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Coordination-driven supramolecular syntheses of new homo- and hetero-polymetallic Cu(I) assemblies: solid-state and solution characterization

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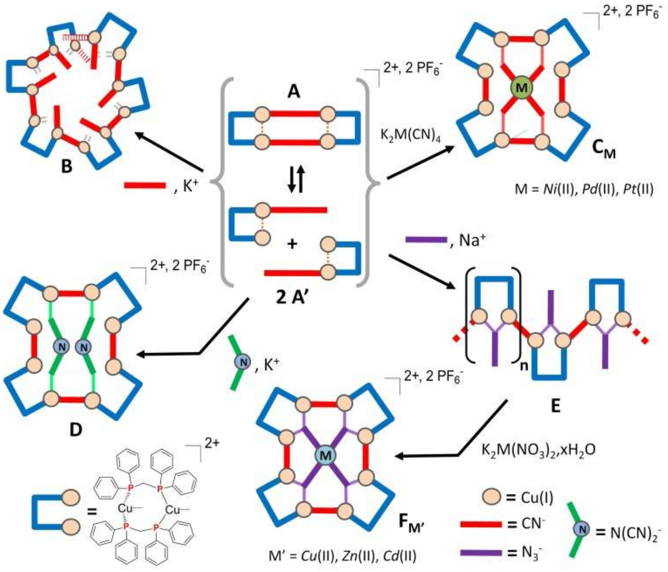
Coordination-Driven Supramolecular Syntheses of New Homo- and Hetero- polymetallic Cu(I) Assemblies: Solid-State and Solution Characterization

Ali Moustafa Khalil,[a] Chendong Xu,[a] Vincent Delmas,[a] Guillaume Calvez,[a] Karine Costuas,[a] Mohamed Haouas,*[b] and Christophe Lescop*[a]

Coordination-driven supramolecular (CDS) syntheses between the pre-assembled tetrametallic flexible precursor **A** and pseudo-halide dicyanamide $N(CN)_2^-$ (DCM) and azido N_3^- ions afforded selectively the discrete Cu_8 assembly **D** and the one-dimensional coordination polymer **E**, respectively. Upon reaction of **E** with M'(II) salts (M' = Cu, Zn, Cd), straightforward self-dissociation/re-organisation processes take place yielding the new discrete Cu_8 assemblies $\mathbf{F_{M'}}$. Preservation in solution of polymetallic Cu(I) CDS assemblies is evidenced for the first time. Solid-state luminescence properties of these derivatives are reported, revealing that **D** is a moderate room temperature luminophore upon UV-vis light excitation (emission quantum yield of 13 %) while derivatives **E**, $\mathbf{F_{Zn}}$ and $\mathbf{F_{Cd}}$ are only weakly luminescent in the solid-state at low temperature.

Introduction



Scheme 1 Synthesis of derivatives **B**,[5b] $\mathbf{C_M}$,[5b] **D**, **E** and $\mathbf{F_{M'}}$.

The preparation of advanced supramolecular materials motivates since two decades impressive synthetic works that have afforded manifold multifunctional systems.[1] In this field, coordination-driven supramolecular (CDS) chemistry[2] constitutes one of the most powerful synthetic approach defined, in which systems based mostly on the Pt(II) and Pd(II) square-planar metal centers have flourished[2] taking benefit of the high structural rigidity and appropriate lability of the coordination sphere of these ions. Importantly, while some of the most impressive achievements obtained in supramolecular syntheses using metal-to-ligand coordination bonds have been based on the coordination chemistry of the 'naked' Cu(I) ion with pre-designed polytopic organic ligands (defining a synthetic approach defined as metal-templated approach),[3] few examples involving the Cu(I) ion accordingly to the CDS chemistry basic principles (formation of dynamic noncovalent interactions between metal centers inserted in pre-assembled precursors and multitopic linkers having both suitable geometries to allow straightforward and selective synthesis of targeted intricate supramolecular assemblies)[2] have been reported so far. Yet, we have recently initiated the rational introduction of pre-assembled precursors based on the Cu(I) ion in self-assembly procedures related to CDS syntheses.[4] In these cases, the typical labile, flexible and low-directional coordination sphere of this ion, initially regarded as strongly restrictive in conventional CDS chemistry, turned out to be valuable to conduct the selective preparation of original polymetallic supramolecular assemblies. In addition, several of the polymetallic derivatives obtained so far present a variety of luminescence properties due to the versatile photophysical processes and the structural flexibility lying in Cu(I)-based CDS derivatives.[4,5] In particular, the pre-assembled solid-state blue luminophore tetrametallic metallacycle **A**[5a] (Scheme 1) allowed conducting adaptive CDS syntheses from its reaction with cyanido-based precursors, affording a helical one-

