}$ cation one obtains another MMX material (**61**) which exhibits an analogous transition from a green CP state to a red CDW state upon heating.¹²⁷ However, in this case the transition occurs between 297 K and 308 K, i. e., at significantly lower temperature than in compound **60** (340 K). Thermogravimetric studies show that up to 350 K compound **61** releases four water molecules per formula unit hence the initial CP compound is to be formulated as $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]_2[\text{Pt}_2(\text{pop})_4\text{I}]\cdot 4\text{H}_2\text{O}$ (**61** $\cdot 4\text{H}_2\text{O}$). Anhydrous **61** sorbs water readily from air at room temperature whereas anhydrous **60** requires water-saturated atmosphere. The higher sensitivity of **61** compared to **60** has been explained by the larger distances between individual MMX chains (caused by the larger cation), facilitating water diffusion into the crystal structure.

3. Gold(I) compounds

3.1 Dicyanoaurates

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3 When reacting $\text{Cu}(\text{ClO}_4)_2$ with $\text{KAu}(\text{CN})_2$ in DMSO, two different polymorphs of
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5 $\text{Cu}[\text{Au}(\text{CN})_2]_2(\text{DMSO})_2$ ($\mathbf{62} \cdot (\text{DMSO})_2$) can be obtained.¹²⁹ Reactant concentrations below 0.2 M
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8 lead to a green polymorph, whereas blue crystals of a second polymorph are obtained at
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10 concentrations above 0.5 M. This concentration dependence suggests that the blue material is a
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12 kinetic reaction product while the green polymorph is presumably the thermodynamically more
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14 stable form. The X-ray crystal structures of the two forms are significantly different, one of the
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16 most evident differences is the five-fold (square-pyramidal) coordination of Cu(II) in the green
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18 polymorph compared to the six-coordinate Cu(II) center in the blue form (Figure 29).
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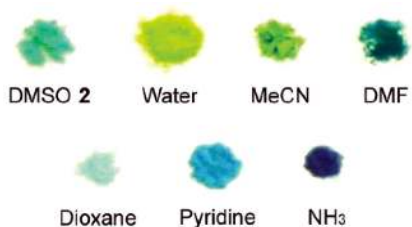


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39 **Figure 29.** Extracts of the crystal structures of the green (left) and blue (right) polymorph of
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41 $\text{Cu}[\text{Au}(\text{CN})_2]_2(\text{DMSO})_2$ ($\mathbf{62} \cdot (\text{DMSO})_2$). Reprinted with permission from ref. ¹²⁹. Copyright 2004
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43 American Chemical Society.
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50 The green structure exhibits an extended 1D zigzag chain structure in which Cu(II) bridges
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52 between individual $\text{Au}(\text{CN})_2^-$ units. Each chain is connected to four neighboring chains through
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54 Au(I)-Au(I) interactions occurring through an intermetallic contact of 3.22007(5) Å. The DMSO
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56 molecules, ligated to Cu(II), occupy the voids between the chains. The blue polymorph contains
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3 2-D layers of interconnected $\text{Au}(\text{CN})_2^-$ units and octahedral $\text{Cu}(\text{II})$ complexes, individual layers
4 are stacked through aurophilic interactions of $3.419(3)$ Å to yield a 3-D network. The different
5 colors of the two polymorphs are due to the different coordination numbers (5 or 6) and
6 geometries (square-pyramidal vs. octahedral) of the $\text{Cu}(\text{II})$ ions, causing substantially different
7 crystal field splittings of the d-d excited states. Both polymorphs are thermally stable up to 100
8 °C, but they easily sorb a variety of different small molecules with N- or O-atoms and thereby
9 release DMSO. Specifically water, acetonitrile, DMF, dioxane, pyridine, and NH_3 were tested. A
10 combination of elemental analysis, thermogravimetry, X-ray diffraction, and IR spectroscopy
11 leads to the conclusion that the compounds generated by vapor uptake are identical to those that
12 can be obtained directly from solutions containing the respective N- or O-atom-containing small
13 molecules. A key finding is that all adsorbed solvent molecules are ligated to $\text{Cu}(\text{II})$ by replacing
14 some or all of the initially present DMSO molecules. This behavior is in clear contrast to many
15 other vapochromic materials in which adsorbed VOCs are loosely trapped in channels or voids of
16 the crystalline host lattice. The ratio of adsorbed molecule to $\text{Cu}(\text{II})$ varies between 1:1 (DMF),
17 2:1 (H_2O , CH_3CN , pyridine), and 4:1 (NH_3), producing color changes which are easily detectable
18 (Figure 30): The maximum visible reflectance varies between 433 ± 7 nm for
19 $\text{Cu}[\text{Au}(\text{CN})_2]_2(\text{NH}_3)_4$ and 560 ± 20 nm for solvent-free $\text{Cu}[\text{Au}(\text{CN})_2]_2$. As the color variations are
20 entirely due to changes in the $\text{Cu}(\text{II})$ coordination number and geometry it might be argued that
21 $\text{Cu}[\text{Au}(\text{CN})_2]_2$ is a copper- rather than gold-based vapochromic material. However, on the one
22 hand the aurophilic interactions between individual cyanoaurate units are crucial for obtaining
23 the vapor-responsive structures of $\text{Cu}[\text{Au}(\text{CN})_2]_2$,¹⁷ and on the other hand the $\text{Au}(\text{CN})_2^-$ units
24 provide a spectroscopic handle which is at least as sensitive to solvent uptake as the changes in
25 the UV-vis (reflectance) spectrum. Specifically, the CN stretching frequency is very susceptible
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3 to π -backbonding from the Cu(II) center to the cyano-groups, producing shifts between 10 cm^{-1}
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5 and 40 cm^{-1} depending on solvent.¹²⁹
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19 **Figure 30.** Vapochromic response of $\text{Cu}[\text{Au}(\text{CN})_2]_2(\text{DMSO})_2$ (**62**·(DMSO)₂) to different vapors.

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27 The solvent exchange on Cu(II) is completely reversible, permitting dynamic vapor sensing, at
28 least for H₂O, CH₃CN, DMF, and dioxane.¹⁴ The stronger pyridine and NH₃ ligands are less
29 easily replaced by other solvents hence in the case of $\text{Cu}[\text{Au}(\text{CN})_2]_2(\text{pyridine})_2$ and
30 $\text{Cu}[\text{Au}(\text{CN})_2]_2(\text{NH}_3)_4$ thermal treatment is necessary to reactivate the vapochromic behavior.
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36 The strong binding of NH₃ to Cu(II) in **62** was one of the motivations for investigating
37 analogous zinc(II) compounds in which the reversibility of NH₃ uptake was anticipated to be
38 better. The second reason why $\text{Zn}[\text{Au}(\text{CN})_2]_2$ (**63**) was studied is that in this material no d-d
39 absorptions of the 3d metal can mask any gold-localized emission.¹³⁰ A vapoluminescence
40 response in lieu of a vapochromic effect would potentially increase the detection sensitivity.
41 Depending on reaction conditions (starting material, solvent, concentration) four different
42 polymorphs of compound **63** were obtained. Particularly noteworthy is the fact that even the
43 counterions of the zinc(II) and $\text{Au}(\text{CN})_2^-$ starting materials influence which polymorph is formed
44 even though these counterions are not incorporated into the final product. Despite careful
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systematic investigations the rationale behind the preferential formation of a particular polymer under a given set of conditions has not become clear. All four polymorphs of $\text{Zn}[\text{Au}(\text{CN})_2]_2$ have been characterized structurally. They all have $\text{Zn}(\text{II})$ in tetrahedral coordination geometry, and they all exhibit short $\text{Au}(\text{I})$ - $\text{Au}(\text{I})$ contacts in the range of 3.11 – 3.34 Å. Two polymorphs exhibit diamond-like networks, among the other two polymorphs there is a quartz-like and a herringbone-like network with different degrees of interpenetration. Because of the presence of aurophilic interactions, UV excitation leads to photoluminescence in three of the four polymorphs. One polymorph shows even two emissions, namely a short-lived ($\tau = 240$ ns) band at 390 nm attributed to fluorescence and a longer lived ($\tau = 930$ ns) band at 480 nm assigned to phosphorescence. Along the series of the three emissive polymorphs the phosphorescence energy is inversely proportional to the $\text{Au}(\text{I})$ - $\text{Au}(\text{I})$ distance, as expected.^{131, 132}

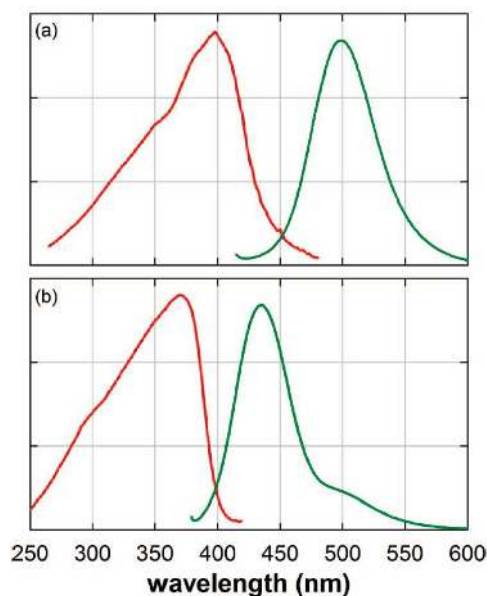


Figure 31. Excitation and emission spectra of (a) $[\text{Zn}(\text{NH}_3)_2][\text{Au}(\text{CN})_2]_2$ and (b) $[\text{Zn}(\text{NH}_3)_4][\text{Au}(\text{CN})_2]_2$ illustrating the vapochromic and vapoluminescent response of compound

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3 **62** to ammonia vapor. Reprinted with permission from ref. ¹³⁰. Copyright 2008 American
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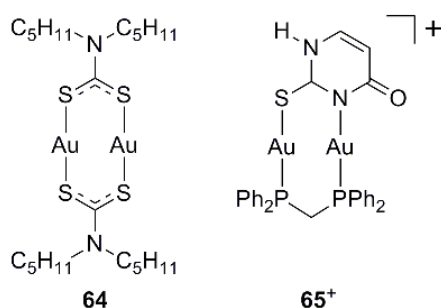
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11 Exposure of any of the four polymorphs to ammonia vapors produces a new emission with a
12 band maximum at 430 nm (Figure 31).¹³⁰ The resulting species, identified as
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14 $[\text{Zn}(\text{NH}_3)_4][\text{Au}(\text{CN})_2]_2$, decomposes fairly rapidly once it is removed from ammonia-rich
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16 atmosphere, and the $[\text{Zn}(\text{NH}_3)_2][\text{Au}(\text{CN})_2]_2$ compound with a lower ammonia content emitting at
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18 500 nm is formed. In IR spectroscopy the CN stretch of $[\text{Zn}(\text{NH}_3)_2][\text{Au}(\text{CN})_2]_2$ shows up as a
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20 single band at 2158 cm^{-1} , and there is evidence for metal-bound NH_3 , suggesting that Zn(II) is
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22 either octahedrally or tetrahedrally coordinated by ammonia. From powder X-ray diffraction data
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24 it was inferred that $[\text{Zn}(\text{NH}_3)_2][\text{Au}(\text{CN})_2]_2$ contains Zn(II) centers in D_{4h} local symmetry with
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26 NH_3 ligands in *trans*-disposition and four equatorial N-bound cyanides. When
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28 $[\text{Zn}(\text{NH}_3)_2][\text{Au}(\text{CN})_2]_2$ was left standing in air for 30 minutes, neat $\text{Zn}[\text{Au}(\text{CN})_2]_2$ was formed, i.
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30 e., the vapoluminescence response has the anticipated higher reversibility compared to
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32 $\text{Cu}[\text{Au}(\text{CN})_2]_2$. Although all four polymorphs of $\text{Zn}[\text{Au}(\text{CN})_2]_2$ show vapoluminescence
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34 behavior, the material made from $\text{Zn}(\text{NO}_3)_2$ and $[(n\text{-Bu})_4\text{N}][\text{Au}(\text{CN})_2]$ exhibits the highest
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36 sensitivity for ammonia with a detection limit of 1 ppb.¹⁷ The permissible long-term exposure
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38 limit for NH_3 is 20 ppm, the human nose starts sensing ammonia at concentrations of 50 ppm.¹³³
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49 3.2 Di- and trinuclear Au(I) complexes 50 51 52

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54 Reaction of $\text{KS}_2\text{CN}(\text{C}_5\text{H}_{11})_2$ with “ AuCl_2^- ” generated in situ from $\text{K}[\text{AuCl}_4]$ and $\text{Na}_2\text{S}_2\text{O}_3$
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56 affords a dimeric gold(I) dithiocarbamate complex (Scheme 29), $[\text{Au}(\text{S}_2\text{CN})(\text{C}_5\text{H}_{11})_2]_2$ (**64**),
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3 which exhibits reversible vapoluminescence upon exposure to polar aprotic molecules such as
4 acetone, CH₃CN, CH₂Cl₂, CHCl₃.¹³⁴ Vapors of protic solvents such as methanol or ethanol
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6 produce no response. X-ray diffraction of single crystals of **64**·DMSO and **64**·CH₃CN shows that
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8 there are infinite chains of Au atoms along the crystallographic c-axis with *intermolecular* Au(I)-
9 Au(I) contacts of 2.9617(7) Å (**64**·DMSO) and 3.0241(12) Å (**64**·CH₃CN). The *intramolecular*
10 Au(I)-Au(I) distances in the two solvates are 2.7690(7) Å and 2.7916(12) Å. In solvent-free **64**
11 the intramolecular metal-metal contacts are equally short (2.7653(3) Å), but the closest
12 intermolecular Au(I)-Au(I) distance increases to 8.135 Å hence there is no infinite chain of
13 mutually interacting gold atoms. Thus, the orange emission ($\lambda_{\text{max}} = 604$ nm) is only observed
14 when *intermolecular* Au(I)-Au(I) interactions between dimers are present, and the emissive
15 excited states are likely to have either (d σ^*)¹(p σ)¹ or (d δ^*)¹(p σ)¹ valence electron
16 configurations.¹³⁵

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35 **Scheme 29.** Dinuclear gold(I) complexes exhibiting vapochromism and tribochromism.



A gold(I) 2-thiouracilato complex with a bridging bis(diphenylphosphino)methane (dppm) ligand (**65a**·CF₃COO) exhibits a somewhat longer (2.8797(4) Å) intramolecular Au(I)-Au(I) distance than complex **64**.¹³⁶ The helical supramolecular arrangement in the crystal structure of

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3 **65a**·CF₃COO precludes the formation of extended chains of interacting gold atoms (Figure 32),
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5 and the substance is not luminescent. When it is gently crushed with a spatula blue
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7 photoluminescence ($\lambda_{\text{max}} = 483 \text{ nm}$) can be detected, i. e., the substance shows luminescence
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9 tribochromism.¹³⁷ The emissive form can also be obtained upon gentle heating (37 °C) or by
10
11 sonication,¹³⁶ and in the course of this treatment acid is released as monitored by using pH paper.
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13 When compound **65a**·CF₃COO is stirred in CH₂Cl₂/CH₃OH solutions over Na₂CO₃ it is possible
14
15 to obtain the deprotonated product **65b** which consists of dimers held together with short
16
17 (2.9235(4) Å) intermolecular Au(I)-Au(I) contacts (Figure 32), i. e., the crystal packing is
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19 completely different. The available experimental evidence including powder X-ray analysis of
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21 crushed **65a**·CF₃COO supports the hypothesis that **65b** is the emissive material resulting from
22
23 mechanical (or thermal) treatment of **65a**·CF₃COO. Thus it appears that the tribochromism is due
24
25 to rearrangement of the molecules in the crystal lattice coupled to release of volatile acid.
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27 Exposure of **65b** to CF₃COOH vapor leads (very slowly) to a loss of the photoluminescence, but
28
29 the emission can be recovered by subsequent exposure to triethylamine vapor. The C-O bond
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31 lengths in the crystal structures of **65a**·CF₃COO and **65b** are similar hence the probable site of
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33 protonation in **65b** is most likely the uncoordinated pyrimidine N-atom.
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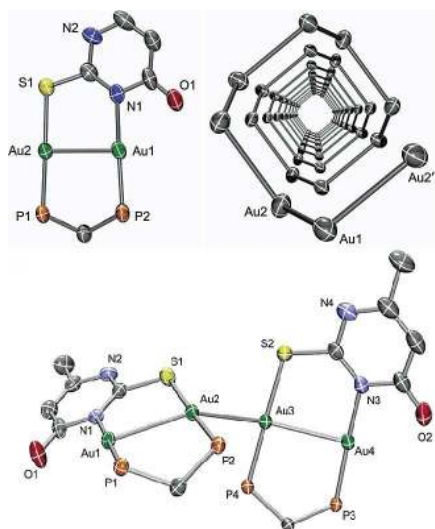
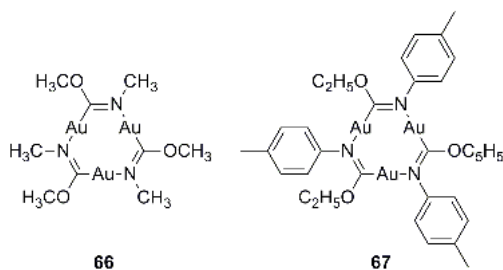


Figure 32. Top left: Crystal structure of compound **65a**·CF₃COO. Top right: helical arrangement of gold atoms in **65a**·CF₃COO. Bottom: Dimers of complexes in compound **65b**. Reprinted with permission from ref. ¹³⁶. Copyright 2003 American Chemical Society.

Scheme 30. Trinuclear gold(I) complexes.



The trinuclear gold(I) complex **66** (Scheme 30) exhibits the unusual phenomenon of solvent-stimulated luminescence.^{138, 139} This means that emission is triggered when liquids are brought into contact with crystals of **66** that have been previously irradiated at 366 nm. Compound **66** features short intra- (3.308(2) Å) and intermolecular Au(I)-Au(I) interactions (3.346(1) Å), and thus it seems plausible that aurophilic interactions are important for the luminescence behavior

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3 of **66**, particularly in view of the fact that a reference compound without any short intermetallic
4 contacts is non-emissive. In the crystal structure of **66** there are extended stacks of individual
5 molecules along the c-axis, and it has been speculated that upon UV irradiation energy might be
6 stored in these stacks in the form of electron-hole pairs which only recombine following addition
7 of solvent. This tentative explanation is plausible because one would expect relatively facile
8 charge migration along these stacks,¹⁴⁰ and electrons or holes can easily be trapped at defect
9 sites. Solvent addition can then trigger minor structural changes such that the electrons and holes
10 are released from the defect sites. Interestingly, CHCl_3 and CH_2Cl_2 in which compound **66** has
11 the highest solubility produce the strongest luminescence. It has been noted that the solvent-
12 stimulated luminescence of **66** is related to the phenomenon of lyoluminescence,¹⁴¹ in which
13 light emission occurs when dissolving a solid that has been previously exposed to ionizing
14 radiation – with the important difference that radiation of much lower energy is required to
15 induce emission in compound **66**.¹³⁸ The solvoluminescence from planar trigold(I) complexes
16 has been reviewed.¹⁴²

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37 The charge mobility in microwires of compound **66** has been explored with a view to obtaining
38 materials with vapor-sensitive conductive properties.¹⁴³ For this purpose a CH_2Cl_2 solution of **66**
39 was drop-cast between two gold electrodes on a SiO_2 surface, and the resulting microwires
40 formed from stacks of **66** were found to bridge the 150 μm gap between the two gold electrodes.
41 Hole mobilities on the order of $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were determined for 10 devices of this type. At a
42 voltage of 1.5 V between the two gold electrodes currents on the order of 0.6 nA flow through
43 the microwires. Exposure to ethanol vapor decreases the flowing current by two orders of
44 magnitude, but this decrease is reversible when purging with pure N_2 afterwards. In addition to
45 ethanol, THF, CH_3CN , acetone, methanol, *n*-propanol, *n*-butanol, *n*-pentanol, benzene, and *p*-
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xylene have been tested, but only ethanol, methanol and CH₃CN were found to produce a significant response. It has been argued that hydrogen-bonding interactions between compound **66** and adsorbed VOCs might disturb the 1D-stacking of the complexes and thereby disrupt efficient charge transfer pathways.¹⁴³

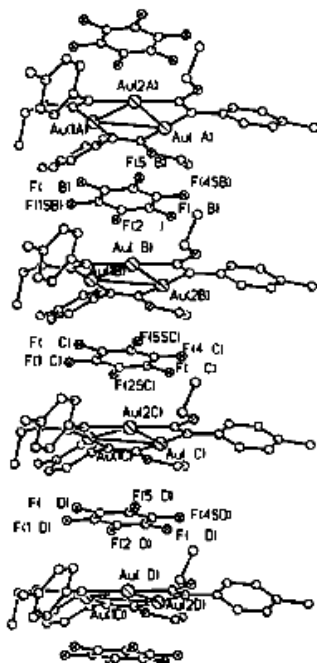


Figure 33. Columnar structure of **67**·C₆F₆. Reprinted with permission from ref. ¹⁴⁴. Copyright 2001 American Chemical Society.

