SYNTHESIS AND CHARACTERIZATION OF NEW ORGANIC MOLECULES AND INORGANIC-ORGANIC HYBRID MATERIALS WITH INTERESTING LINEAR AND SECOND ORDER NON LINEAR OPTICAL PROPERTIES

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La cosa importante è non smettere mai di porsi domande. La curiosità ha le sue buone ragioni di esistere. Non si può che restare sgomenti, quando si contemplano i misteri dell'eternità, della vita, della meravigliosa struttura della realtà. E' sufficiente cercare solo di capire solo un po' di questo mistero ogni giorno. Mai perdere il gusto di una sacra curiosità.

Albert Einstein
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Chapter 1

INTRODUCTION TO NONLINEAR OPTICS (NLO)
1.1 Introduction

Nonlinear optics (NLO) represents optical phenomena caused by the interaction of an oscillating electromagnetic field (light) with specific molecules or bulk materials, with emission of a new electromagnetic field (new light), which differs from the incident one not only in frequency, but also in phase or other optical properties. In general, NLO phenomena result from the interaction of a strong electromagnetic field (as that of a laser radiation) with matter. This is why the first observations of NLO phenomena are subsequent to the laser development. In the last decades, the research has been widely developed, due to the possibility to generate potentially interesting new NLO materials for optical and electro-optical device\(^1\).

Generally, the NLO processes can be classified in two principal categories:

a) Phenomena with frequency conversion: in these processes the interaction of the electromagnetic radiation with the NLO material produces a variation of the frequency of a part of output radiation with respect to incident radiation. The frequency of this new radiation is a multiple of the incident one.

b) Phenomena with the modulation of the refraction index due to the effect of a strong and external electric field: the interaction of a laser radiation with a NLO material, in the presence of electric field which produces a variation of the refraction index of the material, can modulate the velocity of the laser propagation, but not its frequency.

When the applied field is an electric field, we can talk about electro-optic effects (optoelectronics); if it is optic or electromagnetic, and so associated to a strong bright radiation, we can talk about optic-optic effects ( photonics). In general the radiation is a very strong laser, which can modify the electric and optical properties of a material.

In conclusion, the opto-electronic phenomena are referred to a system, in which the material is crossed by a laser radiation while it is also perturbed by a strong external electric field. In the photonic phenomena, instead, the electric field applied is substituted by an electromagnetic field of a strong laser radiation. The photonic phenomena represent the new technology in which the photons, but not the electrons, are used to transfer, to obtain and to analyze data and information with a very high velocity of light respect to the velocity of the electric phenomena. Moreover, the photonic devices are advantageous, because they can also exploit the high frequency, the wide wavelength range and so the available energies of the electromagnetic radiation.
1.1.1 Basic concepts of non-linear optic phenomena\textsuperscript{1,2}

When a bulk material experiences an oscillating external field, there is a perturbation of its electrons and therefore of its polarity, expressed by Eq. (1):

$$\overline{P} = \overline{P}_0 + \overline{P}_{ind} = \overline{P}_0 + \chi^{(1)} \overline{E}$$

Eq. (1)

where $\overline{P}_0$ is the intrinsic polarity, $\overline{P}_{ind}$ is the induced polarization and $\chi^n$ the electrical susceptibility or linear polarizability tensor. If the applied electric field strength $\overline{E}$ is very high, as it happens in the case of laser pulses, the perturbation is not anymore linear with respect to the electric field and the induced polarization is better expressed by a power series according to Eq. (2):

$$\overline{P} = \overline{P}_0 + \chi^{(1)} \overline{E} + \chi^{(2)} \overline{E}^2 + ................. + \chi^{(n)} \overline{E}^n$$

Eq. (2)

where $\chi^{(2)}$, $\chi^{(3)}$ and $\chi^{(n)}$, which are tensors, are, respectively, the second-, third- and $n$-order electrical susceptibilities, which correspond to non-linear responses of the bulk material.

When $\overline{E}$ is relatively low, the perturbation of the electrons can be explained as a simple linear harmonic displacement, but, when $\overline{E}$ is very strong, the perturbation or the polarization of the electronic density is not linear and therefore anharmonic. From the graphic point of view, the perturbation, induced by the electric field $\overline{E}$, can be represented with different diagrams. In fact, if the electric field strength is relatively low, the induced polarization, $\overline{P}_{ind}$, is proportional to the applied field $\overline{E}$ and it can be expressed only as a function of the susceptibility $\chi^{(1)}$ (Figure 1), ignoring the terms which depend on $E^2$ or $E^3$:

$$\overline{P}_{ind} = \chi^{(1)} \overline{E}$$

Eq. (3)

![Figure 1. Weak electric field applied.](image)
In this case the response is linear and the material has a linear optic behavior. When the applied electric field, $\vec{E}$, is very strong the induced polarization in the material has not a linear response and it can be represented by the diagrams reported in Figures 2a and 2b:

![Figure 2](image)

Figure 2. Variation of $\vec{P}_{\text{ind}}$ increasing the applied electric field applied for centrosymmetric (a, left) and noncentrosymmetric (b, right) materials.

This non-linear optical response is associated with strong electric field $\vec{E}$, such as laser radiation, in fact:

$$\vec{E}_{\text{laser}} \geq 10^3 \, \text{V/} \text{cm}$$

(1.4)

This value is enough to perturb the electronic system of a material or a molecule, which is subject to a value of microscopic and atomic electric field of the order of $10^8 - 10^9 \, \text{V/cm}$. In this way the laser perturbs, but it cannot ionize or damage the material. When $n$ increases, the $\chi^{(n)}$ values decreases in considerable way, since the efficiency $\eta$ of a non-linear process is given by:

$$\eta \approx \frac{1}{\lambda_{\text{laser}}} \left( \frac{\vec{E}_{\text{laser}}}{\vec{E}_{\text{atomic}}} \right)^{n-1}$$

(1.5)

Since $\vec{E}_{\text{atomic}} > \vec{E}_{\text{laser}}$, for the greatest part of the materials the effects of the more third order are not observable, because they have a low efficiency and so, generally, they are ignored.

When a material is polarized, from the electric point of view three terms of susceptibility can be considered:

- $\chi^{(1)}$ or linear
- $\chi^{(2)}$ or quadratic or first order NLO effect
- $\chi^{(3)}$ or cubic or second order NLO effect
In the Figure 2a the induced polarization of a centrosymmetric material is reported: in fact the polarization in $+E$ direction (that is $\vec{P}_{\text{ind}}(+\vec{E})$) is identical, but with contrary sign respect to the polarization in $-E$ direction (that is $\vec{P}_{\text{ind}}(-\vec{E})$). The same effect is obtained when the field is inverted. Therefore, in a centrosymmetric material the terms of susceptibility of odd order ($\chi^{(2)}$, $\chi^{(4)}$, ...) must be equal to zero so that $\vec{P}_{\text{ind}}(+\vec{E}) = \vec{P}_{\text{ind}}(-\vec{E})$. In particular a value of $\chi^{(2)}$, different from zero, is attributed to non-centrosymmetric materials. When atoms or molecules are considered the Eq. (2) can be substituted by Eq. (4):

$$\vec{P} = \mu_0 + \alpha\vec{E} + \beta\vec{E}^2 + \gamma\vec{E}^3 + \ldots$$

Eq.(4)

with: $\mu_0$: molecular ground state static electric dipole moment  
$\alpha$: first order polarizability  
$\beta$: second order polarizability or first order (quadratic) hyperpolarizability  
$\gamma$: third order polarizability or second order (cubic) hyperpolarizability