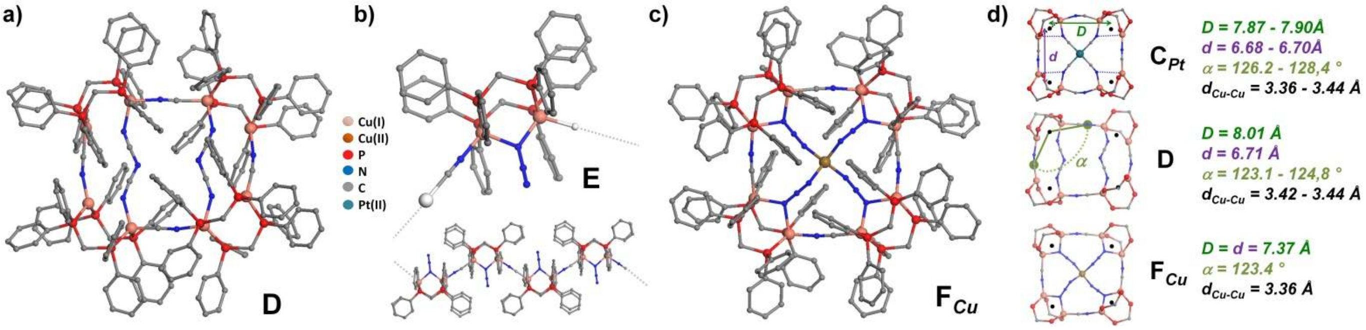


Fig. 1. a) View of the molecular X-ray structure of the derivative **D**; b) Molecular X-ray structure of the bimetallic repetition unit of **E** (top), view of the 1D zig-zag coordination polymer **E** (bottom);[6b] c) Molecular X-ray structure of the derivative $\mathbf{F}_{Cu}$; d) Simplified views and selected metric data of the X-ray structure of derivatives $\mathbf{C}_{Pt}$,[5b] **D** and $\mathbf{F}_{Cu}$ (Counteranions, H atoms and solvent molecules have been omitted for clarity; location of the C and N atoms of the cyanido ligands has been chosen arbitrarily, black dots represent the central points of the Cu-Cu segments of each [$Cu_2(\mu_2$-dppm$)_2$] fragments).

dimensional polymer **B** and the discrete supramolecular assemblies $\mathbf{C}_M$ (Scheme 1).[5b] These self-assembled processes were rationalized assuming that **A** results of the dimerization of two reactive and flexible {[$Cu_2(\mu_2$-dppm$)_2$]CN}$^+$ fragments **A'** (Scheme 1) bearing coordinatively unsaturated Cu(I) metal centers. The versatility of the solid-state photophysical processes of Cu(I)-based CDS derivatives was highlighted by this series of compounds since **A** revealed to be an attractive TADF luminophore[5a] while **B** photophysical behaviour[5b] is typical of multiple emission arising from multiple species and site heterogeneity. Finally, $\mathbf{C}_M$ photophysics highlighted the crucial impact of the spin-orbit coupling offered by the central M metal center on the efficiency of the radiative relaxation processes.[5b] In order to confirm and extrapolate this first series of results, a next step would be to demonstrate that this approach can be adapted to the introduction of other pseudo-halide connecting anions, giving access to new polymetallic derivatives bearing alternative properties. Herein, we report the straightforward preparations (Scheme 1) of new Cu(I) polymetallic assemblies **D**, **E** and $\mathbf{F}_M$ (M = Cu(II), Zn(II) and Cd(II)) introducing pseudo-halide dicyanamide $N(CN)_2^-$ (DCM) and azido N_3^- ions in the CDS assembly processes based on the pre-assembled precursor **A**. Solid-state luminescence properties of these new derivatives are reported, revealing that **D** is a moderate room temperature luminophore upon UV-vis light excitation (emission quantum yield of 13 %) while derivatives **E,** $\mathbf{F}_{Zn}$ and $\mathbf{F}_{Cd}$ are only weakly luminescent in the solid-state at low temperarure ($\mathbf{F}_{Cu}$ being non emissive in the solid-state at any temperature). The rich diversity of the Cu(I)-based supramolecular scaffolds that can be accessed from **A** is therefore highlighted. Finally ~~In addition~~, for the first time, the stability of Cu(I)-based CDS derivatives in solution is demonstrated.

