

# ORGANIC AND ORGANOMETALLIC COMPOUNDS FOR NONLINEAR ABSORPTION OF LIGHT

PER LIND



AKADEMISK AVHANDLING

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**Title**

Organic and Organometallic Compounds for Nonlinear Absorption of Light

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**Abstract**

Nonlinear absorption and associated emission of light by organic and organometallic compounds are of interest for emerging photonics technologies. The demand for protection of eyes and various types of optical sensors from laser-beam pulses has resulted in the search for optical limiting devices that have the property of being transparent at low intensity of light (normal light), but non-transparent towards high intensity (laser) light. This type of protection may be obtained by using an organic material that displays nonlinear optical (NLO) properties. Examples of NLO effects that can be used for optical limiting are reverse saturable absorption and two-photon absorption.

The advantage of using compounds that show such NLO effects is that they can have very fast response and are self-activating, that is, there is no need for externally controlled switching to obtain optical limiting.

In this work, several dialkynyl substituted thiophenes and thiophenyl-alkynyl-platinum(II)-complexes were synthesized and tested for nonlinear absorption of light. A palladium-copper mediated coupling (Sonogashira coupling) was utilized for all reactions between terminal alkynes and aryl halides.

Molecular orbital (MO) calculations were used in order to screen for suitable properties, such as the second hyperpolarizability, in compounds of interest.

Information from absorption and emission spectroscopy was compared to data from MO calculations.

A quantitative structure-activity relationship (QSPR) study using a PLS approach was performed in order to identify important molecular electronic variables for optical limiting of organic compounds.

**Keywords**

Nonlinear absorption, thiophene, platinum (II) complexes, Sonogashira coupling reactions, optical limiting, molecular orbital calculations.

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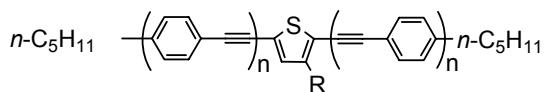
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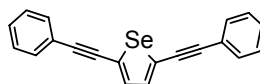
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## STRUCTURES AND NUMBERING OF COMPOUNDS

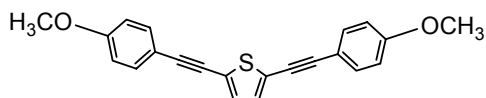
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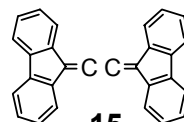
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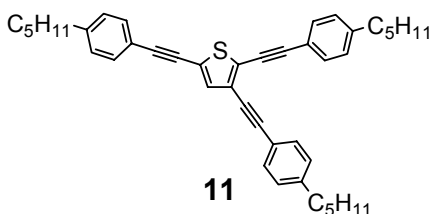
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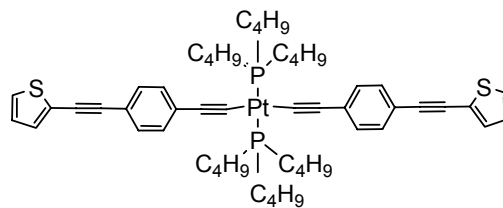
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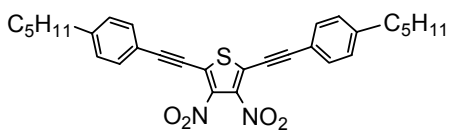
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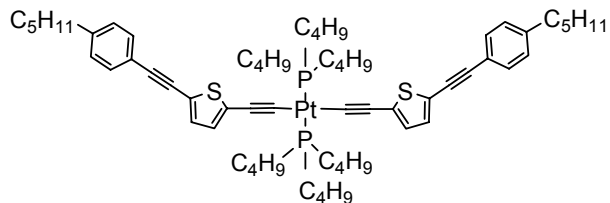
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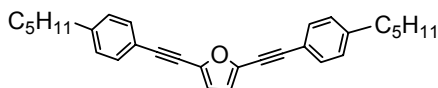
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## List of Papers

This thesis is based on the following papers and will be referred to in the text by their roman numerals I-IV.

- I** A QSPR study on optical limiting of organic compounds  
Per Lind, Cesar Lopes, Kjell Öberg and Bertil Eliasson  
*Chemical Physics Letters* 387 (2004) 238-242
- II** Non-linear absorption of 2,5-dialkynyl thiophenes  
Per Lind, Anders Eriksson, Cesar Lopes and Bertil Eliasson  
*Journal of Physical Organic Chemistry* 18 (2005) 426-433
- III** A theoretical and experimental study of non-linear absorption properties of substituted 2,5-di-(phenylethynyl) thiophenes and structurally related compounds  
Per Lind, Marcus Carlsson, Bertil Eliasson, Eirik Glimsdal, Mikael Lindgren, Cesar Lopes, Linus Boman and Patrick Norman  
*Manuscript*
- IV** Structural, Photophysical and Nonlinear Absorption Properties of *trans*-di-arylalkynyl Platinum (II) Complexes with Phenyl and Thiophenyl Groups  
Per Lind, Dan Boström, Marcus Carlsson, Anders Eriksson, Eirik Glimsdal, Mikael Lindgren and Bertil Eliasson  
*Journal of Physical Chemistry A*, 2007, Accepted

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# 1. INTRODUCTION

## *1.1 Background*

Over the last decades there has been an increasing interest and research activity on nonlinear optical (NLO) properties of organic systems [1-6]. A new photonics technology using optical switching and optical computing instead of, or together with, electronics may well evolve significantly during the coming decades. The use of photons is already speeding up data communication in optical fibres and enhances data storage by laser diodes in computers. The field of nonlinear optics started in 1875 when J. Kerr discovered a change in the refractive index of CS<sub>2</sub> when subjected to an electric field; a process now known as the Kerr-effect. But it was not until the invention of the laser in 1960 that the scope of NLO could really develop [7].

## *1.2 Nonlinear optics*

When a material is subjected to an optical field (i.e. light) of a given frequency, its electrons will oscillate in response. In a linear absorption process this oscillation will be in harmony with the incident light and the absorbed energy could be re-emitted as a secondary light of the same frequency. In a nonlinear process however, the oscillation of electrons will eventually become anharmonic and re-emitted light may differ in frequency and amplitude from the incident light.

Inorganic materials have dominated in the field of NLO, for example, lithium niobate (LiNbO<sub>3</sub>) has been used for electrooptic modulation [8]. Technology based on inorganic electro-optic crystals has not found a broad market though, which is due to the difficulty to grow high-quality single crystals and to incorporate them into electronic devices.

Another drawback of inorganic materials is their relatively slow optical switching, which can be explained by inorganic materials having ionic or covalent bonds throughout the entire solid. This means that the material can be considered as one gigantic molecule where electrons are less accessible than in organic molecules. Furthermore, in inorganic crystals the response to an external electric field comes from setting cations and anions in motion which leads to a rather localized charge separation, and the response time is limited by vibrational time scales [7].

More recently, however, organic materials have come to play a major role in this area of research.

In organic materials, electrons are more accessible and NLO-effects arise from the interaction between light and electrons within individual molecular units,

giving greater and faster responses [7]. This together with the possibility to design an organic molecular structure and synthesise the material to match requirements should make an organic compound generally more advantageous than an inorganic substance.

Especially organic structures with large delocalised  $\pi$ -systems have proven to be useful. The reason for this is that  $\pi$ -electrons are more easily affected by an external optical field as they are relatively loosely bound to the nucleus, and that the delocalised orbitals may be extended over the entire molecule giving large and fast polarization [9,10].

The response of a medium to an induced electric field, i.e. light, is generally described in terms of polarization. On a molecular level this dependence is expressed by equation 1.1. [10]<sup>†</sup>

$$\mathbf{p}_i = \mu_i^0 + \alpha_{ij}\mathbf{E}_j + \beta_{ijk}\mathbf{E}_j\mathbf{E}_k + \gamma_{ijkl}\mathbf{E}_j\mathbf{E}_k\mathbf{E}_l + \dots \text{eqn 1.1}$$

Where  $\mathbf{p}_i$  is the molecular polarization,  $\mu_i^0$  is the permanent dipole moment of the molecule in direction  $i$ ,  $\alpha_{ij}$  is the linear polarizability responsible for effects like light reflection and refraction.  $\beta_{ijk}$  is the second order hyperpolarizability and  $\gamma_{ijkl}$  is the third order hyperpolarizability.  $\mathbf{E}_j$ ,  $\mathbf{E}_k$  and  $\mathbf{E}_l$  are the external electric fields in the  $j, k$ , and  $l$  directions within the molecular co-ordinate system, respectively.

### 1.3 Origin of second and third-order hyperpolarizability

Second order NLO-effects are associated with the tensor  $\beta$  in eqn. 1.1. In order for a molecule to exhibit second order effects it should preferably have a  $\pi$ -electron system which delocalises in response to an applied electric field, resulting in spatial asymmetry of the electron distribution

With a two-state model, the second order hyperpolarizability in a molecule is proportional to the change in dipole moment and the energy difference between the ground and excited state, and the intensity of the transition to that excited state [11].

Charge asymmetry is, as pointed out, essential for large second order responses. In fact, all even order effects vanishes in centrosymmetric systems [4].

Much work has been done in order to design molecules which exhibit these properties and thus have large  $\beta$ -values [12,13]. Generally, one can state that a molecule should possess strong donor and acceptor groups to increase the

<sup>†</sup> Because of simplicity, the variables in equations and formulas in this thesis are not given in italics as is customary.

charge transfer process and secondly have a long conjugated unit linking the donor/acceptor groups together.

Here it can be pointed out that an alkene-bridge is usually a more efficient link than an alkyne-bridge which is due to a greater degree of conjugation inherent in ethylene-linked  $\pi$  systems [14]. Examples of second order NLO-effects are second harmonic generation (SHG) and the electrooptic effect.

Third order NLO-effects are represented by the tensor  $\gamma$  in eqn. 1.1. Again, there is a relationship between electronic structure and molecular geometry; especially the length of the  $\pi$ -system.

Following an excitation of an electron there will be a relaxation of geometry which can lead to the formation of nonlinear excitations.

The geometry relaxation is much slower than the change in  $\pi$ -electron distribution and it is this instantaneous shift in  $\pi$ -electron density that is responsible for the large and fast polarizabilities of  $\pi$ -electron networks [7]. Examples of third order NLO-effects is third harmonic generation (THG) [15] and nonlinear absorption, such as two photon absorption (TPA) [16] and reverse saturable absorption (RSA) [17-19], which are important processes for optical limiting.

#### *1.4 Background of the project*

This work is made as a part of a photonics program initiated by FMV (Swedish Defence Materiel Administration) and performed in cooperation with, among others, FOI (Swedish Defence Research Agency) in Linköping.

The goal for this work is to develop new materials for protection of eyes and optical sensors against laser light. A variety of organic and organometallic compounds will be tested for NLO properties, such as optical limiting, within the frame of this project. All compounds will first be studied in solution and promising substances are then planned to be incorporated into a silica based sol-gel matrix and formed into a glass.

Optical equipment is used by military personal for many different purposes, such as observation, navigation, and reconnaissance. The laser constitutes a great threat towards all optical equipment and, through a sight or by direct exposure, the laser can also severely damage the human eye; undoubtedly our most important optical sensor.

The solution to this problem may be to incorporate a laser protection device within the optical equipment or within a sight to protect the eye.

The protective devices can be either active or passive. An active protection device requires a trigger signal for activation and is therefore not quick enough for the first laser pulses.

The passive device is self-activating which means that it is the optical energy (laser pulse) that is responsible for the activation of the material. Passive devices are based on nonlinear optical absorption and are generally denoted passive optical limiters or power limiters.

Optical limiting (OL) means that a material, through a nonlinear absorption mechanism, absorbs high intensity light, while they are transparent to low intensity light.

During the last decade several promising materials for optical limiting have been presented [17,18,20,21]. Materials like carbon black suspensions, metallophthalocyanines, and others have been tested but still there remains a need for better optical limiting materials to satisfy the requirements.

### *1.5 This work*

The goal of this part of the project has been to design and synthesise new organic and organometallic compounds with thiophene rings for optical limiting. In this work we have performed studies in order to further strengthen our knowledge about the nonlinear optical properties of thiophene derivatives and how to utilize it for optical limiting purposes. All photophysical and optical limiting measurement were performed in solution.

Quantum chemistry (molecular orbital, MO) calculations have been performed in order to identify interesting synthetic targets although it still seems uncertain how well for instance a calculated  $\gamma$ -value can be related to a measured third-order NLO property. Furthermore, it is difficult to calculate properties relevant for optical limiting such as lifetimes of excited singlet and triplet states, quantum yields for intersystem crossing and transition moments for the secondary excitations. However, a calculated  $\gamma$ -value may still give an indication on whether one structure is more promising than another.

The work also includes a QSPR (quantitative structure property relationship) study on the optical limiting ability of organic compounds (see paper I).

Needless to say, we have not reached a level of knowledge necessary to precisely select a molecular structure, with respect to type and number of atoms and their connectivity, that will give a large value of  $\gamma$  for certain photonics application.

Fortunately, it seems likely that progress can continue to be made through experiments and calculations on compounds where relative values or trends are examined.

In this work we have synthesised and investigated nonlinear absorption and optical limiting of a series of dialkynyl substituted thiophenes (papers II and III), as well as some thiophenyl-containing alkynyl platinum(II) complexes (paper IV).

Within the thesis an overview will also be given of the most important physical processes behind optical limiting, along with a short description of the laser measurement technique used to record optical limiting.

A short overview of other organic compounds that have been investigated for NLO properties is also included.

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## 2. NONLINEAR OPTICS IN ORGANIC MOLECULES

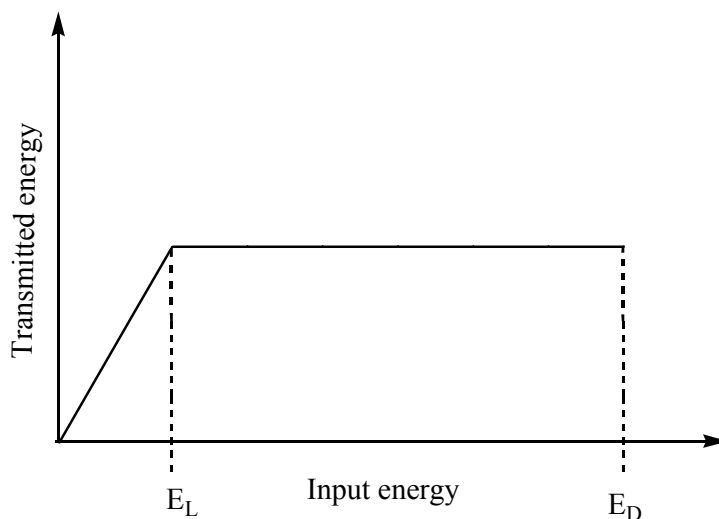
### 2.1 Background

The non-linear optical properties of a material can be used to dramatically reduce the transmittance of a device that is exposed to high energy inputs. Such devices are generally called optical limiters (OL) or optical power limiters (OPL).

For many applications, such as protection of optical sensors and the human eye from laser induced damage, it is considered necessary for an optical limiter to have high linear transmittance [1].

The input-output energy relationship of an ideal optical limiter is shown in figure 2.1.

Under realistic circumstances the limiting threshold (the input corresponding to the breakpoint in the curve) will not be as well defined and the output energy not as constant as for the ideal case, but will change from high to low transmittance gradually.



**Fig. 2.1** The output energy of an ideal optical limiter as a function of the input energy.  $E_L$  is the energy at which limiting begins and  $E_D$  is the energy at which the limiter is damaged.

The general demands put on an optical limiting device is:

- fast response (picoseconds or faster)
- quick recovery (milliseconds)
- high attenuation (more than 99%)
- broad band response (the entire visible region)
- large dynamic range (defined as  $E_L/E_D$ )
- high damage threshold ( $> MW/cm^2$ )
- high linear transmission at low energies ( $> 70\%$ )

Optical limiting methods can be categorised in two groups: dynamic and passive methods [2].

Dynamic control means that the OL device uses some kind of active response. Devices using dynamic control suffer a number of disadvantages such as high complexity and slow responses. A dynamic controlled device usually need some kind of sensor, a processor and an actuation unit to achieve the limiting, which explains the slow responses and high complexity associated with this method. Passive control on the other hand is accomplished by the use of a NLO-material in which the sensing, processing and actuation functions are inbuilt. This means much faster responses as there is no need of communication between separate units.

The physical mechanisms responsible for passive control protection can be divided in two different classes of optical nonlinearities, instantaneous and accumulative nonlinearities [2].

In an instantaneous process the polarization resulting from an applied optical field occurs immediately whereas accumulative nonlinearities arise when the induced nonlinear polarization either develops or decays on a timescale comparable to or longer than the excitation duration. In other words, the instantaneous nonlinearity depends on the instantaneous intensity within the medium whereas the accumulative nonlinearity is dependent on the energy density, fluence, deposited on the medium [2].

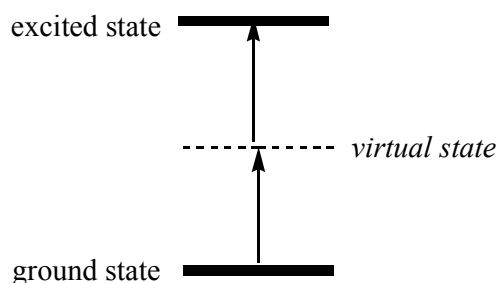
The most important instantaneous process associated with OL is two-photon absorption (TPA)[3], and examples of accumulative nonlinearities in optical limiting is excited state absorption[4,5] and nonlinear refraction [6].

A material that shows OL properties generally exhibits several different mechanisms that work together. The most important mechanisms in optical limiting is two photon absorption (TPA), reverse saturable absorption (RSA), and nonlinear refraction.

Other processes are induced scattering [7] and photorefraction [2] .

## 2.2 Two-Photon Absorption (TPA)

TPA is as mentioned earlier an instantaneous nonlinearity. In this process two photons cause an immediate transition from the ground state of the molecule to an excited state through an intermediate virtual state[3], figure 2.2.



**Fig. 2.2** The molecule absorbs one photon to promote an electron from its ground state to a virtual state followed by absorption of a second photon to promote the electron to its final state

The virtual state can be thought of as a real state with a lifetime approaching zero.

When the linear transmission is high there is no or little ground state absorption at low intensities, but as intensity increases two photons can together promote the molecule to an excited state.