Because of the anisotropy, these quantities are tensors with nine terms of increasing order (correspondent respectively to 9, 27, 81 elements). To connect $\chi^{(1)}$ to $\alpha$, $\chi^{(2)}$ to $\beta$ etc., it is assumed that the atoms or molecules in a material are independently polarized by $\vec{E}$, without interatomic or intermolecular coupling (joining). As a consequence of this approximation it can be reported that:

$$\chi^{(1)} = \Sigma \alpha$$
$$\chi^{(2)} = \Sigma \beta$$
$$\chi^{(3)} = \Sigma \gamma$$

The NLO response observed for a single molecule depends on its own non-linear optical coefficients which are strongly related to its electronic structure. At molecular level the NLO coefficients of even order (for example $\beta$) are zero for centrosymmetric structures, because in absolute value $\vec{P}_{\text{ind}}(+\vec{E}) = \vec{P}_{\text{ind}}(-\vec{E})$. In these cases the first non-linear term different from zero is $\gamma$. However, the non-centrosymmetric molecules have all nonlinear terms and the first is $\beta$. Since the non-linear coefficients have usually very low values, in order to obtain significantly NLO effects, the limit order of magnitude of $\beta$ e $\gamma$ must be respectively $10^{-30}$ esu and $10^{-34}$ esu while for $\chi^{(2)}$ it must be at least $5 \times 10^{-8}$ esu and for $\chi^{(3)}$ at least $3 \times 10^{-15}$ esu.
the electrostatic unity of the non-linear susceptibility, 1 esu = 1 cm/statvolt; 1 volt = 1/299, 8 statvolt).

1.2 Requirements of materials for significant second order NLO properties.

1.2.1 Requirements of organic molecules for significant second order (β) NLO properties

1.2.1.a Influence of the molecular structure

From a molecular point of view, in the last years the research has shown some essential criterions to be follow to have molecules with a quadratic hyperpolarizability (β) value different from zero\textsuperscript{1,2,3}. In particular the molecule:

1) must be polarizable (for example with a wide π electronic conjugation);
2) must have an asymmetric charge distribution (that is a push-pull system with charge transfer);
3) must have one or more excited states energetically similar to the energy of the fundamental state with a significant charge transfer;
4) must have a great difference between the ground and excited state dipole moment.

The effect of these characteristics may be better understood considering the approximate expression for the calculation of β proposed by Oudar\textsuperscript{4}. This model considers that the direction of the excitation is the same of the charge transfer between two energetic levels of a push-pull molecule. So the hyperpolarizability is called β\textsubscript{CT} and it is calculate as reported below:

$$\beta_{CT} = \frac{3e^2}{2} \cdot \frac{h \omega_{eg} f \Delta \mu_{eg}}{\left[(h \omega_{eg})^2 - (2h\omega)^2\right]\left[(h \omega_{eg})^2 - (h\omega)^2\right]}$$

where:

- $h\omega_{eg}$ is the energy of the charge transfer transition
- $h\omega$ is the energy of the laser radiation used in the experiment
- $f$ is the oscillator’s strength of the CT equal to the integral of the absorption coefficient of the CT as reported below

$$f = \int_{\omega_2}^{\omega_1} \varepsilon_{CT} \ d\omega$$

$\Delta \mu = \mu_e - \mu_g$ is the difference of dipole moment between the excited and ground state.
Some inorganic compounds such as LiNbO$_3$ and KH$_2$PO$_4$ give crystals with interesting second order NLO properties. In spite of this, in the last fifteen years many studies have been dedicated to the second order NLO properties of organic structures for different reasons, such as:

- organic materials cost is lower than inorganic materials;
- organic materials show high NLO properties and more quick responses;
- organic structures are more flexible so new materials can be easily obtained.

The best kind of molecule that fulfills the requirements dictated by the Oudar’s model is the push-pull molecules in which a donor (D) and an acceptor (A) group are connected by a conjugated linker. The improvement of the NLO properties can be obtained by increasing $\pi$−delocalization of the molecules (using more conjugated linkers) or increasing the polarizability of the system (for example introducing heteroatoms such as S, Se in the structure). A typical push-pull system is reported Figure 3.

![Figure 3. Structure of a push-pull molecule (A = acceptor group, D = donor group)](image_url)

where in the excited state there is a strong charge transfer between donor and acceptor through the $\pi$ organic polarizable bridge. Experimentally in organic systems it has been found that the $\beta$ value increases with increasing the length of the $\pi$ conjugation and it also depends on the electronic nature of the spacer. In particular, it has been found that the conjugated double bond is better than triple bond and phenyl group (Table 1).
Table 1. Some push-pull molecules with their quadratic hyperpolarizabilities values

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\beta \times 10^{-30}$ esu</th>
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<tr>
<td>$\text{H}_2\text{N}-\text{C}_6\text{H}_4$</td>
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</tr>
<tr>
<td>$\text{O}_2\text{N}-\text{C}_6\text{H}_4$</td>
<td>2.2</td>
</tr>
<tr>
<td>$\text{O}_2\text{N}-\text{C}_6\text{H}_4\text{NH}_2$</td>
<td>9.2</td>
</tr>
<tr>
<td>$\text{O}_2\text{N}-\text{C}_6\text{H}_4\text{N(CH}_3)_2$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{F}_3\text{COC}-\text{C}_6\text{H}_4\text{N(CH}_3)_2$</td>
<td>10</td>
</tr>
<tr>
<td>$\text{NC}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4$</td>
<td>19</td>
</tr>
<tr>
<td>$\text{NC}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{N(CH}_3)_2$</td>
<td>36</td>
</tr>
<tr>
<td>$\text{O}_2\text{N}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$</td>
<td>15</td>
</tr>
<tr>
<td>$\text{O}_2\text{N}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{OMe}$</td>
<td>28</td>
</tr>
<tr>
<td>$\text{O}_2\text{N}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{N(CH}_3)_2$</td>
<td>73</td>
</tr>
</tbody>
</table>
1.2.1.b Effect of the spacer planarity

The planarity of the spacer influences the π−conjugation and, consequently, the polarizability of the compound. Different classes of compounds have been studied in order to rationalize the effect of the planarity, such as stilbenes, azobenzene or Shiff bases (Figure 4a), diphenylpolyenyl (Figure 4b) diphenylalkynescon n > 2 (Figure 4c), polyarylcon n > 2 (Figure 4d), polynes (Figure 4e), polythiophenes (Figure 4f) and condensed thiophenes (Figure 4g).

A general conclusion is that the lack of conjugation due to the lack of planarity of the system reduces interaction between donor and acceptor group and thus to the decrease of β. The lack of planarity may be due to a minor conformational flexibility or to steric hindrance.

Figure 4. Push-pull systems with different kind of conjugated p-delocalized linker.

1.2.1.c Effect of the spacer length

The effect of the extension of the spacing in the push-pull molecules has been widely studied, because it corresponds to a significant β increase and sometimes to a limit saturation length. For molecule as α,ω-diphenylpolynes (Figure 4a), α-phenylpolynes (Figure 4b) and polynes (Figure 4e) hyperpolarizability increases when the conjugation lengt increases, i.e. when the number of double conjugated bonds increase. In fact saturation phenomena have never been observed even to n = 9 and the β values are very high. A very high increase there is in the molecules, where donor and acceptor group are directly bounded to the polyenic chain. The lowest values are in the series, where the terminal groups are phenyl substituted groups. In fact the phenyls do not transmit very well charge transfer, but they act as tampone because of their particular stabilization and so for their small harmonic polarizability.
1.2.2 Requirement for high second order electrical susceptibilities $\chi^{(2)}$

A non-centrosymmetric arrangement of the NLO-phores in the crystalline structure is the main requirement to have a NLO-active material. It has been, however, observed that centrosymmetric polarizable molecules can crystallize with a noncentrosymmetric packing and so the crystals (and also the material deriving from these molecules) can show second order NLO properties. These properties are more significant when in the crystalline architecture of low symmetry there are charge transfers among the molecules (this corresponds to a push-pull process that is an intermolecular charge transfer).