Results and discussion

The reaction of the precursor **A** at room temperature (RT) with NaN_3 or $KN(CN)_2$ in 1:2 and 1:1 ratios respectively afforded colorless solutions from which were obtained the derivatives **D** and **E** (Scheme 1) in good yields (**D** : 68 %; **E** : 69 %) as air-stable colorless polycrystalline powders.[6] Solid-state IR spectra reveal persistence of Cu-CN-Cu fragments in both species (ν(C≡N) stretches: **D**, 2117 cm^{-1}; **E**, 2124 cm^{-1}) together with coordinated DCM ions in **D** (2144, 2205 and 2285 cm^{-1}) and coordinated azido ions in **E** (2045 cm^{-1}) indicating that these new derivatives **D** and **E** combine two different pseudohalide ions. This is confirmed by X-ray diffraction studies[6] performed on single crystals obtained at RT from pentane diffusion into the mother solutions of the respective complexes. It revealed that the derivative **D** is a discrete [$Cu_8(DCM)_2(CN)_4dppm_8$]$(PF_6)_2$ assembly that crystallizes in the *C*2/*c* space group of the monoclinic system. This octanuclear derivative can be described as resulting of the connection of four [$Cu_2(\mu_2$-dppm$)_2$]$^{2+}$ fragments with four μ_2-ditopic cyanido ligands forming a ''$Cu_8(CN)_4$'' metallacycle sub-unit with a slightly twisted rectangular shape (Fig. 1a,d). In each [$Cu_2(\mu_2$-dppm$)_2$]$^{2+}$ fragment, one of the metal centers has a distorted trigonal planar P_2N_1 coordination sphere resulting of the coordination of two 1κP:2κP dppm ligands and of a cyanido ligand. The second Cu(I) metal center presents a distorted tetrahedral coordination P_2N_2 sphere due to an additional coordination with the terminal atom of a DCM ligand. The two DCM ligands are located within the ''$Cu_8(CN)_4$'' metallacycle sub-unit, connecting two-by-two two $Cu_2(\mu_2$-dppm$)_2$ fragments via a $\mu_{1,5}$ coordination mode (d(Cu-N_{DCM} = ca. 2.09 Å). Intermetallic Cu(I) distances in the [$Cu_2(\mu_2$-dppm$)_2$]$^{2+}$ fragments (d(Cu-Cu), ca. 3.43 Å) exceed those recorded in the precursor **A** (d(Cu-Cu) = 2.87 Å)[5a] and are too large for cuprophilic interactions.[7] Conversely to the discrete scaffold observed in **D**, the derivative **E** is a neutral 1D-coordination polymer (1D-CP) that crystallizes in the *P*-1 space group of the triclinic system.[6b] Its repeating unit is based on a [$Cu_2(\mu_2$-dppm$)_2$]$^{2+}$ fragment on which cyanido ligands act as μ_2-ditopic linker between two Cu(I) metal centers of neighboring repeating units (Fig. 1b). Within each Cu(I) dimer, an azido ligand bridges symmetrically the two metal centers in a terminal $\mu_{1,1}$ end-on coordination mode (d(Cu-N_{azido} = ca. 2.1 Å), resulting in distorted tetrahedral P_2N_2 coordination spheres for the Cu(I) metal centers (intermetallic distance (d(Cu-Cu) =