The trinuclear gold(I) complex **67** differs from compound **66** mainly in that the N-atoms bear *p*-tolyl groups instead of methyl-substituents. Solid **67** exhibits blue photoluminescence ($\lambda_{\max} \approx 440$ nm), but when exposed to vapor of C₆F₆ the emission is quenched.¹⁴⁴ X-ray structural investigations provide a plausible explanation for this behavior. Neat **67** crystallizes in such a way that dimers of **67** with short intermolecular Au(I)-Au(I) contacts are formed,¹⁴⁵ whereas the

crystal structure of **67**·C₆F₆ consists of 1D-chains of alternating gold complexes and hexafluorobenzene molecules interacting with each other through (Lewis) acid-base interactions (Figure 33).¹⁴⁴ Thus, uptake of C₆F₆ disrupts intermolecular Au(I)-Au(I) contacts, and this is likely the reason for the emission quenching described above.

A chemically related trinuclear Au(I) complex with imidazolate instead of carbeniate ligands forms analogous 1D chains with intercalating TCNQ molecules, but for the respective complex no vapoluminescence behavior has been reported.¹⁴⁴

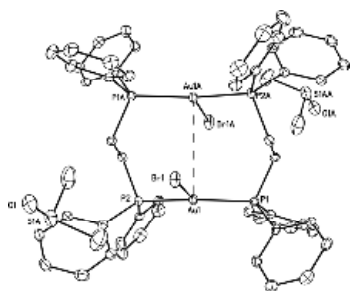
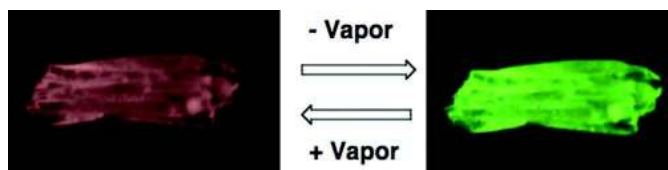


Figure 34. Drawing of the structure of **68**·2DMSO (type A representative). Reprinted with permission from ref. ¹⁴⁶. Copyright 2010 American Chemical Society.

The dimer Au₂(μ-bis-(diphenylphosphino)ethane)₂Br₂ (**68**) was found to exhibit remarkable molecular flexibility and for this reason may be regarded as a molecular accordion with vapoluminescent properties.¹⁴⁶ Depending on crystallization conditions three different types of structures of the same compound are obtained. Type A crystals are obtained for **68**·2DMSO, **68**·2Me₂CO, **68**·2CH₂Cl₂, **68**·2DMF and contain discrete Au₂ dimers (Figure 34). They are colorless and exhibit orange emission ($\lambda_{\text{max}} = 620 - 640 \text{ nm}$) upon UV excitation. The intramolecular Au(I)-Au(I) distances in type A crystals are relatively long and range from 3.8479(3) Å for **68**·2DMSO to 3.5142(3) Å in **68**·2DMF. The expected Au(I)-Au(I) separation

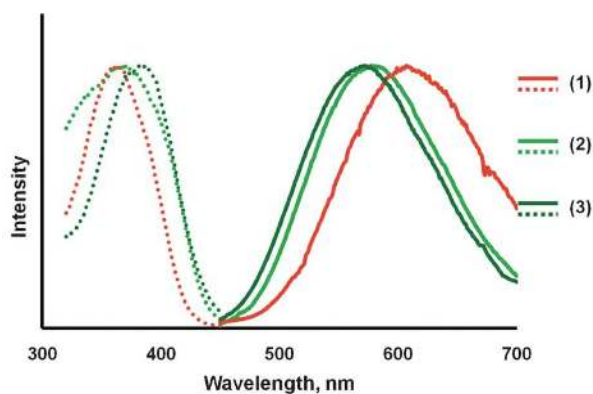
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3 based on the van der Waals radius is about 3.6 Å,¹⁴⁷ i. e., there are little to no aurophilic
4 interactions in these crystals. The solvent molecules merely fill space in the crystal structures but
5
6 do not interact with the metal centers. Type B crystals are green photoluminescent ($\lambda_{\text{max}} = 550$
7
8 nm) and exhibit aurophilic interactions within discrete dimers since there are short Au(I)-Au(I)
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10 contacts between 3.3249(2) Å and 3.09841(18) Å in **68**·2CH₃CN and **68**·0.5Et₂O. Type C
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12 crystals are polymers which are not considered further here because they are not vapochromic or
13
14 vapoluminescent. The finding of intermolecular Au(I)-Au(I) distances varying between
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16 3.09841(18) Å and 3.8479(3) Å for the same compound is highly unusual and justifies usage of
17
18 the term “molecular accordion”.



33
34 **Figure 35.** Vapor-induced luminescence changes in compound **68**. Reprinted with permission
35 from ref. ¹⁴⁶. Copyright 2010 American Chemical Society.

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41 When drying type A crystals of **68**·2CH₂Cl₂ and **68**·Me₂CO their orange emission disappears,
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43 and they begin to exhibit the green luminescence observed for type B crystals (Figure 35).
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45 Subsequent exposure to acetone or CH₂Cl₂ vapor recovers the orange emission of the initial type
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47 A material, but no vapoluminescence response is observed for acetonitrile, diethyl ether, DMF,
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49 DMSO, benzene, pyridine, nitrobenzene, and carbon disulfide. It seems quite obvious that the
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51 remarkable flexibility of the Au₂(μ-dppe)₂Br₂ molecule is responsible for the vapoluminescence
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3 behavior. The different luminescence colors between type A (orange) and type B (green) seem to
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5 be primarily an effect of a smaller Stokes shift in type B crystals.
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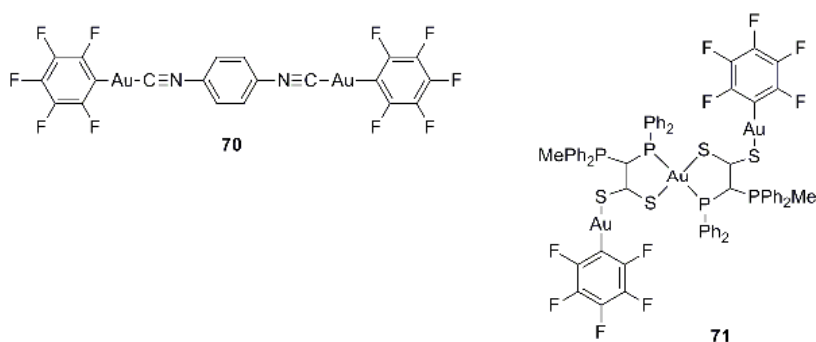


24 **Figure 36.** Excitation (dotted lines) and emission (solid lines) spectra of (a) the α -polymorph of
25 $69 \cdot 2\text{Me}_2\text{CO}$; (b) the β -form obtained after gentle drying of α - $69 \cdot 2\text{Me}_2\text{CO}$ (light green traces); (c)
26
27 the material obtained after drying of α - $69 \cdot 2\text{Me}_2\text{CO}$ for three hours (dark green traces). Reprinted
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29 with permission from ref. ¹⁴⁸. Copyright 2012 The Royal Society of Chemistry.
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37 An analogous gold(I) dimer with iodo- instead of bromo-ligands, $\text{Au}_2(\mu\text{-bis-}$
38 (diphenylphosphino)ethane) $_2\text{I}_2 \cdot 2\text{Me}_2\text{CO}$ ($69 \cdot 2\text{Me}_2\text{CO}$), exhibits similarly spectacular
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40 behavior.¹⁴⁸ Depending on crystallization conditions two different polymorphs of $69 \cdot 2\text{Me}_2\text{CO}$
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42 can be obtained: The α -polymorph luminesces in the orange spectral range ($\lambda_{\text{max}} = 607 \text{ nm}$),
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44 whereas the β -polymorph is a green emitter ($\lambda_{\text{max}} = 577 \text{ nm}$) (Figure 36). The two polymorphs
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46 can be reversibly converted into one another. Gentle drying of α - $69 \cdot 2\text{Me}_2\text{CO}$ crystals in air
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48 transforms them into the green-emitting β -form, and subsequent exposure to acetone or CH_2Cl_2
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50 vapor converts them back to the orange-glowing α -polymorph. This single crystal to single
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52 crystal conversion does not involve any loss or uptake of acetone, but it is possible to remove 2
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4 molecules of acetone from the β -polymorph by prolonged drying. In the course of the conversion
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6 of the α - to the β -form the intramolecular Au(I)-Au(I) distance decreases from 3.6720(2) Å to
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8 3.3955(2) Å.
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13 **Scheme 31.** Di- and trinuclear gold complexes.
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When reacting C_6F_5Au (tetrahydrothiophene) with 1,4-diisocyanobenzene in CH_2Cl_2 one obtains the dinuclear gold(I) complex **70** (Scheme 31) which is a mechanochromic and vapochromic substance.¹⁴⁹ The blue photoluminescence of untreated powder or crystals of **70** was attributed to ligand-localized π - π^* transitions. X-ray diffraction on a single crystal shows that the shortest intermolecular Au(I)-Au(I) distance is 5.19 Å, i. e., there are no aurophilic interactions between individual molecules. When grinding a sample of **70** in an agate mortar the luminescence changes to yellow (Figure 37). Powder X-ray diffraction shows that an amorphous material is formed, and it has been speculated that the yellow luminescence of this material might be due to aurophilic interactions that arise from rearrangement of the individual molecules relative to each other. Significant changes in the $N\equiv C$ stretching frequencies upon mechanical grinding suggest that the coordination mode of the isocyanide ligands is altered, and this could indeed be due to the formation of aurophilic bonds.¹⁵⁰ When exposing a ground sample of **70** to

CH₂Cl₂ vapor the blue luminescence is restored, indicating that the structural transformation is reversible.¹⁴⁹ A simple slipping motion of the planar molecules appears as the most plausible molecular rearrangement accompanying mechano- and vapochromism in compound **70**.

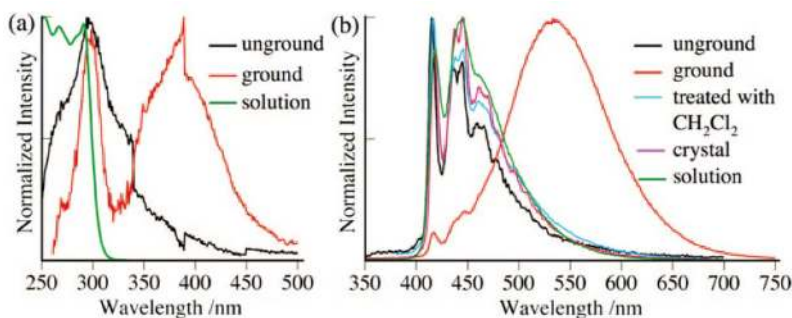


Figure 37. (a) Absorption and (b) photoluminescence spectra of compound **70** in various states.

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The dinuclear complex **71** changes color from orange to black when exposed to vapors of acetone, CH₂Cl₂, or CHCl₃.^{151, 152} This behavior was exploited for the construction of VOC-sensitive optical fibers. The sensors consisted of a standard 1.3 μm optical fiber onto which the vapochromic material was deposited at one end. Since the vapochromic material undergoes a change in refractive index upon solvent exposure, the reflectance of the overall optical fiber changes dramatically in the 500 – 1800 nm wavelength range when the material is exposed to VOCs. Changes of up to 13.5 dB in the transmitted optical power were detected for acetone and CH₂Cl₂, but the devices respond to other solvents as well, for example to CHCl₃, dichloroethane, ethanol, ethyl acetate, THF, and toluene.^{151, 152}

3.3 Gold-thallium complexes

When equimolar quantities of $[\text{NBu}_4][\text{Au}(\text{C}_6\text{Cl}_5)_2]$ and TIPF_6 are brought to reaction in THF one obtains $[\text{Tl}[\text{Au}(\text{C}_6\text{Cl}_5)_2]]_n$ (**72**) as a pale yellow solid.¹⁵³ This vapochromic material contains linear chains of alternating (and nearly planar) $[\text{Au}(\text{C}_6\text{Cl}_5)_2]^-$ anions and Tl^+ cations along the crystallographic z-axis with unsupported Au(I)-Tl(I) interactions at distances of 3.044(5) and 2.9726(5) Å. Theoretical studies lead to the conclusion that this heterobimetallic d^{10} - s^2 interaction (of Lewis acid – Lewis base type) is associated with a stabilization energy of about 275 kJ/mol.¹⁵⁴ Between individual Au(I)-Tl(I) chains there are channels with hole diameters as large as 10.471 Å running parallel to the z-axis hence there is considerable room for incorporation of solvent guests. Compound **72** changes color from yellow to red when exposed to vapors of acetylacetone or pyridine but stays yellow upon exposure to acetone, acetonitrile, THF, triethylamine, 2-fluoropyridine, or tetrahydrothiophene. However, all of these VOCs produce detectable vapoluminescence responses with emission maxima ranging from 507 nm (THF) to 650 nm (acetylacetone) compared to $\lambda_{\text{max}} = 531$ nm for neat **72** (Figure 38).¹⁵³

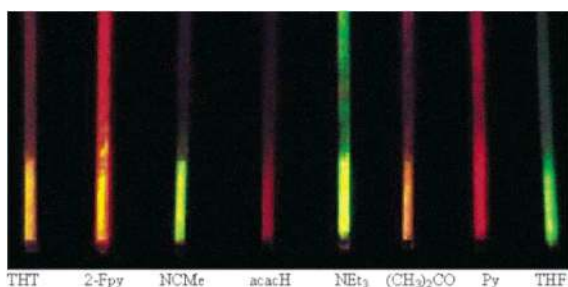
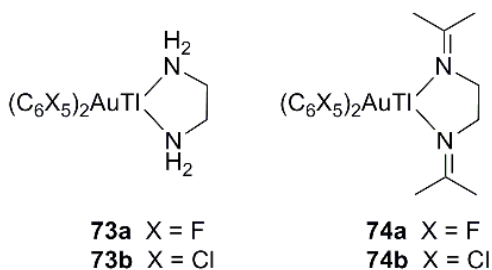


Figure 38. Luminescence vapochromism of compound **72** observed after exposure to various VOCs. Reprinted with permission from ref. ¹⁵⁵. Copyright 2004 American Chemical Society.

Using the appropriate VOCs as solvents, it is possible to synthesize a range of solvent adducts with the general stoichiometry $[\text{TlL}_2[\text{Au}(\text{C}_6\text{Cl}_5)_2]]_n$ (**72L₂**), two of which have been structurally characterized (**72**(tetrahydrothiophene)₂, **72**(2-fluoropyridine)₂).¹⁵⁵ The respective structures contain polymeric chains of cations and anions with unsupported Au(I)-Tl(I) contacts at distances between 2.90894(5) and 3.1981(4) Å which are close to the sum of thallium and gold metallic radii (3.034 Å). The tetrahydrothiophene and 2-fluoropyridine molecules ligate to Tl(I) which is now in pseudo trigonal-bipyramidal coordination with a vacant equatorial coordination site occupied by a lone pair. As a consequence, the Au(I)-Tl(I)-Au(I) interaction is no longer as linear as in neat **72** but more zigzag-like (the Au(I)-Tl(I)-Au(I) angle is 164°). The emission of the individual solvent adducts undergoes a significant red-shift between room temperature and 77 K, suggesting that the luminescence of $[\text{Tl}[\text{Au}(\text{C}_6\text{Cl}_5)_2]]_n$ has its origin in gold-thallium interactions. Time-dependent DFT supports this hypothesis. The geometrical changes around the Tl(I) cation in the course of solvent uptake lead to a change in HOMO-LUMO energy gap because the Au(I)-Tl(I) interaction is perturbed by solvent ligation to the Lewis acid. Importantly, the vapoluminescence response of compound **72** is reversible: Heating of the **72L₂** compounds to 100°C for a few minutes regenerates the solvent-free starting material.

Scheme 32. Vapochromic substances (**73a/73b**) based on ketimine formation (**74a/74b**).



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When reacting equimolar amounts of $[\text{Tl}[\text{Au}(\text{C}_6\text{X}_5)_2]]_n$ ($\text{X} = \text{F}, \text{Cl}$) and 1,2-ethylenediamine (en) one obtains $[\text{Tl}(\text{en})[\text{Au}(\text{C}_6\text{F}_5)_2]]_n$ (**73a**) and $[\text{Tl}(\text{en})[\text{Au}(\text{C}_6\text{Cl}_5)_2]]_n$ (**73b**) as green and white solids, respectively.¹⁵⁶ The ethylenediamine ligand ligates to Tl(I), leading to the pseudo trigonal-bipyramidal coordination geometry discussed above for the **72L₂** compounds. When exposing solid **73a** to acetone or acetophenone vapor it changes color from green to yellow, whereas **73b** changes from white to red with acetone and from white to orange with acetophenone. In order to understand this vapochromic behavior it is important to know that the reaction of **73a** or **73b** with 2 (or more) equivalents of acetone in THF solution yields compounds **74a** and **74b** which are ketimines formed through reaction of the ethylenediamine ligand and acetone. The vapochromism of solids of **73a** and **73b** is most likely due to the same reaction because IR spectroscopy provides clear evidence for the disappearance of the amine N-H stretch in the course of VOC exposure with the simultaneous appearance of imine C=N stretches near 1650 cm^{-1} . Solid **73a/74a** and **73b/74b** are brightly luminescent in different colors hence the compounds can also be used as vapoluminescent sensors. The absorption and emission color changes following ketimide formation have been attributed to perturbation of excitonic states along Tl(I)-Au(I) chains caused by changes in the Tl(I) coordination environment.

3.4 Gold-silver complexes

Bimetallic gold-silver compounds of the general formula $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4\text{L}_2]_n$ (**75L₂**) with a variety of different donor ligands L exhibit vapochromic behavior.^{12, 157} Structural studies of the systems with $\text{L} = \text{Et}_2\text{O}$ (**75(Et₂O)₂**), Me_2CO (**75(Me₂CO)₂**), THF (**75(THF)₂**), and CH_3CN (**75(CH₃CN)₂**) reveal that this class of compounds contains tetranuclear Au_2Ag_2 units linked to

each other along the crystallographic z axis through unsupported Au(I)-Au(I) interactions at distances between 3.1674(11) Å and 3.1959(3) Å, resulting in extended linear-chain compounds (Figure 39).¹⁵⁸

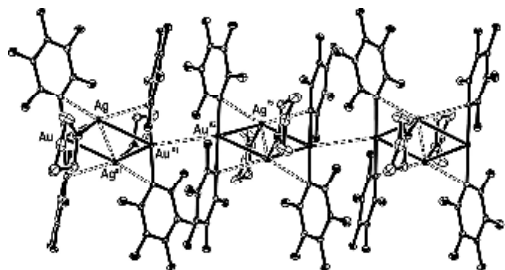
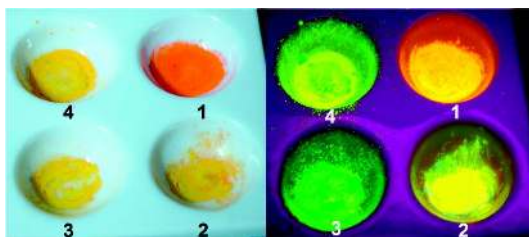


Figure 39. Extract of the crystal structure of compound **75**(THF)₂. Reprinted with permission from ref. ¹⁵⁸. Copyright 2008 American Chemical Society.