The intensity of a beam as it traverses the material is given by eqn. 2.1 [8]:

$$\delta I / \delta z = -[\alpha + \beta I] I \quad \text{eqn 2.1}$$

where  $\alpha$  is the linear absorption coefficient and  $\beta$  is the two photon TPA coefficient.

(Not to be confused with the  $\beta$  that denotes the second order hyperpolarizability tensor on the molecular level.)

As mentioned in section 1, the third order hyperpolarizability tensor is denoted by  $\gamma$ . For bulk material the corresponding tensor is denoted by  $\chi^3$ .

The TPA coefficient,  $\beta$ , is related to the imaginary part of  $\chi^3$  through

the eqn. 2.2 [2]:

$$\beta = (3\omega / 2\varepsilon_0 c^2 n_0^2) \text{Im}[\chi^3] \quad \text{eqn 2.2}$$

Where  $\omega$  is the circular frequency of the light,  $\varepsilon_0$  is the dielectricity constant,  $c$  is the speed of light in vacuum and  $n_0$  is the linear index of refraction.

For a material that is transparent at low intensities,  $\alpha = 0$ , the change in intensity of the light propagating through a material is thus given by eqn. 2.4 [8]:

$$I(L) = I_0 / (1 + I_0 \beta L) \quad \text{eqn 2.3}$$

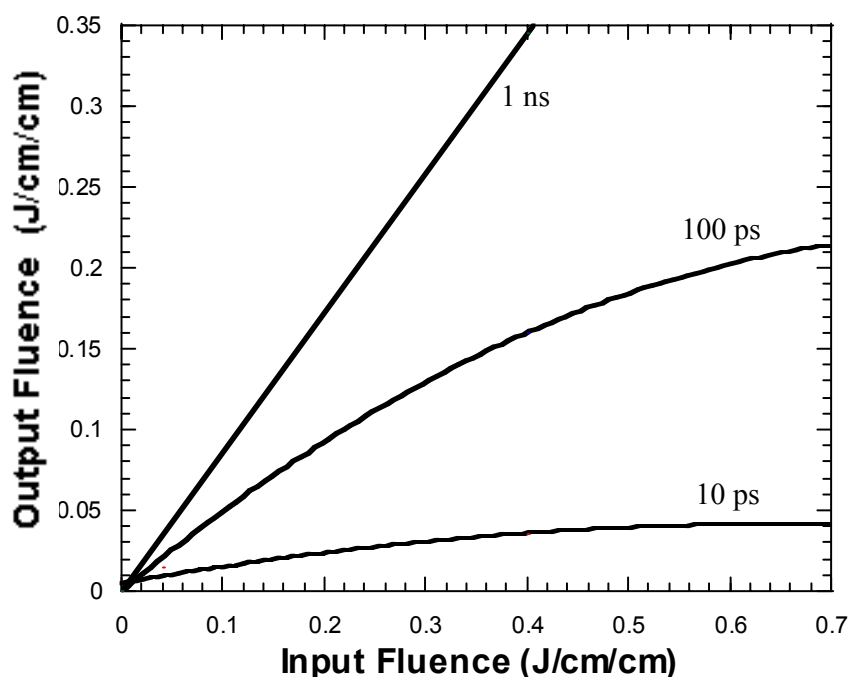
Where  $L$  is the sample length and  $I_0$  is the incoming intensity.

This equation shows that the transmission decreases as the intensity,  $I_0$ , increases.

The decrease in transmission is thus correlated with the TPA coefficient, intensity and material thickness.

However, most materials possess a rather small  $\beta$  value which means that the intensity must be very high in order to see any optical limiting effect due to TPA.

Since intensity is really the energy density (fluence) divided by pulse duration, this also means that TPA is only interesting to use for picosecond pulses or shorter, figure 2.3, in order to achieve any significant clamping [2].



**Fig. 2.3** Calculated results of transmitted fluence of a TPA material for three different pulse durations

Another factor that influences the TPA coefficient is the band gap energy, or the energy difference between the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals. For materials that are transparent at visible wavelengths this band gap is rather wide compared to, for example semiconductors, and according to eqn. 2.4 [9], large band gap energy have a negative impact on the TPA coefficient  $\beta$ .

$$\beta(\omega) = K (E_p^{1/2}/n_0^2 E_g^3) F(2\hbar\omega/E_g) \quad \text{eqn: 2.4}$$

In the eqn.,  $K$  is a material independent constant,  $E_p$  is the Kane energy parameter with a value of approximately 21 eV and which is material independent for direct band gap material, and  $E_g$  is the band gap energy. This equation shows that a large  $E_g$  decreases the TPA coefficient and that  $\beta$  has a frequency dependence, which however is a weaker dependence compared to one-photon absorption.

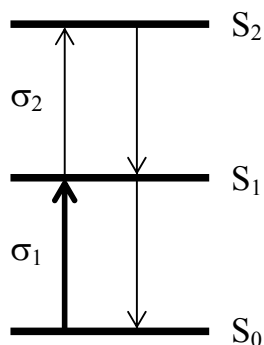
It is obvious that TPA is an important process for optical limiting. It is an instantaneous process, and can thus be thought of as the first line of defence.

However, due to the for most materials low  $\beta$  values, only TPA is not enough for a material to function as a satisfying optical limiter, especially not against longer laser pulse duration [10].

### 2.3 Reverse Saturable Absorption (RSA)

Bleachable dyes are molecules whose absorption can be saturated by high intensity light.

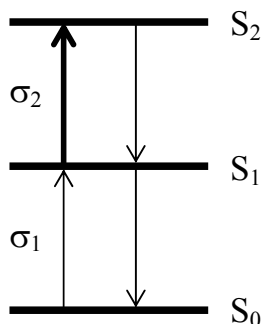
Such a material will absorb light until the ground state is depleted of electrons where after the transmission for a short time will be close to 100 %. The dye will then relax back to its ground state when the light is removed. This process is outlined in figure 2.4.



**Fig. 2.4** Electronic process of saturable absorption .The ground state absorption  $\sigma_1$  is larger than the excited state cross section,  $\sigma_2$ .  $S_1$  is populated until  $S_0$  is depleted followed by relaxation.

Reverse saturable absorption, or reversed bleaching, can be observed in materials that absorbs more in the excited state than in the ground state[4]. As the intensity increases, the absorption increases and transmission decreases. The simplest model to describe this is the three level model outlined in figure 2.5. The ground state cross section is denoted  $\sigma_1$ , and the excited state cross section  $\sigma_2$ . As the material absorbs light the first excited state,  $S_1$ , is populated. If  $\sigma_2$  is smaller than  $\sigma_1$  the material will be more transparent as the ground state is depleted of electrons and bleaching will occur. If, on the other hand,  $\sigma_2$  is larger

than  $\sigma_1$ , absorption will increase as  $S_1$  is populated and reversed bleaching occurs.



**Fig. 2.5** Three level model of RSA. The excited state cross section  $\sigma_2$  is larger than the ground state cross section,  $\sigma_1$ .

Another way to illustrate nonlinear absorptive response for reverse saturable absorbers is illustrated in figure 2.5 [4].

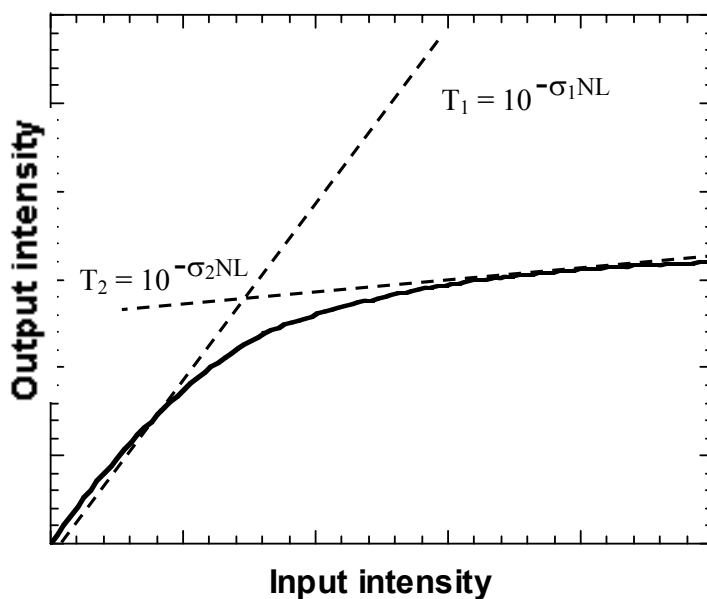
At low intensities the transmittance is determined by the ground state absorption, and transmittance can be written as:

$$T_1 = \exp(-\sigma_1 NL) \quad \text{eqn 2.5}$$

Where  $N$  is the number of active molecules and  $L$  is the sample length.

As the population is transferred from the ground state to the excited state upon excitation the transmittance decreases and becomes governed by the excited state cross section as seen in eqn 2.6:

$$T_2 = \exp(-\sigma_2 NL) \quad \text{eqn 2.6}$$



**Fig. 2.6** Input intensity plotted against output intensity for a three level RSA material

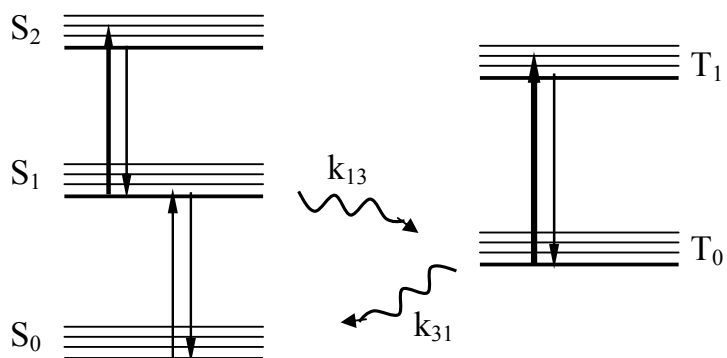
As mentioned above the material must have a large excited-state cross section to ground-state cross-section ratio, to work as a reverse saturable absorber, ( $\sigma_2/\sigma_1 \gg 1$ ). However, the value of  $\sigma_1$  must be adequately large in order to achieve population of the excited state during the pulse [2].

As understood from figure 2.6, RSA is not a truly limiting process as transmittance will still increase with increasing fluence, but it will do so more slowly.

The three level model (fig. 2.5) is the simplest case of RSA but can normally only be applied for sub-nanosecond pulses. For allowed transitions (*singlet*  $\rightarrow$  *singlet*), relaxation is usually very fast and in the case of a long pulse there will be some relaxation to the ground state during the pulse, which will result in a less efficient OL compared to that for a short pulse [2].

In some systems however, there can be a significant intersystem crossing (ISC) from the first excited singlet state to the lowest triplet state. The process involving intersystem crossing and triplet states is illustrated in figure 2.7 [5].





**Fig. 2.7** Five level Jablonski diagram displaying the energy levels involved in RSA

The ISC pathway can become important for compounds that contain a heavy atom such as Au or Pt. The heavy atom provides the pathway for a transition from an excited singlet state to a triplet state through spin-orbit (SO) coupling, a process also known as a “heavy atom effect”.

An effect of the SO coupling, which arises from interaction between the magnetic moments of the electron spin and the electron orbit motion [11], can be described as a mixing of some triplet state character into the singlet state and vice versa.

Intersystem crossing is normally a slow process, on a time scale of ten to several hundred ns [5], since the transition is forbidden. ‘Forbidden’ means that the process is much less likely than for instance internal conversion, but if the rate constant  $k_{13}$  for  $S_1 \rightarrow T_1$  ISC is greater than the inverse of the pulse duration a substantial triplet population can build up during the pulse.

The triplet state is often relatively long lived, and sometimes even denoted a meta-stable state, which is due to the slow relaxation of  $T_1 \rightarrow S_0$  since that is a forbidden transition as well.

The lifetime of the triplet state generally gives an indication of the maximum pulse width for which the material can act as an optical limiter.

This is a reason to design organic molecules to exhibit large intersystem cross section.

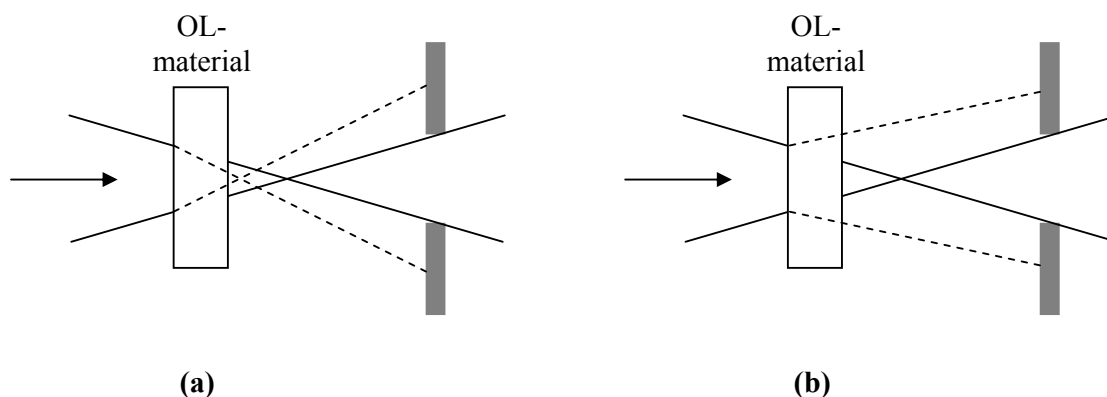
If, on the other hand, pulse duration exceeds the triplet state lifetime, we will see relaxation of the population before the entire pulse have passed through the material and transmission of the tailing part of the pulse would be high.

As mentioned, the relaxation from higher excited states to lower excited states ( $S_2 \rightarrow S_1$ ,  $T_2 \rightarrow T_1$ ) is, as a rule, ultrafast which means that population of these higher states can be ignored for most situations [5]. Nevertheless, in case of very high irradiance optical pumping, which may be obtained with ps or fs pulses, the

upper excited states may start to populate which would lead to a decrease in absorption and increase of transmission, if those new states are not absorbing at the current wavelength.

#### 2.4 Nonlinear refraction

When a NLO-material is subjected to light of high intensity it may demonstrate a change in refraction index. This change can be seen as either positive or negative and cause the material to either defocus or focus the light [2], as illustrated in figure 2.8.



**Fig. 2.8.** (a) Effect of a self-focusing device. (b) Effect of a self-defocusing device.

As understood from figure 2.8, both self-focusing and self-defocusing materials will refract the light away from the optical sensor and thus act as an optical limiter.

A self-defocusing material has the advantage of leading the light away from the beam axis and can thus be regarded as self-protecting, in contrast to a self-focusing material which will suffer a great risk of damaging.

On the other hand, a self-focusing material will be able to activate itself at lower energy input compared to a self-defocusing matter, and an optical limiting device based on non-linear refraction will generally, independent on sign, exhibit a larger dynamic range than devices based on absorption alone [2]. Nonlinear changes of refraction in a material can be a result of both instantaneous and accumulated processes.

For example, a material designed for two photon absorption could, apart from the TPA limiting, also take advantage of the electronic-Kerr effect [2] which is a light-induced change of refractive index.

### *2.5 Organic compounds studied for NLO-properties*

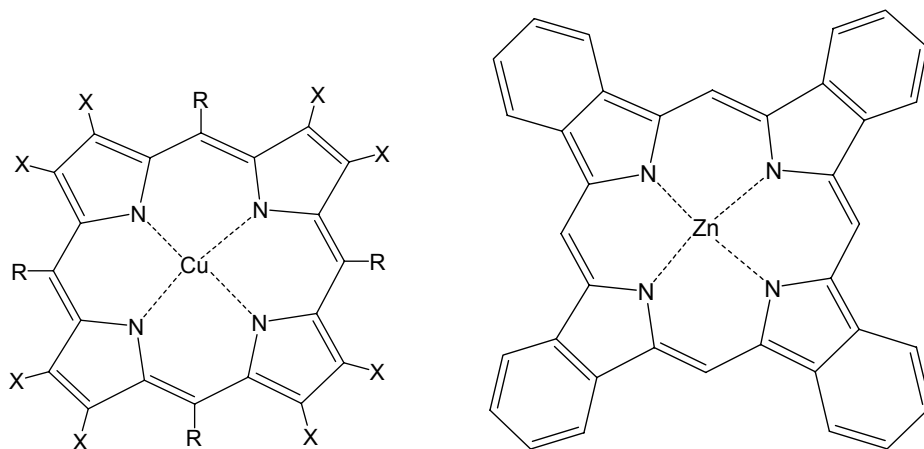
Over the years a large variety of organic structures have been investigated for NLO properties and optical limiting. Some of them, such as phthalocyanines, cumulenes and platinum acetylides will be discussed later in this thesis (see chapter 5) but in this section a short review is given of other classes of organic structures studied by other groups. The purpose of this is to give the reader some idea of the diversity of this field.

As a general rule, a large first and/or second hyperpolarizability is found for compounds or complexes with an extended  $\pi$ -electron system; consequently this review concentrate on molecules with this structural feature. Since a standard is not defined for measuring and reporting optical limiting characteristics of compounds and materials, this assessment will point out important differences between the classes of compounds rather than report numbers.

#### *2.5.1 Porphyrins*

Porphyrins (Pf) have been much studied with respect to electron and energy transfer processes. Metal ion complexation often increases the third order nonlinear optical susceptibility. Metallo-Pf typically have a Soret band ( $\pi$ - $\pi^*$  transition to second excited state) in the region of 400-450 nm and a less intense Q band (to first excited state) in the region of 500-600 nm. Additional charge transfer bands are sometimes present and arise from Pf-metal interactions. Also the Q band is affected by the presence of a metal. The photophysics of this class of compounds is well known and the Pf generally show good thermal stability[12]. Several Pf systems have been studied with respect to optical limiting and have shown rather good characteristics. A recent example of a Cu-Pf with various degree of bromine substitution (figure 2.9) shows that the bromines result in a distinct improvement of the optical limiting at 532 nm, ( $\lambda_{\max}$  at 562-573 nm)[13]. This is attributed to a more efficient S  $\rightarrow$  T intersystem crossing, as compared with the parent Pf without the Br atoms. Another example is a tetrabenzo-Pf (figure 2.9), which shows good optical limiting at 750 nm (near IR)[14].

Porphyrins are not considered as the most interesting optical limiters because of the absorption of visible light. Still, such structures may be optimized to give efficient optical limiting in other regions, such as near IR mentioned above.