The acentricity requirement constitutes a major impediment when we attempt to engineer materials with large $\chi^{(2)}$ because about 75% of organic molecules crystallize in centrosymmetric space groups. Different strategies to overcome this issue have been developed in the last years:

- introduce chiral groups in the molecule;
- use hydrogen bond to drive crystallization;
- introduce steric hindrance groups;
- use ionic chromophores.

During my PhD I succeed in the preparation on new NLO-active material following the latter strategy and in particular exploiting:

1) the organization of ionic chromophores in non-centrosimmetric crystalline systems. In fact, for ionic compounds, Coulombic interactions should overwhelm the unfavorable dipole-dipole interactions and allow an asymmetric assembly of polar ionic moieties.

2) the application of external forces, such as an electric filed, in order to address the non-centrosimmetric arrangement of the ionic chromophores in a polymeric matrix.
1.3 Techniques to measure the non-linear optical effects

1.3.1 Determination of second order electrical susceptibilities $\chi^{(2)}$ of bulk materials with Kurtz-Perry technique

At the bulk level, the most used method to investigate the second order NLO activity for powder samples has been developed by Kurtz and Perry in 1968\textsuperscript{15}. This is a very simple and fast technique that allows an initial screening of the NLO properties of the system by the measure of the intensity of the second harmonic radiation (SHG). Since the measured efficiency depends on the bulk electric susceptibility $\chi^{(2)}$, this method gives an indirect evaluation of the order of magnitude of $\chi^{(2)}$ which is referred to a standard, usually urea. The analyzed sample is in a crystalline powder form, that is a condition easily attainable in many cases and as a consequence this method has a very large applicability. A typical instrument to determine the second harmonic generation of powders consists of a Nd:YAG Q-switched laser followed by an hydrogen Raman shifter. A very thin section (ca. 0.2 mm) of the powder is irradiated with the pulsed laser radiation and the second harmonic emitted light is focused by the elliptical mirror on the photomultiplier and compared to that of a reference compound such as urea or quartz while the fundamental radiation is cut off by filters. The scheme of the instrument is reported in Figure 8.

![Diagram of Kurtz-Perry technique](image)

**Figure 8.** Experimental set-up for Kurtz measurements

The SHG measure consists of four steps:

1. sample preparation;
2. calibration of the sensitivity respect to a standard;
3. measure of the sample activity and comparison with the standard;
4. control of the validity of the result.

In general, the results obtained with this technique must be considered semiquantitative because they are influenced by the size of the particles. Therefore, the analysis on powders with unknown granulometry is useful a for qualitative measure and for initial screening while
the procedure is more complex for quantitative measurements. In this case, in fact, grain of a fixed size (usually 75-150 μ) are selected by standard sieves and then put in a quartz cell with a defined thickness. A regular packaging is obtained through a vibrator, while the particle dimensions are controlled with the common techniques of optical microscopy.

1.3.2 Experimental measurement of quadratic hyperpolarizability of molecular species: The EFISH Technique (Electric Field Induced Second Harmonic Generation) \(^1,13\)

The EFISH technique has been used widely for the experimental measurement of quadratic hyperpolarizability of polar molecules which are NLO active. This technique allows to calculate both the sign and the absolute value of the scalar product \(\mu \beta\), where \(\mu\) represents the ground state molecular dipole moment and \(\beta\) is the projection of the vectorial component of the tensor of the quadratic hyperpolarizability along the dipole moment axis. The ground state dipole moment can be measured independently and so \(\beta\) can be calculated by EFISH measurement. In our laboratory the dipole moment of species in solution is determined with the Guggenheim method (see Appendix 1). It is important to limit the possible increase of real value of \(\beta\) due to resonance phenomena, working systematically the EFISH measurement at a fundamental wavelength of 1.9 μm (0.65 eV), so that the values of radiations \(2\omega\) (1.9/2 μm = 0.950 μm) are distant to the absorption bands (\(\pi \rightarrow \pi^*\), CT, MLCT and/or LLCT) of the studied organic or organometallic molecules (generally these bands are not beyond 0.6-0.8 μm). In the EFISH technique the dipoles of the molecules, dissolved in a suitable solvent (usually CHCl₃, but also CH₃COCH₃ or THF), are aligned by a strong dc electric field (ca. 30 KW/cm) which is required to break the statistical centrosymmetry of the solution. A laser beam at fundamental frequency \(\omega\) is directed through the cell in the presence of this field. By translating the cell perpendicularly to the laser beam, the thickness of the solution is modified; therefore interference occurs, causing Maker fringes by which \(\beta\) can be evaluated. It is possible to point out the presence of two radiations in output, the incident radiation (with frequency \(\omega\)) and a radiation with frequency \(2\omega\) (second harmonic) generated thanks to the interaction between the laser and the sample. The fundamental radiation is removed by filters, and only the second harmonic radiation reaches the photomultiplier. The intensity and the properties of this radiation depend on the non linear hyperpolarizability of the first order of the analyzed sample and so they can be defined by the \(\beta\) value and by the cell characteristics. The schematic diagram of EFISH system is reported in Figure 5.
Chapter 1

Figure 5. A = photomultiplier tube; B = filer; C = cell; D = doubler of the beam; E = mirror; F = electric field generator; G = photomultiplier and monochromator; H = crystals of the reference; I = integrator; J = register.

The measurements are carried out in a cuneiform cell, constituted by two quartz windows opportunely angled and assembled on a stainless steel support (Figure 6). The windows are the most delicate part of the system, in fact, if the laser beam is not perfectly focused in the center of the cell, it can cause their breaking. For this reason the main radiation is, at first attenuated with filters and then focused on the right position with a He-Ne laser.

Basic concepts for β calculation

After the introduction in the cuneiform cell, the solution of the sample is submitted to an impulse with high tension (ca. 5 KV), synchronized with the emission impulses of the laser. In this way the generated electrostatic field breaks the statistical centrosymmetry of the solution, producing a dipolar orientation of the solvent and of the molecules. The impulse is used to minimize electrolysis phenomena of the samples or polarization processes of the electrodes into the cell. During the experiment the cell is translated respect to the incident beam in order to change its optic path into the cell. By the use of suitable filters, the fundamental frequency ω of the incident laser cannot reach the detector while the second harmonic 2ω is measured as function of the cell position.
The necessity to use a cuneiform cell and to measure the intensity of harmonic radiation $2\omega$ as function of the optic path is related to the process of phase shift between the fundamental and harmonic waves into the medium. By the cell translation, the signal of the intensity of the second harmonic radiation is modulated as interference fringes, known as Maker fringes (Figure 7). The intensity of $I_{2\omega}(x)$, $I(x)$, and the coherence length $l_c(x)$ can be determined by the resulting diagram.

![Figure 7. Interference fringes or Maker fringes](image)

The width and the periodicity of the fringes are correlated to the macroscopic susceptibility $\Gamma(x)$ of the solution that depends on $I_{2\omega}(x)$ and on $l_c(x)$, according to this relation:

$$\Gamma(x) = \left. \frac{1}{l_c(x)} \right| \left[ A \cdot \sqrt{\frac{I_{2\omega}(x)}{I_{2\omega}(0)}} \cdot \frac{E(0)}{E(x)} + B \right] \cdot 10^{-12} \quad \text{Eq. (5)}$$

(in the unity of the electrostatic c.g.s. system)

where $I_{2\omega}(x)$ is the intensity of the harmonic at $x$ concentration (0 is the solvent), $E(x)$ is the intensity of the electric field, $A$ and $B$ are constants depending on the solvent.