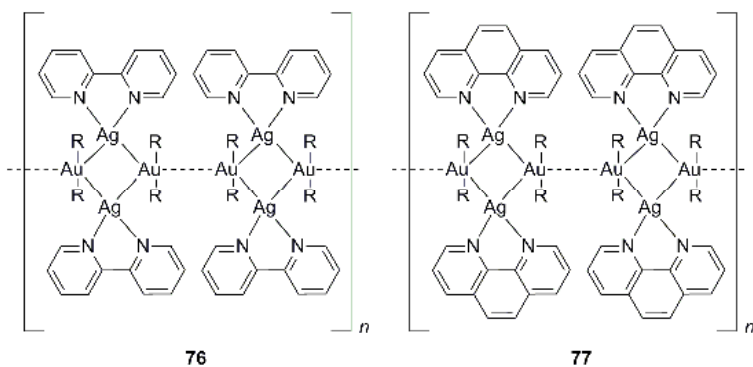
Compound **75**(Et₂O)₂ is obtained by reacting equimolar quantities of [Bu₄N][Au(C₆F₅)₂] and AgClO₄ in a CH₂Cl₂/Et₂O solvent mixture and can be used as a starting material for the syntheses of the other **75**L₂ compounds.^{159, 160} Moreover, exposure of solid **75**(Et₂O)₂ to vapors of acetone, THF or acetonitrile produces rapid color changes that are consistent with replacement of Et₂O by the respective other VOCs (Figure 40).



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3 **Figure 40.** Left: Samples of compound **75**(Et₂O)₂ before (1) and after exposure to vapors of
4 acetone (2), THF (3), CH₃CN (4). Right: Reprinted with permission from ref. ¹⁵⁸. Copyright
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8 2008 American Chemical Society.
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13 IR spectroscopy provides clear evidence for the substitution of the initial O-donor by the
14 stronger N-donor ligand. The exchange ability of the individual VOCs follows the order CH₃CN
15 > Me₂CO > THF > Et₂O, i. e., acetonitrile is able to replace all oxygen donor ligands but not vice
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This observation suggests that true ligand substitution reactions take place at the Au₂Ag₂
core and that the vapochromic behavior of this class of compounds is not simply due to
adsorption of the VOCs into the crystal lattice. Thermogravimetric analyses of the **75L**₂
compounds reveal significant differences between the temperatures at which the donor ligands
(L) are lost, and these variations were interpreted in terms of different boiling points of the
individual VOCs and the strengths of their interactions with the Ag(I) centers.¹⁵⁸ The **75L**₂
compounds are emissive at room temperature and 77 K, presumably involving electronic
transitions on the Au₂Ag₂ core which may be perturbed by changes in the Au(I)-Au(I) and Au(I)-
Ag(I) interactions.

Scheme 33. Vapochromic Au₂Ag₂ compounds. R = C₆F₅.



Several compounds of the stoichiometry $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4\text{L}_2]_n$ have been the subject of more application-oriented studies in which these vapochromic materials were deposited on optical fibers.¹⁶¹⁻¹⁶³ VOC-induced changes in reflected optical power on the order of 2.5 dB – 4 dB were detected.¹⁶¹⁻¹⁶³ In one set of experiments it was possible to distinguish isopropanol from ethanol and methanol, but discrimination between the two shorter alcohols proved more difficult.¹² In several of these vapochromic sensor materials the donor ligand L was a bidentate 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) ligand, i. e., these materials can be formulated as $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{bpy})_2]_n$ (**76**) and $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{phen})_2]_n$ (**77**) (Scheme 33).^{12, 162} Prior to VOC exposure many of these materials are bright yellow but then turn colorless upon sorption of different donor solvents. The loss of color has been attributed to the rupture of intermolecular Au(I)-Au(I) contacts between individual Au_2Ag_2 metallacycles.^{157, 159, 162}

The reaction between $[\text{Bu}_4\text{N}][\text{Au}(4\text{-C}_6\text{F}_4\text{I})_2]$ and AgClO_4 affords a creme-colored solid which can be identified as $[\text{Au}_2\text{Ag}_2(4\text{-C}_6\text{F}_4\text{I})_4]_n$ (**78**).¹⁶⁴ Utilization of the 4- $\text{C}_6\text{F}_4\text{I}$ group instead of C_6F_5 was motivated by the possibility that the *p*-iodo-substituent might form noncovalent halogen-bonds to Lewis donor atoms.¹⁶⁵ Compound **78** is vapochromic toward Me_2CO , THF, or CH_3CN , but no response is detected for non-coordinating solvents such as diethyl ether or toluene. Solvates of compound **78** with the general formula $[\text{Au}_2\text{Ag}_2(4\text{-C}_6\text{F}_4\text{I})_4\text{L}_2]_n \cdot x\text{L}$ (**78L₂·xL**) are

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3 readily obtained when reacting $[\text{Au}_2\text{Ag}_2(4\text{-C}_6\text{F}_4\text{I})_4]_n$ in Me_2CO , THF, or CH_3CN . The respective
4 substances are brightly colored and contain the desired halogen bonds with I-O, I-F, and I-N
5 distances in the range from 2.837(23) to 3.494(15) Å.¹⁶⁴ The acetone solvate
6 (**78**(Me_2CO)₂·2 Me_2CO) and the THF solvate (**78**(THF)₂) can both be converted to the
7 acetonitrile solvate (**78**(CH_3CN)₂) by exposure to vapors of CH_3CN , manifesting in an emission
8 color change from red to bright yellow. Combined structural and emission studies (the latter in
9 fluid solution) lead to the conclusion that two factors drive the vapoluminescence response: (i)
10 the degree of aggregation of individual Au_2Ag_2 clusters into polymeric chains, and (ii) the
11 geometry of the Au_2Ag_2 clusters itself.¹⁶⁴ The aggregation of individual clusters results from an
12 interplay between aurophilic interactions (with Au(I)-Au(I) distances in the range from
13 2.7853(14) to 2.9481(3) Å) and noncovalent halogen bonds. TD-DFT calculations indicate that
14 in the acetone solvate the HOMO is mostly spread over the 4- $\text{C}_6\text{F}_4\text{I}$ ligands with a some
15 contribution of $5d_{z^2}\sigma^*$ character from interacting Au(I)-Au(I) centers. The LUMO is a mixture of
16 $5p\sigma$ bonding density between the Au(I) and Ag(I) centers.

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18 Analogous tetranuclear Au_2Ag_2 compounds with vapochromic properties can be obtained
19 when using 3,5- $\text{C}_6\text{Cl}_2\text{F}_3$ or C_6Cl_5 groups as ligands to the gold atoms.¹⁶⁶ From $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$
20 solution one obtains compounds with the formulas $[\text{Au}_2\text{Ag}_2(3,5\text{-C}_6\text{Cl}_2\text{F}_3)_4(\text{Et}_2\text{O})_2]_n$ (**79**(Et_2O)₂)
21 and $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{Cl}_5)_4(\text{Et}_2\text{O})_2]_n$ (**80**(Et_2O)₂).¹⁶⁶ Upon exposure to the respective VOCs the diethyl
22 ether molecules in **79**(Et_2O)₂ and **80**(Et_2O)₂ can be replaced with THF, acetone or acetonitrile,
23 manifesting itself in a vapochromic response. X-ray crystal structure analyses of $[\text{Au}_2\text{Ag}_2(3,5\text{-}$
24 $\text{C}_6\text{Cl}_2\text{F}_3)_4(\text{THF})_2]_n$ and $[\text{Au}_2\text{Ag}_2(3,5\text{-C}_6\text{Cl}_2\text{F}_3)_4(\text{toluene})_2]_n$ demonstrate that there are polymeric
25 chains of Au_2Ag_2 units held together via aurophilic interactions. The intermolecular Au(I)-Au(I)
26 distances are 2.8617(7) and 2.8863(7) Å in **79**(THF)₂ which is appreciably shorter than in the
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related pentafluorophenyl derivative with THF (**75**(THF)₂) (3.1959(3) Å). However, the compounds with the 3,5-C₆Cl₂F₃ ligand were found to exhibit a relatively poor thermal stability when compared to the pentachlorophenyl derivatives. Contrary to the behavior of compound **75** which has a strong preference for acetonitrile over Et₂O, THF, or acetone (see above),¹⁵⁸ in the [Au₂Ag₂(3,5-C₆Cl₂F₃)₄(CH₃CN)₂]_n material acetonitrile is displaced by vapors of THF or acetone.¹⁶⁶ Similarly, the THF molecules of **79**(THF)₂ can be displaced by acetone from the gaseous phase, but exposure to vapors of acetonitrile leads only to solvate mixtures and incomplete THF substitution.

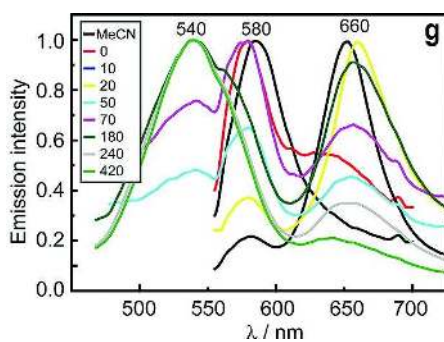


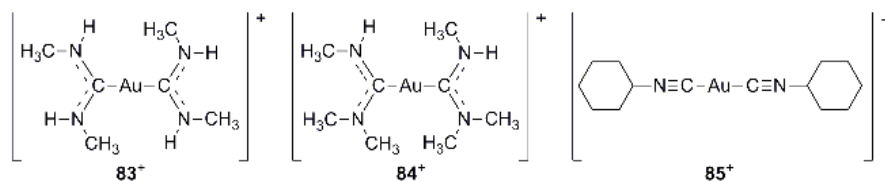
Figure 41. Luminescence changes of compound **81** observed in the course of solvation with fluid CH₃CN. The inset marks the reaction time in minutes. Reprinted with permission from ref.¹⁶⁷. Copyright 2011 American Chemical Society.

When using 2-C₆F₄I instead of 4-C₆F₄I as a ligand to gold(I), the iodine-atom can ligate to Ag(I), thereby mitigating the propensity for polymerization of this class of materials.¹⁶⁷ Accordingly, reaction of Ag(tfa) (tfa = trifluoroacetate) with an equimolar amount of NBu₄[Au(2-C₆F₄I)₂] in CH₂Cl₂ affords (NBu₄)₂[Au₂Ag₂(2-C₆F₄I)₄](tfa)₂ (**81**) which is comprised of tetranuclear monomers with Au(I)-Ag(I) distances in the range from 2.7738(7) to 2.9269(7) Å.

Both 2-C₆F₄I ligands of Au(I) coordinate to Ag(I) with Ag-I distances of 2.7987(9) – 2.9011(9) Å. Solvation of green emitting **81** with fluid CH₃CN leads to the rapid formation of a yellow glowing intermediate (Figure 41), and finally a red luminescent polymeric compound of stoichiometry [Au₂Ag₂(2-C₆F₄I)₄(CH₃CN)₂]_n is obtained. The yellow intermediate is believed to be a material of stoichiometry [Au₂Ag₂(2-C₆F₄I)₄]₂ (**82**) composed of dimers of tetranuclear Au₂Ag₂ clusters. The dimer compound **82** can be obtained from reaction of NBu₄[Au(2-C₆F₄I)₂] with AgClO₄ and is selectively vapochromic toward coordinating solvents such as CH₃CN, THF, and acetone. The fact that the Ag(I) ions in **82** are coordinatively unsaturated seems to be key to the vapochromic behavior.

3.5 Other Au(I) complexes

Scheme 34. Solvoluminescent gold(I) complexes.



Three carbene complexes of gold(I) (**83**PF₆, **83**BF₄, **84**PF₆) (Scheme 34) are frequently cited in the context of vapochromism even though they show the phenomenon of solvoluminescence rather than true vapochromism or vapoluminescence.¹⁶⁸ The 77 K emission of **83**PF₆ is green in acetonitrile, blue in DMSO and pyridine, and orange in acetone (Figure 42).

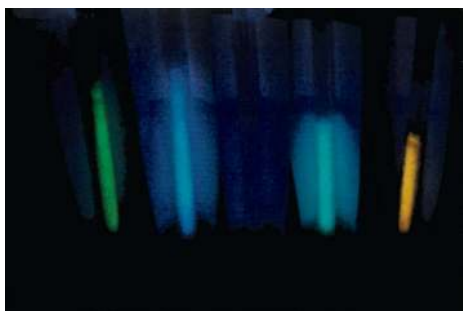


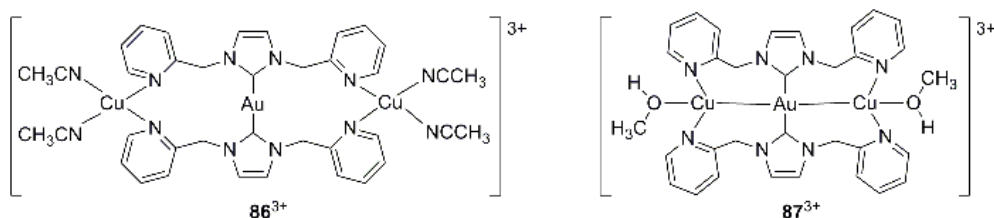
Figure 42. Photoluminescence of frozen solutions of compound **83PF₆** in CH₃CN, DMSO, DMF, pyridine, and acetone. Reprinted with permission from ref. ¹⁶⁸. Copyright 2002 American Chemical Society.

Detailed structural and spectroscopic studies lead to the conclusion that the emission changes induced by concentration and temperature variation are due to the formation of aggregates (dimers, trimers, and higher oligomers) of emissive gold(I) complexes. Thus it appears that aurophilic attractions can overcome the Coulomb repulsion between individual cationic complexes. This can lead to the formation of a band of orbitals made from overlapping (filled) 5d_{z²} orbitals of interacting Au(I) centers and a corresponding unoccupied band made from 6p_z orbitals of gold. The X-ray crystal structure of **83PF₆**·0.5(Me₂CO) features extended columns of cations with an Au(I)-Au(I) separation of only 3.1882(1) Å. Hydrogen-bonding interactions between the emissive cations and the anions could potentially play an important role for the emission properties, at least this would explain the observable differences between **83PF₆** and **83BF₄**. The observation of a hydrogen-bonding network in the abovementioned crystal structure supports this interpretation.

The [(cyclohexyl-isocyanide)₂Au](PF₆) compound (**85PF₆**) exhibits similarly spectacular solvoluminescence behavior as the carbene compounds **83PF₆**, **83BF₄**, and **84PF₆**.¹⁵⁰ A colorless

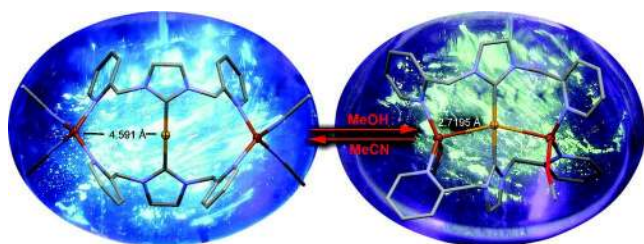
polymorph of the isocyanide compound **86**PF₆ exhibits linear chains with regular Au(I)-Au(I) distances of 3.1822(3) Å, whereas the structure of a yellow polymorph is more complicated with 4 independent Au(I)-Au(I) contacts ranging from 2.9643(6) to 2.9803(6) Å. Such distances are clearly on the short end of known aurophilic interactions.²⁸

Scheme 35. A vapochromic Cu(I)-Au(I)-Cu(I) complex (**86**³⁺) and its reaction product (**87**³⁺) after exposure to MeOH vapor.



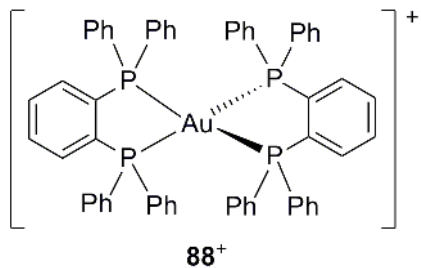
The heterotrimeric Cu(I)-Au(I)-Cu(I) complex **86**³⁺ (Scheme 35) is one out of comparatively few vapochromic substances in which the VOC-induced color change is a direct consequence of a ligand exchange reaction.¹⁶⁹ This complex formed by addition of [Cu(CH₃CN)₄](PF₆) to an acetonitrile solution of the gold(I) imidazole (im) complex [Au(im(CH₂-py)₂)₂](PF₆) which has pendant pyridine (py) units that can bind to copper(I). The intermetallic distances are long (~ 4.6 Å) and presumably repulsive. Single crystals of **86**(PF₆)₃ grown from acetonitrile solution contain two lattice CH₃CN molecules which are lost upon evacuation or prolonged exposure to air, resulting in solvent-free and blue photoluminescent **86**(PF₆)₃. Subsequent exposure of dry **86**(PF₆)₃ to methanol, H₂O, or acetone causes a change in luminescence color from blue to green (Figure 43). THF and CH₂Cl₂ do not induce any change in emission behavior. Crystallization of the trinuclear complex from MeOH/Et₂O mixture directly yields the green emitting compound, which has been identified as **87**(PF₆)₃. X-ray diffraction on single crystals of **87**(PF₆)₃ reveals the

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3 presence of short (2.7915(7) Å) Au(I)-Cu(I) distances. This attractive interaction between
4 individual metals is likely the consequence of the replacement of two CH₃CN molecules per
5 Cu(I) center by only one methanol ligand, making one coordination site of the tetrahedral
6 copper(I) centers available for metal-metal bonding. Compound **87**(PF₆)₃ can be converted to
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8 Cu(I) center by only one methanol ligand, making one coordination site of the tetrahedral
9 copper(I) centers available for metal-metal bonding. Compound **87**(PF₆)₃ can be converted to
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11 **86**(PF₆)₃ by exposure to CH₃CN vapor, i. e., the vapoluminescence is reversible.
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26 **Figure 43.** Crystal structures and emission colors of complexes **86**³⁺ and **87**³⁺. Reprinted with
27 permission from ref. ¹⁶⁹. Copyright 2010 American Chemical Society.
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34 **Scheme 36.** A cationic gold(I) complex whose vapochromic properties strongly depend on the
35 counter-anion.
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52 The tetrahedral gold(I) complex [Au(dppb)₂]⁺ (**88**⁺) (Scheme 36) with two bidentate dppb
53 (dppb = 1,2-bis-(diphenylphosphino)benzene) ligands was isolated with seven different
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55 anions.¹⁷⁰ Small anions such as NO₃⁻, Cl⁻ or BF₄⁻ permit symmetrical coordination of the two
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dppb ligands to the Au(I) center in the crystal lattice, resulting in blue phosphorescence for **88**NO₃ (Figure 44), **88**Cl, and **88**BF₄. Larger cations (e. g., PF₆ or B(4-C₆H₄F)₄⁻) enforce small conformational changes of the dppb ligands in the solid state, resulting in yellow-orange phosphorescence for **88**PF₆ and **88**B(4-C₆H₄F)₄. The nitrate salt is a vapoluminescent substance (Figure 44).¹⁷⁰ Solid **88**NO₃ emits blue light, and the luminescence spectrum is similar to that of free dppb, indicative of ligand-localized phosphorescence ($\tau = 3.3 \mu\text{s}$). Exposure of microcrystalline **88**NO₃ to vapors of ethanol and methanol leads to a rapid change in emission color from blue to orange-yellow (Figure 44), but longer alcohols trigger no response. The respective solvent adducts (**88**NO₃·2EtOH and **88**NO₃·3MeOH) were characterized by single crystal X-ray diffraction and were found to contain structurally distorted [Au(dppb)₂]⁺ units similar to what has been noted above for larger anions. When heating the solvent adducts to 100 °C for ~20 minutes, blue-emitting neat **88**NO₃ is restored.