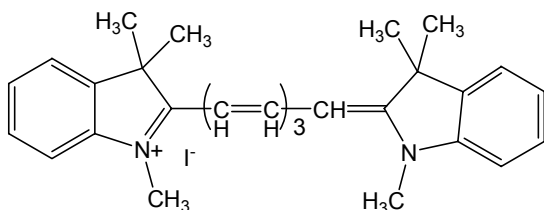
**Fig 2.9** Structure of a Cu-porphyrin with Br substitution at various positions X (left) and a Zn-tetrabenzporphyrin (right)

### 2.5.2 Fullerenes

**C-60 and C-70 fullerenes** have been extensively studied during the last decade, including nonlinear optical limiting[14-16]. Both compounds show good optical limiting with C-60 being somewhat better, at least partly due to its lower linear absorption at the studied wavelength of 532 nm. The dominant mechanism is thought to be RSA with the lowest excited triplet state as the major absorbing state. C-60 is thermally stable and commercially available at a reasonable price. Still, it is not straightforward to obtain derivatives of this system, a feature that may limit the use of C-60 as an OL material.

### 2.5.3 Carbocyanines.

Carbocyanines is a class of dyes that have a positive charge spread along a  $\pi$ -system of double-bonds. An example is the hexamethylindotricarbocyanine iodide (HITCI), see figure 2.10. Similar dyes may contain sulfur or oxygen instead of the saturated carbon in the five-membered rings. Generally, these dyes often have strong absorbance in the visible region. HITCI has  $\lambda_{\max}$  at the red-end (740 nm) and was found to show good optical limiting[17].



**Fig 2.10** HITCI

As for carbocyanines, *polyenes* have alternating single and double bonds. The all-trans polyenes are relatively stable and this class of compounds has shown rather high second and third order NLO properties [18,19].

A variety of other types of *polymers* have also been tested for NLO [20-22].

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### 3. PHOTOPHYSICS AND OPTICAL POWER LIMITING MEASUREMENTS

When matter is subjected to light a number of different processes may take place. Generally, a distinction is made between photochemical and photophysical processes [1]. In a photochemical process the interaction of light with matter causes a structural change within the material [2]. These phenomena may actually be used for synthetic purposes but can be somewhat difficult to control.

In a photophysical process however the chemical structure remains unchanged at the end and it is these types of processes that are interesting for optical limiting purposes. But why do light have an influence on matter and what is light? Below is given a short description on the nature of light and the ways it influences matter

#### 3.1 The nature of light

The nature of light is dual and may be illustrated in two different ways. On one hand it can be described as a particle and on the other hand as a wave [2]. When looked upon as a particle we call this element a *photon*. A photon can thus be exemplified as a particle with a certain amount of energy but no mass. As a wave, light is described as electromagnetic fields that oscillate in time and space with different wavelengths and travel with the speed of  $3 \times 10^8$  m/s.

The energy of light, or irradiation, is proportional to the frequency and inversely proportional to the wavelength.

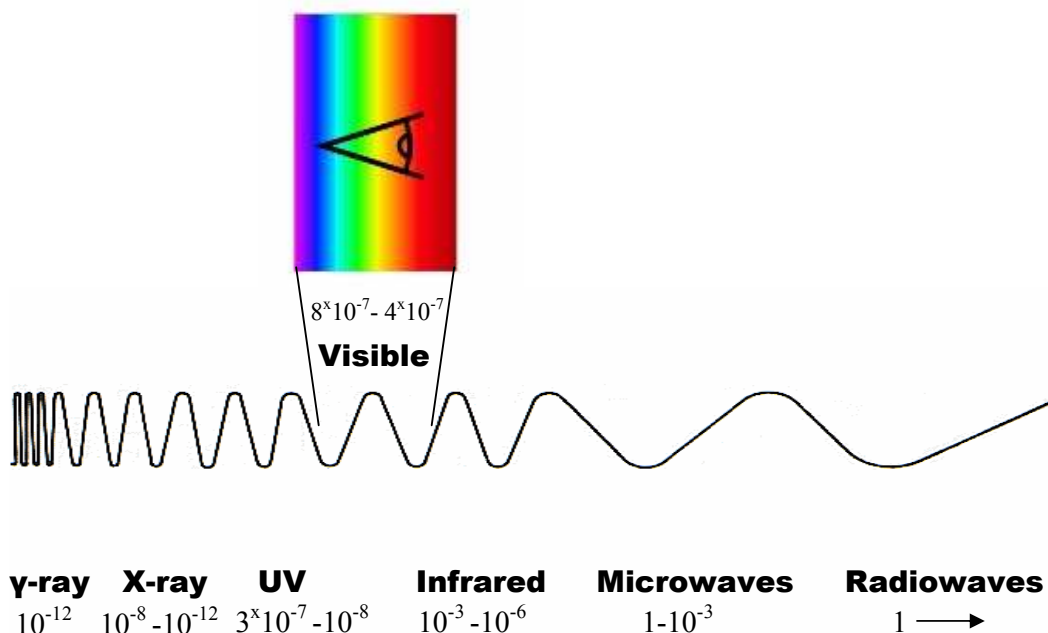


Fig. 3.1 Electromagnetic spectrum

The wavelength of visible light is, as seen from the figure 3.1, in the interval of ca. 400-800 nm. At the right end of the spectrum, microwave radiation is indicated, with wavelengths between ca. 0.5-300 mm. The energy of microwaves is enough to increase rotational motion of molecules, an effect frequently used in lunchrooms all over the world for heating leftovers from yesterday's dinner.

Infrared radiation lies between ca. 0.8-300  $\mu\text{m}$  and may be used to affect vibrational motion in molecules. Ultraviolet (100-300 nm) and visible light have enough energy to excite electrons in molecules. In this interval and especially in the ultraviolet region the energy may even be high enough to actually break bonds in molecules. Use of ultraviolet and blue light is typical for initiating photochemistry reactions.

At even shorter wavelengths (higher energy), such as x-ray and  $\gamma$ -ray irradiation the energy is so high it may cause ejection of electrons from atoms and molecules, a process called ionization.

We should however bear in mind that there is a difference between energy and power of light. The energy of light is, as stated, dependent on the wavelength of the radiation whereas the power is also dependent on the number of photons at any given time. The power of the light is given in the unit of watts (W). A third commonly encountered concept of light is intensity. Intensity may be defined as power per unit area.

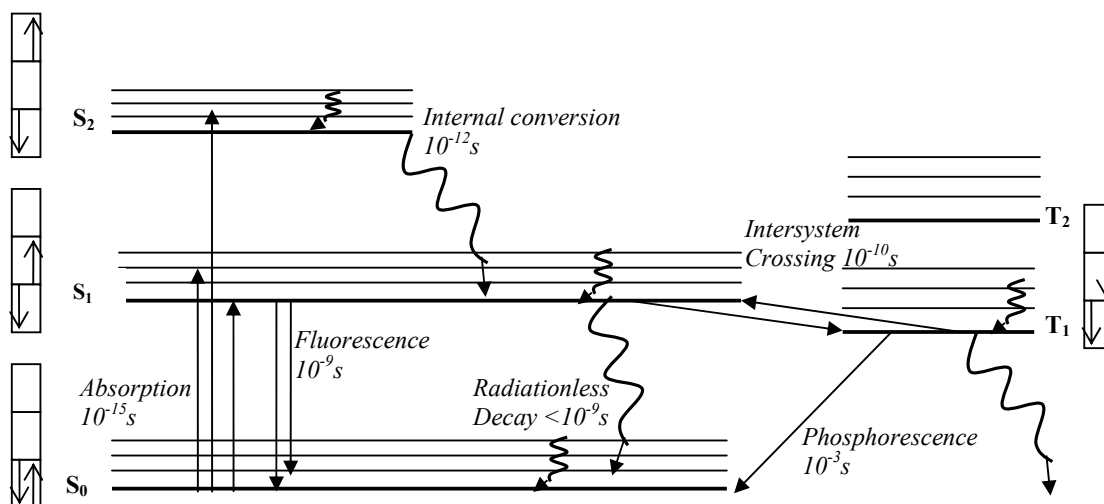
However, as this work focuses on compounds for materials that may function as absorbers or attenuators of high intensity light it is the photophysical properties that are the most important. In the section below is given a short description of different photophysical processes that may take place as light interacts with matter.

How to monitor these processes and what information that may be extracted from the obtained data is briefly discussed together with techniques used to measure the optical power limiting ability of a material.

### *3.2 The Jablonski diagram*

The first Jablonski diagram was presented by Jablonski in 1935. A slightly modified form of the Jablonski diagram is shown in figure 3.2, and herein is described the different fates in the life history of an excited electron [3,4].





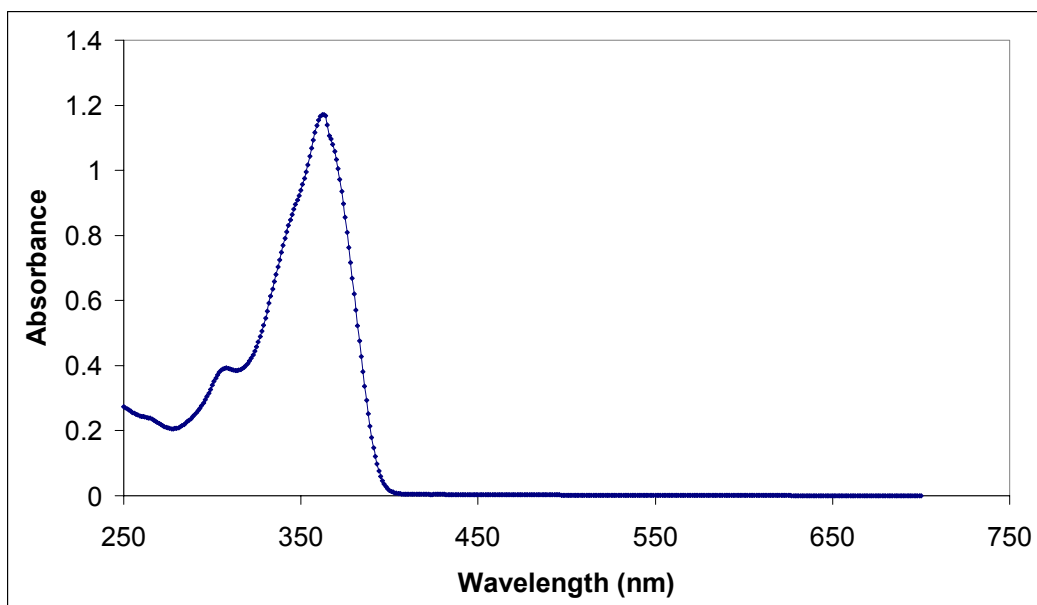
**Fig. 3.2** The Jablonski diagram. Arrows in boxes describes the relative spin states of the paired electrons

In the figure, S<sub>0</sub> represents the electronic ground state while S<sub>1</sub> and S<sub>2</sub> represent the first and second excited singlet state, respectively. The first and second triplet states are denoted T<sub>1</sub> and T<sub>2</sub> in that order.

### 3.3 Absorption

Virtually all organic molecules in the ground state (S<sub>0</sub>) have a closed-shell electron configuration, that is, all electrons are paired. However, when the molecule is subjected to light, this can be described as an electron being promoted to an upper energy level if the energy of the light matches the energy difference of the ground and excited state. As seen from the figure, excitation to higher vibrational levels of S<sub>1</sub> or even to a higher excited state is possible. Relaxation from an upper excited state to the lowest vibrational level of S<sub>1</sub> through internal conversion is extremely fast though and takes place before any other relaxation process can compete.

The absorption spectrum of compound **24** is shown in figure 3.3.



**Fig. 3.3** Absorption spectrum of compound 24

An absorption spectrum, often denoted UV/vis-spectrum, is recorded using a UV/vis-spectrophotometer. The sample is irradiated with monochromatic light normally ranging from 250-800 nm and the output intensity for every wavelength is measured. The absorption ( $A$ ) at any given wavelength is then calculated using the equation  $A = \log(I_0/I_1)$  and plotted versus the wavelength to acquire the absorption spectrum.

### 3.4 Fluorescence

One of the relaxation pathways from  $S_1$  to  $S_0$  involves re-emission of an absorbed photon, i.e. emission of light. This process is known as fluorescence and spectra that show light intensity versus wavelength are referred to as fluorescence spectra or emission spectra.

A fluorescence spectrum is obtained by initial irradiation of the sample at a single wavelength, normally where the molecule exhibit maximum absorption. A very popular irradiation source for luminescence studies is a Ti:Sapphire laser, which is a common type of tunable (ca 650 -1100 nm) laser for short (typically 100-200 fs) pulses. The wavelength dependence of the fluorescence intensity is then detected at a  $90^\circ$  angle to the incident light in order to avoid element of residual incident light.

### 3.4.1 Steady state fluorescence

Figure 3.4 displays the absorption and emission spectrum of **24**. It can be seen that the emission spectrum resembles the mirror image of the absorption spectrum. This is in full accordance with the fact that relaxation to the lowest vibrational level of  $S_1$  occurs prior to emission of a photon. The difference between  $\lambda_{\text{max}}$  of the longest wavelength absorption band and the shortest wavelength emission band is known as the *Stokes shift*. The magnitude of the Stokes shift gives an indication of the extent of geometry difference between the ground and excited state of a molecule, and/or solvent reorganization[5]. Hence, a small Stokes shift implies a small change in geometry between the  $S_0$  and the relaxed  $S_1$  states.

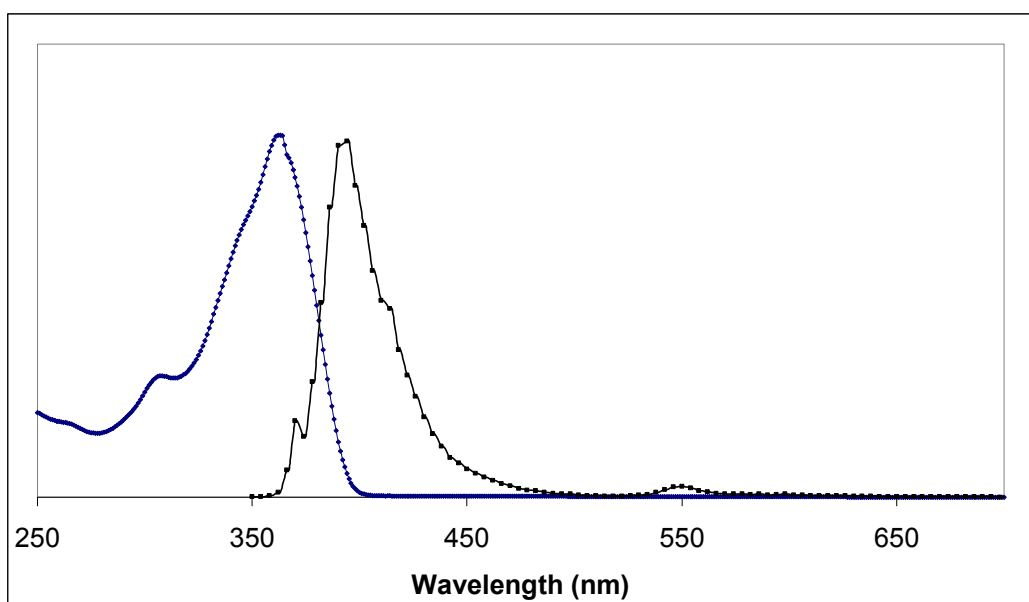
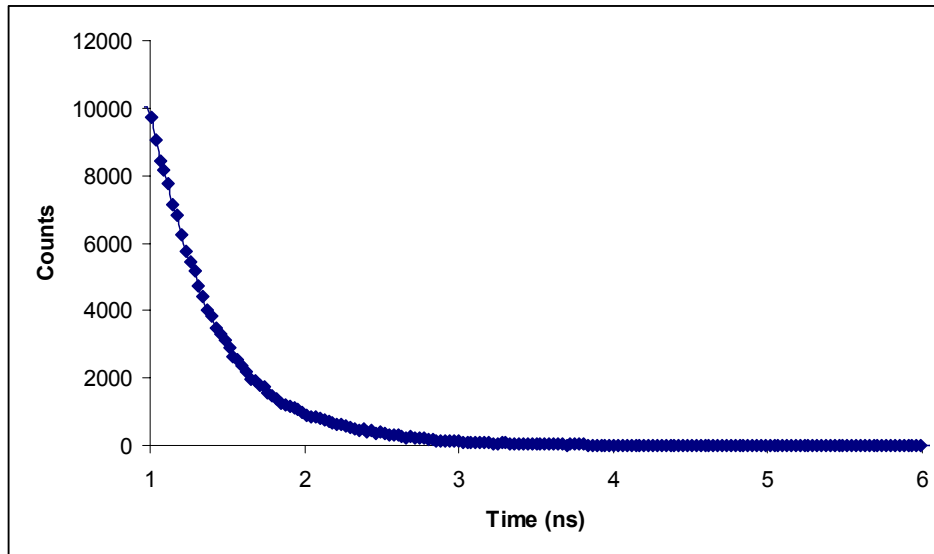


Fig 3.4 Absorption (left) and emission (right) spectra of **24**

### 3.4.2 Time-resolved fluorescence

Below (figure 3.5) is given an example of a time-resolved fluorescence decay. Such a decay of signal intensity gives information of the lifetime of the  $S_1$  state. A fast decay of the fluorescence may indicate an efficient ISC to the  $T_1$  state, which can be favorable for an optical limiting material. As seen from the spectrum below the fluorescence decay of compound **8** (paper II) is in the ns region.

For most organic structures the fluorescence decay range from 100  $\mu\text{s}$  to 10 ns. For compounds **23** and **24** though, the fluorescence decay is only a few ps (see paper IV).



**Fig. 3.5** Fluorescence decay of compound **8**, with excitation at 355 nm.

### 3.4.3 Fluorescence quantum yield.

A key concept in photophysics and photochemistry is the *quantum yield*, generally denoted  $\Phi$ . The quantum yield of a process is equal to the number of photons undergoing the process divided by the total number of photons absorbed. If all possible processes are considered then the sum of all quantum yields will be equal to 1,

$$\Phi_{\text{tot}} = \Phi_{\text{heat}} + \Phi_{\text{fluorescence}} + \Phi_{\text{ISC}} = 1$$

The fluorescence quantum yield,  $\Phi_{\text{fl}}$ , of a molecule may be obtained from the emission spectra by plotting a graph of the integrated fluorescence at a number of different concentrations *vs* the absorbance at the same concentrations. The result is a straight line with gradient  $m_X$  and intercept = 0.