Since as

$$\gamma_{EFISH} = \frac{M}{\rho N_a f x} \cdot [(1+x)\Gamma(x) - \Gamma(0)] \quad \text{Eq. (6)}$$

where $N_a$ is the Avogadro’s number, $M$ the molecular weight of the solute, $\rho$ the density of the solvent, $x$ the molar fraction of the solute and $f$ a correction factor of the applied electric field $E$, it is possible to obtain the $\beta$ value (projection of the vectorial component of the tensor of the quadratic hyperpolarizability along the dipole moment axis) by this relation:

$$\gamma_{EFISH} = \frac{\mu_0 \beta_{\text{vec}} (-2\omega,\omega,\omega)}{5kT} + \gamma(-2\omega,\omega,\omega,0) \quad \text{Eq. (7)}$$
where the first term of the sum represents the contribution of the second order hyperpolarizability and the second one represents the contribution of the third order of the radiation $2\omega$.

Since the contribution of the third order hyperpolarizability of the radiation $2\omega$ is usually lower than the contribution of the second order, generally $\gamma$ can be ignored. In this way the $\mu_0\beta_{vec}$ value can be calculated directly from $\gamma_{EFISH}$ value.

If the ground state dipole moment $\mu$ is known, it’s possible to calculate the $\beta$ value, defined according the phenomenological convention\textsuperscript{14}.

\textit{Experimental procedure}

The cell for the measure has a volume of \textit{ca.} 4 ml. The measurements are carried out in CHCl\textsubscript{3} solution (but also in CH\textsubscript{3}COCH\textsubscript{3} or THF). The incident radiation, produced by a laser Nd: YAG Q-switched with impulses of a period of 15 o 90 ns at a frequency of 10 Hz, has a wavelength of 1.06 $\mu$m. By a Raman shifter, using the Raman effect on the hydrogen, an incident radiation of 1.904 $\mu$m can be obtained. By the substitution of the laser source, it’s possible to use an incident radiation of a wavelength of 1.34 $\mu$m. It is necessary to prepare, for every compound, two solutions at different concentration (with ponderal values $x$ in the range $10^{-2}$ e $10^{-3}$, but it depends on the NLO properties of the sample). Then it can continue according the scheme:

• A scanning for pure CHCl\textsubscript{3}
• A scanning for the compound solution
• Another scanning for pure CHCl\textsubscript{3}.

In this way the possible errors, due to the decrease of the energy of the incident radiation during the measure, are nullified. Usually it is convenient to repeat the sequence of measures for three times, and calculate the average of the three $\beta$ values during data calculations. After a very scanning, the cell is carefully washed (it is possible to use all solvent, but it is necessary to rinse the cell with CHCl\textsubscript{3} before the new measure) and dried with compress air.
1.4 H and J aggregates

As discussed in the section 1.2.1, the condition *sine qua non* in the preparation of NLO-active materials is the non-centrosimmetric arrangement of the molecules in the crystal. It has also been observed that the value of $\chi^{(2)}$ can be affected by the orientation of the chromophores, for example, if molecules crystallize in an acentric fashion but the polarization vectors are organized in a pseudo-centric way, the value of $\chi^{(2)}$ is zero. Moreover, measurements of $\beta$ in solution showed a variation of the value of the first order hyperpolarizability (either increase or decrease) due to an aggregation effect observed changing the concentration of the solution. The most important kinds of aggregation are:

- **H aggregate**: domains with high concentration of chromophores aligned in a side-by-side arrangement. The dipole moment of the molecules might be oriented in the same direction (Figure 7a, cofacial arrangement) or in opposite directions (Figure 7b, eclipsed cofacial arrangement)

![Figure 7](image)

*Figure 7*: Scheme of chromophores organized as H aggregates. The narrow is the direction of the dipole moments in the molecule.

- **J aggregates**: domains at high concentration of chromophores aligned in an head-to-tail arrangement forming chains shifted by half a molecule each one to the adjacent one (Figure 8)

![Figure 8](image)

*Figure 8*: Scheme of chromophores organized as J aggregates. The narrow is the direction of the dipole moments in the molecule.

The presence of these two kinds of aggregation is easily detected by spectroscopic analysis. It is well known that H aggregates leads to a blue-shift of the UV-Vis absorption band ($\pi \rightarrow \pi^*$ transition), compared to the absorption spectrum of the free chromophore, and to a red-shift of
the fluorescent emission band. J aggregates lead to a formation of a new sharp band red-shifted in comparison to the absorption band of the free chromophore\textsuperscript{16} while a red-shift and an enhancement of photo-luminescent quantum yield is often observed\textsuperscript{17} in the emission spectrum.

The shifts of $\lambda_{\text{max}}$ in absorption and emission spectra caused by the presence of H or J aggregates can be rationalized using the “excitonic splitting” model\textsuperscript{18}. The molecules in the aggregates are close one to each other and it leads to a strong electronic perturbation of $\pi$ orbitals energetic level that imply the formation of new excited states associated to intermolecular charge transfer transitions. So, the energy needed for the electronic excitation is a “wave packet” and it is delocalized all over the aggregate and no more on the single molecule. This “wave packet” is called exciton.

The selection rules of these new transitions, and the shift of $\lambda_{\text{max}}$ and $\lambda_{\text{em}}$, are related to the disposition of the chromophores in the aggregates. The Figure 9 shows the splitting of energy level for H and J aggregates and in particular:

- for H aggregates the excitonic splitting gives a high-energy allowed transition and a low-energy forbidden band. Absorption is dominated by the high energy band (blue-shift of $\lambda_{\text{max}}$), but the long-lived fluorescence occurs from the low-energy band and is thus strongly red-shifted.
- for J aggregates the low-energy allowed transition dominates both absorption and emission spectra which are both red-shifted.

![](image_url)

**Figure 9.** Energy levels for H and J aggregated on the basis of “excitonic splitting” model.
The magnitude of the microscopic parameter $\beta$ and the macroscopic $\chi^{(2)}$ are related to the energy of the charge transfer, $E_{\text{CT}}$, that it’s lower for J aggregate than for H aggregate leading to a higher value of $\beta$ and $\chi^{(2)}$ in case of J aggregates. However not only $E_{\text{CT}}$ affect the second order NLO parameters, when aggregation’s phenomena exist, in fact variation of $f$ (oscillator’s strength) and $\Delta\mu$ (difference between dipole moment of the molecule at the excited state and at the ground state) also play an important role. A theoretical study of second order NLO properties of push-pull molecules showed how much distance and orientation of chromophores in a dimeric structure affect $E_{\text{CT}}, f$ and $\Delta\mu$. In particular, for a cofacial arrangement of the chromophores, decreasing the intermolecular distance $R$ till the limit value 3.3 Å (average distance value for a van der Walls interaction in organic crystalline systems) the calculations predict:

- decrease of $\Delta\mu$
- decrease of $f$
- decrease of $\lambda_{\text{max}}$ (increase of $E_{\text{CT}}$)

that lead to a decrement of the value of $\beta$ calculated with the Oudar equation (section 1.2.2). On the other hand the eclipsed cofacial arrangement of chromophores, typical of the second type of H aggregates, leads to a centrosimmetric structure of the aggregate so to a material with no second order NLO properties.

For what concerns J aggregates, keeping $R$ constant an increasing $R'$ starting from zero, we may observe:

- increase of $\Delta\mu$
- increase of $f$
- increase of $\lambda_{\text{max}}$ (decrease of $E_{\text{CT}}$)

and these variations lead to an increase of the value of $\beta$, calculated using the Oudar equation, that reaches a maximum when the donating group of one chromophore and the withdrawing group of a chromophore of an adjacent chain are overlapped.

These theoretical predictions have been demonstrated in quite a few experimental studies. For example, the compound trans-4-(4-dimethylaminostyryl)-1-methylpyridinium $p$-toluensulfonate or DAST is often use as standard during the measurements of SHG of materials with extremely high second order NLO properties. It crystallizes in a non-
centrosymmetric space group with the cations (called [DAMS$^+$]) organized in J aggregates (Figure 10) and its SHG has been reported to be equal to 1000 times that of the standard urea$^{20}$.