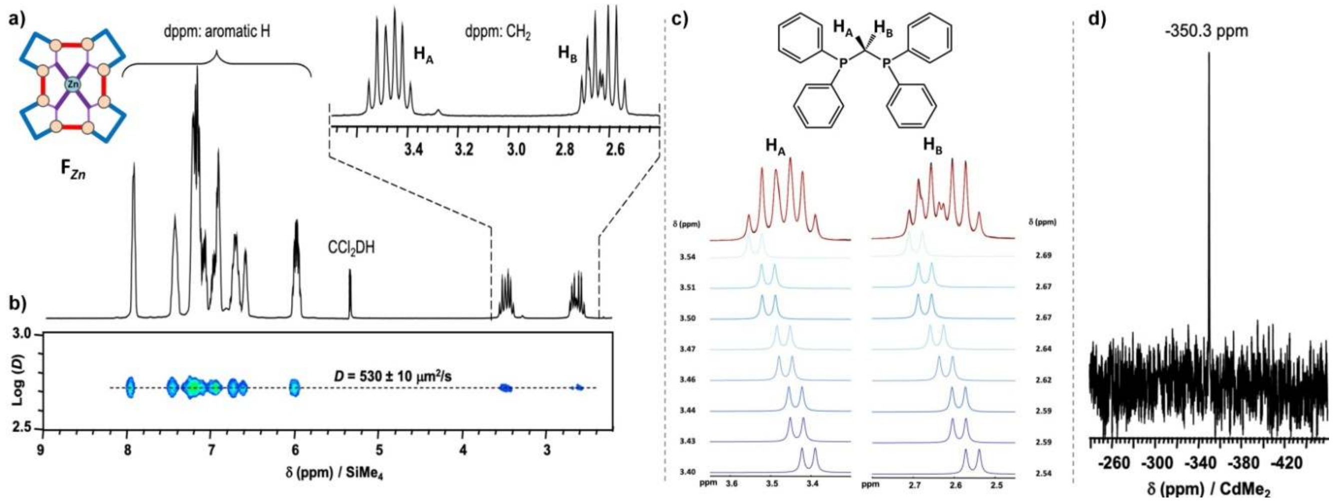


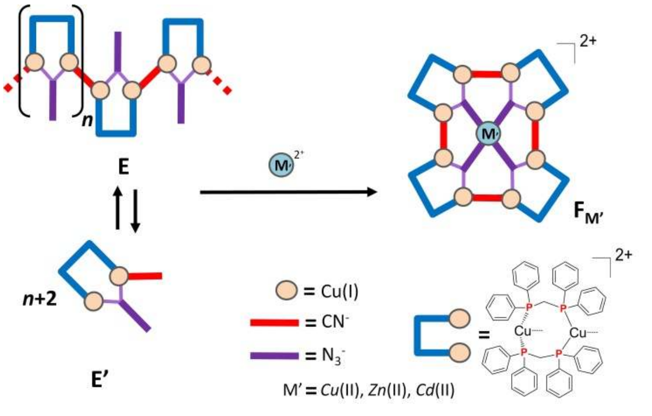
Fig. 2. a) $^1H\{^{31}P\}$ NMR and b) $^1H\{^{31}P\}$ DOSY RT spectra of derivative **F*$_{Zn}$*** in CD_2Cl_2; c) Spectral decomposition of $^1H\{^{31}P\}$ NMR resonances for methylenic protons in **F*$_{Zn}$***, using 8 equal doublets with $J_{H\text{-}H} \approx 13.1$ Hz. Black line = experimental spectrum, Red line = calculated spectrum, Blue lines = components. Chemical shifts of each individual component are indicated; d) ^{113}Cd NMR RT spectrum of derivative **F*$_{Cd}$*** in CD_2Cl_2.

ca. 3.23 Å). The connection of these repetition units leads to the formation of a 1D-CP having ~~a~~ 'zig-zag' geometry. Regarding the synthetic processes that can account for the formation of these new polymetallic scaffolds, the self-assembly paths can be rationalized considering that, on the one hand, the azido anions insert between the metal centers of the $\{[Cu_2(\mu_2\text{-dppm})_2]CN\}^+$ fragments **A'** (Scheme 1) affording $[Cu_2(\mu_2\text{-dppm})_2](CN)_1(N_3)_1$ sub-units that self-assemble in the solid-state forming the 1D-CP scaffold of **E**. On the other hand, the DCM anion behaves as a bended ditopic template that connects two **A'** moieties in tetrametallic sub-units that subsequently self-assemble forming the discrete Cu_8 derivative **D**. Thus, the bottom-up synthetic processes established to explain the preparation of derivatives **B** and **C** (Scheme 1) can also be applied for **D** and **E**. The multiplicity, the variety and the versatility of coordination modes associated to the DCM and the azido anions are clearly key factors insuring the selective preparation of these polymetallic Cu(I) species. The difference observed in the secondary structures of the 1D-CPs **B** (helicoidal) and **E** (zig-zag) can be assigned to the longer dimension of the azido anions (ca. 2.30 Å) versus the cyanido anions (ca. 1.15 Å) that likely induces destabilization of the helicoidal geometry type as observed in **B** for the benefit of the selection of the 'zig-zag' 1D-CP backbone of **E**. Conversely, and quite remarkably, **C$_M$** (Scheme 1) and **D** scaffolds present comparable architectures based on ''$Cu_8(CN)_4$'' metallacycle sub-units (Fig. 1d) in which can be inserted, respectively, one dianonic $M(CN)_4$ and two monoanionic DCM fragments in spite of the different geometries and charges displayed by these building-blocks. This is allowed by the significantly large extend of structural alteration that the ''$Cu_8(dpmm)_8(CN)_4$'' metallacyclic sub-unit can bear when hosting these different templates while preserving its coarse geometry (Fig. 1d). This highlights a strong tendency of the CDS self-assembly processes based on the flexible adaptive $\{[Cu_2(\mu_2\text{-dppm})_2]CN\}^+$ pre-organized fragments **A'** to yield well-defined discrete and stable multimetallic multicyclic assemblies.