The same procedure is done using a standard sample with known  $\Phi_{\text{fl}}$ , yielding a second line with gradient  $m_{ST}$ . The fluorescence quantum yield of X is then calculated from,  $\Phi_{\text{fl}(X)} = \Phi_{\text{fl}(ST)} (m_X / m_{ST})$ .

A more thorough description is given in [6].

A small  $\Phi_{\text{fl}}$  fluorescence quantum yield together with fast fluorescence decay implies an efficient ISC to the triplet state and/or an efficient thermal deactivation. A large  $\Phi_{\text{fl}}$  on the other hand suggest small contribution from other processes.

### 3.5 Phosphorescence

Measurements of the phosphorescence follow much of the reasoning for fluorescence. Phosphorescence originates from the conversion from the first excited triplet state to the ground singlet state with the associated emission of a photon. As for fluorescence the phosphorescence spectrum will be red shifted in comparison to the absorption spectrum. The effect may be even more apparent since the  $T_1$  level is lower in energy than the  $S_1$  level, as seen in figure 3.2. Time-resolved phosphorescence gives information on the lifetime and population of  $T_1$ . Results of this give indication of the efficiency of ISC and the possibility of ESA from the  $T_1$  state.

### 3.6 Two-photon induced emission

A two-photon induced emission (TPE) spectrum may be obtained by excitation of the sample at twice the wavelength of the one-photon absorption. A TPE spectrum similar to the OPE spectrum indicates that the same  $S_x$  level is populated. By integration of the TPE spectrum it is possible to calculate the two-photon absorption cross section  $\sigma_{\text{TPA}}$ , by the use of eqn 3.1 where  $c$  is the concentration of the sample. This operation relates the integrated TPE and  $\Phi_{\text{fl}}$  of the sample to a reference sample with known  $\sigma_{\text{TPA}}$  and  $\Phi_{\text{fl}}$ .

$$\sigma_{\text{TPA}} = (\text{TPE}_{\text{int}} / (\Phi_{\text{fl}} c)) * ((\Phi_{\text{fl-ref}} \sigma_{\text{TPA-ref}} c_{\text{ref}}) / \text{TPE}_{\text{int-ref}}) \quad \text{eqn 3.1}$$

The absorption cross section  $\sigma$  is frequently given in the unit area/molecule and describes the effective area of the molecule that a photon needs to traverse in order to be absorbed. The larger  $\sigma$ , the easier it is to excite the molecule.  $\sigma_{\text{TPA}}$  is in turn proportional to the TPA coefficient  $\beta$  and can thus be used to calculate  $\beta$ .

### 3.7 Optical power limiting measurements

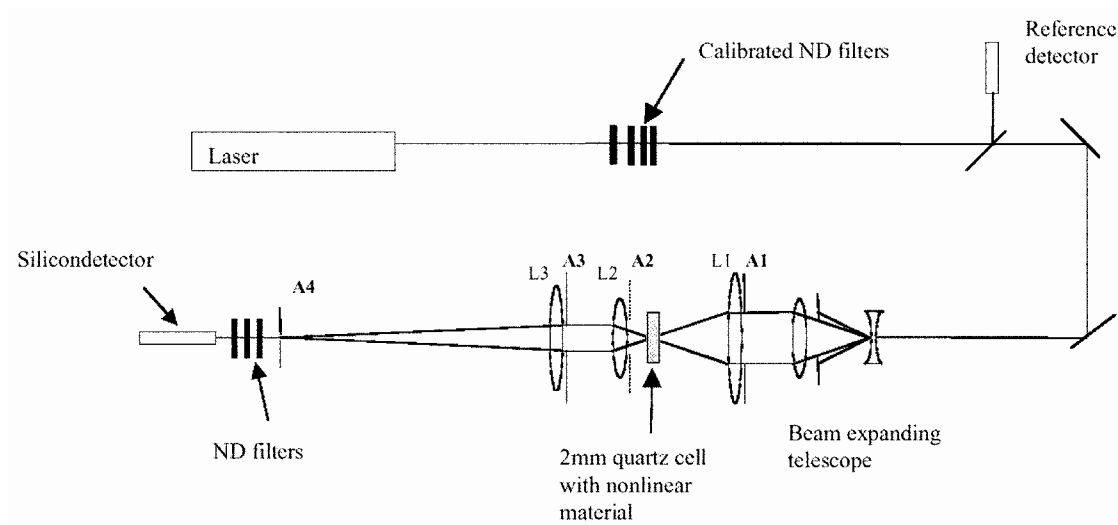
All optical-limiting testing in this work were performed by co-workers at FOI in Linköping. These experiments are briefly described below. The laser measurements were performed using a standardized test-bed at 532 nm.

### 3.7.1 Sample preparation and transmission spectra

The optical limiting material was dissolved in a common organic solvent such as THF or dichloromethane. A 2 mm quartz cell was typically used. Transmission spectra were recorded, as well as the photopic transmission which is calculated from the normal transmission spectra. The photopic transmission is defined as the product of the spectral luminous efficiency of the eye and the percent transmission of a material. In other words, the photopic transmission is the transmission recalculated with consideration of the sensitivity of the eye at different wavelengths. One of our requirements on the OPL compounds has been a photopic transmission of 70% or above at 532 nm.

### 3.7.2 The optical limiting test-bed

The arrangement for the optical-limiting measurements is shown in figure 3.6.



**Fig. 3.6** Test-bed for optical limiting measurements

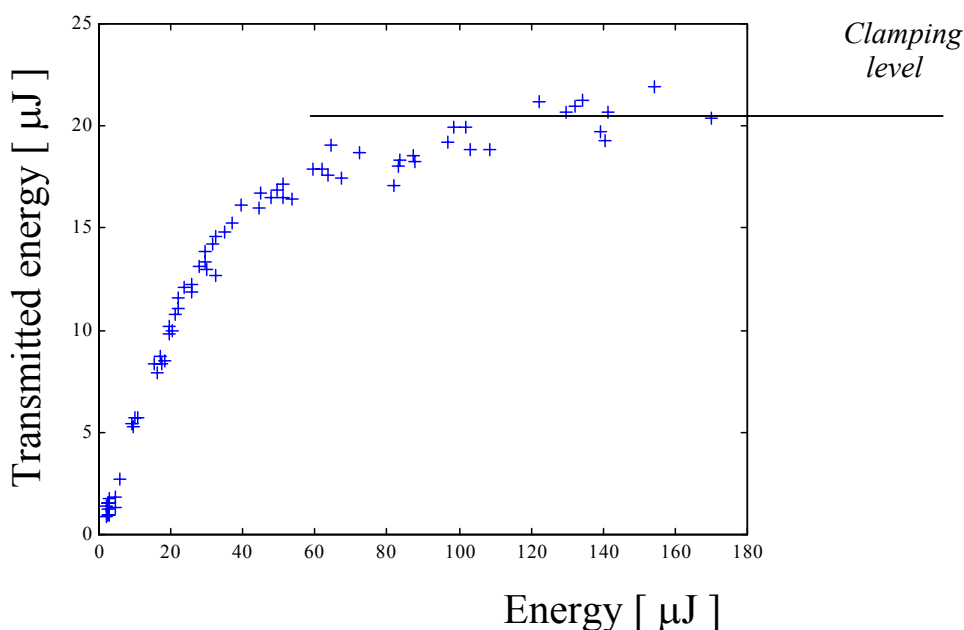
The output energy of the laser source was varied by changing the number of filters in the beam. A uniform illumination of the objective was achieved by the use of a beam-expanding telescope in front of the test-bed, thus resembling a laser beam from a distant source. The cell containing the NLO material was positioned to obtain the focus from objective lens L1 centered on the cell.

The outgoing beam was collected and focused by lenses L2 and L3, and finally detected by the silicon detector. Apertures A1-A4 was used to produce a uniform beam profile.

The laser used was a frequency doubled Nd:YAG laser delivering 5 ns pulses at 532 nm with a repetition rate of 10 Hz and several tens of kW pulsed output power. Nd:YAG (neodymium-doped yttrium aluminium garnet;  $\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$ ) is a crystal that is used as a lasing medium for solid-state lasers.

Nd:YAG lasers typically emit light with a wavelength of 1064 nm; thus 532 nm is the second harmonic (doubled frequency) of 1064 nm.

The detected energy was then plotted against the output energy to give an optical limiting spectrum, figure 3.7. The clamping level (CL) is the energy level at which the transmitted energy is clamped.



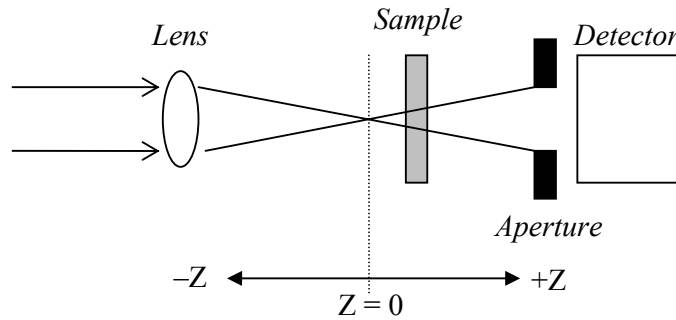
**Fig 3.7** Example of an OL spectrum where transmitted energy is plotted against incident energy.

### 3.8 Z-Scan

Another widely used method for determination of the OL ability of a material is the frequently used Z-scan technique, which was first developed by Sheik-Bahae and co-workers in 1989[7]. This is a sensitive technique for

determination of the non-linear absorption coefficient  $\beta$ , as well as for the sign and magnitude of the nonlinear refractive index  $n_2$ .

The general principle of the Z-scan technique is to move a sample of the OL-material along and through the focus of the laser beam (figure 3.8) with concurrent detection of the transmitted radiation.



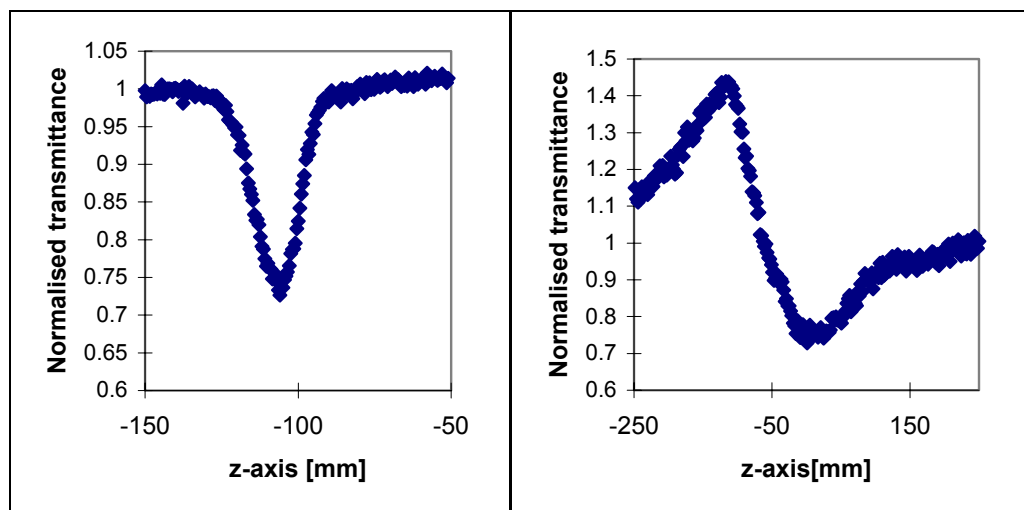
**Fig. 3.8** Schematic illustration of the apparatus set up of the Z-scan experiment

An aperture is placed in front of the detector and by varying the size of the aperture it is possible to distinguish between nonlinear absorption and refractive effects. By using an open detector aperture the detected transmittance will only be sensitive to nonlinear absorption since the whole beam enters the detector at all times. A small aperture, on the other hand, will also be sensitive to changes in the refractive index of the medium.

In figure 3.9 is shown an example of a transmittance spectrum generated from a Z-scan experiment. As expected for materials that possess NLO properties the transmittance decreases as the intensity increases and the lowest transmittance is recorded at  $z = 0$  where the laser beam is focused within the sample.

From this curve, the magnitude of the nonlinear absorption coefficient  $\beta$  and the nonlinear refractive index  $n_2$  can be extracted. These mathematical expressions are however beyond the scope of this thesis.





**Fig 3.9** Z-scan measurements of **15**. The experiment to the left shows a significant nonlinear absorption, while the experiment to the right shows a nonlinear refraction with a negative refraction index ( $n_2$ ).

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## 4. QUANTUM CHEMISTRY CALCULATIONS

### 4.1 General considerations

The use of computers in modern chemistry is today widespread due to rapid improvements in both software and hardware. Chemists worldwide perform calculations as a matter of routine in order to obtain information about parameters of molecular geometry and electronic properties.

The foundation of quantum chemistry is the solution of the Schrödinger equation,  $\hat{H}\Psi = E\Psi$ , that provides a wave function  $\Psi$ , which theoretically contains all information about the current molecule. In the Schrödinger equation  $\hat{H}$  is the *Hamiltonian*, an operator which represents the total energy of the system, and  $E$  is the energy of the stationary system. A complete solution of the Schrödinger equation is today only possible for a two-body problem, i.e. hydrogen. In order to solve the equation for larger molecules the calculations rely on a number of estimations. The two most important simplifications are the Born-Oppenheimer approximation and the LCAO approximation. The Born-Oppenheimer approximation states that nuclei may be viewed upon as fixed in space, or static, compared to electrons due to the large difference in mass. The LCAO (linear combination of atomic orbitals) approximation reduces the many-body problem (molecule) to a single-body problem (atom). Linear combination of the atomic orbitals thus forms molecular orbitals.

Quantum chemistry molecular orbital (MO) methods can be divided into three different categories: semiempirical, ab initio and density functional theory (DFT) methods. For textbooks discussing these methods see references [1-4]. The semiempirical approaches generally treat interactions involving only valence s and p electrons, and use empirical parameters for describing various effects from inner electrons. Further, the atomic orbitals (AOs) are described by rather simple functions, i.e. ‘small basis sets’. The semiempirical techniques have abbreviations such as ETH, CNDO, MNDO, PPP, INDO, MINDO, AM1 (Austin Model 1), and PM3 (Parameterization Model 3) [2,4]. Other semiempirical methods, such as INDO/S (also denoted ZINDO) [5-7] and CNDO/S [8,9] are aimed at calculations of electronic excitations. The different methods produce somewhat different results with respect to the molecular properties of interest, which may be geometry data, energies (of MOs, bond dissociation and transition states etc), electron densities, excitation energies and oscillation strengths.

The ab initio methods explicitly take all electrons into account, and can be performed on many different levels of complexity [1,4]. Except for the choice of basis set, the type of Hamiltonian, i.e. energy operators, is important for the accuracy of the results from the calculations. The Hartree-Fock (HF) Hamiltonian is the most common, in which the energy of each electron is evaluated in the average field of the other electrons. A disadvantage with this is

that electron correlation is not specifically treated. To some degree, electron correlation is accounted for in configuration interaction (CI) approaches. For hyperpolarizability calculations, electron correlation should be included to produce good results [10,11]. The more elaborate Møller Plesset (MP2, MP3, MP4) methods are aimed at dynamic electron correlation [12-14].

Unfortunately, calculations of hyperpolarizabilities, two-photon absorption and excited-state absorption based on such methods can be very time consuming, if at all incorporated in the standard quantum chemistry program packages.

In the DFT methods, molecular energy and geometry is calculated from functions describing the overall molecular electron density [3,4]. DFT methods are computationally somewhat less demanding than HF calculations when the same type of basis set is applied, except for calculations on small molecules using relatively small basis sets, where the HF method is faster. Because of improvements in DFT theory during the last decades, the DFT calculations now typically reproduce molecular geometries with accuracy comparable to those from the most sophisticated HF+MP methods, and therefore receive increased popularity. Nevertheless, hyperpolarizabilities and excited state properties do not yet belong to standard DFT calculations.

With today's workstation or desktop computers, DFT and ab initio methods become time-consuming for calculations on normal molecular structures having more than 20-30 carbon atoms. The calculations may also be troublesome for molecules with fewer atoms if some atoms are from the third row or below. For most transition metals, basis sets for inner electrons have not been evaluated, and computations with such elements have to be performed using effective core potentials (ECPs) instead of individual basis sets for inner electrons.

In contrast, semiempirical calculations are much faster than ab initio and DFT approaches.

A geometry optimization of a 20-30 carbon-atom molecule may take less than a minute on a desktop PC, and molecules with several hundreds or more of third-row atoms are routinely handled with these techniques. At this date, parameters for interesting heavy atoms such as Ru, Pd and Pt are becoming available in commercial software using for instance the AM1-d Hamiltonian [15,16].

Nevertheless, because the parameterization normally is derived from a limited number of known, stable (well-behaving) molecules, one should be very careful to draw conclusions from calculations on new compounds. Before a computation study is undertaken, some knowledge about what molecular systems that were used in the parameterization is required, and suitable test calculations should be performed.

#### 4.2 Configuration interaction for calculation of electronic excitation energy

UV-VIS spectroscopic transitions can be calculated by the CI method, where additional electronic configurations, often called micro-states, to that of the normal ground-state configuration are formed by promoting one electron (and sometimes also two electrons) from filled orbitals to virtual orbitals of the ground-state configuration. Excited states are derived as solutions of linear combinations of several or many of the new configurations.

#### 4.3 Calculation of third order hyperpolarizability

A rationale for a relationship between OPL and  $\chi^{(3)}$  (and  $\gamma$ ) is that the imaginary and real parts of  $\chi^{(3)}$  describe two-photon absorption and nonlinear reflection, respectively. Both these effects can contribute to OPL.

At least two different approaches for calculation of  $\gamma$  are incorporated in the available semiempirical MO calculation program packages; the ‘sum-over-states’ (SOS) [17] and ‘Time-dependent Hartree-Fock’ (TDHF) methods [18]. Both methods relate hyperpolarizability to the electric-field induced mixing of the ground state and various excited states. One important parameter in the expression of hyperpolarizability is the inverse dependence of the energy difference between the ground state and the excited states.

#### 4.4 Chemometrics methods; PC/PLS study.

Although nature sometimes tends to be somewhat obstinate, the possibilities to tailor organic molecules with modern synthetic methods are virtually limited only by our own imagination. The great number of synthetic methods has made it feasible to modify a molecular structure in order to improve a desired property. Nevertheless, synthetic work is often time consuming and computational methods to predict molecular responses have been developed in order to save resources[19-21].