Another very interesting examples are new hybrid inorganic-organic materials in which polymeric anionic inorganic chains are layered between chains of [DAMS$^+$] organized in J aggregates, as clearly observed in the UV-Vis spectra of the compounds (e.g. [DAMS]-MPS$_3$ ($M = Mn, Cd, Zn$); [DAMS][M$^{II}$Cr(C$_2$O$_4$)$_3$] ($M^{II} = Mn, Fe, Co, Ni, Cu$)$^{21,22,23,24}$; [DAMS][Cu$_5$I$_6$]$^{25}$). These new materials have shown very interesting second order NLO properties.
References


Chapter 2

NEW SELF-ASSEMBLED MATERIALS
WITH INTERESTING SECOND ORDER
NON LINEAR OPTICAL PROPERTIES
2.1 New polyfunctional inorganic-organic hybrid materials containing mixed metal oxalate chains

In the last years, polyfunctional inorganic-organic materials have been subjected to a lot of attention in the scientific world\(^1\). Within this wide new field, the coupling of magnetic and nonlinear optical properties seems to be quite attractive\(^2\), and yet largely unexplored. In particular, although some magnetic materials displaying efficient second harmonic generation (SHG) properties have been reported\(^3\), systems in which the magnetic properties can be easily and rationally tuned, without affecting the SHG efficiency, are still rare. In a previous PhD thesis the synthesis and characterization of a new family of hybrid materials of formula \([\text{DAMS}]_4\text{M}^{\text{III}}_2\text{M}^{\text{II}}\text{(C}_2\text{O}_4)_6\cdot\text{DAMBA}\cdot2\text{H}_2\text{O}\) (where \(\text{M}^{\text{III}}=\text{Rh, Fe, Cr}; \text{M}^{\text{II}}=\text{Mn, Zn}, \text{DAMS} = \text{trans-4-(4-dimethylaminostyryl)-1-methylpyridinium}; \text{DAMBA} = \text{para-dimethylamino)}\) benzaldehyde; formula in Figure 1) characterized by a strong SHG and very interesting magnetic properties was reported\(^4\).

![Figure 1. Formula of [DAMS]\(\text{I}\) (a) and DAMBA (b)](image)

These new materials are characterized by a layered structure in which “strips” of polymeric mixed \(\text{M}^{\text{II}}/\text{M}^{\text{III}}\) oxalates, linked by hydrogen bonds through DAMBA and water molecules. The para-dimethylaminobenzaldehyde plays a rather unique role because it stabilizes the organic-inorganic layer and therefore induces the segregation of second-order NLO-phores, \([\text{DAMS}]^+\), in layers of self-organized head-to-tail J aggregates that guarantee a very high SHG. In such layered structure any structural distortions induced by the substitution of the magnetic ion into the inorganic framework can be easily absorbed without significantly altering the whole crystalline framework and therefore the SHG efficiency which, in fact, remains constant for each pair of \(\text{M}^{\text{II}}/\text{M}^{\text{III}}\). On the other hand, the magnetic property can be tuned changing the \(\text{M}^{\text{II}}/\text{M}^{\text{III}}\) pair. In particular the interaction between magnetically active Mn\(\text{II}\) ions is rather weak in combination with the diamagnetic Rh\(\text{III}\) ions, but it is more relevant if associated with Cr\(\text{III}\) or Fe\(\text{III}\) ions (with ferri- or ferromagnetic nature, respectively). The weak antiferromagnetic interactions characterizing compounds containing Mn/Rh, Zn/Fe and Zn/Cr as \(\text{M}^{\text{II}}/\text{M}^{\text{III}}\) pairs and the stronger magnetic interactions of compounds containing Mn/Fe and Mn/Cr reveal that the spin-staircase systems of this class of mixed oxalates can be described by a next-nearest interactions along the \(\text{M}^{\text{II}}/\text{M}^{\text{III}}\) ions of the polymeric chains of the
inorganic “stripes”. The magnetic shielding of the “stripes”, due to the organic bridge of DAMBA and the intercalation of NLO-phores layers, is extremely efficient in lowering 2D and 3D magnetic interactions and ordering. All these evidences facilitate the 1D anisotropic magnetic interaction along the polymeric chain of these “stripes” in the crystalline network. 

In view of this tunability of the magnetic properties and of the particular structural arrangement, the investigation has been extended to the Ni\textsuperscript{II} and Co\textsuperscript{II} members of this class of hybrid mixed oxalates with the attempt to improve the magnetic behavior since the magnetic orbitals of these metals are usually more delocalized along the chains\textsuperscript{5} producing unexpectedly strong magnetic interactions.

Co\textsuperscript{II} is particularly interesting since it can produce Single Chain Magnets (SCMs), as the cobalt-organic radical system\textsuperscript{6} reported by Bogani et al., defined as 1D magnetic polymers whose magnetization relaxes slowly at low-temperatures. In order to observe this behavior the compound must be characterized by a good isolation between adjacent magnetic chains and, at least one of the magnetic center, must have a strong anisotropy. The new Co\textsuperscript{II} derivatives of the family hybrid M\textsuperscript{II}/M\textsuperscript{III} oxalates should be the perfect candidate because i) M\textsuperscript{II}/M\textsuperscript{III} oxalate chains are 1D polymers; ii) the chains are isolated from the others by the presence of DAMBA molecules and [DAMS\textsuperscript{+}] layers; iii) Co\textsuperscript{II} is known to have an higher anisotropy.

It is worth noting that the possibility of obtaining oxalate-based SCM, in spite of their relatively weak exchange interactions has been recently reported by Coronado and coworkers\textsuperscript{7}.

### 2.1.1 Synthesis and characterization of the M\textsuperscript{III}/Ni\textsuperscript{II} and M\textsuperscript{III}/Co\textsuperscript{II} derivative

The best general synthetic way to obtain compounds of the family of mixed oxalates of formula \([M^{\text{III}}_2M^{\text{II}}(C_2O_4)_6][\text{DAMS}]_4\cdot 2\text{DAMBA} \cdot 2\text{H}_2\text{O} \quad (M^{\text{III}} = \text{Rh; Fe; Cr}; \quad M^{\text{II}} = \text{Mn; Zn})\) consists in a two step procedure\textsuperscript{4}. The first step leads to the formation of the intermediated phase Am\textsuperscript{II}/M\textsuperscript{III}, by mixing in a mixture of water and methanol \(K_3[M^{\text{III}}(C_2O_4)_3] \cdot n\text{H}_2\text{O} \quad (M^{\text{III}} = \text{Rh, Fe, Cr}); \quad M^{\text{II}}X \quad (M^{\text{II}}X = \text{Mn(NO}_3)_2 \cdot n\text{H}_2\text{O}; \quad \text{ZnSO}_4 \cdot 7\text{H}_2\text{O})\) and [DAMS]\textsuperscript{I} while in the second step the phase Am\textsuperscript{II}/M\textsuperscript{III} is dissolved in H\textsubscript{2}O in presence of DAMBA.

The same strategy has been suited and successfully applied to obtain both Ni\textsuperscript{II} and Co\textsuperscript{II} derivatives.
2.1.1.1 Synthesis and characterization of Phases A\textsuperscript{Ni,II}/M\textsuperscript{III} and A\textsuperscript{Co,II}/M\textsuperscript{III}

This first step is the same of the one reported for Mn and Zn derivatives\textsuperscript{4}. In a two-necked flask [DAMS]I (0.50 mmol) is dissolved in 40 mL H\textsubscript{2}O/CH\textsubscript{3}OH (1:1). The solution was heated at 60°C and 0.5 mmol K\textsubscript{3}[M(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}]\textsubscript{n}H\textsubscript{2}O (M = Rh, Fe, Cr), previously dissolved in 20 mL H\textsubscript{2}O/CH\textsubscript{3}OH (1:1), are added. The heating is turned off and 0.5 mmol of M\textsuperscript{II}X (M\textsuperscript{II}X = 123.6 mg of NiCl\textsubscript{2}•6H\textsubscript{2}O; 145.4 mg of Co(NO\textsubscript{3})\textsubscript{2}•6H\textsubscript{2}O), dissolved in CH\textsubscript{3}OH (2–3 mL), are added to the still hot solution. In both cases, a brownish-black powder start immediately to precipitate as phase A. After 1 h 30 min stirring at room temperature the solid is filtered, washed with few drops of H\textsubscript{2}O/CH\textsubscript{3}OH (1:1) and dried under vacuum.