Importantly while the crystallization experiments of the derivative **D** always gave selectively this compound whatever the conditions and duration of crystallization applied, we noticed in a few cases, the apparition after one week of few dark blue crystals in the crystallization experiments that initially only afforded the derivative **E**. X-ray diffraction study[6] reveals the formation of a new discrete $\{Cu_9(N_3)_4(CN)_4dppm_8\}(PF_6)_2$ supramolecular assembly **F*$_{Cu}$*** (Fig. 1c) that crystallizes in the non-centric *I*-43*d* space group of the cubic system with a $[Cu_2(\mu_2\text{-dppm})_2(Cu)_{1/4}(CN)_1(N_3)_1]$ fragment in the asymmetric unit. Similarly to **D**, this nonanuclear Cu(I) derivative can be first described as based on a ''$Cu_8(CN)_4$'' metallacycle sub-unit having in the case of **F*$_{Cu}$*** a slightly twisted square shape (Fig. 1c,d). The backbone of the derivative **F*$_{Cu}$*** results then of the connection of this unit to a rare '$Cu(N_3)_4$' internal fragment bearing a highly distorted tetrahedral metal center (N-Cu(II)-N angles: 99.48(14)° and 132.10(4)°) coordinated to four N_3^- ligands. The assembly **F*$_{Cu}$*** is dicationic since two PF_6^- anions are observed in the unit cell. An oxidation degree of +2 is therefore formally assigned to the central metal ion, while the eight metal centers of the ''$Cu_8(CN)_4$'' metallacycle sub-unit are endowed a +1 oxidation state.[8] In the derivative **F*$_{Cu}$***, the azido ligands connect the central Cu(II) ion up to eight Cu(I) metal centers owing to the four peripheral $Cu_2(\mu_2\text{-dppm})_2$ fragments, via a $\mu_{,1,1,3}$ coordination mode in which the metal centers of the Cu(I) dimers (d(Cu-Cu) = 3.354(9) Å) are symmetrically bridged ($d(Cu(I)\text{-}N_{N3}$ = 2.134(6) and 2.149(6) Å). After two months, the amount of crystals of **F*$_{Cu}$***

did not significantly increased at the expense of those of **E**. It suggests that the apparition of crystals of $\mathbf{F}_{Cu}$ can likely be assigned to residual traces of free Cu(I) ions in the synthesis conducted under air, that upon time are oxidized in Cu(II) ions. The characterization of $\mathbf{F}_{Cu}$ reveals that equilibria in solution take place in these preparations, along which the templating action of the Cu(II) ion favors the formation of the discrete species $\mathbf{F}_{Cu}$. This motivated us to react pre-prepared amount of **E** (in suspension in CH_2Cl_2) with the adequate stoichiometric ratio of Cu(II) ions (dissolved in MeOH). As a result, a deep blue and clear solution was instantaneously obtained from which single crystals of $\mathbf{F}_{Cu}$ were selectively grown after two days in a good yield (85 %), without any traces of the 1D-CP **E**. Therefore, similarly to **A** (scheme 1), **E** behaves as a source of heteroleptic $[Cu_2(\mu_2\text{-dppm})_2](CN)_1(N_3)_1$ reactive fragments **E'** (Scheme 2) allowing the rational and selective preparation of the discrete nonametallic species $\mathbf{F}_{Cu}$. Supporting this hypothesis, the diamagnetic $\mathbf{F}_{Zn}$ and $\mathbf{F}_{cd}$ heterometallic assemblies were also selectively prepared in high yields ($\mathbf{F}_{Zn}$: 91 %; $\mathbf{F}_{cd}$: 88 %) as colorless polycrystalline powder by reacting **E** with, respectively, Zn(II) and Cd(II) ions. Single crystal X-ray diffraction studies revealed that both derivatives are isostructural with $\mathbf{F}_{Cu}$, having therefore a $M(II)(N_3)_4$ internal fragment bearing a highly distorted tetrahedral metal center inserted in a ''$Cu_8(CN)_4$'' metallacycle sub-unit due to the coordination of four $\mu_{,1,1,3}$ azido ligands.