Multivariate data analysis has proven to be useful for extracting relevant information from large data collections. By principal components (PC) analysis, a limited number of new variables (often only 2-3) are obtained from a matrix consisting of many variables that describe a number of objects (compounds)[22]. When the principal components are plotted against each other, one can often see the dominant patterns in the data, such as groups and outliers. The partial least squares (PLS) analysis provides a method to find

relations between variables[23]. This can be used to predict one important variable from the (hidden) information in a large number of other variables. These variables, obtained in our case (paper I) from quantum chemical calculations, are used to comprise an X-matrix which is then related to a response matrix (Y).

Subsequently, the dataset is analyzed to build a model to be used for prediction of the response of a new compound.

To confirm the certainty of the model, cross-validation can be used [22].

Cross-validation is a statistical method where objects of the dataset are left out in order to be predicted by the model. This procedure is repeated until every object has been left out once and the results thus obtained are compared to the observed results. This operation leads to a  $Q^2$ -value that states the usefulness of the model.

The model thus obtained constitutes a useful tool for computational prediction of a physical response.

In paper I we implemented a QSPR study on the OL of organic compounds using a PLS approach. The variables were, as stated above, provided by MO ab initio calculations and the response matrix was derived from the read output energy at an input energy of 150  $\mu$ J. Six variables that play an important role for the optical limiting in organic molecules were identified.

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## 5. DESIGN, SYNTHESIS AND STRUCTURAL DETERMINATION OF OPTICAL LIMITING MATERIALS

### 5.1 Choice of compounds

As mentioned earlier a large number of different organic substrates have been investigated for optical limiting applications [1-6]. In the design of a compound for OL many different physical requirements have to be met, such as transparency in combination with a large delocalised  $\pi$ -system, thermal stability and high solubility. The compound should also be fairly easy to synthesise and non-toxic in order to be of practical use.

The work presented in this thesis focuses on two different types of compounds where the first is 2,5-dialkynyl-thiophenes, and the second type is alkynyl-platinum (II) complexes.

A motivation for the selection of these compounds as well as a synthetic overview is presented below.

### 5.2 2,5-Dialkynyl thiophenes

In the first study we wanted a compound that could easily be derived from only a few smaller subunits where each subunit would exhibit significant TPA/RSA in relation to its number of atoms and  $\pi$ -electrons. We decided to look for a symmetrical system where two subunits, A, were connected through another subunit B. The use of a symmetrical system was assumed to facilitate a theoretical description of various excited states.

The compounds should be rigid to avoid having the OL response being averaged by molecular conformations of unknown distribution, which would complicate the interpretation of the results.

The compounds should also be easy to prepare and should display chemical and thermal stability.

Both subunits should be transparent in the visible region and the electronic interaction between the subunits should not cause the molecule to absorb significantly more at longer wavelength.

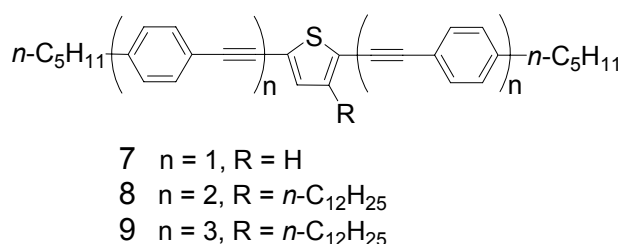
Thiophene was chosen as the “bridging unit” B. In comparison to benzene, thiophene is a slightly better  $\pi$ -electron donor [7] and is also more easily polarized. It can take part in electron delocalisation without displaying much enhanced absorption in the visible region. Experiments [8] as well as theoretical studies [9,10] have shown that thiophene displays instantaneous third-order polarizability, a purely electronic process which is likely to originate from the localized electrons on the sulphur.

It has also been shown that thiophenes with unsaturated substituents in 2,5-positions exhibit large TPA at 602 nm [11-13].

Other studies of thiophene and oligophenes show that these structures have fast triplet state formation originating from a TPA populated singlet excited state [14,15].

As subunits A, the groups to be connected through the thiophene, we chose phenyl-ethynyl groups. One obvious reason was synthetic convenience, but also their thermal stability and transparency in the visible region were reasons for this choice.

We also extended the number of phenyl-ethylene units from compound 7 to 8 and 9 in order to investigate the effect of a longer conjugated  $\pi$ -system, figure 5.1.



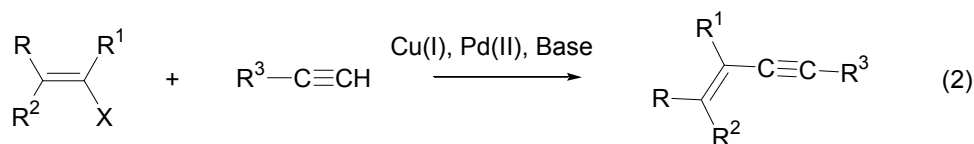
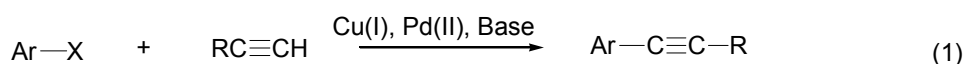
**Fig. 5.1** Thiophene derivatives studied in paper II

An ethynyl linkage instead of an ethenyl should have the advantage of a blue-shifted absorption and a more transparent molecule. This can be accounted for by orbital energy mismatch between the  $sp$  hybridised alkynyl and the  $sp^2$  hybridised phenyl carbons. Such a slightly poorer conjugation has been found to lead to somewhat lower  $\gamma$  values in diphenyl-substituted acetylenes in comparison with stilbenes [16], but is for our needs justified by better transparency using alkynyl groups.

In addition, the  $C_\infty$  symmetry of the alkynyl group results in fewer conformations for the chosen molecules which was assumed to simplify MO calculations and interpretation of results.

### 5.3 The Sonogashira coupling reaction

The syntheses of the different alkynes as well as the three alkynyl thiophenes were performed using a palladium-copper mediated coupling reaction. This type of reaction, where an ethynyl or ethylene unit is coupled to an aromatic or heteroaromatic halide is known as the Sonogashira coupling [17]. In 1975 Sonogashira presented the coupling of terminal alkynes with aromatic and vinyl halides [17], figure 5.2. Both Heck [18], and Cassar [19], had earlier presented similar couplings, but these reactions did not involve copper and required much harder conditions. The form of copper used for the Sonogashira coupling is the cuprous ion (+1), which is less stable than the cupric ion (+2). The cuprous ion is easily oxidized.

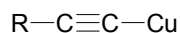


**Fig. 5.2** The Sonogashira coupling of terminal alkynes with aromatic (1) and vinyl (2) halides

The reaction is of wide scope as it is possible to couple a large number of different substrates with different functionalities [20], under very mild conditions. The introduced triple bond can itself be transformed into other functionalities or simply removed by hydrogenation.

#### 5.3.1 Mechanism of the Sonogashira coupling

The detailed mechanism of the Sonogashira coupling still remains somewhat unclear. Especially the role of the copper co-catalyst is not yet totally clarified, although the most common proposal is that it forms an organo-copper substrate with the alkyne, figure 5.3:

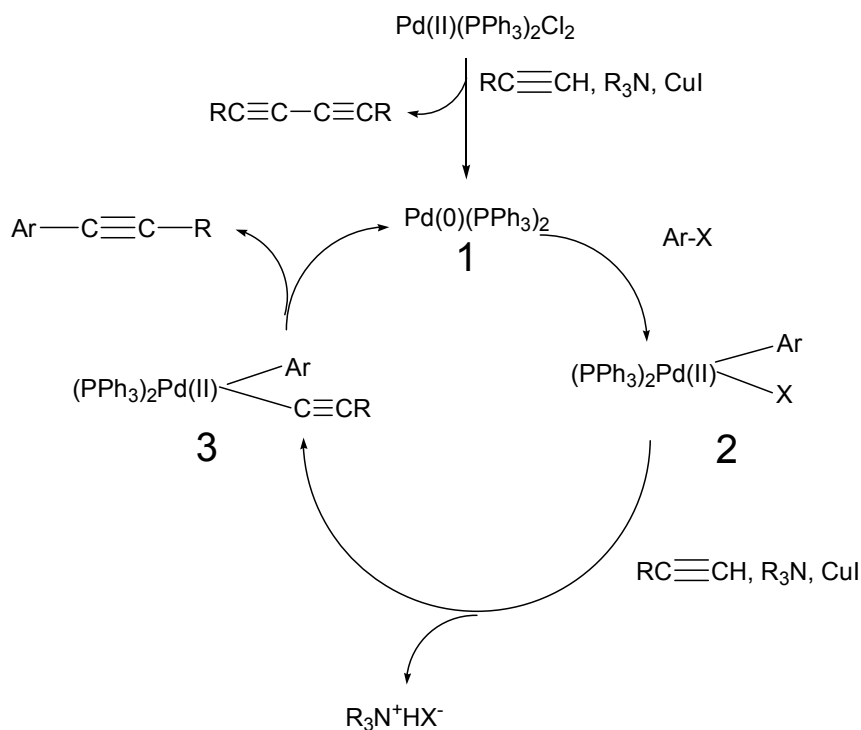


**Fig. 5.3** Proposed structure of organo-copper substrate

The mechanism proposed by Sonogashira [17], figure 5.4, starts with an in situ reduction of the Pd(II) to the catalytic species Pd(0), **1**. This takes place on the expense of the double amount of alkyne, which through an oxidative coupling forms a di-yne substrate, probably involving the copper.

Subsequent oxidative addition of the arylhalide to **2**, followed by reaction with the alkyne, possibly via a copper-acetylid intermediate leads to derivative **3**. Reductive elimination of Pd yields the desired acetylide and regenerates the Pd(0) catalyst **1**.

The amine may have dual utility, acting to aid the formation of the organo-copper substrate, and to neutralize the hydrogen halide formed.



**Fig. 5.4** Reaction cycle of the Sonogashira coupling as proposed by Sonogashira and Hagihara.

The rate-determining step of the reaction is the oxidative addition of the arylhalide to the Pd(0) catalyst. Substrates carrying electron withdrawing substituents *ortho* or *para* to the halide will therefore generally react faster as an electron deficient halide-bearing carbon will undergo addition more readily [21].

### 5.3.2 *Scope of the reaction*

The Sonogashira coupling of terminal alkenes or alkynes to an aryl or vinyl halide represent an important method for C-C bond formation.

The most common form of the Sonogashira coupling is when an aromatic halide is coupled to a terminal alkyne utilizing catalytic palladium, a metal co-catalyst, normally CuI, and a base.

The Pd-catalyst most frequently used for the reaction is the same that Sonogashira and Hagihara used in their original publication [17]; Pd(II)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The efficiency of this catalyst has made the search for alternative Pd-species redundant [20]. The active catalyst in the reaction is as proposed the Pd(0)-species, but such catalysts, for example Pd(0)(PPh<sub>3</sub>)<sub>4</sub>, rapidly deteriorates unless very carefully stored, whereas the Pd(II) catalysts generally exhibit good long term stability.

The amount of copper and palladium catalysts used in the Sonogashira coupling is generally in the range of 1-5 mol% for both. However, Sing and Just found in their study that the most effective Cu(I) to Pd-ratio was 3:2 [22]. They also showed that an increase of Cu(I)-catalyst from 3 mol% to 6 mol% resulted in a doubled reaction rate.

In the early reports triethylamine or diethylamine was used both as solvent and amine, but in 1998 Thorand and Krause published an investigation that showed that these experiments often were difficult to reproduce and pointed to several difficulties surrounding the Sonogashira coupling [23]. Among the problems, they pointed at the harsh conditions that needed to be used in the coupling of aromatic bromides to alkynes, the need of purification, and the oxidative homocoupling (Glaser coupling) of the alkynes in the presence of oxygen. They found that most of these problems were solved by the use of THF as solvent together with an amine as base. We also obtained somewhat better yields with the procedure using THF, including a simplified reaction work-up.

Several different solvents have been reported to work in the reaction, for example DMF, MeCN, pyridine, toluene; all together with an amine as base [20,24].

The most widely used metal co-catalyst is, as mentioned earlier, copper (I) iodide which tentatively forms an organo-copper substrate with the alkyne. However, the use of copper salt request, as noted, anaerobic conditions in order to prevent oxidative homocoupling of alkynes.

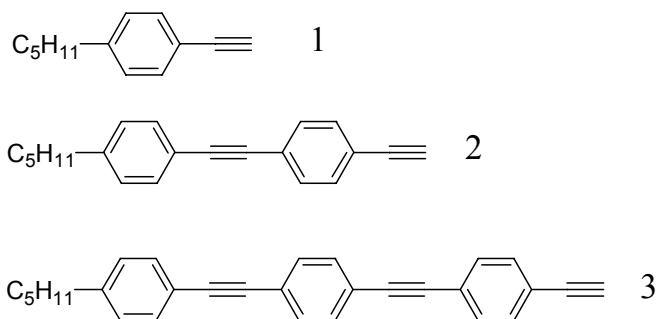
Since absolute anaerobic conditions may be hard to achieve several methods for copper-free Sonogashira couplings have been developed over the last couple of years[25-27]. For example, Liang et.al have coupled terminal alkynes to substituted aryl iodides with PdCl<sub>2</sub> as catalyst in water under aerobic conditions[28]. The palladium-free Sonogashira coupling have also been demonstrated[29].

Development of microwave assisted synthesis in recent years have proven to be of great use for synthetic chemists and the technique has also been established for

the Sonogashira coupling reaction[30-33]. The use of microwaves in organic synthesis tends to give higher yields at shorter reaction times when compared to classical methods although the technique may not always be successful.

#### 5.4 Synthetic pathway

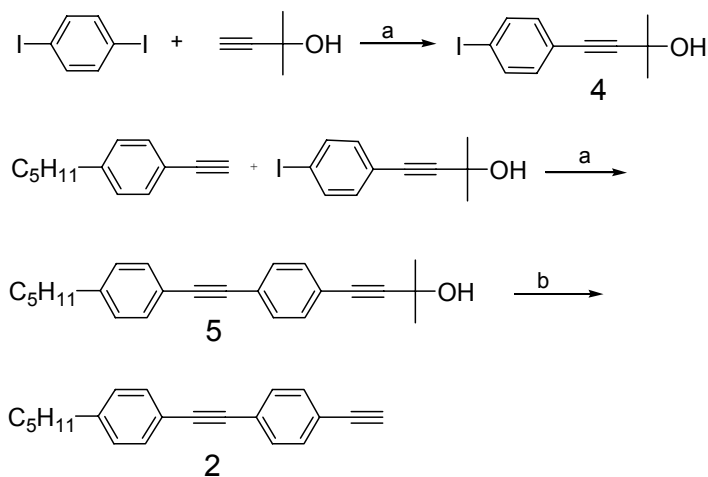
The three different alkynes used were the commercially available 4-pentyl-1-ethynylbenzene (1), 1-ethynyl-4-(4-pentylphenylethynyl)benzene (2), and 1-ethynyl-4-(4-(4-pentylphenylethynyl)phenylethynyl)benzene (3), outlined in figure 5.5.



**Fig. 5.5** Alkynes used for coupling reactions with 2,5-dibromo thiophenes (paper II)

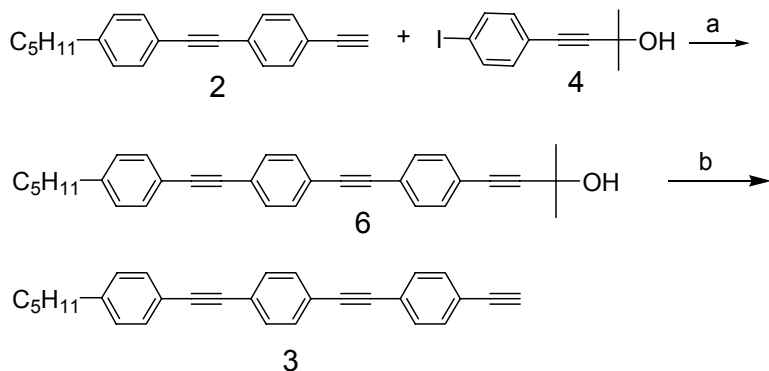
The optical limiting of compounds **7-9** in solution at 532 nm is presented in paper II together with a discussion on the relationship between OL and parameters obtained from molecular-orbital based calculations. For instance, these calculations show a greater increase of second-order hyperpolarizability ( $\gamma$ ) effects from compound **5** to **6** than from **6** to **7**. The synthetic details on the preparation of these compounds are outlined in paper II, together with spectroscopic data, but a short overview is outlined in figures 5.6 – 5.10.

## 5.4.1 Synthesis of alkynes



**Fig. 5.6** Synthesis of alkyne 2. a) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, PPh<sub>3</sub>, pyridine, triethylamine  
b) NaH, C<sub>6</sub>H<sub>6</sub>

The crude alkyne was obtained as yellow crystals after recrystallisation from hexane, but after filtering through a short aluminum oxide column using hexane, white fluffy leaflets were obtained.



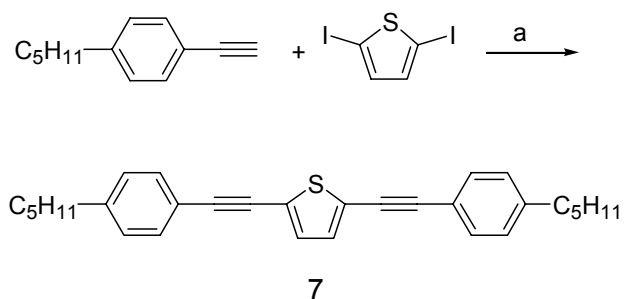
**Fig. 5.7** Synthesis of alkyne 3: a) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, PPh<sub>3</sub>, pyridine, triethylamine.  
b) NaH, C<sub>6</sub>H<sub>6</sub>

Several filtrations through a short aluminum oxide column using 5 % chloroform in petroleum ether afforded the alkyne as white leaflets, similar to alkyne 2.

This alkyne is less soluble in common solvents than alkyne 1 and 2. The alkynes were stored at room temperature for several months without any noticeable degradation.