As also reported for Mn\textsuperscript{II} and Zn\textsuperscript{II} derivatives, any attempts to grow suitable single crystals for X-ray diffraction failed and XRPD analysis can be performed. The phases A\textsuperscript{Ni,III} is characterized by a XRPD pattern, mainly controlled by the inorganic layer, and speaking of isomorphous relationship with the previously characterized phases A\textsuperscript{M\textsuperscript{II}/M\textsuperscript{III}} species (Figure 2). Kurtz–Perry measurements showed a SHG of the same order of magnitude of [DAMS][p-toluenesulfonate] (i.e. 1000 times that of urea), when working at 1907 nm incident wavelength\textsuperscript{8,9}. The same is true for the phases A\textsuperscript{Co,III} (Figure 2) even if, interestingly, the XRPD pattern for A\textsuperscript{Co/Cr} is consistently different to the others reported for “A” intermediate, although it showed comparable crystallinity and SHG efficiency.

The synthesis is very reproducible as confirmed by elemental analysis (see Experimental Section).

![Figure 2. XRPD pattern diffraction of Phases A\textsuperscript{Ni/Fe}, A\textsuperscript{Co/Fe} and A\textsuperscript{Zn/Fe}](image-url)
2.1.1. Synthesis and characterization of $[\text{M}^{\text{III}}_{2}\text{M}^{\text{II}}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}$ ($\text{M}^{\text{III}} = \text{Rh}; \text{Fe}; \text{Cr}; \text{M}^{\text{II}} = \text{Ni}; \text{Co}$)

Since the formula of all the phases A is unknown, the amount of p-dimethylaminobenzaldehyde is calculated as weight/weight ratio compared to the quantity of phase A. For the Ni$^{\text{II}}$ derivative, the synthesis way that has been applied is the same reported for Mn$^{\text{II}}$ and Zn$^{\text{II}}$ derivatives: 20mg of DAMBA are added to a water solution of 80mg of phase ANi/M$^{\text{III}}$ ($\text{M}^{\text{III}} = \text{Fe}, \text{Cr}, \text{Rh}$), the solution is heated under reflux for 1h 30min and then cooled down at room temperature. Crystals of formula $[\text{M}^{\text{III}}_{2}\text{Ni}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}$, suitable for XRD analysis, grow in few days (in general indicated as M$^{\text{III}}_{2}\text{Ni}$).

A little bit harder is to grow crystals of the Co$^{\text{II}}$ phases probably because the higher water affinity of the ion. In particular, $[\text{M}^{\text{III}}_{2}\text{Co}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4[\text{DAMBA}]_2\cdot2\text{H}_2\text{O}$ where M = Cr, Fe (respectively indicated as Cr$^2\text{Co}$ and Fe$^2\text{Co}$) have been succesfully isolated keeping the w/w ratio between DAMBA and Phase ACo/M$^{\text{III}}$ equal to 1/4 but using a mixture of H$_2$O and methanol 1:1 v/v as solvent while $[\text{Rh}^{\text{II}}\text{Co}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4[\text{DAMBA}]_2\cdot2\text{H}_2\text{O}$ (also indicated as Rh$^2\text{Co}$) has been obtained working with water as solvent but a 1/1 w/w ratio DAMBA/phase ACo/Rh.

The new compounds M$^{\text{III}}_{2}\text{Ni}$ and M$^{\text{III}}_{2}\text{Co}$ have been found to be isomorph to the already reported M$^{\text{III}}_{2}\text{Zn}$ and M$^{\text{III}}_{2}\text{Mn}$ by comparison of the XRPD powder diffraction and they all crystallize in the polar acentric Fdd2 space group$^4$. The crystalline structure of the Fe$^2\text{Ni}$ and Fe$^2\text{Co}$ compounds are solved by XRD analysis of suitable single crystals (see the Experimental Section) and the crystallographic data are reported in Table 1. For all the compounds, the large asymmetric unit contains two independent [DAMS$^+$] ions, one DAMBA, one water molecule, three oxalate anions, one Fe$^{\text{III}}$ atom in a general position and one M$^{\text{II}}$ in a twofold special position. Differently from other mixed layered metal-oxalates of [DAMS$^+$]$^{10}$, all these hybrid materials are characterized by layers of mixed metal oxalates based on an organic-inorganic 2D framework, rather than a purely inorganic one. The inorganic part of this compound is composed by the metal ions and the coordinated oxalates, forming infinite stripes (~14 Å large) (see Figure 3), elongated along the c axis. The M$^{\text{II}}$ cations are bound to four oxalate groups in a distorted square anti prismatic coordination environment while the M$^{\text{III}}$ cations are octahedrically coordinated by three oxalate groups. One of these latter stretches out from the stripe, whereas the other two oxalates bridge M$^{\text{III}}$ and M$^{\text{II}}$, forming a peculiar -M$^{\text{II}}$-(M$^{\text{III}}$)$_2$-M$^{\text{II}}$-(M$^{\text{III}}$)$_2$-M$^{\text{II}}$- 1D motif quite unusual. Details over the metal to oxygen bond length of this rather uncommon, at least for Co$^{\text{II}}$ and Ni$^{\text{II}}$, cubic anti-
prismatic coordination are reported on Table 2; notably the Co environment is closer to that of Ni rather than that of Mn in the corresponding Fe\textsubscript{2}M\textsuperscript{II} compounds.

Table 1. Crystallographic data for [Fe\textsubscript{2}Ni(C\textsubscript{2}O\textsubscript{4})\textsubscript{6}][DAMS]\textsubscript{4}·2DAMBA·2H\textsubscript{2}O and [Fe\textsubscript{2}Co(C\textsubscript{2}O\textsubscript{4})\textsubscript{6}][DAMS]\textsubscript{4}·2DAMBA·2H\textsubscript{2}O

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<td>Goodness-of-fit on $F^2$</td>
<td>1.009</td>
<td>1.009</td>
</tr>
<tr>
<td>Final $R$ indices [I&gt;2$\sigma$(I)]</td>
<td>$R_1 = 0.0841$, $wR_2 = 0.1979$</td>
<td>$R_1 = 0.0924$, $wR_2 = 0.2127$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.1626$, $wR_2 = 0.2397$</td>
<td>$R_1 = 0.2095$, $wR_2 = 0.2801$</td>
</tr>
</tbody>
</table>

$R_{int} = \Sigma|F_o^2 - F_c^2| / \Sigma F_o^2$, $R_\sigma = \Sigma\sigma(F_o^2) / \Sigma F_o^2$, $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = (\Sigma(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$
Table 2. \( \text{M}^{\text{II}}-\text{O} \) distances in \([\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}\) compounds structurally characterized by single crystal X-ray diffraction analysis.