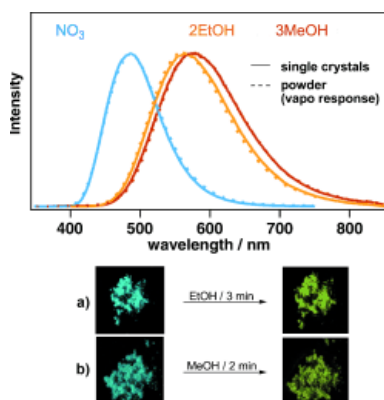


Figure 44. Vapochromic response of **88**NO₃ to ethanol and methanol. (M. Osawa, I. Kawata, S. Igawa, M. Hoshino, T. Fukunaga, D. Hashizume: Vapochromic and Mechanochromic Tetrahedral Gold(I) Complexes Based on the 1,2-Bis(diphenylphosphino)benzene Ligand. *Chem.*

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3 *Eur. J.*, 2010, 16, 12114-12126. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.
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6 Reproduced with permission.)
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11 The tetrafluoroborate salt of **88**⁺ exhibits mechanochromism.¹⁷⁰ Upon extensive grinding the
12 emission color eventually changes from blue to yellow-orange, suggesting that a conformational
13 change of the [Au(dppb)₂]⁺ complex can be induced mechanically. Ground **88**BF₄ is
14 vapoluminescent and exhibits the reverse emission color change following exposure to vapors of
15 acetone, acetonitrile, CH₂Cl₂, diethyl ether, and THF.
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23 A referee of this review article speculated that the cations in some of the emissive salts formed
24 with **88**⁺ have gold(I) only in a three-coordinate state, because luminescence is a common
25 phenomenon for three-coordinate Au(I) but almost unknown for four-coordinate Au(I).
26 Potentially, a hydrogen bond from an alcohol to an anion or to a phosphorus atom can give rise
27 to structural changes, and mechanical stress might cause a flattening of the cations from a quasi-
28 tetrahedral structure.
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39 4. Compounds with metals other than platinum or gold 40 41 42 43

44 Most of the platinum compounds and many of the gold materials from the previous two
45 sections are type I vapochromic systems according to the definition used in section 1.3, i. e.,
46 changes in weak intermolecular interactions (e. g., metal-metal interactions, π -stacking,
47 hydrogen-bonding, or C-H- π interactions) as a result of analyte uptake trigger the vapochromic
48 response. This common theme and the large number of platinum and gold based vapochromic
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3 substances compared to other VOC-sensitive materials provided the rationale for grouping them
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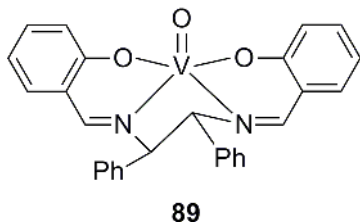
8 Section 4 contains many 3d metal complexes which are inherently more labile than complexes
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10 of 4d or 5d elements. As a consequence type II vapochromic behavior, defined in section 1.3 as
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12 the vapochromism or vapoluminescence response triggered by analyte-induced changes in the
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14 first coordination sphere of the metal, is a unifying theme for many of the VOC-sensitive
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16 materials in this section. Specifically, this encompasses roughly 20 compounds which are treated
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18 in subsection 4.1, sorted along the metal component from vanadium to cobalt, nickel, copper,
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20 and tin; an additional short chapter on metalloporphyrins with various metal centers concludes
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22 this subsection on type II vapochromic materials containing metals other than Pt or Au. In the
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24 majority of the compounds presented in section 4.1, vapochromism is a *direct* consequence of
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26 changes in the ligand field around the metal leading to significant changes in the d-d and/or
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28 MLCT absorptions.
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34 Subsection 4.2 contains about 15 coordination compounds in which the vapochromism is the
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36 result of changes in weak intermolecular interactions. As a matter of fact, the origin of the
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38 vapochromism in these 15 type I materials is quite diverse, and the identification of common
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40 themes for the different classes of materials presented in this subsection is rather difficult; an
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42 attempt to do so has resulted in the division of subsection 4.2 into 5 individual chapters.
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48 4.1 Vapochromism as a result of analyte-induced changes in the first coordination sphere of
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50 the metal
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Scheme 37. A vapochromic oxovanadium(IV) complex.



The oxovanadium(IV) complex **89** (Scheme 37) is the only vapochromic vanadium complex known to date.¹⁷¹ Green crystals are obtained from chloroform solution (**89**·CHCl₃) whereas recrystallization from acetonitrile affords orange crystals (**89**·CH₃CN). The two forms can be converted into one another and contain either monomeric complexes or polymeric chains thereof.¹⁷²⁻¹⁷⁴ In the monomeric green form, the vanadium(IV) center is in square-pyramidal coordination with the V=O group in apical position, in the orange form the vanadyl oxygen atom of one complex ligates to the sixth coordination site of the neighboring vanadium center, resulting in an infinite -V=O-V=O- chain. The polymeric acetonitrile adduct (**89**·CH₃CN) contains two independent molecules per unit cell with V=O bond distances of 1.625(5) and 1.636(5) Å, the distances between the vanadium center and the oxygen atom of a neighboring vanadyl group are 2.188(5) and 2.196(5) Å. When exposing orange crystals of **89**·CH₃CN to chloroform vapor they turn green (Figure 45). Conversely, green crystals of **89**·CHCl₃ change color to orange when exposed to acetonitrile vapor. Due to changes in V=O stretching frequencies the interconversion between the two forms can also be detected by IR spectroscopy. Another interesting observation is the occurrence of mechanochromism in the orange form: Grinding of **89**·CH₃CN affords a green powder, and subsequent addition of a small volume of

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CH₃CN regenerates the initial orange material. Thermochromism is observed for the green form as it turns orange when heated to 120 °C for a few minutes.¹⁷¹

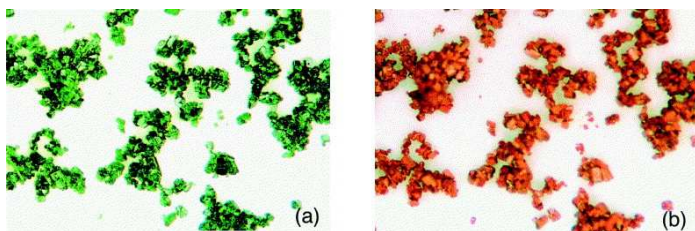


Figure 45. Vapochromism of compound **89** observed following exposure to CH₃CN (green to orange) or CHCl₃ (orange to green). Reprinted with permission from ref. ¹⁷¹. Copyright 2003 Elsevier.

4.1.2 Cobalt complexes

Cobalt(II) complexes are known to undergo relatively facile inter-conversion between octahedral and tetrahedral coordination geometries accompanied by drastic color changes.¹⁷⁵ This property forms the basis of the vapochromic behavior of a few compounds in which octahedral clusters of [Re₆S₈(CN)₆]⁴⁻ or [Re₆Se₈(CN)₆]⁴⁻ connect partially hydrated Co(II) complexes in extended solid frameworks with porous structures.¹⁷⁶ The crystal structure of [Co₂(H₂O)₄][Re₆S₈(CN)₆]₂·12H₂O (**90**·12H₂O) exhibits a three-dimensional network comprised of [Re₆S₈]²⁺ and [Co₂(μ-OH)₂]⁴⁺ cations linked by cyanides (Figure 46).

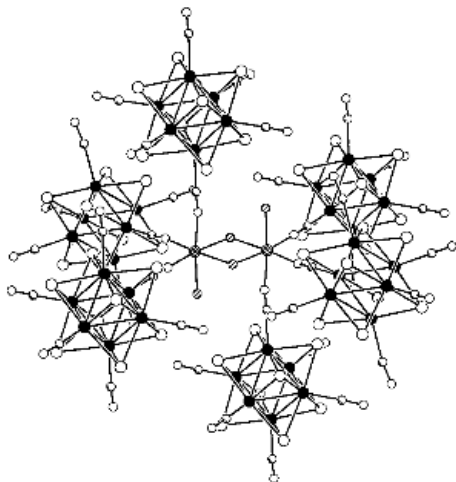


Figure 46. Extract from the crystal structure of $(\mathbf{90}\cdot 12\text{H}_2\text{O})$ showing the $[\text{Co}_2(\mu\text{-OH}_2)_2]$ in the middle and the $[\text{Re}_6\text{S}_8]^{2+}$ clusters around it. Reprinted with permission from ref. ¹⁷⁶. Copyright 2000 American Chemical Society.

The Co(II) ions are in *fac*-configuration with three N-atoms from cyanide and three water ligands, each Re_6 moiety is in turn connected to six Co_2 clusters yielding a Prussian blue type structure. The relatively large size of the $[\text{Re}_6\text{S}_8]^{2+}$ and $[\text{Co}_2(\mu\text{-OH}_2)_2]$ cations entails the formation of large cube-like cages within the Prussian blue type structure comprising a volume of 258 \AA^3 . Each of these cages contains 6 water molecules. The structure of $[\text{Co}(\text{H}_2\text{O})_3]_4[\text{Co}_2(\text{H}_2\text{O})_4][\text{Re}_6\text{Se}_8(\text{CN})_6]_3\cdot 44\text{H}_2\text{O}$ ($\mathbf{91}\cdot 44\text{H}_2\text{O}$) contains a mixture of isolated Co(II) complexes with octahedral coordination and $[\text{Co}_2(\mu\text{-OH}_2)_2]^{4+}$ clusters which are linked via cyanide to the $[\text{Re}_6\text{Se}_8]^{2+}$ units. All framework atoms together occupy only 56% of the total volume of this structure hence the large content of crystal water. Exposure of $\mathbf{90}\cdot 12\text{H}_2\text{O}$ or $\mathbf{91}\cdot 44\text{H}_2\text{O}$ to vapors of diethyl ether leads to a rapid change in color from orange to blue-violet and blue, exposure to THF induces a change to violet or green (Figure 47).



Figure 47. Powder samples of $90 \cdot 12\text{H}_2\text{O}$ (upper line) and $91 \cdot 44\text{H}_2\text{O}$ (lower line) treated with water (as prepared), THF, and diethyl ether (from left to right). Reprinted with permission from ref. ¹⁷⁶. Copyright 2000 American Chemical Society.

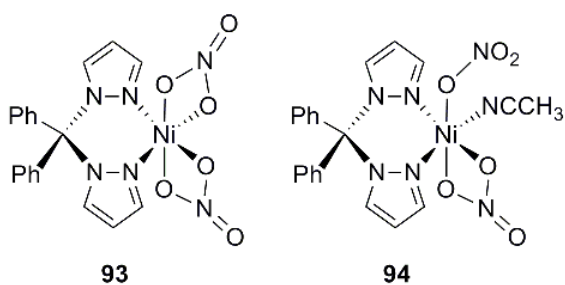
A range of VOCs influence the absorption properties of these two compounds, but diethyl ether leads to the most rapid response. For $90 \cdot 12\text{H}_2\text{O}$ substantial color changes are detected by the naked eye for nitromethane, THF, acetone, propionitrile, *n*-octanol, *n*-propanol, ethyl acetate, isopropanol, and diethyl ether. For $91 \cdot 44\text{H}_2\text{O}$ the most important color changes occur upon exposure to vapors of triethylamine, acetonitrile, THF, EtOH, DMF, acetone, propionitrile, *n*-octanol, methyl *tert*-butyl ether, ethyl acetate, *n*-propanol, isopropanol, and diethyl ether. The changes in the optical absorption spectrum following VOC exposure are fully consistent with inter-conversion of some or all of the Co(II) ions from octahedral to tetrahedral coordination geometry. Specifically, one observes the characteristic ${}^4\text{T}_1(\text{F}) \leftarrow {}^4\text{A}_2$ and ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2$ transitions of tetrahedral $e^4t_2^3$ species. As far as the mechanism of this conversion is concerned, it has been proposed that VOCs enter the cavities and channels of compounds $90 \cdot 12\text{H}_2\text{O}$ and $91 \cdot 44\text{H}_2\text{O}$, thereby disrupting the hydrogen-bonding network which stabilizes the octahedral coordination of Co(II). With bulkier VOC molecules present, labile water ligands are released and the tetrahedral coordination geometry is adopted.

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Reaction of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ with the N,N' -ditopic 2-aminopyrazine (ampyz) ligand in aqueous solution gives a coordination framework with the composition $[\text{Co}(\text{H}_2\text{O})_4(\text{ampyz})_2][\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_2(\text{H}_2\text{O})_2$ (**92**).¹⁷⁷ Intermolecular hydrogen-bonding and π - π interactions lead to the formation of 2D sheets with the sulfate anion playing a key role as a structural element. In diffuse reflectance one detects d-d absorptions of high-spin Co(II) at ~ 9000 cm^{-1} and $19500 - 22000$ cm^{-1} due to ${}^4\text{T}_{2g} \leftarrow {}^4\text{T}_{1g}$ and ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}$ transitions. When heating compound **92** to 220 $^\circ\text{C}$, a color change from orange to purple occurs, accompanied by a loss in crystallinity due to collapse of the supramolecular framework. The color change is most likely the result of a change in the coordination environment of the Co(II) centers, leading to shifts of the d-d absorption bands. Thermogravimetric analysis reveals that the resulting material has the composition $[\text{Co}_2(\text{ampyz})_2](\text{SO}_4)$. Exposure of the dehydrated compound to laboratory air during 8 hours restores the initial orange crystalline material. An isostructural Fe(II) compound and a mixed Co(II)/Fe(II) compound exhibit similar behavior, but their water-vapor sensing properties are less favorable because the color changes occurring upon water uptake are minor.¹⁷⁷

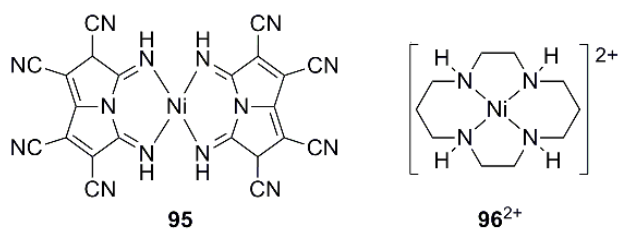
4.1.3 Nickel complexes

Scheme 38. A vapochromic Ni(II) complex (**93**) and its reaction product with acetonitrile (**94**).



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6 A nickel(II) complex with a chelating diphenyl(dipyrazolyl)methane and two nitrate ligands
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8 (**93**) (Scheme 38) shows enough flexibility in its coordination sphere that one of the nitrates can
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10 undergo a change in hapticity from η^2 to η^1 as a function of temperature or acetonitrile vapor
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12 pressure.¹⁷⁸ This ability makes complex **93** a thermochromic and vapochromic substance because
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14 the conversion of **93** into **94** is associated with a color change from green to blue. Shifts in d-d
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16 absorption bands due to electronic transitions from the $^3A_{2g}$ ground state to $^3T_{2g}$, $^3T_{1g}$ (3F), and
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18 $^3T_{1g}$ (3P) excited states are responsible for this change in color. The nitrate hapticity switch is
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20 further associated with a change in the IR spectrum. Complexes **93** and **94** were both
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22 characterized structurally, and their most notable feature is the small bite angle of the bidentate
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24 nitrate ligands leading to *cis*-O-Ni-O angles of about 62° , causing significant distortions from the
25
26 ideal octahedral geometry. The vapor-induced conversion from **93** to **94** can be reversed by
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28 heating to 100°C for a few minutes. The formation of the η^2 complex is favored at higher
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30 temperatures due to entropic effects associated with the release of CH_3CN and chelation of the
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32 nitrate ligand.
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41 **Scheme 39.** Vapochromic Ni(II) complexes.
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The bis(pyrrolizinato)nickel(II) complex **95** (Scheme 39) acts as a vapochromic substance in polyvinylbutyral (PVB) matrices.¹⁷⁹ The initially prepared spin-coated film containing about

0.02 moles of **95** per liter of PVB is light blue but changes to colorless on heating to 90 °C for a few minutes. The colorless state persists at room temperature unless the films are exposed to vapors of various VOCs with alcohols triggering the most rapid response and manifesting in the appearance of an absorption maximum at 661 nm. It is believed that the blue form of **95** is in fact an octahedral complex with two solvent molecules completing the coordination sphere of Ni(II) whereas the colorless form corresponds to the four-coordinate NiN₄ complex represented by structure **95**. The selectivity for alcohols has been attributed to their coordinating ability, the poor response to acetonitrile vapor has been explained by the observation that this solvent shows little tendency to coordinate to **95** even in solution. Curiously, toluene triggers a vapo-chromic response as well, but this has been ascribed to the affinity of the PVB matrix for this particular solvent.

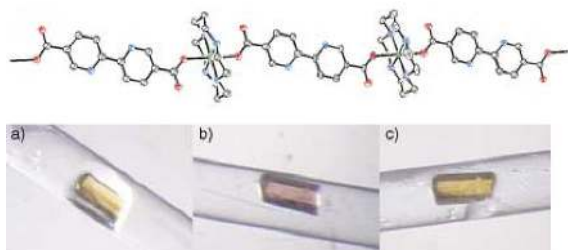


Figure 48. Top: 1D chain structure of [Ni(cyclam)]²⁺ and 5,5'-dcbpy²⁻. Bottom: (a) Crystal of [Ni(cyclam)(dcbpy)]·5H₂O in the mother liquor; (b) same crystal after evacuation at 150°C; (c) same crystal after subsequent exposure to water vapor. (E. Y. Lee, M. P. Suh: A Robust Porous Material Constructed of Linear Coordination Polymer Chains: Reversible Single-Crystal to Single-Crystal Transformation upon Dehydration and Rehydration. *Angew. Chem. Int. Ed.*, 2004, 43, 2798-2801. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

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6 The $[\text{Ni}(\text{cyclam})]^{2+}$ complex (**96**²⁺) and 2,2'-bipyridine-5,5'-dicarboxylate ($5,5'$ -dcbpy²⁻) form
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8 together a robust metal-organic open framework of composition $[\text{Ni}(\text{cyclam})(\text{dcbpy})]\cdot 5\text{H}_2\text{O}$
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10 which is able to undergo reversible single crystal to single crystal transformations.¹⁸⁰ The Ni(II)
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12 center is octahedrally coordinated with axial $5,5'$ -dcbpy²⁻ ligands binding in monodentate fashion
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14 and resulting in a linear coordination polymer chain (Figure 48). Individual chains are linked to
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16 each other through C-H- π interactions involving a carbon atom of the macrocycle and the pyridyl
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18 rings of $5,5'$ -dcbpy²⁻. When heating single crystals of $[\text{Ni}(\text{cyclam})(\text{dcbpy})]\cdot 5\text{H}_2\text{O}$ to 150 °C
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20 under 10^{-5} Torr for several hours there is a color change from yellow to pink. The packing of the
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22 porous framework stays intact, and it appears that the C-H- π interactions are largely responsible
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24 for this. The Ni-O(carboxylate) bonds shorten by 0.025 Å upon dehydration which may be
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26 responsible for the observed color change. In this sense, complex **96**²⁺ is not a clear type II
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28 vapochromic substance (according to the definition used in section 1.3), yet the metal-ligand
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30 bond length change is clearly a significant modification of the first coordination sphere of the
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32 metal center. When exposing the pink dehydrated crystals to air the yellow color is restored
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34 within minutes with retention of single crystallinity.
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44 4.1.4 Copper complexes

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49 When adding excess 4-picoline (4-pic) to a solution of CuI in concentrated aqueous KI one
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51 obtains the material $[\text{CuI}(4\text{-pic})]_{\infty}$ (**97**) which crystallizes in a double-zigzag configuration with -
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53 Cu(I)-I-Cu(I)- connections propagating along the crystallographic b axis (Figure 49). The
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55 shortest Cu(I)-Cu(I) distances in this compound are 2.8087(8) Å,^{181, 182} and this polymeric
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3 material is blue photoluminescent ($\lambda_{\text{max}} = 437 \text{ nm}$) due to the presence of an emissive XLCT
4 (halogen-to-ligand charge transfer) state.²⁰ When exposing it to toluene vapors in a sealed vial
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6 for 2 days, it converts into $[\text{CuI}(4\text{-pic})]_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ (**98**·2C₆H₅CH₃). The tetrameric copper(I)
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8 species of the toluene adduct exhibits comparatively short Cu(I)-Cu(I) distances ranging from
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13 2.651 to 2.735 Å, and the yellow emission of this compound ($\lambda_{\text{max}} = 580 \text{ nm}$) has been attributed
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15 to a cluster-centered (³CC) electronic transition.²⁰ The incorporation of toluene molecules
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17 permits arrangement of the tetrameric units into chains without leaving too many voids between
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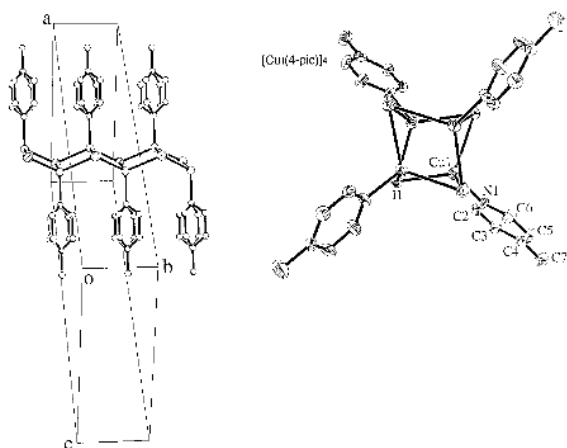


Figure 49. Left: Polymer chain of $[\text{CuI}(4\text{-pic})]_{\infty}$ (**97**) propagating along the b-axis. Right: Structure of the $[\text{CuI}(4\text{-pic})]_4$ (**98**) cluster. Reprinted with permission from ref. ¹⁸⁰. Copyright 2000 American Chemical Society.