While the 1D-CP **E** is insoluble in CD_2Cl_2, the discrete derivatives **D**, $\mathbf{F}_{Cu}$, $\mathbf{F}_{Zn}$ and $\mathbf{F}_{Cd}$ are moderately (**D**) or readily soluble ($\mathbf{F}_{Cu}$, $\mathbf{F}_{Zn}$ and $\mathbf{F}_{Cd}$) allowing to conduct solution multinuclear NMR studies of the diamagnetic compounds **D**, $\mathbf{F}_{Zn}$ and $\mathbf{F}_{Cd}$. In a general point of view, as a result of the lability and fluxionality of the coordination sphere of the Cu(I) ions in the Cu(I)-based CDS derivatives reported so far, rapid and reversible intramolecular conformational re-organizations dominate the dynamics of such assemblies in solution.[4,5] So far, this hindered the observation of sharp NMR patterns that would be clearly diagnostic of the persistence of the specific molecular architectures observed in solid state structures. This situation is in marked contrast with the plethora of Pt(II) and Pd(II)-based CDS assemblies for which multinuclear NMR spectroscopies constitute a standard and routine key characterization technique that allows to probe the stability and reactivity in solution of these derivatives.[2] The same stands for the Cu(I)-based supramolecular assemblies obtained according to the metal-templated approach in which the specific design of the multitopic assembling ligands insure a high conformational stability to the resulting derivatives.[3] Indeed, in the case of the compound **D**, the $^{31}P\{^1H\}$ NMR spectrum reveals two broad multiplets centered at −15.0 and −18.2 ppm which are upfield shifted compared to the signals observed for **A** (two broad singlets at $\delta = -8.5$ ppm and −10.5 ppm, Fig. S2).[6] The ^1H NMR spectrum of **D** presents typical resonances of non-equivalent dppm methylene protons splitted into two broad multiplets centered at + 2.70 and + 3.55 ppm, underlying the $1\kappa P$:$2\kappa P$-coordination of the dppm ligands. Such NMR spectra patterns are comparable with those recorded for the derivatives $\mathbf{C}_{\mathbf{M}}$,[5b] which is in agreement with their overall similar solid-state supramolecular backbones. Yet, it does not allow to formally confirm the preservation in solution of the multimetallic multicyclic scaffolds of these derivatives since one cannot exclude that similar self-dissociation and re-organization equilibria could take place for derivatives **D** and $\mathbf{C}_{\mathbf{M}}$. Conversely, and unexpectedly, the $^1H\{^{31}P\}$ NMR (Fig. 2a) and $^1H\{^{63}Cu\}$ spectra of $\mathbf{F}_{Zn}$ display well-defined sharp signals as a signature of a frozen molecular system.[6] In particular, an intriguing pattern of two apparent multiplets (Fig. 2a) centered at +2.61 ppm and +3.48 ppm is observed, accounting for the non-equivalent methylene protons of the coordinated dppm ligands. 2D $^1H\{^{31}P\}$ *J*-Resolved NMR experiment (Fig. S13) revealed that these methylene multiplets are assigned to a distribution of overlapping independent doublets with average geminal $^2J_{H\text{-}H}$ values of 13.1 Hz, which is confirmed by simulation of these multiplets with eight equivalent $^2J_{H\text{-}H}$ 13.1 Hz doublets (Fig. 2c). This reveals the preservation of the solid state X-ray molecular structure of $\mathbf{F}_{Zn}$ in solution. Indeed, a non-centric S_4 point group symmetry lies in the polycyclic solid-state backbone of $\mathbf{F}_{Zn}$ and renders the four $[Cu_2(\mu_2\text{-dppm})_2]^{2+}$ fragments non-equivalent. Moreover, on each of these $[Cu_2(\mu_2\text{-dppm})_2]^{2+}$ dimers, the four methylene protons are symmetrically inequivalent, two of them pointing inward the metallacycle while the two other are orientated outward. Persistence in solution of such a molecular structure should result in the methylene protons signals zone in a total of sixteen signals divided into two groups of eight doublets embedded with geminal $^2J_{H(inward)\text{-}H(outward)}$ coupling, which is indeed experimentally observed. A variable temperature $^1H\{^{31}P\}$ NMR study (Fig. S17) confirmed the rigidity of $\mathbf{F}_{Zn}$ backbone in solution, showing that the general pattern observed at RT is preserved over



Scheme 2 Suggested mechanism of adaptive self-dissociative assembling processes based on the derivative **E** and its reaction with M'(II) metals salts.

the temperature range investigated. In the case of the derivative **F**$_{Cd}$ the ^{1}H{^{31}P} spectrum[6] exhibits broader signals than those obtained for **F**$_{Zn}$ which probably indicate a larger