#### 5.4.2 Syntheses of 2,5-dialkynyl thiophenes

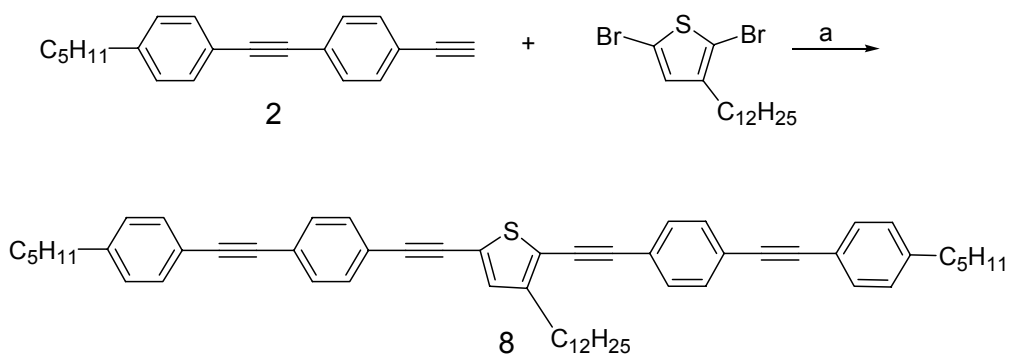
Synthesis of 2,5-di(4-pentylphenylethynyl)thiophene (7):



**Fig. 5.8** Synthesis of 2,5-di(4-pentylphenylethynyl)thiophene.  
a) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, PPh<sub>3</sub>, pyridine, triethylamine

The product was obtained as pinkish crystals and is readily soluble in most organic solvents.

Synthesis of 3-dodecyl-2,5-di-(4-(4-pentylphenylethynyl)-phenylethynyl)-thiophene (8):

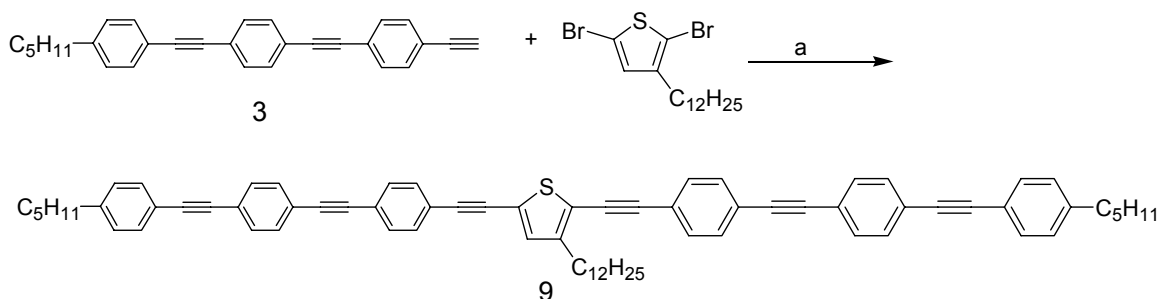


**Fig. 5.9** Synthesis of 3-dodecyl-2,5-di-(4-(4-pentylphenylethynyl)-phenylethynyl)-Thiophen a) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, PPh<sub>3</sub>, pyridine, triethylamine



The product was obtained after filtration through silica followed by recrystallisation from hexane as yellow crystals. The product was fairly soluble in common organic solvents.

Synthesis of 3-dodecyl-2,5-di-(4-(4-(4-pentylphenylethynyl)-phenylethynyl)-phenylethynyl)-thiophene (9):



**Fig. 5.10** Synthesis of 3-dodecyl-2,5-di-(4-(4-(4-pentylphenylethynyl)phenylethynyl)-phenylethynyl)-thiophene.

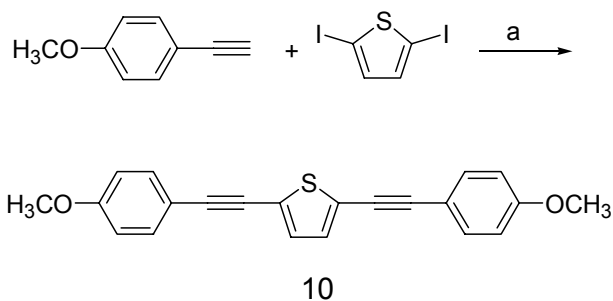
a) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, PPh<sub>3</sub>, toluene, triethylamine

The product was obtained as yellow crystals after several recrystallisations from dichloromethane/hexane.

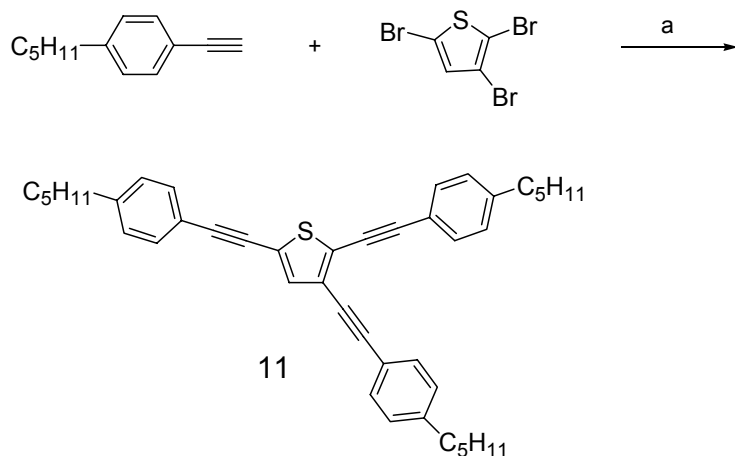
The product proved to have surprisingly low solubility in common organic solvents.

Yields of di-substituted thiophenes were lowered as the number of phenyl units on the alkyne increased. Furthermore, difficulties in the purification step increased with the size of the compound. This is likely due to the decrease in solubility of both products and by-products.

In figure 5.11–5.15 is outlined the synthesis of a few compounds closely related to those described above. These compounds, including furan and selenophene equivalents to **7**, were studied for OL and photophysical properties in paper III which also includes synthetic details.



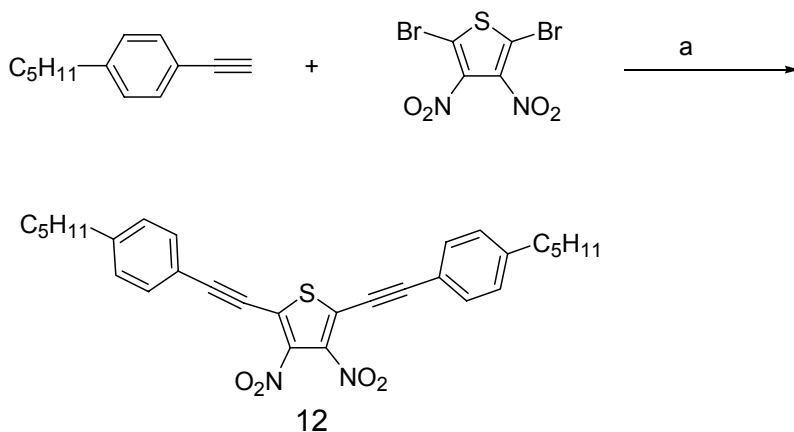
**Fig.5.11** Synthesis of 2,5- di(4-methoxyphenylethynyl)thiophene.  
a) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, PPh<sub>3</sub>, pyridine, triethylamine



**Fig. 5.12** Synthesis of 2,3,5-tri(1-(4-pentylphenyl)ethynyl)thiophene  
a) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, pyridine, triethylamine

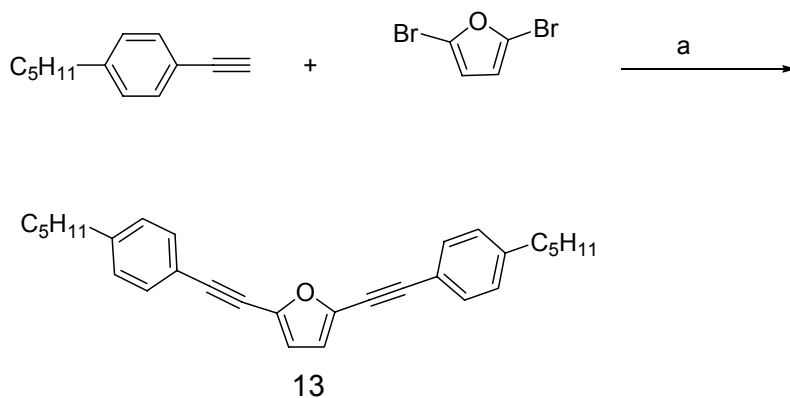
The tri-substituted thiophene was obtained after chromatography on a silica column as an orange oil, and was soluble in common solvents, such as chloroform and THF.

The introduction of the third alkyne at position 3 on the thiophene made it necessary to use very harsh conditions.



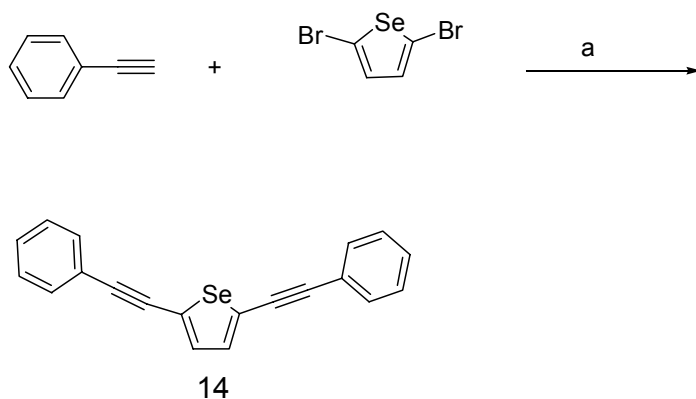
**Fig. 5.13** Synthesis of 2,5- di(4-pentylphenylethynyl)-3,4-dinitrothiophen  
 a) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, , THF, triethylamine

This compound was obtained as orange crystals and was soluble in solvents like, THF, chloroform and dichloromethane.



**Fig. 5.14** Synthesis of 2,5- di(4-pentylphenylethynyl)furan  
 a) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, THF, triethylamine

The disubstituted furan was obtained as white crystals and was very soluble in solvents like THF, chloroform and dichloromethane.



**Fig. 5.15** Synthesis of 2,5- di(phenylethynyl)selenophene  
a)  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ,  $\text{CuI}$ , THF, triethylamine

The disubstituted selenophene was obtained as greyish crystals and was very soluble in solvents like THF, chloroform and dichloromethane

Common for all coupling reactions performed using alkynes is a variable amount of alkyne-alkyne coupling.

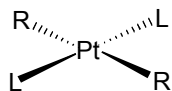
To decrease the amount of such homocouplings of alkynes great accuracy should be taken to remove oxygen from air, and from solvents, in the reaction flask. Further, use of freshly purified  $\text{Cu(I)I}$  is preferred to exclude any presence of  $\text{Cu(II)}$ , which is a catalyst for homocoupling of acetylenes.

### 5.5 Dialkynylplatinum(II) complexes

The second class of compound studied in this work (paper IV) is alkynylplatinum (II) complexes, where we have used two different alkynes. In these organometallic compounds the large transition metal contributes to the delocalized  $\pi$ -system [34,35].

These types of molecules are interesting because they possess triplet levels which are coupled to singlet transition through intersystem crossing [36], which may result in enhanced excited state absorption, a quality which is of course very useful for optical limiting, see Ch. 2.

In addition to the two carbanions, platinum(II) complexes include nucleophilic phosphine molecules in a square planar configuration [37], figure 5.16.



**Fig. 5.16** The square planar structure of a *trans* PtL<sub>2</sub>(alkynyl)<sub>2</sub> compound

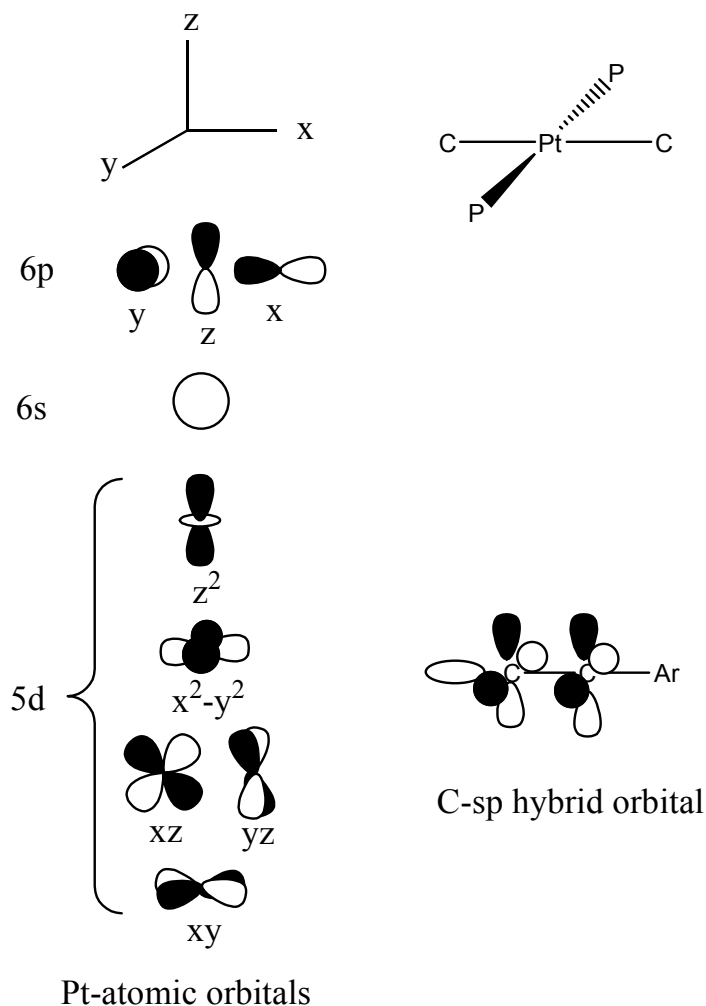
The reason for platinum to attach two ligands can be explained by the 18-electron rule, which states that the molecule is stable when the transition metal has the same electronic configuration as the noble gas in the same row [38].

For platinum(II)-complexes used in this work the electron counting would be: Pt<sup>2+</sup>, 10-2=8 electrons; 2 alkynyl<sup>-</sup>, 2×2=4 electrons and, 2 PBu<sub>3</sub>, 2×2=4 electrons. All in all, this means that platinum have 16 valence electrons with this configuration. The complex does not fulfill the 18-electron rule, but by attaching two ligands, thus reaching 16 valence electrons, the platinum complex is still fairly stable.

The nature of the ligand is also of importance for the molecular stability since different ligands bind with different strength. The stronger the attachment, the less is the molecule subjected to ligand displacement. The strength of attachment is in the following order: H<sub>2</sub>O, OH, NH<sub>3</sub>, pyridine, < Cl, Br, < SCN, I, NO<sub>2</sub>, Ph, < Me, SC(NH<sub>2</sub>)<sub>2</sub>, <H, PR<sub>3</sub>, < C<sub>2</sub>H<sub>4</sub>, CN, CO,[38].

As seen from this series, trialkyl-phosphines constitute a good choice of ligand for creating a stable compound. An explanation for the strong attachment of phosphines may be that it has the capability of π-back bonding and several studies have shown that Pt-P backbonding in phosphine-platinum complexes involves significant d-σ\* interaction[34,39].

The exact nature of the bonding between the alkynyl carbon and platinum in Pt(II) complexes may be difficult to identify. Nevertheless it is often described by a σ-type overlap of a C sp hybrid orbital and a Pt hybrid orbital mainly constructed from the 6s, 6p<sub>x</sub> and 5d<sub>x<sup>2</sup>-y<sup>2</sup></sub> atomic orbitals (see figure 5.17) [34].



**Fig. 5.17** Coordination and orbital mixing of Pt(II)L<sub>2</sub>(C≡C)<sub>2</sub> complexes

Additional bonding of  $\pi$ -type ( $\pi$ -backbonding) may result from overlap of  $d_{xy}$  and  $d_{xz}$  orbitals with alkyne  $\pi_y^*$  and  $\pi_z^*$  orbitals respectively. The fact that both alkynyl groups may interact mutually through the metal d-orbitals creates a long conjugate system[40].

However, recent studies of similar platinum acetylides have shown that the molecular structure changes upon conversion to the excited triplet state, in such manner that the acetylenic and adjacent carbons have cumulenenic character[41]. Further it has been demonstrated that the triplet state is confined to one ligand and not delocalized across the central platinum atom[42].

### 5.5.1 Choice of alkynyl platinum(II) complexes

For monomeric platinum (II)alkynyl complexes we selected two alkynes which differ somewhat from those previously used. We wished to include thiophene in the conjugated system for the same reason as previously described for the substituted thiophenes.

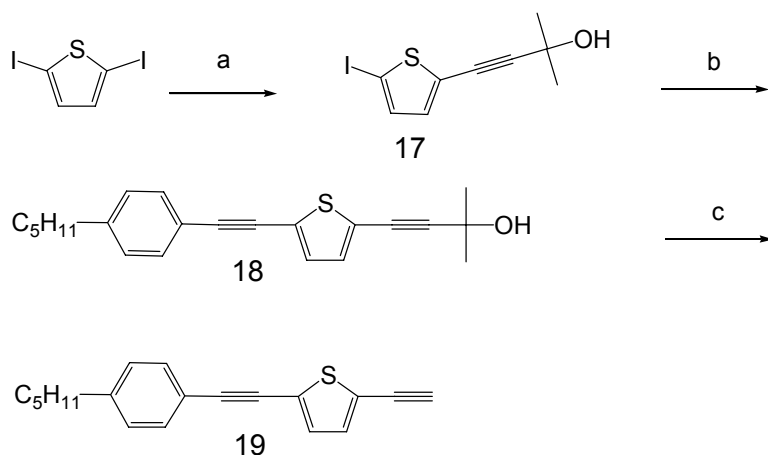
The first alkyne was 2-ethynyl-5-(4-pentyl-phenylethynyl)-thiophene **19**, a structure which allows the thiophene unit to be attached to platinum through the ethynyl linkage.

In the second alkyne used, 2-(4-ethynyl-phenylethynyl)-thiophene **22**, the terminal ethynyl group is instead connected to the phenyl unit.

The precursor to the Pt complexes was *trans*-dichloro-*bis*-tri-*n*-butylphosphine-platinum(II),  $\text{PtCl}_2(\text{PBu}_3)_2$  [43]. The reason to use the *trans* compound was to allow the two alkynes to be positioned in a linear fashion instead of having a perpendicular arrangement that is expected from reaction with *cis*- $\text{PtCl}_2(\text{PBu}_3)_2$ . A more pronounced delocalization of  $\pi$ -electrons, and a larger hyperpolarizability, should result from the *trans* arrangement. The coupling of the alkynides to platinum were performed according to [44], which is similar to the regular Sonogashira coupling.

### 5.5.2 Synthetic scheme

The general synthetic method to produce these molecules resembles those already described and will not be explained in detail but rather outlined in a schematic manner. Experimental details are given in Paper IV.