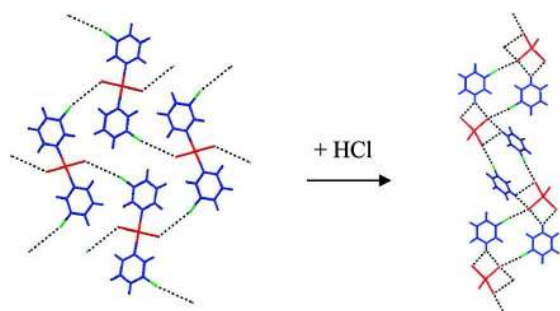


Figure 50. 2D network of compound **99** (with square-planar Cu(II)) and 1D network of compound **100** (with tetrahedral Cu(II)). Reprinted with permission from ref. ¹⁸². Copyright 2007 American Chemical Society.

Reaction of CuCl_2 and 3-chloropyridine (3-Clpy) in methanol solution affords the charge-neutral coordination compound *trans*- $[\text{CuCl}_2(3\text{-Clpy})_2]$ (**99**) in which the copper(II) center is in square planar coordination.^{183, 184} This material is blue and reacts with gaseous HCl to form the yellow salt $(3\text{-ClpyH})_2[\text{CuCl}_4]$ (**100**) in which Cu(II) is tetrahedrally coordinated. This vapor-induced conversion is remarkable because it not only involves cleavage of two Cu-N coordination bonds but also the rupture of the covalent H-Cl bonds to form two new Cu-Cl and N-H bonds. The crystal structure changes from a 2D-network propagated via Cu-Cl – Cl-C halogen bonds (**99**) (Figure 50) to a 1D-network propagated via N-H – Cl_2Cu hydrogen bonds and Cu-Cl – Cl-C halogen bonds (**100**). HCl uptake has been monitored by FTIR spectroscopy from which an equilibrium constant of $1.03(5) \cdot 10^{-5}$ was determined, indicating good sensitivity for HCl detection in the 200 – 20000 ppm concentration range. Temperature dependent FTIR studies show that HCl extrusion is endothermic. X-ray diffraction at a synchrotron facility was used to search for intermediate crystalline phases present at small concentrations but occurring in the process of interconversion between **99** and **100**. However, no such phase could be found and

Rietveld analysis of X-ray powder patterns gave an excellent fit to a two-phase model without the need for involvement of an intermediate (amorphous) phase. This study shows that the molecular solid state can be far more flexible and dynamic than it is generally perceived to be.¹⁸³

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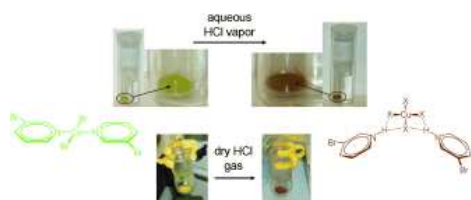


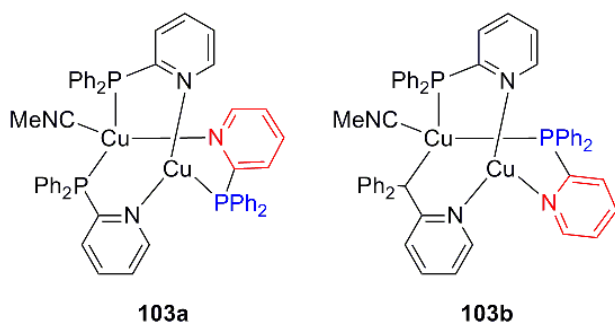
Figure 51. Reaction of *trans*-[CuBr₂(3-Brpy)₂] (**101**) to (3-BrpyH)₂[CuBr₂Cl₂] (**102**). (G. Mínguez Espallargas, J. van de Streek, P. Fernandes, A. J. Florence, M. Brunelli, K. Shankland, L. Brammer: Mechanistic Insights into a Gas-Solid Reaction in Molecular Crystals: The Role of Hydrogen Bonding. *Angew. Chem. Int. Ed.*, 2010, 49, 8892-8896. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

Subsequent related work focused on the isostructural *trans*-[CuBr₂(3-Brpy)₂] (**101**) complex and its reaction with gaseous HCl.¹⁸⁵ This study provided significant new insight into the mechanism of HCl uptake. One important observation is that upon conversion of green **101** to brown (3-BrpyH)₂[CuBr₂Cl₂] (**102**) (Figure 51) the initially present bromo-ligands are not lost. It has been hypothesized that insertion of HCl into Cu-N bonds of **101** is followed by a structural reorientation of the [CuBr₂Cl₂]²⁻ anions which is driven by the formation of hydrogen bonds and halogen bonds. Indeed it was found that the chloride population of a given crystallographic site correlates with the total number of strong intermolecular interactions formed, either hydrogen or halogen bonds. Thus, the hypothesis from above makes sense because the respective noncovalent

(and mainly electrostatically driven) interactions are expected to be stronger with chloride than with bromide due to the more negative electrostatic potential of Cl^- . Methodologically, the reaction of *trans*- $[\text{CuBr}_2(3\text{-Brpy})_2]$ with HCl resembles isotope labeling experiments only that Cl and Br exhibit sufficiently different X-ray scattering power that differentiation of the two halides becomes easily possible with X-ray diffraction.

Green *trans*- $[\text{CuBr}_2(3\text{-Brpy})_2]$ (**101**) reacts with HBr to brown $(3\text{-BrpyH})_2[\text{CuBr}_4]$, but this material has a different crystallographic structure with different supramolecular connections than **100** and **102**.¹⁸⁶ However, release of HBr from $(3\text{-BrpyH})_2[\text{CuBr}_4]$ or HCl from **100/102** leads to an isostructural series of compounds.

Scheme 40. Vapochromism based on ligand flip isomerization.



An interesting case of linkage isomerism has been reported for $[\text{Cu}_2(\text{dppy})_3(\text{CH}_3\text{CN})](\text{BF}_4)_2$ (dppy = diphenylphosphino-pyridine) (Scheme 40).¹⁸⁷ This binuclear complex has its dppy ligands arranged in head-to-tail fashion with two phosphorus atoms binding to one copper(I) center and the third to the other one (**103a**). Recrystallization of **103a** from a mixture of CH_2Cl_2 and CH_3OH affords the methanol adduct (**103b**· CH_3OH) which has one of its dppy ligands flipped, resulting in head-to-head orientation of all three ligands. Because of the hemilability of

the dppy ligand it is further possible to convert blue photoluminescent **103a** ($\lambda_{\text{max}} = 489 \text{ nm}$) into green emissive **103b**·CH₃OH ($\lambda_{\text{max}} = 520 \text{ nm}$) by exposure of solid **103a** to methanol vapor, and this process can be fully reversed when heating the methanol adduct to 203 °C. The linkage isomerization reaction is accompanied by a significant increase of the Cu(I)-Cu(I) separation from 2.721(3) Å in **103a** to 2.7961(4) Å in **103b**·CH₃OH and by an increase of π - π interactions manifesting by short distances between the phenyl and pyridyl planes in the methanol adduct. These two structural changes are most likely jointly responsible for the shift in emission wavelength upon CH₃OH uptake.

Scheme 41. A copper complex exhibiting concentration lumichromism.

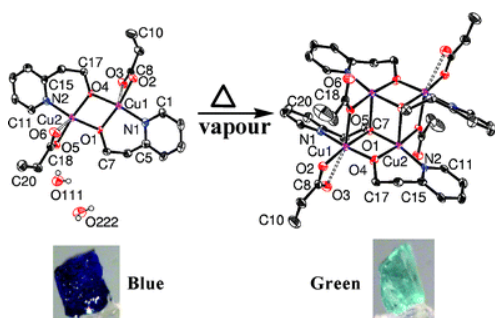
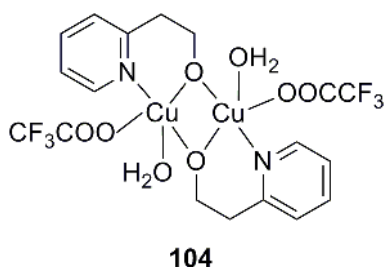


Figure 52. Conversion of dimeric blue **104**·2H₂O to a tetrameric green product. Copyright 2010

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A dinuclear copper(I) complex with 2-(2-hydroxyethyl)pyridine (μ -hep) and *n*-propionate (O^nPr) ligands (**104**) shows the unusual phenomenon of a vapor-induced single crystal to single crystal transformation.¹⁸⁸ Initially the $[(O^nPr)Cu(\mu\text{-hep})_2Cu(O^nPr)]$ complex is obtained as a dihydrate (**104** \cdot 2H₂O). When heated to 110 °C this blue compound releases water and undergoes a structural change to a green tetrameric complex under retention of its crystallinity (Figure 52). The tetramer has the structure of a double open cubane. The same structural conversion can be induced at room temperature when exposing **104** \cdot 2H₂O to various VOCs, albeit with different response times. Whereas CH₃OH produces a response within 5 minutes, ethanol, isopropanol, and acetonitrile require exposure times of 2 hours, 24 hours, and 8 days, respectively. In view of the fact that multiple bond breaking and bond making processes must occur, this structural conversion in the single crystalline state is remarkable. However, the overall process is irreversible. Analogous compounds with acetate instead of *n*-propionate were also investigated but did not show vapo-chromic behavior.¹⁸⁸

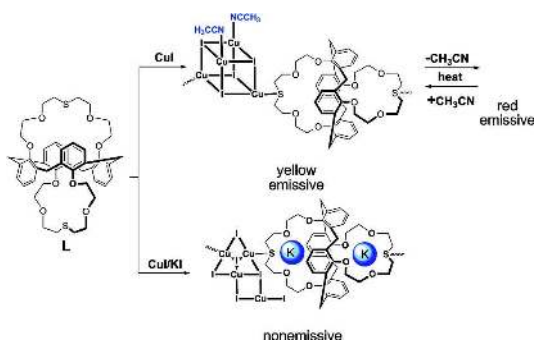


Figure 53. Reactivity and luminescence behavior of $[(Cu_4I_4)L(CH_3CN)_2]_n$ (**105** \cdot (CH₃CN)₂).

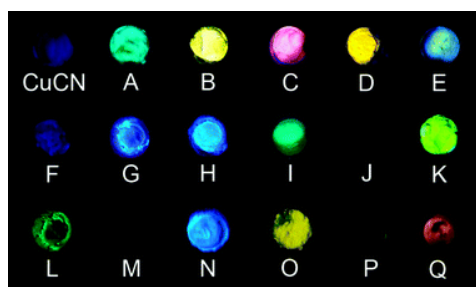
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3 Reaction of a calix[4]-*bis*-monothiacrown (L) with CuI in acetonitrile leads to the formation of
4 a 1D polymeric material with the formulation $[(\text{Cu}_4\text{I}_4)\text{L}(\text{CH}_3\text{CN})_2]_n$ (**105**·(CH₃CN)₂) (Figure
5 53).¹⁸⁹ It contains cubane-like Cu₄I₄ clusters which are linked to one another by the calix[4]-*bis*-
6 monothiacrown ligands through two of the four Cu(I) ions, while the two other metal centers
7 bear acetonitrile ligands. The yellow photoluminescence of compound **105** ($\lambda_{\text{max}} = 567$ nm) was
8 assigned to a cluster-centered excited state with admixed halide-to-metal charge transfer (XLCT)
9 character. Addition of KI leads to the incorporation of K⁺ ions into the thiacycrowns, a process
10 which is accompanied by emission quenching, perhaps because of η^5 -type cation – π
11 interactions. When heating potassium-free samples to 150 °C for 1 hour the acetonitrile ligands
12 are released, producing a red photoluminescent ($\lambda_{\text{max}} = 600$ nm) compound. Bulk crystallinity is
13 maintained and thus the process is reversible, manifesting in a vapoluminescence response upon
14 exposure of the de-solvated material to CH₃CN.
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32 Six different coordination compounds have been isolated as products from the reaction
33 between CuI and triphenylphosphine (PPh₃).¹⁹⁰ One out of two cubane-type polymorphs with the
34 stoichiometry $[\text{CuI}(\text{PPh}_3)_4]$ (**106a**) converts to an isomer when exposed to vapors of acetonitrile,
35 dichloromethane or ethanol. In the product (**106b**), two opposite edges of the cubane-like
36 structure are broken up, and a molecular structure resembling that of cyclooctane is formed.
37 Compound **106a** emits green light ($\lambda_{\text{max}} = 518$ nm, $\tau = 3.2$ μs) upon UV excitation at room
38 temperature whereas its isomer **106b** is essentially nonluminescent under these conditions,
39 paving the way to vapor-induced luminescence on/off switching.
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51 Copper(I) cyanide (**107**) reacts with a variety of different amines (both in the liquid and vapor
52 phase) to produce adducts of the stoichiometry $\text{CuCN}\cdot\text{L}_n$ with $n = 0.75 - 2.0$.¹⁹¹⁻¹⁹³ Neat CuCN
53 emits at the edge of the visible spectral range with $\lambda_{\text{max}} = 392$ nm, but the solvent adducts
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3 luminesce with different colors throughout the visible spectral range with λ_{max} depending on the
4 exact nature of the amine (L) (Figure 54).¹⁹¹ The $\text{CuCN}\cdot\text{L}_n$ adducts can be obtained on the
5 preparative scale by heating CuCN suspensions in neat amines and hence can be characterized
6 structurally. Single crystals suitable for X-ray diffraction were obtained with $\text{L} =$ pyridine, 2-
7 methylpyridine, 4-methylpyridine, 3-ethylpyridine, 4-(*t*-butyl)pyridine, piperidine, *N*-
8 methylmorpholine, and *N,N*-dimethylcyclohexane. Each of these structures contains chains of
9 CuCN with the cyano C/N positions disordered in most cases, and in each structure (except for
10 $\text{CuCN}\cdot 4$ -(*t*-butyl)pyridine) the amine is directly bonded to copper(I). Depending on the amine
11 content (n), the Cu(I) centers are either 3- or 4-coordinate. The photoluminescence behavior of
12 these authentic solvent adducts is identical to that observed for samples of CuCN that have been
13 exposed to vapors of the respective amines. However, powder X-ray diffraction reveals that only
14 a fraction of vapor-exposed CuCN reacts to the adduct $\text{CuCN}\cdot\text{L}_n$, and thus it seems that only the
15 surface of CuCN is able to react with the amine vapors. This interpretation is compatible with the
16 high reversibility of the vapoluminescent response. Based on DFT calculations the HOMO of the
17 $\text{CuCN}\cdot\text{L}_n$ compounds is mostly comprised of the $3d_{z^2}$ orbital of the metal while the LUMO is a
18 mixture of 4p orbitals of Cu(I) and π^* orbitals of the cyano ligand,¹⁹⁴ and consequently it might
19 be argued that the emission has mixed d-d and MLCT character.
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3 **Figure 54.** Luminescence of neat CuCN (upper left) and various solvent adducts of CuCN (A-
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6 Q). Copyright 2010 The Royal Society of Chemistry.
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11 The reaction of CuI with selected *N,N'*-disubstituted piperazines (pip) in acetonitrile yields
12 (CuI)₂(pip) compounds consisting of chains with piperazine-linked Cu₂I₂ rombs.¹⁹⁵ These
13
14 structures with 3-coordinate Cu(I) are obtained only for sterically crowded *N,N'*-
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16 diethylpiperazine (Et₂pip), *N,N'*-dibenzylpiperazine (Bnpip), *N,N'*-bis-phenylethylpiperazine
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18 (PhEtpip), producing compounds (CuI)₂(Et₂pip) (**108a**), (CuI)₂(Bn₂pip) (**108b**), and
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20 (CuI)₂((PhEt)₂pip) (**108c**), whereas sterically less demanding piperazines lead to structures with
21
22 4-coordinate Cu(I). The Cu(I)-Cu(I) distances in **108a-c** range from 2.4716(11) to 2.4837(14) Å
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24 and are significantly below the van der Waals distance (~2.80 Å), indicative of substantial
25
26 metallophilic interactions. Exposure of **108a** and **108b** to vapors of amine and sulfide
27
28 nucleophiles (Nu) leads to brightly photoluminescent materials which show identical
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30 luminescence properties as the respective (CuI)₄(Nu)₄ compounds, suggesting that Nu vapor
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32 exposure induces the reaction 2 (CuI)₂(pip) + 4 Nu → (CuI)₄(Nu)₄ + 2 pip. Depending on the
33
34 nucleophile, luminescent materials with emission colors ranging from blue (Nu = 2-
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36 methylpyridine) to red (Nu = morpholine) are obtained. Other nucleophiles which give a
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38 vapoluminescence response are pyridine, 3-methylpyridine, , piperidine, pyrrolidine, pyrrolidine,
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40 diethylamine, dimethyl sulfide.¹⁹⁵ Vapors of 2-chloropyridine, 3-chloropyridine, and *N*-
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42 methylpiperidine yield non-emissive compounds.
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4.1.5 Tin

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Four commercial tin(II) salts were found to be useful for optical sensing of amine vapors at concentrations as low as 100 ppb.¹⁹⁶ Specifically, tin(II) sulfate (SnSO_4 , **109a**), tin(II) methanesulfonate ($\text{Sn}(\text{CH}_3\text{SO}_3)_2$, **109b**), tin(II) triflate ($\text{Sn}(\text{OTf})_2$, **109c**), and tin(II) fluorophosphate (SnPO_3F , **109d**) were found to display visible room temperature emission after exposure to vapors of NH_3 , EtNH_2 , Et_2NH , Et_3N , or $\text{N}(\text{C}_5\text{H}_5)_3$. Importantly, each of the four tin(II) salts responds differently to the five amines, and consequently similar analytes can be distinguished from each other rather easily. Many other nucleophilic analytes have little impact on the emission properties, but it has been noted that for real-world applications the water-sensitivity of several of the tin(II) salts is problematic. For instance the emission intensity of amine-vapor exposed $\text{Sn}(\text{CH}_3\text{SO}_3)_2$ and $\text{Sn}(\text{OTf})_2$ drops considerably in presence of atmospheric humidity. The fundamental reasons for the luminescence turn-on response in presence of amines is unclear,¹⁹⁶ it was merely noted that tin(II) is known to form complexes with amine-containing molecules.^{197, 198}

4.1.6 Metalloporphyrins

Due to their intense colors and the presence of axial binding sites metalloporphyrins are of interest for sensing of coordinating VOCs. An application-oriented study falling into the category of “electronic nose” research made use of arrays containing 11 different tetraphenylporphyrin-based compounds for achieving chemoselective vapor visualization. The tetraphenylporphyrin was either used as a free base, or with Sn(IV), Co(III), Cr(III), Mn(III), Fe(III), Co(II), Cu(II), Ru(II), Zn(II) and Ag(II).¹⁹⁹ These metals span a wide range of ligand affinity which opens the possibility for obtaining unique color fingerprints upon VOC exposure

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3 at analyte concentrations below 2 ppm. A wide range of ligating solvents including alcohols,
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5 amines, thiols, thioethers, and phosphines can be detected and distinguished from each other by
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7 taking the difference before and after vapor-exposure of the scanned images of the arrays. The
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9 porphyrins were dissolved in dibutylphthalate in polystyrene matrix, and deposition of small spots
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11 with 0.5 mm diameter was found to optimize the response time. The porphyrin spots can be
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13 deposited using an ink-jet technique in order to obtain cheap disposable sensor arrays.
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17 Zinc(II) tetraphenylporphyrin (**110**) dissolved in silicone rubber can be used for detection of
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19 ammonia vapor at concentrations as low as 0.7 ppm.²⁰⁰ In the course of NH₃ ligation to ZnTPP
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21 the Soret band shifts from 414 to 424 nm, and similar spectral changes were observed on
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23 exposure to triethylamine. Silicone films of ZnTPP produce significantly better results than
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25 Nafion or ethyl cellulose support matrices. The latter is apparently impermeable for ammonia gas
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27 while the Nafion films were very thin (10 μm) and resulted in weak absorption.
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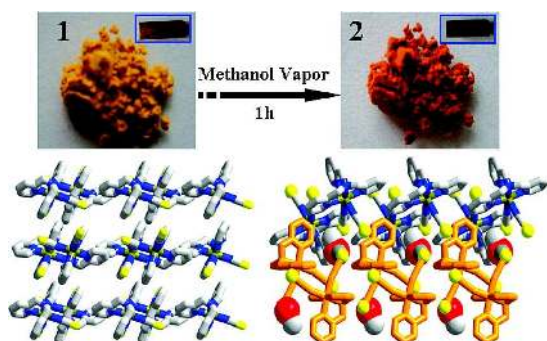
34 4.2 Vapochromism as a result of indirect analyte-metal interactions 35 36 37 38

39 This subsection treats the remainder of metal-containing vapochromic substances that cannot
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41 easily be grouped according to a single unifying theme. These materials contain different metals
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43 and their vapochromism has diverse origins. The division into 5 chapters is an attempt to group
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45 these substances according to common themes and/or origin of their vapochromic properties.
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50 4.2.1 Vapochromism as a consequence of a change in spin state 51 52 53 54 55 56 57 58 59 60

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3 A single crystal to single crystal transformation has been reported for the spin-crossover
4 compound $\text{Fe}(\text{tpa})(\text{NCS})_2$ (**111**) (tpa = tris-(2-pyridylmethyl)amine).²⁰¹ This molecule
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crystallizes in a relatively open structure with individual molecules arranged via π - π interactions in one direction and hydrogen bonds in a second direction. The Fe-N distances are between 1.977(8) to 2.091(6) Å, which is typical for low-spin Fe(II)-N bonds. Exposure to methanol vapor leads to a new compound which is best formulated as $[\text{Fe}(\text{tpa})(\text{NCS})_2] \cdot [\text{Fe}(\text{tpa})(\text{NCS})_2 \cdot \text{CH}_3\text{OH}]$ (**111**·**[111**· CH_3OH]). In the crystal structure determined at 120 K this methanol adduct exhibits Fe-N distances contracted by about 0.2 Å, indicating that a low-spin to high-spin transition has taken place. The change in spin state has been confirmed by Mössbauer spectroscopy and is accompanied by a change in color from yellow (**111**) to red (**111**·**[111**· CH_3OH]) (Figure 55). Remarkably, the methanol molecule is not directly interacting with any of the two metal centers, but it merely changes the way individual molecules interact with each other yet this suffices to induce the spin transition. As an additional subtlety the two crystallographically distinct iron centers give rise to three different spin crossover phases: At 120 K both metal centers are low-spin, at 298 K one Fe(II) is high-spin while the other is low-spin, and at 350 K both metals are high-spin.