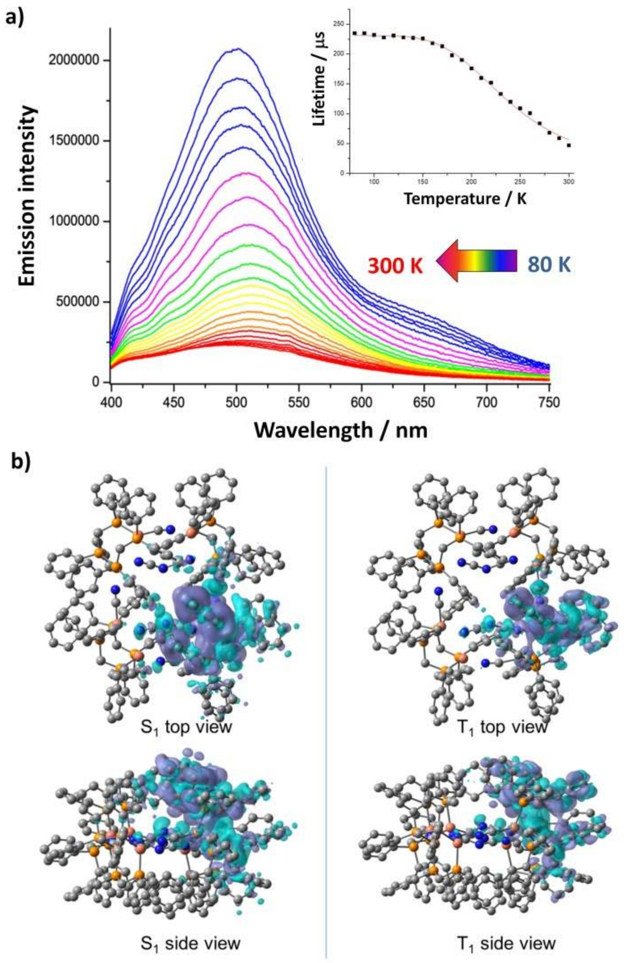


Fig. 3. a) Non-normalized solid-state temperature dependant emission spectra of **D** (λ_{ex} = 365 nm); insert: plot of the emission decay lifetime (long-lived component) against temperature (80 K to 300 K), the red line represents the fit according to the TADF Boltzmann-type equation S1; b) Isosurface representations of the electronic charge-density difference between the first vertical singlet (S_1) and triplet (T_1) excited states, and the one of the ground state (S_0) of **D** (violet = density depletion, cyan = density increase) (± 1.10^{-4} e.bohr^{-3}).

degree of conformational flexibility in the backbone of **F**$_{Cd}$ in solution at RT. Yet, variable temperature NMR study shows that the resolution of the ^{1}H{^{31}P} spectra of **F**$_{Cd}$ improves upon temperature cooling (Fig. S18), presenting at low temperature pattern very similar to the ^{1}H{^{31}P} spectra of **F**$_{Zn}$. The ^{31}P{^{1}H} NMR spectrum of **F**$_{Zn}$ (Fig. S21) shows two complex multiplets centered at -14.7 and -17.9 ppm.[6] These signals are observed at similar chemical shifts than the broad signals recorded for **F**$_{Cd}$, **D** (Fig. S2) and **C**$_{M}$,[5b] which is in agreement with the ''Cu$_8$(CN)$_4$'' metallacycle sub-units featured by all these derivatives. The preservation of the solid state discrete molecular structure of **F**$_{Zn}$ and **F**$_{Cd}$ in solution is definitively confirmed by DOSY NMR analysis (Fig. 2b and S14) which revealed that all of the proton signals correspond to the same diffusion coefficient *D*, and thus the same supramolecular object. The hydrodynamic radius R_h as