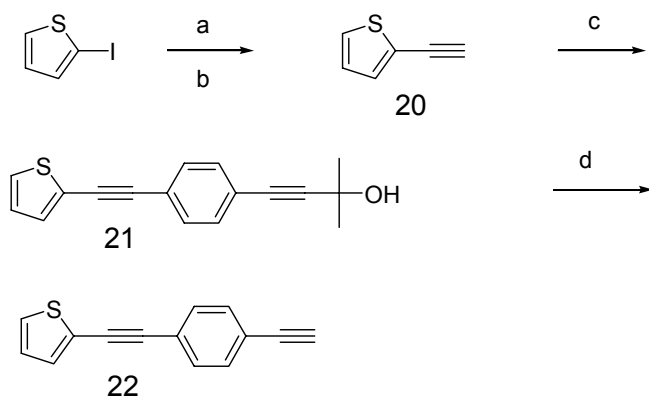


**Fig. 5.18** Synthesis of 2-ethynyl-5-(4-pentylphenylethynyl)thiophene.

- $\text{PdCl}_2(\text{PPh}_3)_2$ , CuI, THF, triethylamine.
- 4-Pentyl-1-ethynylbenzene,  $\text{PdCl}_2(\text{PPh}_3)_2$ , CuI, THF, triethylamine.
- NaH, toluene.

The alkyne was obtained as white crystals after chromatography on a silica column.

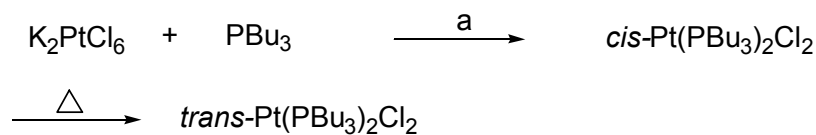
The other alkyne was synthesised as outlined below [45]:



**Fig. 5.19** Synthesis of 2-(4-ethynyl-phenylethynyl)-thiophene  
 a) 2-Methyl-3-butyn-2-ol,  $\text{PdCl}_2(\text{PPh}_3)_2$ , CuI, THF, triethylamine.  
 b) NaH, benzene.  
 c) **4**,  $\text{PdCl}_2(\text{PPh}_3)_2$ , CuI, THF, triethylamine.  
 d) NaH, benzene.

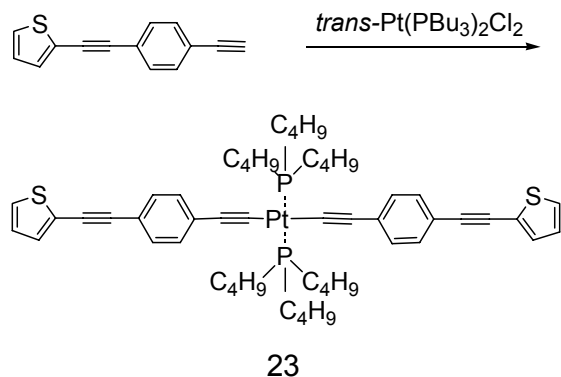
Also this alkyne was obtained as white crystals.

The alkynes were then reacted with *trans*-dichloro-bis-tributylphosphine-platinum(II) which was prepared from  $\text{K}_2\text{PtCl}_6$  as outlined in figure 5.20. The *trans*-isomer is obtained as yellow crystals by heating the white *cis*- isomer [46]. The coupling of the alkynes to *trans*-dichloro-bis-tributylphosphine-platinum(II), giving the square-planar bis(tertiary phosphine) dialkynyl complexes of Pt(II), were performed as described in figure 5.21, and 5.22.



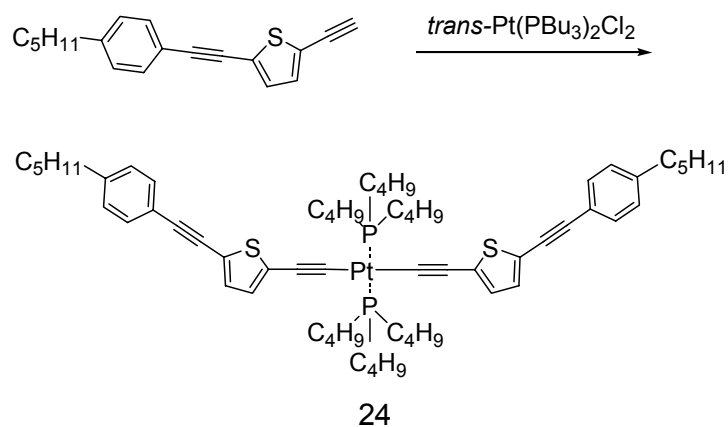
**Fig. 5.20** Synthesis of *trans*-dichloro-bis-tributylphosphine-platinum(II)  
 a)  $\text{Na}_2\text{SO}_3$ ,  $\text{H}_2\text{O}$





**Fig. 5.21** Synthesis of  $trans\text{-Pt}(\text{P}(n\text{-Bu})_3)_2(\text{C}_{14}\text{H}_8\text{S})_2$

The product was obtained as orange crystals after flash chromatography on silica gel.



**Fig. 5.22** Synthesis of  $trans\text{-Pt}(\text{P}(n\text{-Bu})_3)_2(\text{C}_{19}\text{H}_{17}\text{S})_2$

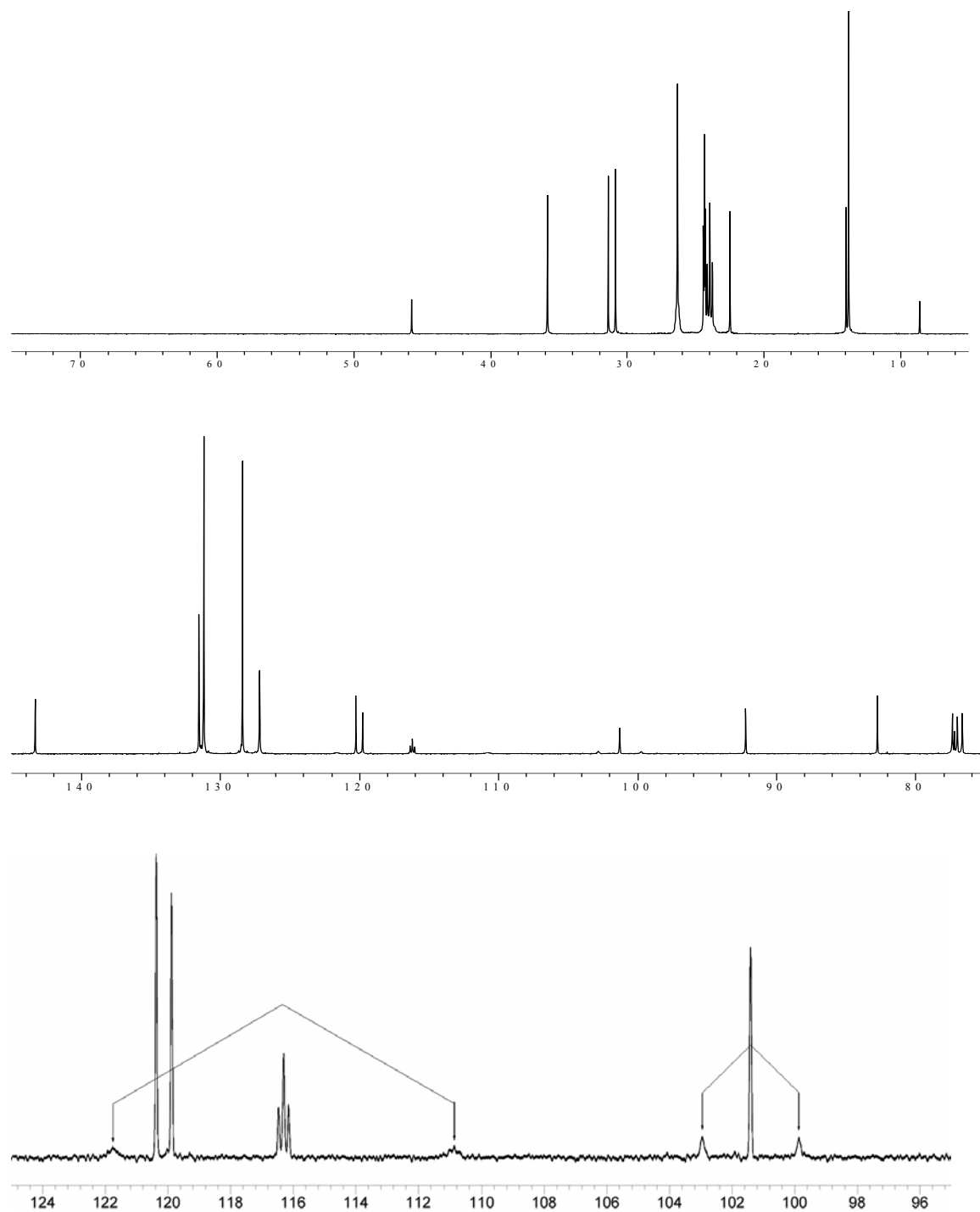
Compound **24** was also obtained as orange crystals following chromatography on a silica column.

### 5.6 Structure determination of Pt(II) complexes using NMR

As mentioned above, the synthesis of alkynyl Pt(II)-complexes may result in a mixture of two possible isomers, *cis* or *trans*. To determine what isomer/isomers that is present in the product mixture we have used NMR spectroscopy where  $^{13}\text{C}$  and  $^{31}\text{P}$ -NMR presents most information on the nature of isomers, due to the coupling between  $^{13}\text{C}$ - $^{31}\text{P}$  and  $^{195}\text{Pt}$ .

The  $^{13}\text{C}$  NMR spectrum of 24 is shown in figure 5.23.

The triplet structure at  $\delta = 116.3$  of the carbon bonded to Pt is consistent with a *trans* configuration, that is, a  $^{13}\text{C}$ - $^{31}\text{P}$  coupling ( $^2J_{\text{CP}} = 14.3$  Hz) to two magnetically equivalent  $^{31}\text{P}$  nuclei. Both carbons in the Pt-C $_1$ ≡C $_2$  link show coupling to  $^{195}\text{Pt}$ , with  $^1J = 985$  and  $^2J = 280$  Hz for C $_1$  and C $_2$ , respectively. ( $^{195}\text{Pt}$  has  $I = 1/2$  and a natural abundance of 33.8 %). The  $^{31}\text{P}$  NMR spectrum contains only one singlet at  $\delta = 4.1$  relative to external 85%  $\text{H}_3\text{PO}_4$ , and  $^{195}\text{Pt}$  satellites with  $^1J_{\text{PPt}} = 2319$  Hz. This value of  $^1J_{\text{PPt}}$  is comparable with for instance that of *trans*-PtCl $_2$ (PBU $_3$ ) $_2$  in CH $_2$ Cl $_2$  (2392 Hz) [47], or for CDCl $_3$  solution (2367 Hz) as measured by us. A larger value for *cis*-PtCl $_2$ (PBU $_3$ ) $_2$ ,  $^1J_{\text{PPt}} = 3500$  Hz [47] (or 3508 Hz in CDCl $_3$  [48]) can be rationalized by invoking the strength of the bond *trans* to the P-Pt bond. The P-Pt bonds will experience less competition in the *cis* isomer, where the rather weak Pt-Cl bonds are *trans* to the stronger P-Pt bonds[47,49-51]. This is an example of ‘*trans* influence’ which is common in complexes of heavier transition metal ions.

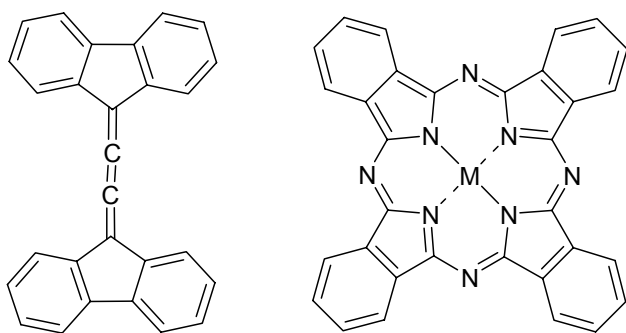


**Fig. 5.23**  $^{13}\text{C}$  NMR spectrum of **24**, with solvent signals at 77 ppm. Top: nine signals from butyl and pentyl groups and two from impurities (at 46 and 9 ppm); middle: twelve peaks from unsaturated carbons, of which the 131.4 and 131.5 ppm signals are not resolved in the figure; bottom:  $^{195}\text{Pt}$  satellite signals of the alkyne carbons at 116.3 and 101.3 ppm are indicated.

### 5.7 Other compounds

Within the frame of this project there has been a lot of synthetic work aiming for structures different from those described above, but for various reasons the synthetic goal was never reached. However I would like to take the opportunity to summarize a few years of synthetic struggle that didn't result in any useful substances for optical limiting but nevertheless gave me the chance to school my synthetic skills.

The synthetic work was predominantly focused on substituted di-fluorenylidene ethylenes (DFE) and phtalocyanines.



**Fig. 5.24** Left: di-fluorenylidene ethylene; right: a metallo-phtalocyanine

#### 5.7.1 Phtalocyanines

Phtalocyanines (Pc) form complexes with ions and ionic groups and have been relatively much studied for optical limiting purposes. Several compounds have been found that show very good limiting. Examples are Pc with substituents on the phenylene ring and InCl or VO complexed to the four nitrogens [52,53]. Some improvements with heavy substituents are noticed (iodo vs t-butyl or alkoxy). Indium tetra (t-butyl) Pc chloride in toluene has a linear transmittance of 0.7 and attenuate 8-ns laser pulses at 532 nm approximately by a factor of 7.6 compared to C-60 and a factor of 3 compared to aluminium Pc chloride (AlPcCl). A three-disk system made from In(*t*-Bu)<sub>4</sub>PcCl in polymethylmethacrylate (PMMA) is reported to attenuate 8-ns laser pulses at 532 nm up to a factor of 540 [53]. The good limiting is thought to be RSA enhanced by S<sub>1</sub> → T<sub>1</sub> intersystem crossing, increased by the paramagnetic In ion.

AlPcCl mentioned above is another well studied limiter and the excited manifolds for this compound have been investigated [54]. In parallel to many other Pc systems, two  $\pi$ - $\pi^*$  transitions are found in the visible region. Generally, for metallo-Pc, these appear in the region of 300-400 and 500-700(-800), but in contrast to metalloporphyrins, metallo-Pc have the longer wavelength absorption as the more intense. AlPcCl has a low absorption at 532 nm, which was the laser wavelength in the experiments. The Pc was compared with a dye, (HITCI discussed in Ch. 2.5), with the conclusion that AlPcCl was a better limiter due to shorter lifetime of the second excited state, i.e.  $S_2 \rightarrow S_1$  relaxation was faster than for HITCI.

Lead complexed Pc compounds also belong to the best known limiters[3]. Again, RSA is the dominant process. Pb tetra( $\beta$ -cumylphenoxy)Pc has a large dynamic range and is a limiter in almost the whole visible area, with the best effect around 520 nm. Pb octa( $\alpha$ -butoxy)Pc is another compound, with the best limiting around 570-580 nm, not far from the optimum response for human eye. This shows that changes in the peripheral substitution can significantly alter this important property. In a comparison of Pc with different ions: Al, Ga, In, Si, Ge, Sn, Pb,<sup>1</sup> all showed optical limiting, but In and Pb, were found to have more efficient  $S_1 \rightarrow T_1$  cross-over [52].

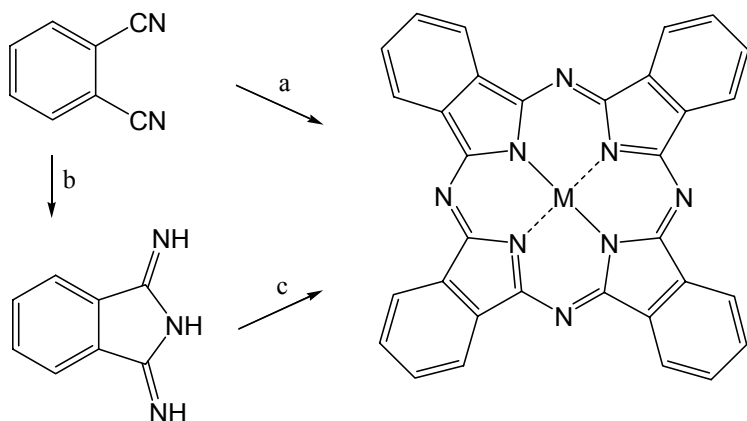
Their major drawback as an optical limiter is their absorption of light of normal intensity within the visible region which makes them very colourful compounds. Normally a phthalocyanine display large absorption at around 300 nm and 700 nm but possess an “optical window” of low absorption around 500 nm. Our object was to broaden the “optical window” by varying the extent of the  $\pi$ -system and insert heteroatoms within the framework.

The general synthetic strategies to obtain phthalocyanines are outlined in figure 5.25. The most straightforward way is to use the di-nitriles, but sometimes the path via a 1,3-diiminoisoindoline derivative may give better result.

The synthesis is generally performed in a highboiling solvent and usually requires a base catalyst. The metal salt may be either halogenides or acetates. Recently microwave assisted methods for synthesising phthalocyanines have been developed which greatly reduce the reaction times and enhance the yield [55].