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3 **Figure 55.** Change in appearance and crystal structure of compound **111** upon exposure to
4 MeOH vapor. The red form contains two crystallographically distinct types of Fe complexes and
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6 is best formulated as **111**·[**111**·CH₃OH]. Reprinted with permission from ref. ²⁰¹. Copyright 2010
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8 American Chemical Society.
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17 Ethanol gives an adduct of similar stoichiometry as methanol (**111**·[**111**·C₂H₅OH]), i. e., a
18 compound with two crystallographically distinct Fe(II) centers. By contrast, all other tested
19 solvents (*n*-PrOH, *i*-PrOH, CH₃CN, CH₂Cl₂, and CHCl₃) yield adducts of the same stoichiometry
20 as the solvent-free parent compound (**111**) in which all Fe(II) centers are identical.²⁰² Adducts of
21 **111** with any of the latter five solvents undergo a color change from yellow/brown to red
22 following exposure to ethanol vapor, indicating that a similar low-spin to high-spin transition as
23 discussed above for methanol is occurring. When **111**·[**111**·C₂H₅OH] is exposed to vapors of
24 CH₂Cl₂ or CHCl₃ the color reverts to yellow. Comparison of magnetic and structural properties
25 within this family of materials has led to the conclusion that hydrogen-bonding interactions
26 between solvent molecules and the metal complexes tend to enhance the ligand field exerted on
27 the Fe(II) center, and this obviously plays a key role for the spin-crossover behavior.²⁰³
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4.2.2 Hydrogen-bonded proton transfer assemblies

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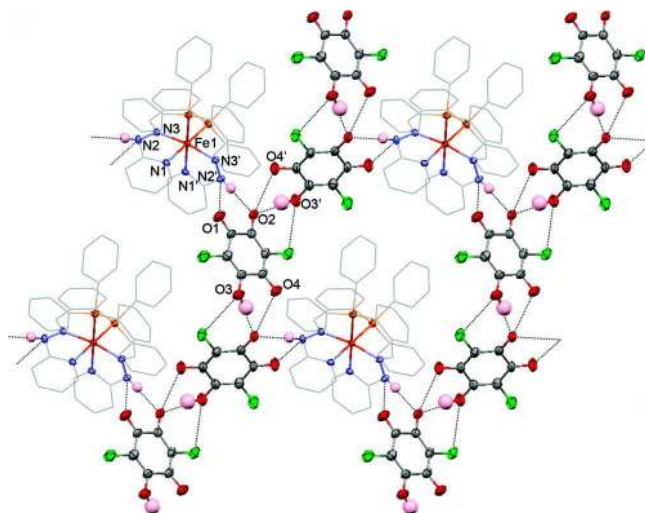
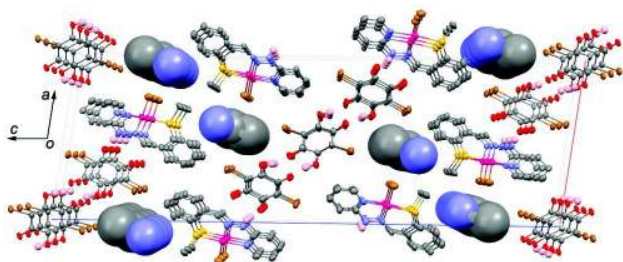


Figure 56. Extract from the crystal structure of **112·2THF**. Reprinted with permission from ref.
²⁰⁴. Copyright 2011 American Chemical Society.

A vapochromic hydrogen-bonded proton transfer (HBPT) assembly is obtained from reaction between $\text{Fe}(\text{pbph})_2 \cdot 3\text{H}_2\text{O}$ ($\text{pbph} = 2\text{-(diphenylphosphino)benzaldehyde-2-pyridylhydrazone}$) and chloranilic acid (H_2CA) in THF.²⁰⁴ The stoichiometry of the final compound is $\text{Fe}(\text{Hpbph})_2(\text{HCA})_2 \cdot 2\text{THF}$ (**112·2THF**), i. e., two protons are transferred from two chloranilic acid molecules to the pbph ligands. In the crystal structure of this compound (Figure 56) there are two 2D hydrogen-bonded sheets containing interactions between cationic metal complexes and HCA^- , as well as interactions between individual HCA^- anions. The THF guest molecules are located between these sheets. When **112·2THF** is heated to 158 °C all THF molecules are eliminated from the lattice. Subsequent exposure to vapors of THF restores the initial assembly. Adduct **112·2THF** itself is susceptible to various organic vapors including aprotic and protic solvents. Diffuse reflectance reveals spectral changes around 610 nm with CH_2Cl_2 and Et_2O producing distinctly different changes than MeOH, EtOH or acetic acid. The spectral changes

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3 occurring with the protic solvents are perceived as a color change from brick-red to orange,
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5 resulting presumably from perturbation of hydrogen-bonding interactions in the HBPT assembly.
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8 The iron(II) center does not appear to be directly involved in the vapochromic behavior.
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11 Palladium has also been incorporated into a vapochromic hydrogen-bonded proton transfer
12 (HBPT) assembly.²⁰⁵ Specifically, a Pd(II)-hydrazone complex (PdBr(Hmtbhp); Hmtbhp = 2-(2-
13 (2-methylthio)benzylidene)hydrazinyl)pyridine) was combined with bromanilic acid (H₂BA), a
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15 widely used building block for supramolecular architectures known for its ability to accept one
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17 electron and donate two protons.^{206, 207} The HBPT assembly **113**
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19 ([PdBr(Hmtbhp)]₂(HBA)₂(H₂BA)) can uptake CH₃CN reversibly, resulting in a color change
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21 from reddish purple to dark red. In the resulting solvent adduct the acetonitrile molecules form
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23 1D channels along the crystallographic b-axis (Figure 57), and upon heating to 100 °C in argon
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25 atmosphere the guest-free assembly can be recovered.
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43 **Figure 57.** Packing diagram of HBPT assembly **113** with CH₃CN guest molecules shown as
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45 space filling models. Reprinted with permission from ref. ²⁰⁵. Copyright 2010 American
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54 However, acetonitrile removal alters the powder X-ray diffraction pattern significantly,
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56 indicating that the supramolecular assembly is not robust enough to retain its structure without
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3 the CH₃CN guests. Depending on what solvent vapors HBPT assembly **113** is exposed to, the
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5 lowest energetic absorption band either blue-shifts (DMF, pyridine, dimethylacetamide,
6
7 DMSO) or red-shifts (1,4-dioxane, CH₃CN, MeOH, EtOH). The absorption band shifts seem to
8
9 correlate with Gutmann donor and acceptor numbers of the solvents.²⁰⁸ Presumably, the
10
11 hydrogen-bonding mode of the supramolecular assembly is fundamentally changed upon
12
13 sorption of solvents with a high donor number, and such proton-accepting solvents seem to be
14
15 adsorbed more easily than proton-donating solvents with a large acceptor number. Palladium
16
17 does not appear to be directly involved in the vapochromic behavior of assembly **113**; in this
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19 regard the classification of this material as a Pd-based vapochromic substance is not optimal.
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27 4.2.3 Metallophilic, π - π , and donor-acceptor interactions

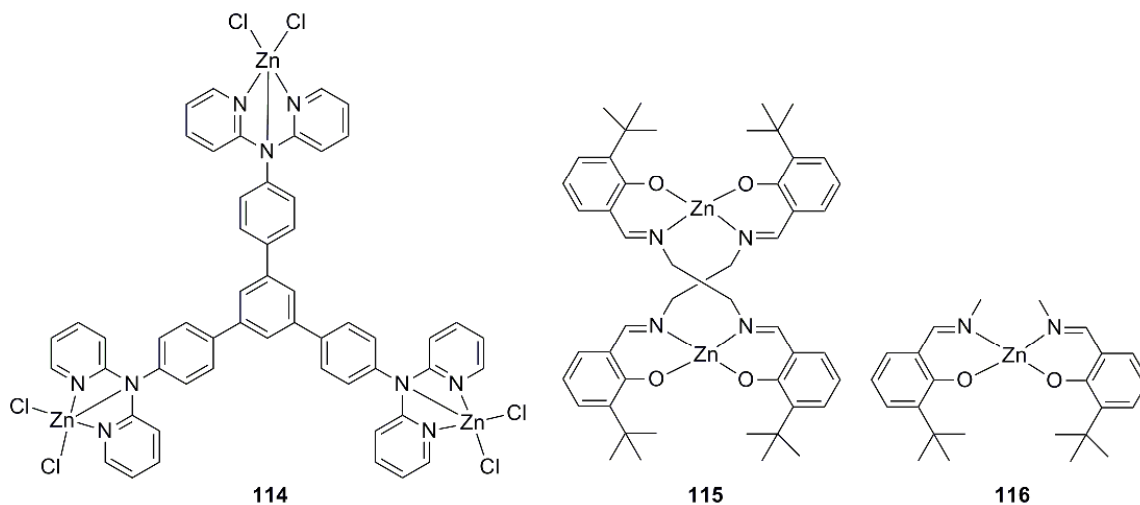
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32 A zinc(II) complex of 1,3,5-tris(*p*-(2,2'-dipyridylamino)phenyl)benzene (TPDPB) (Scheme
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34 42) can selectively detect benzene vapors at concentrations of ~500 ppm.²⁰⁹ Depending on
35
36 crystallization conditions, two different forms are obtained. When using a small amount of
37
38 benzene in CH₂Cl₂, form A with the composition [(ZnCl₂)₃(TPDPB)]·3CH₂Cl₂·0.25C₆H₆
39
40 (**114**·3CH₂Cl₂·0.25C₆H₆) crystallizes, whereas a 1:1 mixture of benzene and CH₂Cl₂ affords form
41
42 B with the composition [(ZnCl₂)₃(TPDPB)]·3C₆H₆ (**114**·3C₆H₆). In the crystal structure of form
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44 A individual molecules of **114** build pairs with a separation of 3.85(1) Å between their central
45
46 phenyl rings, and the TPDPB ligands are rotated by 120° relative to each other to give a
47
48 staggered face-to-face orientation. Benzene guest molecules are sandwiched between two pairs
49
50 of host molecules, undergoing π - π stacking with the central phenyl rings of **114** at an interplanar
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52 distance of 3.60(1) Å. In form B the molecular packing is fundamentally different with both
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edge-to-edge and face-to-face interactions between benzene and the host present. The occurrence of two forms of benzene inclusion structures was taken as evidence for the affinity of **114** for benzene, and hence the benzene-sensing properties of this compound were tested by depositing it onto a polydimethylsiloxane (PDMS) bead which was attached onto an optical fiber tip. In the solid state, **114** is blue photoluminescent ($\lambda_{\text{max}} = 430 \text{ nm}$) with an emission band resembling that of the free TPDPB ligand, only red-shifted by $\sim 30 \text{ nm}$. Upon exposure to vapors of benzene the emission is quenched, presumably because the benzene guests undergo π - π stacking with the host, similar to what is observed in the two crystal structures discussed above. Interestingly, toluene, xylene, and ethyl benzene induce a much weaker response, similar to what is observed for hexane, cyclohexane, methanol, ethanol, CH_2Cl_2 , trichloroethylene, or perchloroethylene. Thus, compound **114** exhibits a remarkable selectivity for benzene vapors.

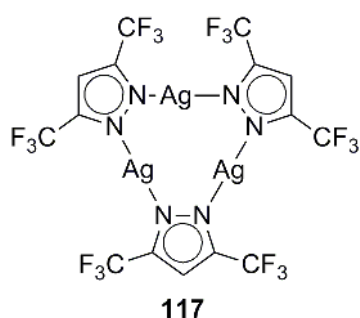
Scheme 42. Zinc(II) complexes investigated in the context of vapochromism.



A helical zinc(II) dimer complex with two 3,3'-di-*tert*-butylsalen (*t*-Busalen) ligands (**115**) shows mechanochromic and vapochromic behavior.²¹⁰ The $[\text{Zn}_2(\textit{t}\text{-Busalen})_2]$ complex is green

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3 photoluminescent ($\lambda_{\text{max}} = 473$ nm), quite different from its monomer analogue (**116**) which emits
4
5 blue light upon UV irradiation ($\lambda_{\text{max}} = 456$ nm). The X-ray crystal structure of the dimer
6
7 complex **115** reveals significant intramolecular π - π stacking interactions between individual
8
9 phenyl rings of the 'Busalen ligands. Mechanical grinding of **115** or exposure to THF vapor
10
11 produces a blue luminescent substance, suggesting at first glance that these external stimuli
12
13 disrupt the intramolecular π - π interactions, leading to non-interacting luminophors which exhibit
14
15 similar emission properties as the monomer reference substance (**116**). However, careful analysis
16
17 of X-ray diffraction and emission data of **115**·THF and **115**·MeOH reveals that the emission
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19 color is in fact correlated with the crystal packing structure and that *intermolecular* π - π stacking
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21 is the key to the change in photoluminescence color.²¹⁰
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30 **Scheme 43.** A vapo-chromic silver(I) complex.
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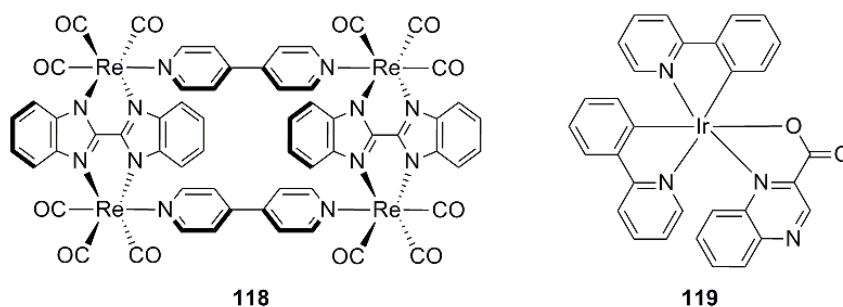
46
47 The trinuclear pyrazolyl-bridged silver(I) complex $[[3,5-(\text{CF}_3)_2\text{pz}]\text{Ag}]_3$ (**117**) (Scheme 43)
48
49 forms π -acid/ π -base binary adducts with benzene and some of its methylated derivatives.²¹¹ X-
50
51 ray crystal structure analysis of a benzene adduct reveals the presence of discrete tetramolecular
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53 units comprised of a benzene/**117**/**117**/benzene sequence. Being a stronger π -base than benzene,
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55 mesitylene is able to overcome the argentophilic interactions between neighboring complexes,
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3 and consequently an infinite chain of **117**/mesitylene/**117**/mesitylene units is formed with this
4
5 compound. This difference in packing structure between benzene and mesitylene adducts has
6
7 important implications for the photoluminescence behavior. While neat **117** is non-emissive, the
8
9 benzene adduct shows green luminescence ($\lambda_{\text{max}} \approx 520$ nm) and the mesitylene adduct emits in
10
11 the blue spectral range ($\lambda_{\text{max}} \approx 410$ nm). The green luminescence has been attributed to excimeric
12
13 states involving argentophilic interactions,²¹² the disruption of these intermetallic contacts in the
14
15 mesitylene adduct leads to blue emission. Thin films of **117** respond to vapors of benzene,
16
17 toluene, and mesitylene with a luminescence turn-on response, in line with the formation of the
18
19 solvent adducts described above. Aromatic solvents with electron-withdrawing substituents such
20
21 as chlorobenzene and hexafluorobenzene do not switch on the luminescence. Similarly, non-
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23 aromatic solvents such as acetone, methanol, and THF do not trigger a response. These
24
25 observations support the notion of π -acid/ π -base interactions in the benzene, toluene, and
26
27 mesitylene adducts.
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34 Hupp and coworkers explored a variety of molecular rectangles based on rhenium(I)
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36 tricarbonyl diimines,²¹³ and one of them exhibits vapoluminescence.²¹⁴ Notably, it is a charge-
37
38 neutral compound (**118**) (Scheme 44) in which no counterions are blocking the channels formed
39
40 within and between individual rectangles. The crystal structure of $[\text{Re}(\text{CO})_3(\text{bibzim})(4,4'$ -
41
42 $\text{bpy})\text{Re}(\text{CO})_3]_2$ (**118**) (bibzim = 2,2'-bibenzimidazole) contains both intra- and intermolecular
43
44 vacancies of rectangular shape and similar size (~ 10 Å \times 6 Å). The emission intensity of **118**
45
46 changes upon exposure to various VOCs, the affinity of thin films of **118** for aromatic
47
48 compounds decreases along the series toluene > 4-fluorotoluene > benzene > fluorobenzene >
49
50 hexafluorobenzene. This order suggests that electron donor/acceptor (host/guest) interactions
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52 might play an important role for guest uptake. The host/guest stoichiometry can exceed unity,
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3 indicating that the guest molecules fill both intra- and intermolecular cavities. The estimated
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5 internal surface area is $\sim 120 \text{ m}^2/\text{g}$.
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11 **Scheme 44.** Vapochromic rhenium(I) and iridium(III) complexes.
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Many cyclometalated iridium(III) complexes exhibit favorable emission properties which makes them interesting for triplet harvesting in OLEDs.^{215, 216} The $[\text{Ir}(\text{ppy})_2(\text{qxn})]$ (ppy = 2-phenylpyridine, qxn = quinoxaline-2-carboxylate) complex (**119**) can be crystallized in two differently colored forms one of which can be converted into the other by exposure to CH_3CN vapor.²¹⁷ From mixed ethanol/chloroform solution one obtains black crystals of **119** $\cdot 0.25\text{EtOH}\cdot 0.5\text{CHCl}_3$ while from acetonitrile/chloroform red crystals of **119** $\cdot \text{CH}_3\text{CN}$ are formed. In the black form there are π - π interactions between qxn ligands from different complexes which may lead to an energetic stabilization of the ligand-based LUMO with respect to the red structure in which such π - π interactions are absent hence the different colors of the two forms. The black form is weakly emissive with $\lambda_{\text{max}} = 692 \text{ nm}$ and a decay time of only 43 ns, but the red form exhibits intense photoluminescence at 654 nm with a lifetime of 130 ns. Exposure of black **119** $\cdot 0.25\text{EtOH}\cdot 0.5\text{CHCl}_3$ to acetonitrile vapor converts it to the red form within ~ 1 minute while several other VOC vapors (propionitrile, acetone, acetic acid, ethyl

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3 acetate, methanol, ethanol, 2-propanol, pyridine, THF, diethyl ether, CH₂Cl₂, CHCl₃, CH₃I,
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5 hexane, benzene) gave no response. Reconversion of the red form to the black form does not
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7 occur as easily, and the most efficient procedure is to dissolve the complex in CHCl₃ followed by
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9 subsequent evaporation of the solvent.
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12 13 14 15 4.2.4 Vapochromism in coordination polymers and metal-organic frameworks 16 17 18 19



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29 **Figure 58.** Left: Anhydrous Cu(pz)₂ (**120**); middle: Cu(pz)₂·H₂O (**120**·H₂O); right: Cu(pz)₂·NH₃
30
31 (**120**·NH₃). Reprinted with permission from ref. ²¹⁸. Copyright 2009 American Chemical Society.
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37 The Cu(pz)₂ compound (pz = pyrazolato) (**120**) is most easily obtained in the form of a pink
38
39 hydrate (**120**·H₂O). This material forms a 1D coordination polymer with weakly bound water
40
41 molecules and Cu-O distances of 2.913(4) Å.²¹⁹ Gentle heating leads to the anhydrous beige
42
43 form. In humid air the beige substance readily reconverts to the pink hydrate but under dry
44
45 conditions anhydrous **120** can be used for detection of NH₃, methylamine, methanol, ethanol,
46
47 acetonitrile, and pyridine vapors. The resulting materials are solvent adducts of the general
48
49 formula **120**-solvent and exhibit colors ranging from pink (methanol and acetonitrile adduct) to
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51 blue (other adducts). However, vapor uptake is slow and requires between 20 minutes (NH₃) and
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2 days (ethanol) in order to be complete.