<table>
<thead>
<tr>
<th>( \text{M}^{\text{II}} )</th>
<th>( \text{Fe} )</th>
<th>( \text{Fe} )</th>
<th>( \text{Fe} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{M}^{\text{II}} )</td>
<td>( \text{Mn}^{4+} )</td>
<td>( \text{Ni} )</td>
<td>( \text{Co} )</td>
</tr>
<tr>
<td>Bridging oxalate 2</td>
<td>2.592(3)</td>
<td>2.589(6)</td>
<td>2.56(1)</td>
</tr>
<tr>
<td></td>
<td>2.265(3)</td>
<td>2.416(6)</td>
<td>2.39(1)</td>
</tr>
<tr>
<td>Bridging oxalate 3</td>
<td>2.472(3)</td>
<td>2.530(6)</td>
<td>2.52(1)</td>
</tr>
<tr>
<td></td>
<td>2.295(3)</td>
<td>2.451(6)</td>
<td>2.43(1)</td>
</tr>
</tbody>
</table>

Figure 3. (a) View, along the crystallographic \( a \) axis, of the inorganic/organic layer. Grey: Carbon atoms; Red: oxygen atoms; Blue: nitrogen atoms; Green: \( \text{M}^{\text{II}} \) sites; Yellow: \( \text{M}^{\text{III}} \) sites. Hydrogen atoms are not shown, for the sake of clarity. The three independent oxalates (1, 2 and 3) are indicated, as well as the stronger hydrogen bonding connections, that involve the “lateral” oxalate ligands (having two free oxygens), the DAMBA molecules and the water molecules. Weaker C-H-O connections are not represented. Two metal-oxalate stripes, elongated along the direction of the \( c \) crystallographic axis, can be recognized. (b) View, along the crystallographic \( b \) axis, of the layered structure formed by the \([\text{DAMS}^+]\) layers and the inorganic/organic layers. The layers are alternatively charged with positive and negative charges. (c) View of the layered crystal structure along the crystallographic \( c \) axis, showing the packing of two layers and the disposition of the oxalate-based chains in the structure. Hydrogen atoms are omitted for clarity. (d) View, along the \( a \) axis, of the relative organization of the \([\text{DAMS}^+]\) molecules.
As already reported for this family of mixed metal oxalates, each pair of stripes is spaced by ~10 Å and shifted by 1/2 along c, producing a mismatch of the lateral branches, as shown in figure 1a. The volume between the stripes is used to accommodate bridges formed by DAMBA and water molecules. Such 2D layer is held together by medium/strong O-H---O hydrogen bonds (Oxalate---water---DAMBA, water acting as HB donor with O---O distances of about 2.9 Å) and weaker C-H---O hydrogen bonds (DAMBA---oxalate, DAMBA being the donor). This entanglement produces a compact but flexible mixed organic/inorganic layer parallel to (100), where DAMBA acts as a fundamental building block, not just as a spacer.

The mixed inorganic/organic layers are negatively charged, with a surface density of charge of about 0.008 e/Å² (a charge of -4 spread over a surface of ca. 462 Å², corresponding to the (1 0 0) plane). Inside the organic layer, the main inertial axis of the [DAMS+] chromophores is oriented along the direction [0116], thus forming an angle of ca. 22° with the polar axis c, see fig. 1c. The macroscopic polarities of the [DAMS+] molecules in each layer are all parallel one to another (despite having two symmetry independent cations), a necessary condition to generate a large SHG.

The [DAMS+] cations are stacked, spaced by 3.55 Å, with about half a molecule mismatch, see Figure 4. This structural motif, typical of J aggregates, is instrumental to introduce intermolecular cooperative effects into the system and thus create Frenkel excitons, which are particularly effective at producing large second-order NLO responses. Interestingly, two adjacent strata of cations alternate different chain inclinations with respect to the polar axis c (+22° and -22°). The consequent formation of a full organic layer, instead of the piling of just a single chain, allows to host the [DAMS+] chromophores with dipolar moment directions more properly oriented for superior SHG activity.

Figure 4. A view of one organic cationic layer formed by J type arrangement of [DAMS+] molecules. The two independent [DAMS+] molecules are shown in light and dark gray, respectively.
All the members of this new family of compound show the same UV-Vis spectrum in solution and at the solid state. In Figure 5 are reported the spectra of the [Rh₂Ni(C₂O₄)₆][DAMS]·2DAMBA·2H₂O derivative as an example. The solid state UV-Vis spectra is characterized by the superposition of two bands: a broad and strong band centered around 464 nm and a strong, narrow signal at 568 nm. This latter is red-shifted with respect to the absorption band of other [DAMS⁺] salts and should be originated by the presence of a Frenkel exciton, clearly indicating the presence of J aggregates of the [DAMS⁺] chromophore. In acetonitrile all the compounds show absorption spectrum identical to that of [DAMS]I, with an absorption band at 471 nm due to the disruption of the ordered J aggregates by dissolution in a polar organic solvent.

The efficient SHG of this family of mixed hybrid oxalates and therefore also the new N⁰ and Co⁰ derivatives can be rationalized according to the so-called ‘Zyss model’, with the molecular second-order NLO response of [DAMS⁺] ascribed, according to the ‘‘two level model‘‘ to the major internal charge-transfer process (ILCT). When the chromophores are arranged within a crystalline lattice, the total SHG efficiency can be approximated as the sum of the molecular contributions weighted for the orientation of the individual molecular entities with respect to the crystal axes. According to this ‘‘oriented gas” model, the already high SHG efficiency could be further optimized (possibly with efficiency even 10 times larger) if the CT axis of [DAMS⁺] formed an angle of 54° (instead of 22°) with the c-axis. However, engineering such structures is so difficult that at the moment the most interesting feature of this family is that the orientation of [DAMS⁺] chromophores is not significantly modified by introducing different M⁰/M³ pairs. Therefore, all mixed hybrid oxalates of this family show comparable SHG efficiencies, which indicates that the d–d transition of the various metals ions and/or the metal to ligand charge transfer of the inorganic stripes are negligible in comparison to the strong contribution of the [DAMS⁺] to the SHG efficiency.
2.1.2 Magnetic properties

The magnetic properties are given by the presence of magnetic ions embedded in the inorganic network, where the strength of the magnetic interactions between the M\textsuperscript{II} and M\textsuperscript{III} ions can be tuned also by the insertion of diamagnetic M\textsuperscript{II} or M\textsuperscript{III} ions in the bivalent and trivalent sites of the polymeric inorganic “stripes”. While the magnetic coupling is expected to be weak in the compounds containing the diamagnetic Rh\textsuperscript{III} ion, the insertion of the magnetic Cr\textsuperscript{III} and Fe\textsuperscript{III} ions in the polymeric inorganic stripes is expected to potentially lead to interesting magnetic properties of their derivatives. In a previous paper, Cariati et al\textsuperscript{4} reported the study of the magnetic properties of the M\textsuperscript{III}\textsubscript{2}Mn and M\textsuperscript{III}\textsubscript{2}Zn derivatives, performed by the Prof. Gatteschi research group in Firenze, which are summarized in Table 3. These measurements on Mn\textsuperscript{II} and Zn\textsuperscript{II} derivatives show a very interesting tunability of the magnetic ordering, obtained by choosing the proper pair of M\textsuperscript{II}/M\textsuperscript{III} ions. In particular, the interaction between magnetically active Mn\textsuperscript{II} ions is rather weak in combination with the diamagnetic Rh\textsuperscript{III} ions, but it is more relevant if associated with Cr\textsuperscript{III} or Fe\textsuperscript{III} ions (with ferri- or ferromagnetic nature, respectively). The weak antiferromagnetic interactions characterizing compounds Rh\textsubscript{2}Mn, Cr\textsubscript{2}Zn and Fe\textsubscript{2}Zn as well as the stronger magnetic interactions of Cr\textsubscript{2}Mn and Fe\textsubscript{2}Mn reveal the absence of long-range three-dimensional (3D) magnetic ordering and the presence of only moderate intrachain coupling. Therefore such structure is naturally suited to produce inorganic stripes of almost perfect mono-dimensional magnets.