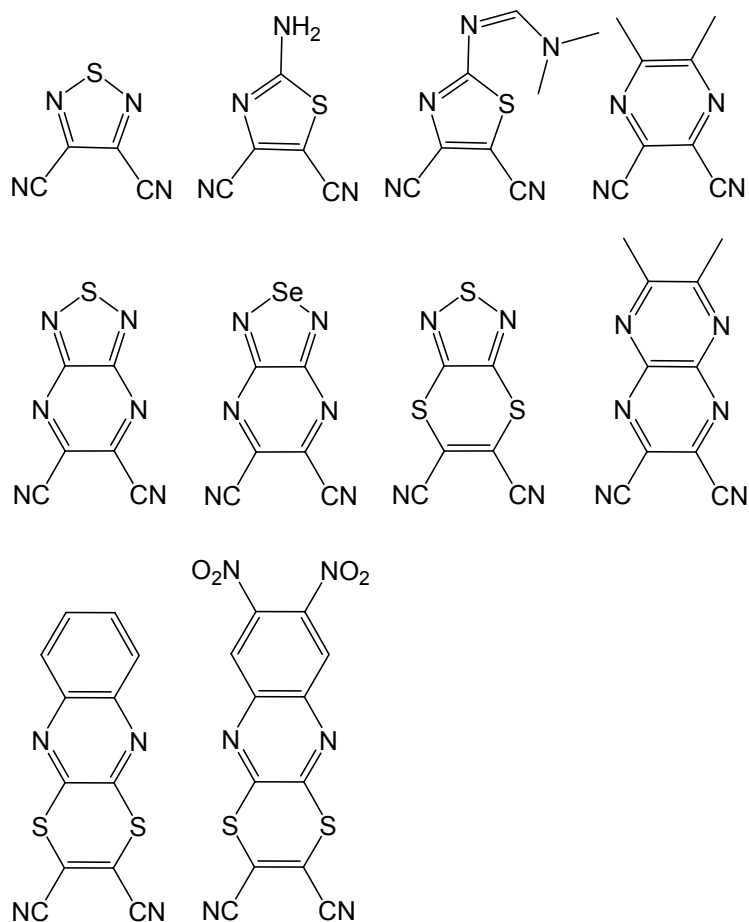
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<sup>1</sup> For Al, Ga, In, in the form tri(n-hexyl)siloxy-MPc, where M is the metal atom. For Si, Ge, Sn, in the form bis[tri(n-hexyl)siloxy]-MPc. The Pb compound was tetra(t-butyl)-PbPc.



**Fig. 5.25** General synthetic pathway for phthalocyanines

Unfortunately, no phthalocyanines was ever isolated within the frame of this project, but a number of different di-nitriles were synthesized and these are outlined below (figure 5.26).



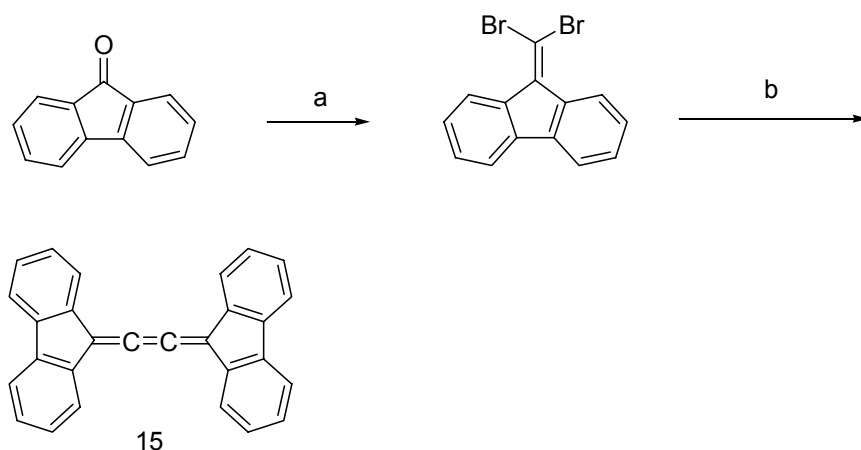
**Fig. 5.26** Di-nitriles used for synthesis of Phtalocyanines

### 5.7.2 Cumulenes

Cumulenes is a class of compounds with similarities to polyenes, but with a linear carbon chain that makes the compounds more rigid than polyenes. The general formula is  $R_1R_2C=(C)_n=CR_3R_4$ , with allene ( $H_2C=C=CH_2$ ) and butatriene ( $H_2C=C=C=CH_2$ ) as the smallest molecules in this class. Only the compounds with an odd number of cumulated double bonds have the four substituents in the same plane. Some theoretical studies have analyzed the linear polarizability and hyper-polarizabilities in cumulenes of variable length [56-58]. At short chain length, up to eight carbons, polyenes are predicted to have larger hyper-polarizabilities than cumulenes, but this would be reversed with longer chains. A Z-scan study reports that cumulenes have relatively low resonant third order nonlinear optical properties [59]. Another study on third-harmonic generation measurements show that cumulenes have high values of the THG intensity [60]. Because of this cumulenes are considered interesting for optical limiting purposes.

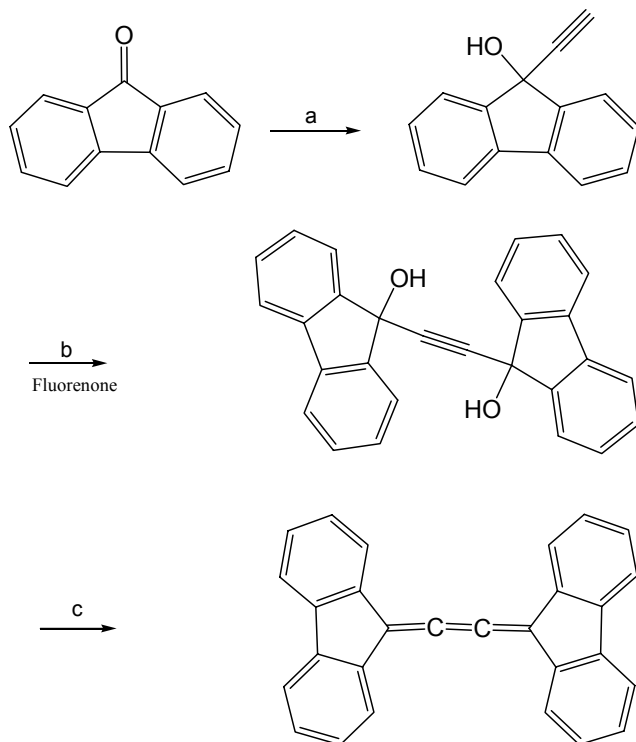
A strong absorption band is typically found with  $\lambda_{max}$  in the region of 450-600 nm, but this can most certainly be altered further to the red-light region by appropriate structural design

The general procedure for synthesis of di-fluorenylidene ethylenes (DFE) is outlined in figure 5.27.



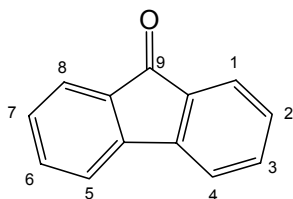
**Fig. 5.27** Synthesis of di-fluorenylidene ethylene  
a)  $CBr_4$ ,  $PPh_3$ ,  $CH_2Cl_2$ . b)  $n-BuLi$ , THF

An alternative route to obtain cumulenes was described by Fischer [61]. Here, the ketone is reacted with an acetylenic Grignard reagent to obtain a propinol (figure 5.28). This propinol is then treated with a base and a second fluorenone is added to yield a butindiol. Subsequent treatment of the butindiol with  $\text{SnCl}_2$  results in the desired cumulene.



**Fig. 5.28** Alternative synthetic route to di-fluorenylideneethylene

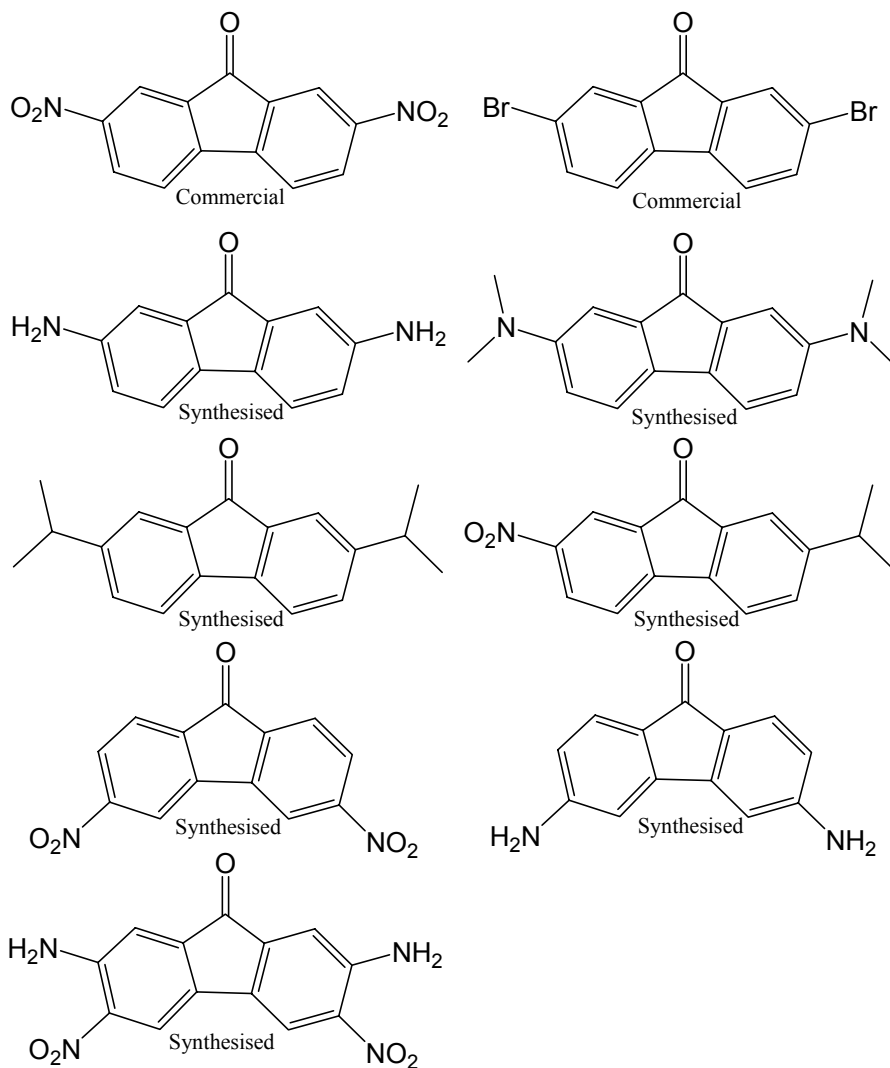
Much of the work was focused on synthesizing various 2,7- and 3,6-di-substituted fluorenones (figure 5.29) to be used for cumulene production.



**Fig. 5.29** Numbering of carbon positions in fluorenone



The following fluorenones (see figure 5.30), either synthesised or commercially obtained, were used for cumulene synthesis. As indicated earlier none of the desired tetra- substituted cumulenes was isolated.



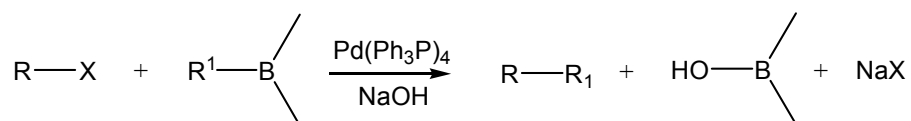
**Fig. 5.30** Fluorenones used for cumulene synthesis

### 5.8 Other cross-coupling reactions

In this work, the major synthetic tool has been the Sonogashira-Hagihara coupling reaction. However, this is by no means the only tool in the synthetic toolbox for cross-coupling reactions. Below is given a short overview of some palladium catalyzed coupling reactions slightly different from, but related to, the Sonogashira reaction.

#### 3.8.1 Suzuki reaction

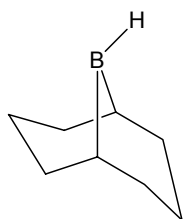
The Suzuki reaction [62] utilize palladium to couple an aryl- or alkenylhalide to an organoborane moiety (figure 5.31)



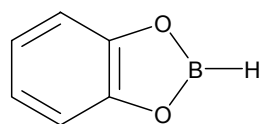
R = aryl or alkenyl, X = I or Br

**Fig. 5.31** The Suzuki reaction

The R group of the borane can be practically any group. Often the organoborane is prepared from catecholborane or 9-BBN-H.



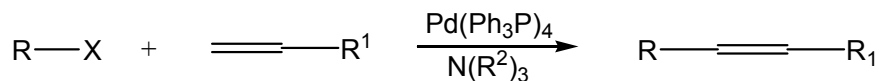
9-BBN-H



Catecholborane

### 5.8.2 The Heck reaction

The Heck reaction [18,63] is a palladium catalyzed coupling of aryl, benzyl, or vinylhalides or triflates to alkenes in a basic solution (figure 5.32).

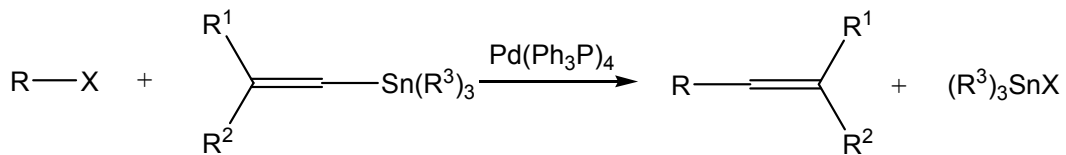


R = aryl, benzyl or vinyl  
X = I, Br or triflate

**Fig. 5.32** The Heck reaction

### 5.8.3 The Stille reaction

In the Stille reaction [64] an aryl, benzyl, or vinylhalide or triflate is coupled to an organostannane, preferentially aryl or vinylstannane, in a palladium catalyzed reaction (figure 5.33).



R = aryl, benzyl or vinyl  
X = I, Br or triflate

**Fig. 5.33** The Stille reaction

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## 6. SUMMARY AND FUTURE WORK

In this work, we have presented the synthesis, photophysical data and optical limiting properties of a few novel organic and organometallic thiophene derivatives. Further, a QSPR study using a PLS approach identified six molecular electronic variables that play an important role for the optical limiting ability of organic compounds.

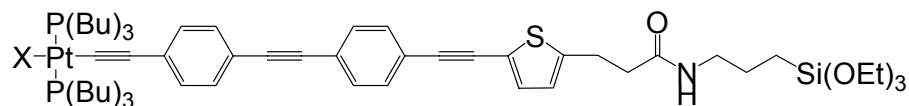
The goal of this part of the project has been to increase our knowledge of the utility of compounds with thiophene rings for optical power limiting. Although the required degree of attenuation was not achieved in the measurements presented here, the molecular frameworks do have interesting OL properties. The thiophene **7** displays surprisingly good clamping considering the size of the molecule. Thiophenes **8-9** display good transmission despite the length of the delocalised  $\pi$ -system. Of compounds **10-14** only **12** displays significantly better attenuation than **7**. The OL of **12** is comparable to that of **9**, and this may be explained by fast triplet formation in **12** due to the nitro groups. The use of a heavier atom in the heteroaromatic ring (Se or Te) does not seem to have any major impact on the OL ability of this class of compounds at 532 nm.

The platinum compound **24** seems to be a slightly better optical limiter than **23**, at 532 nm. Structural examination of **23** and **24** reveals a difference in conformation in such manner that in **24** the aromatic rings are almost coplanar with the P-Pt bonds while they are almost at right angle in **23**. As a result the spin density at the Pt nucleus is increased in **24** during vertical excitation. This may in turn result in a more efficient intersystem crossing of **24** compared to **23**. The work to further improve the NLO properties, primarily of the Pt (II) complexes, has continued after the conclusion of this part of the project.

The alkynyl unit has been extended with, for instance, a third aromatic ring with the thiophene unit at the end positions, and substituents have been included in the aromatic rings in order to favour a conformation of the Pt complex where the plane of the rings in the arylalkynyl entity are perpendicular to the P-Pt bonds.

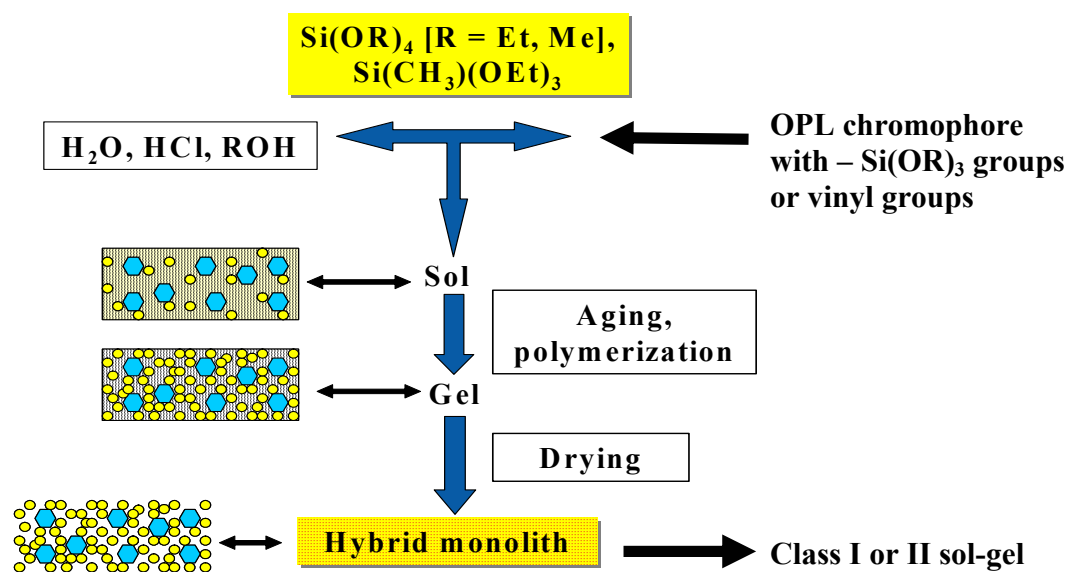
A few attempts to obtain glass materials of the NLO chromophore have been carried out as well. Two different approaches to manufacture such glass have been tested. In the first procedure a terminal alkenyl group is attached to the chromophore, which is dissolved in a matrix of styrene or acrylate followed by polymerization. The chromophore is thus bonded covalently into the matrix. Glass obtained by this method will have a homogenous composition. However, the organic matrix has proven to suffer from insufficient thermal stability, a characteristic which may render such glass less useful for power limiting purposes.

In a similar approach, the NLO chromophore has a  $\text{Si}(\text{OR})_3$  group as shown in figure 6.1. The chromophore is dissolved in a silica based solution and is after hydrolysis allowed to solidify (figure 6.2).



**Fig. 6.1** Example of NLO chromophore with  $\text{Si}(\text{OR})_3$  substituent

The glass thus obtained is cut in appropriate size and polished. Materials obtained in such manner are denoted class II organic-inorganic hybrid materials.



**Fig. 6.2** Schematic approach for manufacturing of class I and II glasses.

Glass materials can also be produced by addition of a NLO chromophore to a pre-polymer solution. After polymerization, the glass incorporates the NLO compound. (When the matrix is an inorganic material, the doped glass is often denoted a class I organic-inorganic hybrid glass).

This method is more straightforward but may result in a non-homogenous glass since there are no covalent bonds between the chromophore and the matrix. To this date no glass has been produced that corresponds to the all demands put on an optical limiting device. Nevertheless, thiophenyl-containing alkynyl platinum(II) complexes have great potential and further modification of this class of compound may well result in a material with adequate properties.

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