The structural changes accompanying water sorption of **120** have been studied in detail.²¹⁸ Interestingly the anhydrous form has no pores yet H₂O uptake occurs with remarkable ease (within 2 minutes), and hence it has been noted that this material exhibits “porosity without pores”.

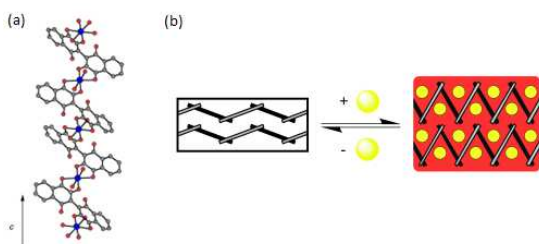


Figure 59. (a) Chain of [Cu(bhnq)(H₂O)₂] complexes in (**121**·H₂O·3EtOH); (b) schematic representation of the hinge-like behavior of the 2,2'-bi(3-hydroxy-1,4-naphthoquinone) ligand upon VOC uptake. (K. Yamada, S. Yagishita, H. Tanaka, K. Tohyama, K. Adachi, S. Kaizaki, H. Kumagai, K. Inoue, R. Kitaura, H.-C. Chang, S. Kitagawa, S. Kawata: Metal-Complex Assemblies Constructed From the Flexible Hinge-Like Ligand H₂bhnq: Structural Versatility and Dynamic Behavior in the Solid State. *Chem. Eur. J.*, 2004, 10, 2647-2660. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

When reacting CuSO₄ and the 2,2'-bi(3-hydroxy-1,4-naphthoquinone) ligand (H₂bhnq) in water-ethanol mixtures one obtains a coordination polymer of formulation [[Cu(bhnq)(H₂O)₂(H₂O)(EtOH)₃]_n (**121**·H₂O·3EtOH) which has infinite 1D chains of [Cu(bhnq)(H₂O)₂] units (Figure 59) with interstitial ethanol and water molecules.²²⁰ The chelating bhnq²⁻ ligands bridge neighboring Cu(II) centers in an *anti* fashion to form zigzag

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3 chains, the coordination sphere around each metal is a distorted octahedron with four O-atoms
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5 from two bhnq^{2-} ligands and two water molecules. Once removed from the mother liquor red
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7 crystals of $\mathbf{121}\cdot\text{H}_2\text{O}\cdot 3\text{EtOH}$ turn black due to loss of ethanol, but this process is reversible for
8
9 example when using MeOH or EtOH vapor. Crystallographic investigations show that the
10
11 Cu(II)-Cu(II) distance shortens when going from the black to the red form, the reason being that
12
13 sorbed EtOH molecules establish a hydrogen-bonding network with the bhnq^{2-} ligands and the
14
15 coordinated waters. These noncovalent interactions lead to a contraction of the 1D chains which
16
17 is possible thanks to the flexible hinge-like structure of the bhnq^{2-} ligand (Figure 59).
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21 In THF the reaction between CuSO_4 and the H_2bhnq ligand leads to the compound
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23 $[[\text{Cu}(\text{bhnq})(\text{THF})_2](\text{THF})]_n$ ($\mathbf{122}\cdot\text{THF}$).²²¹ This material forms similar 1D chains as compound
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25 $\mathbf{121}\cdot\text{H}_2\text{O}\cdot 3\text{EtOH}$ only with THF ligands and additional interstitial THF molecules which can be
26
27 removed in vacuum. The de-solvated form has a longer Cu(II)-Cu(II) distance than the THF
28
29 solvate (6.45 vs. 7.8 Å), and a shift of the absorption band maximum in the visible spectral range
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31 from 500 to 540 nm accompanies de-solvation. THF uptake restores the initial material, and the
32
33 reversibility of this transformation has been attributed to the hinge-like bhnq^{2-} ligand.
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40 Depending on reaction conditions two different forms of a vapochromic metal-organic
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42 framework (MOF) can be obtained from the reaction of CuI with 1,4-diazabicyclo[2.2.2]octane
43
44 (DABCO).²²² In both forms DABCO completes the coordination sphere of Cu(I) by ligating to
45
46 four corners of the Cu_4I_4 cubane-like clusters. In form A (obtained from aqueous solution) the
47
48 supertetrahedral $[\text{Cu}_4\text{I}_4(\text{DABCO})_4]$ units are arranged in a self-interpenetrating network ($\mathbf{123a}$).
49
50 In form B (obtained from CH_3CN solution, $\mathbf{123b}$) two independent networks interpenetrate each
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52 other. In both forms there is ~20% of volume accessible for solvent molecules because there are
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54 channels of ~7 Å diameter propagating through the crystalline lattices. Both forms exhibit long-
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lived ($\tau = 8.0, 13.4 \mu\text{s}$) emission from cluster-centered excited states (${}^3\text{CC}$) which might have some admixture from XMCT states resulting from iodide-to-copper charge transfer. Emission occurs with large Stokes shifts (11400 and 10700 cm^{-1}) indicative of strong excited-state distortions and significant structural reorganization of the photoexcited cubane-like clusters. The clusters are not exactly identical in both forms, consequently, the emission occurs at slightly different wavelengths (form A: $\lambda_{\text{max}} = 580 \text{ nm}$; form B: $\lambda_{\text{max}} = 556 \text{ nm}$). This fact can be exploited for vapoluminescence sensing because exposure of form A to vapors of acetonitrile induces a structural conversion to form B.

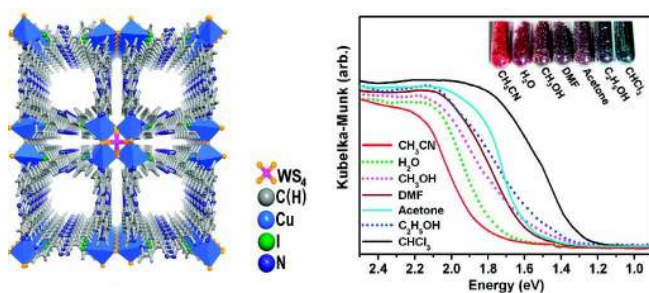


Figure 60. Left: Nanotubular structure of $[(\text{WS}_4\text{Cu}_4)\text{I}_2(\text{dptz})_3]_n$ (**124**); right: UV-Vis spectra and photographs of different solvent adduct of **124**. Reprinted with permission from ref. ²²³. Copyright 2011 American Chemical Society.

Reaction of $(\text{NH}_4)_2\text{WS}_4$, CuI , and dptz ($\text{dptz} = 3,6\text{-}(\text{dipyridin-4-yl})\text{-}1,2,4,5\text{-tetrazine}$) in DMF yields a nanotubular metal-organic framework with the stoichiometry $[(\text{WS}_4\text{Cu}_4)\text{I}_2(\text{dptz})_3 \cdot \text{DMF}]_n$ (**124**· DMF) in which each WS_4^{2-} anion chelates four Cu(I) cations (Figure 60).²²³ Each Cu(I) center is tetrahedrally coordinated, individual $\text{WS}_4\text{Cu}_4^{2+}$ units are paired up by pyrazines which exhibit π - π interactions at interplanar distances of $3.578(2) \text{ \AA}$.

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3 There are square-shaped ($5.4 \times 5.3 \text{ \AA}$) nanotubes along the c-axis containing DMF guests which
4 can be removed at $100 \text{ }^\circ\text{C}$. Immersion of the de-solvated MOF into various organic solvents
5 causes significant color changes that can also be induced by exposure to the respective vapors,
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There are square-shaped ($5.4 \times 5.3 \text{ \AA}$) nanotubes along the c-axis containing DMF guests which can be removed at $100 \text{ }^\circ\text{C}$. Immersion of the de-solvated MOF into various organic solvents causes significant color changes that can also be induced by exposure to the respective vapors, albeit leading to a much slower response. Systematic studies revealed a negative solvatochromic effect with a solvent-induced absorption band shift of 245 nm between CH_3CN and CHCl_3 (Figure 60). Moreover, there is a good correlation between the magnitude of the absorption band shift and the Reichardt solvent polarity parameter.²²⁴ The strong π -acceptor property of the dptz ligand is believed to play a key role for this solvatochromic and vapochromic behavior, a structurally analogous MOF with 2,2'-bipyridine instead of dptz does not show such behavior.²²³

4.2.5 Vapochromism in cyanometallates

2,2'-Bipyridinetetracyanoruthenate(II) complexes exhibit strongly solvent-dependent absorption and luminescence properties,²²⁵⁻²²⁹ and a few of them (or closely related complexes) are sensitive to *vapors* of certain chemical substances. For instance, the $\text{Ru}(4,4'\text{-}^t\text{Bubpy})_2(\text{CN})_2$ complex (**125**) is responsive to water vapor.²³⁰ **125**, **125** $\cdot\text{H}_2\text{O}$, and **125** $\cdot 2\text{H}_2\text{O}$ exhibit luminescence band maxima at 740 , 685 , and 640 nm , i. e., there is a correlation between emission peak and number of crystal waters. Simultaneously, the increase in the number of crystal waters is accompanied by a decrease of the CN stretching frequency in the IR spectrum. Thin films of **125** are most sensitive to moisture, operating at water vapor pressures as low as 10^{-2} Pa . Complex **125** is also responsive to vapors of various VOCs.²³¹ Neat **125** has an emission band maximum at 740 nm , but λ_{max} shifts to 700 nm when exposed to benzene, to 660 nm for quinoline, 650 nm for CH_2Cl_2 , and 640 nm for MeOH and pyridine. Thus, complex **125** has a

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3 certain discrimination capability for several VOCs, which parallels its solvatochromic behavior.
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5 In fluid solution there is a good correlation between the MLCT energy and the acceptor number
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7 (AN)²³² of the solvent, furthermore the CN stretching frequencies correlate with AN.
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10 The tetrakis(bis-3,5-trifluoromethylphenylborate) (tfpb⁻) salt of tris(5,6-dimethyl-1,10-
11 phenanthroline)ruthenium(II) (**126**) is an excellent sensor for benzene vapors at concentrations
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13 down to 7600 ppm.²³³ The vapoluminescence effect manifests in a rapid spectral change
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15 dominated by a shift in emission band maximum from 572 to 558 nm. The most interesting
16
17 aspect of [Ru(5,6-Me₂phen)₃](tfpb)₂ is its cross-sensitivity for the simultaneous sensing of
18
19 benzene and oxygen. O₂ quenches the luminescence of neat **126**, but simultaneous exposure to
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21 vapors of benzene and O₂ leads to benzene uptake and very little emission quenching is
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23 observed. A crystal structure of **126**·1.5C₆H₆ reveals that benzene guest molecules block
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25 channels in the crystal structure in such a way that oxygen diffusion can be suppressed.
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34 5. Summary of detectable VOCs

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39 Even though many of the vapochromic and vapoluminescent coordination complexes from the
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41 previous sections cannot realistically be used in real-world applications for reasons explained for
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43 each individual case above, a summary of analytes which can be detected and, where available,
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45 quantitative information regarding sensitivity is given in Table 1. The table lists the vapochromic
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47 substances in the same order as they appear in the text, for the abbreviations used the reader is
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49 referred to the text.
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55 **Table 1.** Summary of vapochromic sensing materials and analytes considered in this review.
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sensing material	analyte
[Pt(bpy)(CN) ₂] (1)	HF, H ₂ O, H ₂ S ^{35, 38}
[Pt(5,5'-Me ₂ bpy)(CN) ₂] (5)	H ₂ O ³⁷
[Pt(4,4'-H ₂ dc bpy)(CN) ₂] (6)	DMSO, DMF, CH ₃ CN, EtOH, MeOH, Me ₂ CO, CH ₂ Cl ₂ , CHCl ₃ , CH ₃ COOH, CCl ₄ , C ₆ H ₆ ^{13, 39}
Na ₂ [Pt(dcbpy)(CN) ₂]·2H ₂ O (7 ·2H ₂ O)	MeOH, Me ₂ CO, DMF ⁴⁰
[Pt(4,4'-H ₂ dc bpy)(SCN) ₂] (8)	DMSO, DMF, dimethylacetamide, MeOH, EtOH, Me ₂ CO, CH ₃ CN ⁵⁰
Zn[Pt(5,5'-dcbpy)(CN) ₂] (Zn9)	H ₂ O ⁴¹
Mg/Ca/Sr/Ba[Pt(5,5'-dcbpy)(CN) ₂] (Mg/Ca/Sr/Ba 9)	H ₂ O, MeOH ⁴²
[Pt(^t Bu ₂ bpy)(4-ethynylpyridine) ₂] (10)	CH ₂ Cl ₂ (25 ppm), CHCl ₃ (450 ppm) ⁵⁹
[Pt(^t Bu ₂ bpy)(C≡C-C ₆ F ₅) ₂] (11)	CH ₂ Cl ₂ ⁵⁹
Pt(^t Bu ₂ bpy)(ethynyltriarylboron) ₂] (12)	CH ₂ Cl ₂ , CHCl ₃ , Me ₂ CO, EtOH, CH ₃ CN, THF: green luminescence; toluene, hexane, MeOH: luminescence quenching; benzene, cyclohexane: red emission ⁶⁰
[Pt(5,5'-bis(TMS-C≡C)-bpy) ₂ (5-ethynyl-bpy) ₂] (13)	Me ₂ CO, CH ₂ Cl ₂ , <i>n</i> -hexane, and many others ⁶⁶
[Pt(5,5'-bis(TMS-C≡C)-bpy) ₂ (C≡CC ₆ H ₅) ₂] (14)	CH ₂ Cl ₂ , CHCl ₃ , CH ₃ I ⁶⁷
[Pt(5,5'-bis(TMS-C≡C)-bpy) ₂ (C≡CC ₆ H ₄ F-3) ₂] (15)	CHCl ₃ ⁶⁸
[Pt(5,5'-bis(TMS-C≡C)-bpy) ₂ (C≡CC ₆ H ₄ F-4) ₂] (16)	CH ₂ Cl ₂ , CHCl ₃ ⁶⁸
[Pt(5,5'-bis(TMS-C≡C)-bpy) ₂ (C≡CC ₆ H ₄ -CF ₃ -4) ₂] (17)	dioxane, THF, THP ⁶⁹
<i>cis</i> -[Pt(CN-C ₆ H ₄ -C ₂ H ₅) ₂ (CN) ₂], (<i>cis</i> - 18)	toluene, benzene, chlorobenzene, <i>p</i> -xylene, mesitylene, EtOH ⁷⁰
<i>cis</i> -[Pt(CN- ⁱ C ₃ H ₇) ₂ (CN) ₂] (<i>cis</i> - 19)	benzene (selective) ⁷²
[Pt(CN- ^t Bu) ₂ (CN) ₂] (20)	MeOH, CH ₃ CN, toluene; no response to: THF, Me ₂ CO, EtOAc, Et ₂ O, petroleum

	ether, hexane, CH ₃ NO ₂ , NH ₃ , chlorobenzene, cyclohexane, CH ₂ Cl ₂ , CHCl ₃ , N ₂ H ₄ ^{73, 74}
[Pt(CN- ⁱ C ₃ H ₇) ₄][Pt(CN) ₄] (21)	H ₂ O, MeOH, CF ₃ CH ₂ OH, CHCl ₃ ⁷⁵
[Pt(CN-C ₆ H ₄ -C ₁₀ H ₂₁) ₄][Pd(CN) ₄] (23)	CHCl ₃ (response time 350 ms), MeOH, CH ₂ Cl ₂ , acetone ^{76, 77} detection limit for CHCl ₃ : a few mg/m ³
[Pt(CN-C ₆ H ₄ -C ₁₀ H ₂₁) ₄][Pt(CN) ₄] (24c)	CHCl ₃ (response time 500 ms), CH ₂ Cl ₂ , MeOH, EtOH, 2-propanol, Et ₂ O, CH ₃ CN, hexanes, acetone, C ₆ H ₆ ⁷⁸
[Pt(CN-C ₆ H ₄ -C ₁₀ H ₂₁) ₄][Pt(NO ₂) ₄] (25)	Me ₂ CO ⁸¹
electronic nose made from 26, 27, 28	CHCl ₃ , H ₂ O, MeOH, CH ₂ Cl ₂ , 1-PrOH, <i>n</i> -hexane, cyclohexane ⁸³
electronic nose made from 26, 27, 29	Me ₂ CO (12% saturation, 75g/m ³), MeOH (3% saturation, 6 g/m ³) ⁸⁴
[Pt(CN-cyclododecyl) ₄][Pt(CN) ₄] (30)	H ₂ O (unique two-step response); CH ₂ Cl ₂ /CHCl ₃ (weaker two-step response); benzene, toluene, <i>p</i> -xylene (one-step response) ⁸⁶
[Pt(<i>R/S</i> -β-methylphenethylisocyanide) ₄][Pt(CN) ₄] (31)	differentiates between <i>R</i> -2-BuOH and <i>S</i> -2-BuOH at 90% confidence level ⁸⁷
[Pt(<i>R</i> -tpy)Cl]X (R = H, OC ₄ H ₉ , OC ₆ H ₁₃ , OC ₈ H ₁₇ , OC ₁₂ H ₂₅ ; X = Cl ⁻ , ClO ₄ ⁻ , PF ₆ ⁻ (32 ⁺ X ⁻); [Pt(^t Bu ₃ -tpy)Cl]X (X = Cl ⁻ , ClO ₄ ⁻ , PF ₆ ⁻) (33 ⁺ X ⁻)	CH ₃ CN, piperidine, DMF, and other VOCs with lone pairs ⁸⁸
[Pt(Cl-tpy)Cl]Cl (34Cl)	MeOH (selective) ⁹⁰
[Pt(tpy)(NCS)]SCN (35SCN)	MeOH, two-step response ⁹¹
[Pt(tpy)(NCS)]SCN (35SbF₆)	selective for CH ₃ CN, DMF, pyridine ⁹²
[Pt(tpy-nicotinamide)Cl](PF ₆) ₂ (37(PF₆)₂)	MeOH, CH ₃ CN, pyridine ⁹³
[Pt(pentaphenyl-benzene-tpy)Cl]Cl (38)	selective for CH ₂ Cl ₂ , EtOH, CH ₃ CN, EtOAc ⁹⁴
[Pt(Me ₂ bzimpy)Cl]Cl (39Cl)	MeOH, EtOH, CHCl ₃ , CH ₃ CN ⁹⁵
[Pt(Me ₂ bzimpy)Cl]PF ₆ (39PF₆)	CH ₃ CN, DMF (unresponsive to H ₂ O, MeOH, EtOH, 2-PrOH, Et ₂ O, CH ₂ Cl ₂ , CHCl ₃ , CCl ₄ , Me ₂ CO, hexanes, benzene) ⁹⁵ ,