Crystalline samples of **D** display at 300 K an eye-perceived yellowish luminescence upon excitation at 365 nm (Fig. 3a). This corresponds to a broad and featureless RT emission band with an emission maximum λ_{em} at 500 nm associated with a bi-exponential emissive lifetime τ_1 = 52 µs and τ_2 = 18 µs and an emission quantum yield (EQY) of 21 %. Upon cooling to 80 K, the emission spectrum of derivative **D** presents a gradual enhancement of its emission band is associated with a moderate red-shift of the emission maximum λ_{max} down to ca. 200 K and then a slight blue-shift of the λ_{max} is observed as the temperature decreases to 80 K (λ_{em} = 512 nm at 80 K). The overall unsymmetrical shape of these spectra suggests that several radiative relaxation pathways could be operant in this system, with relative efficiencies that could be dependant of the temperature. Note moreover that the rise of a shoulder at ca. 650 nm at low temperature. The detailed study of the temperature dependence of the emission lifetime (Fig. 3a) was conducted, revealing bi-exponential decay times all along the temperature range with a short-lived component having an almost linear and moderate progression upon cooling (at 80 K, τ_2 = 56 µs). Conversely the long-lived component presents a larger amplitude variation (at 80 K, τ_1 = 238 µs, Fig. 3a) bearing a sigmoidal profile that resembles the temperature dependant profile typically observed in the case of thermally activated delayed fluorescence (TADF).[10] Yet, a single radiative relaxation pathway operant along the entire temperature window is quite unlikely regarding the thermal dependence of the emission spectra and a precise assignment of the relaxation processes occurring after UV-Vis excitation in derivative **D** would be uncertain. Attempting a fit of the thermal variation of the τ_1 component to the Boltzmann-type equation S1 in SI,[10a] the values of $\Delta E(S_1\text{-}T_1)$ = 978 cm^{-1}, $\tau(S_1)$ = 229 ns and $\tau(T_1)$ = 231 µs can be eventually obtained. This set of values ranges among those determined for the other Cu(I) CDS assemblies based on the $[Cu_2(\mu_2\text{-dppm})_2]^{2+}$ fragment (including the precursor **A**) that were identified as TADF luminophores,[5] suggesting that a TADF process could take part in the radiative relaxation processes occurring in derivative **D**. Note that the calculated $\Delta E(S_1\text{-}T_1)$ = 978 cm^{-1} is a priori not supported by the spectral shifts observed in the temperature dependant emission spectra, which supports the hypothesis of multiple emission processes. Interestingly, **D** and the structurally related derivative **C**$_{Pd}$ (Scheme 1a) share significantly similar radiative relaxation parameters despite a larger room temperature EQY for **D** (EQY **C**$_{Pd}$ = 2 %).[5b] Quantum chemical calculations at the DFT level were performed for **D**. The geometry optimization[6] of the ground state S_0 reveals that the metallacycle frame is preserved in vacuum which confirms the stability of such nanosized scaffold. The first lowest singlet and triplet excited states were calculated by time dependent DFT (vertical excitation).[6] They are highly similar (Fig. 3b) and correspond to electronic transitions from the metal-dppm centered molecular orbitals (MOs) to exclusively ligand-centered MOs involving both cyanido and DCM ligands together with the phenyl rings of the dppm ligands. This demonstrates that introduction of different pseudo-halide ligands impacts not only the geometries and the self-assembling processes but also the photophysical properties of CDS Cu(I) assemblies. Conversely, derivatives **E**, **F**$_{Zn}$ and **F**$_{Cd}$ present only very weak luminescence in the solid-state upon UV-vis light excitation[6] (derivative **F**$_{Cu}$ is non emissive). This is very likely due to the intense stretching vibrational modes typically associated with the coordinated azido ligands that are responsible of very efficient non-radiative relaxation pathways.

Conclusions

With the preparation of the new polymetallic assemblies **D**, **E** and $\mathbf{F_{M'}}$, we demonstrate that the variety of building blocks embedded in Cu(I) CDS processes can be extended to different pseudo-halide ions giving access to a rich diversity of original intricate heteroleptic and heterometallic supramolecular scaffolds. Thus, the scope offered by CDS syntheses that be conducted using Cu(I) pre-assembled precursors is greatly enlarged since a large number of alternative ligands can be involved in these rational self-assembly processes. Moreover, we show that the derivative **E**, as its precursor **A**, can also be used as a new adaptive Cu(I) pre-assembled precursor for CDS syntheses, enlarging the possible accesses to large family of new Cu(I)-based heterometallic CDS assemblies. Importantly, the preservation of these large complex supramolecular architectures in solution is demonstrated for the first time. This shows that, if the amplitude of the conformational flexibility of Cu(I) CDS scaffolds can be important at RT in solution inducing ill resolved and poorly informative NMR spectra, this do not imply systematic dissociative and re-organisation equilibria in solution. Such behaviour of Cu(I) CDS assemblies may be due to the high thermodynamic stability of these intricate scaffolds bearing multiple chelates and metallacycle sub-units that disfavours self-dissociative processes in solution. This study opens new perspectives for solution-route processes luminescent molecular-based devices (OLEDs, luminescent sensors, …)[10,11] based on Cu(I) CDS assemblies whose photophysics can be modulated thanks to the combination of different pseudo-halide ligands with pre-assembled polymetallic Cu(I) precursors, a field of investigation that attracts currently a large interest for the preparation of new light-emitting devices or stimuli-sensitive luminescent multifunctional materials based in this cheap metal ion.[10,11]

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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