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[Pt(Me ₂ bzimpy)Cl]Cl in ZrP (39 ⁺ in ZrP)	H ₂ O, MeOH, CH ₃ CN, Me ₂ CO, CH ₂ Cl ₂ , THF, benzene, toluene, <i>n</i> -hexane ⁹⁸
[Pt(R ₂ bzimpy)Cl]X (40a : R = C ₈ H ₁₇ , 40b : C ₁₂ H ₂₅ , 40c : C ₁₆ H ₃₃ ; X = Cl, PF ₆ , BF ₄ , ClO ₄ , OTf, OAc)	Me ₂ CO, CH ₃ CN, MeOH, EtOH, CH ₂ Cl ₂ , CHCl ₃ , EtOAc, benzene ⁹⁹
[Pt(2,6-bis(1 <i>H</i> -imidazol-2-yl)pyridine)Cl]Cl (41)	CH ₂ Cl ₂ , CH ₃ CN, CH ₃ OH, Me ₂ CO ¹⁰⁰
[(Pt(2,6-diphenylpyridine)) ₂ (dppm)] (42)	CH ₂ Cl ₂ , CH ₃ OH, Me ₂ CO, benzene, pentane ¹⁰¹
[Pt(2,6-di(hexanoylamide-phenyl)pyridine)] (43)	DMF, CH ₃ OH ¹⁰²
[Pt(4,6-di(phenyl)-2,2'-bipyridine)] (44) on silica gel	pentane, benzene, CH ₂ Cl ₂ , CHCl ₃ ¹⁰³
[(Pt(C [^] N [^] N [^] N [^])) ₂ (<i>cis</i> -1,2-bis(diphenylphosphino)ethylene)](ClO ₄) ₂ (45 (ClO ₄) ₂)	CH ₃ CN, EtOH, Et ₂ O, THF, EtOAc, CH ₂ Cl ₂ , CHCl ₃ ¹⁰⁴
[(Pt(2,6-di(2'-naphthyl)pyridine)) ₂ (dppm)] (46)	strong response: CH ₂ Cl ₂ , CH ₂ Br ₂ , CHCl ₃ , ClCH ₂ CH ₂ Cl, BrCH ₂ CH ₂ Br, CH ₃ I; weak response: Me ₂ CO, Et ₂ O, THF, EtOAc; no response: CH ₃ CN, MeOH, EtOH, benzene, toluene, <i>n</i> -hexane ¹⁰⁵
K[Pt(bzq)(CN) ₂]·H ₂ O (K47 ·H ₂ O)	MeOH (response time: ~5 s), EtOH (~10 s), CH ₃ CN (~30 s), Me ₂ CO (~2 min), THF (~45 min) ¹⁰⁶
K[Pt(bzq)(CN) ₂] (K47)	H ₂ O ¹⁰⁶
K[Pt(ppy)(CN) ₂] (K48)	H ₂ O ¹⁰⁶
[Pt(NCN-pincer)Cl] (49)	SO ₂ ¹⁰⁷
[Pt(NCN-pincer)Cl] ₃ -dendrimers (50 and 51)	SO ₂ at conc. of 100 μM (6 μg SO ₂ cm ⁻³), response time: 2 ms ¹⁰⁸
[Pt(NHC-butyl) ₂ Cl]Cl (53)	H ₂ O ¹¹⁶
[Pt(NHC-mesityl) ₂ (CO)](PF ₆) ₂ (54)	MeOH, H ₂ O, THF, Et ₂ O, DMF, pyridine; no response to CH ₂ Cl ₂ , CHCl ₃ , benzene ¹¹⁷
[Pt(bpy)(pyridine-2-thiolate)](PF ₆) ₂ (55)	Rapid response: MeOH, CH ₃ CN; slow response: EtOH, ^t PrOH; no response: ^t BuOH ¹¹⁸

[Pt(dithiooxamide) ₂] (56)	HCl ¹¹⁹
[Pt ₂ Ag ₂] cluster made from two Pt(II) benzoquinoline pyrrolidinedithiocarbamate units (57 (ClO ₄) ₂)	CH ₃ CN; does not respond to MeOH, H ₂ O, CH ₂ Cl ₂ , Et ₂ O, DMF, DMSO, <i>n</i> -hexane, toluene ¹²¹
<i>cis</i> -[Pt(aminophosphine) ₂] (58)	MeOH, EtOH, ^t PrOH; no response: ^t BuOH ¹²²
[PtI ₂ (diarsinine) ₂] (59)	CH ₂ Cl ₂ , Me ₂ CO, toluene ¹²³
[NH ₃ (CH ₂) ₄ NH ₃] ₂ [Pt ₂ (pop) ₄] (60)	H ₂ O ^{126, 128}
[NH ₃ (CH ₂) ₅ NH ₃] ₂ [Pt ₂ (pop) ₄] (61)	H ₂ O ¹²⁷
Cu[Au(CN) ₂] ₂ (DMSO) ₂ (62 ·(DMSO) ₂)	H ₂ O, CH ₃ CN, DMF, dioxane, morpholine pyridine, NH ₃ ^{14, 129}
Zn[Au(CN) ₂] ₂ (63)	NH ₃ (1 ppb detection limit) ^{17, 130}
[Au(S ₂ CN(C ₅ H ₁₁) ₂) ₂] (64)	Me ₂ CO, CH ₃ CN, CH ₂ Cl ₂ , CHCl ₃ , insensitive to: MeOH, EtOH ¹³⁴
[Au ₂ (μ-thiouracilato)(μ-dppm)CF ₃ COO] (65 CF ₃ COO)	Et ₃ N vs. CF ₃ COOH ¹³⁶
[Au ₃ (CH ₃ N=COCH ₃) ₃] (66)	solvent-stimulated luminescence strongest with CHCl ₃ and CH ₂ Cl ₂ ¹³⁸
[Au ₃ (CH ₃ N=COCH ₃) ₃] (66)	conductivity in microwires (not vapo-chromism): significant response for: MeOH, EtOH, CH ₃ CN; no response: THF, acetone, <i>n</i> -PrOH, <i>n</i> -BuOH, <i>n</i> -pentanol, benzene, and <i>p</i> -xylene ¹⁴³
[Au ₃ (H ₃ C- <i>p</i> -C ₆ H ₄ -N=COC ₂ H ₅) ₃] (67)	C ₆ F ₆ ¹⁴⁴
Au ₂ (μ-bis-(diphenylphosphino)ethane) ₂ Br ₂ (68)	CH ₂ Cl ₂ , Me ₂ CO; no response to: CH ₃ CN, Et ₂ O, DMF, DMSO, benzene, pyridine, nitrobenzene, CS ₂ ¹⁴⁶
Au ₂ (μ-bis-(diphenylphosphino)ethane) ₂ I ₂ ·2Me ₂ CO (69 ·2Me ₂ CO)	CH ₂ Cl ₂ , Me ₂ CO ¹⁴⁸
[(C ₆ F ₅ Au) ₂ (μ-1,4-diisocyanobenzene)] (70)	CH ₂ Cl ₂ ¹⁴⁹
[Au(PPh ₂ C(CSSAuC ₆ F ₅)PPh ₂ Me) ₂](ClO ₄) (71)	Me ₂ CO, CH ₂ Cl ₂ , CHCl ₃ , ClCH ₂ CH ₂ Cl, EtOH, EtOAc, THF, toluene ^{151, 152}
[Tl[Au(C ₆ Cl ₅) ₂]] _n (72)	Me ₂ CO, Hacac, CH ₃ CN, THF, Et ₃ N,

	pyridine, 2-fluoropyridine, or tetrahydrothiophene ^{153, 155}
[Tl(en)[Au(C ₆ X ₅) ₂] _n (73a X = F; 73b X = Cl)	Me ₂ CO, acetophenone ¹⁵⁶
[Au ₂ Ag ₂ (C ₆ F ₅) ₄ L ₂] _n (L = Et ₂ O) (75 (Et ₂ O) ₂)	Me ₂ CO, THF, CH ₃ CN ¹⁵⁸
[Au ₂ Ag ₂ (C ₆ F ₅) ₄ (bpy) ₂] _n (76)	MeOH, EtOH, <i>i</i> PrOH ¹²
[Au ₂ Ag ₂ (C ₆ F ₅) ₄ (phen) ₂] _n (77)	MeOH, EtOH, Me ₂ CO ¹⁶²
[Au ₂ Ag ₂ (4-C ₆ F ₄ I) ₄] _n (78)	Me ₂ CO, THF, CH ₃ CN; insensitive to: Et ₂ O, toluene ¹⁶⁴
[Au ₂ Ag ₂ (4-C ₆ F ₄ I) ₄ (Me ₂ CO) ₂] _n ·2Me ₂ CO (78) (Me ₂ CO)·2Me ₂ CO	CH ₃ CN ¹⁶⁴
[Au ₂ Ag ₂ (4-C ₆ F ₄ I) ₄ (THF) ₂] _n (78 (THF) ₂)	CH ₃ CN ¹⁶⁴
[Au ₂ Ag ₂ (3,5-C ₆ Cl ₂ F ₃) ₄ (Et ₂ O) ₂] _n (79 (Et ₂ O) ₂)	Me ₂ CO, THF, CH ₃ CN ¹⁶⁶
[Au ₂ Ag ₂ (3,5-C ₆ Cl ₂ F ₃) ₄ (THF) ₂] _n (79 (THF) ₂)	Me ₂ CO, partial reaction with CH ₃ CN ¹⁶⁶
[Au ₂ Ag ₂ (3,5-C ₆ Cl ₂ F ₃) ₄ (CH ₃ CN) ₂] _n (79 (CH ₃ CN) ₂)	Me ₂ CO, THF ¹⁶⁶
[Au ₂ Ag ₂ (C ₆ Cl ₅) ₄ (Et ₂ O) ₂] _n (80 (Et ₂ O) ₂)	Me ₂ CO, THF, CH ₃ CN ¹⁶⁶
[Au ₂ Ag ₂ (2-C ₆ F ₄ I) ₄] ₂ ·4NBu ₄ ClO ₄ ·THF (81 ·4NBu ₄ ClO ₄ ·THF)	Me ₂ CO, THF, CH ₃ CN ¹⁶⁷
[Au(im(CH ₂ -py) ₂) ₂ (Cu(CH ₃ CN) ₂) ₂](PF ₆) ₃ (86)	MeOH, H ₂ O, Me ₂ CO; insensitive to: THF, CH ₂ Cl ₂ ¹⁶⁹
[Au(im(CH ₂ -py) ₂) ₂ (Cu(CH ₃ OH) ₂)](PF ₆) (87b)	CH ₃ CN ¹⁶⁹
[Au(dppb) ₂](NO ₃) (88 NO ₃)	MeOH, EtOH; insensitive to longer alcohols ¹⁷⁰
[Au(dppb) ₂](BF ₄) (88 BF ₄)	Me ₂ CO, CH ₃ CN, CH ₂ Cl ₂ , Et ₂ O, THF ¹⁷⁰
[VO(sal-(R,R)-stien)]·CHCl ₃ (89 ·CHCl ₃)	CH ₃ CN ¹⁷¹
[VO(sal-(R,R)-stien)]·CH ₃ CN (89 ·CH ₃ CN)	CHCl ₃ ¹⁷¹
[Co ₂ (H ₂ O) ₄][Re ₆ S ₈ (CN) ₆] ₃ ·12H ₂ O (90 ·12H ₂ O)	CH ₃ NO ₂ , Me ₂ CO, CH ₃ CH ₂ CN, <i>n</i> -octanol, 1-PrOH, 2-PrOH, EtOAc, Et ₂ O, THF ¹⁷⁶
[Co(H ₂ O) ₃] ₄ [Co ₂ (H ₂ O) ₄][Re ₆ Se ₈ (CN) ₆] ₃ ·44H ₂ O (91 ·44H ₂ O)	Et ₃ N, CH ₃ CN, CH ₃ CH ₂ CN, THF, EtOH, DMF, Me ₂ CO, <i>n</i> -octanol, MTBE, EtOAc, 1-PrOH, 2-PrOH, Et ₂ O ¹⁷⁶

[Co ₂ (ampyz) ₂](SO ₄) (= dry form of 92)	H ₂ O ¹⁷⁷
[(dppm)Ni(η ² -NO ₃) ₂] (93)	CH ₃ CN ¹⁷⁸
Bis(1,2,6,7-tetracyano-3,5-dihydro-3,5-diiminopyrrolizinido)nickel(II) (95)	CH ₃ OH, toluene; poor response to CH ₃ CN ¹⁷⁹
[Ni(cyclam)(dcbpy)] (96 (dcbpy))	H ₂ O ¹⁸⁰
[CuI(4-pic)] _∞ (97)	toluene ^{181, 182}
[CuI(4-pic)] ₄ ·2C ₆ H ₅ CH ₃ (98 ·2C ₆ H ₅ CH ₃)	pentane ^{181, 182}
<i>trans</i> -[CuCl ₂ (3-Clpy) ₂] (99)	HCl ¹⁸⁴
<i>trans</i> -[CuBr ₂ (3-Brpy) ₂] (101)	HCl, HBr ^{185, 186}
[Cu ₂ (dppy) ₃ (CH ₃ CN)](BF ₄) ₂ (103)	CH ₃ OH ¹⁸⁷
[(O ⁿ Pr)Cu(μ-hep) ₂ Cu(O ⁿ Pr)]·2H ₂ O (104 ·2H ₂ O)	MeOH, EtOH, ^t PrOH, CH ₃ CN with response times of 5 min, 2 h, 24 h, 8 d ¹⁸⁸
[(Cu ₄ L ₄)(calix[4]- <i>bis</i> -monothiacrown)] _n (105)	CH ₃ CN ¹⁸⁹
[CuI(PPh ₃) ₄] (106a)	CH ₃ CN, CH ₂ Cl ₂ , EtOH ¹⁹⁰
CuCN (107)	amines (Py, 2-MePy, 3-MePy, 4-MePy, 3-EtPy, 4-EtPy, 4- ^t BuPy, piperidine, <i>N</i> -methylpiperidine, <i>N</i> -ethylpiperidine, Me ₂ NCy) and other nucleophilic VOCs (<i>N</i> -methylmorpholine) ¹⁹¹
(CuI) ₂ (Et ₂ pip) (108a), (CuI) ₂ (Bn ₂ pip) (108b)	Py, 2-MePy, 3-MePy, pyrrolidine, pyrrolidine, morpholine, Et ₃ N, dimethyl sulfide ¹⁹⁵
SnSO ₄ (109a), Sn(CH ₃ SO ₃) ₂ (109b), Sn(OTf) ₂ , (109c), SnPO ₃ F (109d)	NH ₃ , EtNH ₂ , Et ₂ NH, Et ₃ N, N(C ₅ H ₅) ₃ ¹⁹⁶
Zn(II)tetraphenylporphyrin (110)	NH ₃ , Et ₃ N ²⁰⁰
Fe(tris-(2-pyridylmethyl)amine)(NCS) ₂ (111)	MeOH ²⁰¹
[Fe(tpa)(NCS) ₂] ₂ ·[[Fe(tpa)(NCS) ₂] ₂ ·EtOH] (111 ·[111 ·EtOH])	CH ₂ Cl ₂ , CHCl ₃ ²⁰²
Fe(Hpbph) ₂ (HCA) ₂ ·2THF (112 ·2THF)	CH ₂ Cl ₂ , Et ₂ O, MeOH, EtOH, CH ₃ COOH ²⁰⁴
Fe(Hpbph) ₂ (HCA) ₂ (112)	THF ²⁰⁴

[PdBr(Hmtbhp)] ₂ (HBA) ₂ (H ₂ BA) (113)	DMF, pyridine, dimethylacetamide, DMSO, 1,4-dioxane, CH ₃ CN, MeOH, EtOH; with discrimination ability ²⁰⁵
[(ZnCl ₂) ₃ (1,3,5-tris(<i>p</i> -(2,2'-dipyridylamino)phenyl)benzene)] (114)	benzene (500 ppm) ²⁰⁹
[Zn ₂ (3,3'-di- <i>tert</i> -butylsalen)] ₂ (115)	THF ²¹⁰
[[3,5-(CF ₃) ₂ pz]Ag] ₃ (117)	selective to: benzene, toluene, mesitylene ²¹¹
[Re(CO) ₃ (bibzim)(4,4'-bpy)Re(CO) ₃] ₂ (118)	toluene, 4-fluorotoluene, benzene, fluorobenzene, hexafluorobenzene, THF ²¹⁴
[Ir(ppy) ₂ (qxn)]·0.25EtOH·0.5CHCl ₃ (119 ·0.25EtOH·0.5CHCl ₃)	CH ₃ CN ²¹⁷
[Cu(pz) ₂] (120)	NH ₃ , CH ₃ OH, EtOH, CH ₃ CN, pyridine, MeNH ₂ ^{218, 219}
[[Cu(bhnq)(H ₂ O) ₂ (H ₂ O) _n] _n (121 ·(H ₂ O) _n)	MeOH, EtOH ²²⁰
[Cu(bhnq)(THF) ₂] _n (122)	THF ²²¹
[Cu ₄ I ₄ (DABCO) ₂] (123)	CH ₃ CN ²²²
[(WS ₄ Cu ₄)I ₂ (dptz) ₃] _n (124)	CH ₃ CN, H ₂ O, CH ₃ OH, DMF, Me ₂ CO, C ₂ H ₅ OH, CHCl ₃ ²²³
Ru(4,4'- <i>t</i> -Bubpy) ₂ (CN) ₂ (125)	H ₂ O ²³⁰ , MeOH, CH ₂ Cl ₂ , benzene, quinoline, pyridine with discrimination ability ²³¹
[Ru(5,6-Me ₂ phen) ₃](tfpb) (126)	benzene, detection limit: 7600 ppm ²³³

Challenges associated with the use of vapochromic substances in practical sensor device applications differ from material to material; details are found in sections 2 – 4. Some frequently occurring issues are the following: Long-term stability of the chemical sensors, interference by atmospheric oxygen or humidity, reversibility of the vapochromic response, selectivity to certain

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3 VOCs, and sufficiently rapid response times. The targeted synthesis of vapochromic materials is
4 very difficult because even the most basic structure / function relationships have remained
5 elusive for many vapochromic substances. Even the optimization of known vapochromic
6 materials is difficult since very minor structural changes may lead to complete disappearance of
7 the vapochromic property. In many cases the application potential of newly discovered
8 vapochromic materials was apparently considered low and therefore quantitative analytical
9 measurements were only performed in rather few selected cases.^{17, 84, 108, 130, 209, 233} It seems fair
10 to state that with respect to quantified sensitivity data, the field is still much in its infancy.
11 Changing this situation is certainly a challenge for the future in this field.
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31 6. Concluding remarks

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36 Vapochromism and vapoluminescence in coordination complexes is possible through a variety
37 of different mechanisms. Changes in metal-metal interactions play an important role in many
38 platinum(II) and gold(I) based substances,^{13, 14, 17, 35, 37, 36, 50, 41, 66, 67, 68, 69, 70, 72, 73, 88, 91, 92, 93, 95, 97,}
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Occasionally, vapochromism is triggered through reaction of the analyte at a remote ligand site

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3 in a complex.^{156, 181, 182, 234} Host-guest interactions in materials with vapor-accessible channels
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5 are quite prominently represented and in the future are likely to become increasingly important
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7 since much current effort appears to be devoted to the synthesis of new functional metal-organic
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9 frameworks.^{69, 70, 220, 222, 190, 223, 234, 205, 214}
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13 Until now the field of vapochromism and vapoluminescence was mostly driven by
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15 coordination chemists with a strong interest in understanding the vapor-induced phenomena at a
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17 fundamental (mechanistic) level. The application potential of many of the investigated
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19 substances was considered rather limited, and hence quantitative analytical data is available only
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21 for relatively few cases. However, it is clear that sensors based on vapochromic and
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23 vapoluminescent materials are potentially very sensitive towards VOCs, especially when a
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25 luminescence turn-on response can be induced. Provided a sufficiently rapid response time can
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27 be obtained, such sensing materials therefore hold great promise for real-time monitoring of
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29 VOCs in air. This might be a less cumbersome procedure than adsorbing VOCs on adsorbates for
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31 later extraction and chromatographic analysis. When compared to electrochemical gas sensors
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33 vapochromic or vapoluminescent sensors have the advantage that detection is not limited to
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35 redox-active analytes. However, selectivity for a certain specific analyte is very difficult to
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37 achieve with vapochromic or vapoluminescent materials. An important basic problem in this
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39 context is that the discovery of such substances frequently relies on serendipity because there is
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41 no other choice: In many cases even very minor modifications of the chemical structure of a
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43 known vapor-responsive substance leads to disappearance of the vapochromism /
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45 vapoluminescence phenomena.
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53 For real-world analytical applications, the future of vapochromic and vapoluminescent
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55 substances probably lies in cross-reactive sensor arrays in which many different sensing
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3 materials are combined, and in which characteristic fingerprint responses for individual analytes
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5 can potentially be obtained. On the other hand, the phenomena of vapor-induced color and
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7 luminescence changes are interesting in their own right and are likely to continue to fascinate
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9 chemists in academic research.
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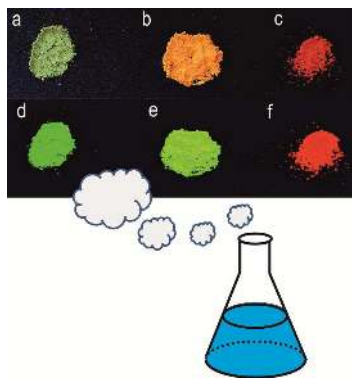
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