Table 3. Magnetic behavior of the [M\textsuperscript{III}\textsubscript{2}M\textsuperscript{II}(C2O4)6] [DAMS]\textsubscript{4} 2DAMBA 2H2O where M\textsuperscript{II} = Mn, Zn

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coupling</th>
<th>M\textsubscript{sat} at 2K (\mu\textsubscript{B})</th>
<th>Constant Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh\textsubscript{2}Mn</td>
<td>Weak antiferromagnetic</td>
<td>4.04</td>
<td>J = -0.023 ± 0.002K</td>
</tr>
<tr>
<td>Fe\textsubscript{2}Mn</td>
<td>Ferromagnetic</td>
<td>5.03</td>
<td>J = -34.5 ± 0.2K</td>
</tr>
<tr>
<td>Cr\textsubscript{2}Mn</td>
<td>Ferrimagnetic</td>
<td>11.09</td>
<td>J = 3.23 ± 0.04K</td>
</tr>
<tr>
<td>Fe\textsubscript{2}Zn</td>
<td>Weak antiferromagnetic</td>
<td>9.64</td>
<td>J = -1.0 ± 0.1K</td>
</tr>
<tr>
<td>Cr\textsubscript{2}Zn</td>
<td>Weak antiferromagnetic</td>
<td>5.75</td>
<td>J = -0.7 ± 0.1K</td>
</tr>
</tbody>
</table>

In the Rh\textsubscript{2}Ni compound only Ni\textsuperscript{II} ions contribute to the magnetic behavior. The high temperature value of \chi T, 1.14 emu K/ mol at 300 K, is consistent with the presence of isolated high spin Ni\textsuperscript{II} centers (S = 1, g = 2.12), but the interaction between the Ni\textsuperscript{II} centers appears to be surprisingly strong, since the \chi T value almost immediately starts decreasing, decreasing the temperature, as shown in fig. 6a.
Such high magnetic couplings for even well-spaced Ni$^{II}$ centers in chain compounds are already well-documented\textsuperscript{16,17} but, in this case, the phenomenon is particularly relevant, given the long distance between the Ni$^{II}$ ions, separated by one Rh$^{III}$ ion and two bridging oxalate ligands. The observed $\chi T$ decrease is due to antiferromagnetic interactions between the Ni$^{II}$ centers, whose presence is clearly observable when plotting $1/\chi$ versus T (Fig. 6b).

Figure 6. Magnetic behavior of [Rh$_2$Ni(C$_2$O$_4$)$_6$][DAMS]$_4$·2DAMBA·2H$_2$O. (a) Temperature dependence of the product $\chi T$ (circles) together with the fit with equation 2 and the parameters in the text (gray line). The field dependence of the magnetization at 2 K is reported in the inset. (b) Temperature dependence of the inverse of the susceptibility $\chi$ (circles) together with the Curie–Weiss linear regression at high temperatures (dark gray line) and the fitting of the experimental data with the $S = 1$ chain model of equation 2 (light gray curve).

Linear fitting of the data above 150 K afforded not only very good agreement (R = 0.9991) to a Curie–Weiss behavior ($\chi = C/(T-\theta)$) with $C = 0.74 \pm 0.01$ and $\theta = -57 \pm 1$ K, but also surprisingly strong antiferromagnetic interactions along the chain since measurement of the magnetization as a function of the field at 2 K, reported in the inset of Fig. 6a, shows the effect of such strong interactions, which the field is incapable of completely overcoming. The experimental data has been fitted with a Heisenberg chain model\textsuperscript{17}, using a Hamiltonian $\mathcal{H}$ of the form:

$$\mathcal{H} = -\sum_{i=1}^{N} (JS_i S_{i+1} + \mu_B S_i g H)$$

Eq. (1)

the summation over the $i$ index runs all over the $N$ chain sites, being $J$ the exchange interaction, $S_i$ the spin coordinates at the $i^{th}$ site of the chain, $g$ the Landé factor, $\mu_B$ the Bohr magneton and $H$ the externally applied magnetic field. The theoretical background for classical $S = 1$ chains with antiferromagnetic interactions has already been developed\textsuperscript{15}: experimental data could be fitted by the expression:

$$\chi T = \frac{N_{Av} g^2 \mu_B^2}{k_B} \frac{2 + 0.0194x + 0.777x^2}{3 + 4.346x + 3.232x^2 + 5.834x^3}$$

Eq.(2)
in which $N_A$ is Avogadro’s number, $\mu_B$ the Bohr magneton, $k_B$ Boltzmann’s constant and $J$ the magnetic coupling constant. Very good agreement ($R^2 = 0.9989$) is obtained for $J = -42 \pm 1$ K, and $g = 2.12 \pm 0.01$.

The low-temperature experimental data show a slight discrepancy with this approach as the height of the peak experimentally observed in the $1/\chi$ versus $T$ plot is not quantitatively reproduced, while the peak temperature is accurately calculated (Fig.6). This slight discrepancy in the low-temperature regime can be due to the external magnetic field used in the measurement, as equation (2) is strictly valid only for zero field, but it could also be induced by the onset of more complex physical phenomena.

The dramatic effect of the substitution of the diamagnetic Rh$^{III}$ ion by the Cr$^{III}$ magnetic center is clear in Figure 7, where the temperature dependence of its $\chi T$ curve is reported. The high temperature value of $\chi T$ (4.72 emu K/mol at 300 K) is in good agreement with both the crystal structure and the theoretical value calculated considering the presence of two Cr$^{III}$, $S = 3/2$, and one Ni$^{II}$ ions in every monomeric unit of the polymeric chain of an inorganic “stripe”. Unexpectedly, the $\chi T$ product smoothly increases as the temperature is lowered, indicating the presence of very weak ferromagnetic interactions.

![Figure 7. Magnetic behavior of $[\text{Cr}_2\text{Ni(C}_2\text{O}_4)_6][\text{DAMS}]_{2\text{DAMBA}\cdot 2\text{H}_2\text{O}}$. (a) Temperature dependence of the product $\chi T$ (circles). The field dependence of the magnetization at 2.5 K is reported in the inset (b) Temperature dependence of the inverse of the susceptibility $\chi$ (circles) together with the Curie–Weiss linear regression at high temperatures (dark gray line).](image)

Only at rather low-temperatures, around 50 K, the $\chi T$ product starts rising sharply, leading to a peak value of 4.86 emu K/mol at 7 K. This behavior is rather typical of chain structures, which often display a peak in the susceptibility due to the growth of the correlation length along the chain. A similar behavior was reported for the analogue containing the Mn$^{II}$ ion in the chain$^4$. The peak shall not be ascribed to the transition to three-dimensional long-range order, as interchain interactions are efficiently shielded by the organic chromophores surrounding the chains. The intrachain magnetic interactions are thus surprisingly much weaker than those observed in Rh$_2$Ni compound between the Ni$^{III}$ centers alone. A fit of the
high temperature data with the Curie–Weiss law, with excellent agreement (R = 0.99991) down to 40 K, gave an estimate of the strength of the interactions of \( \theta = 1.21 \pm 0.05 \) K. This very low value is surprising because of two reasons: i) it shows an antiferromagnetic coupling between the Ni\(^{II}\) and Cr\(^{III}\) centers lower than the coupling between Ni\(^{II}\) ions in the Rh\(_2\)Ni derivative; ii) usually Cr\(^{III}\)–Ni\(^{II}\) interactions mediated by oxalate bridges are known to be ferromagnetic\(^\text{18}\). Such unexpected magnetic behavior can possibly rise from a competition between Ni\(^{II}\)–Ni\(^{II}\) antiferromagnetic interactions and Cr\(^{III}\)–Ni\(^{II}\) ferromagnetic ones that can lead to the stabilization of very complex magnetic states. Magnetization versus field measurements has been performed at 2.5 K and it gives a saturation value of 6 \( \mu B \) (inset Figure 7a). Saturation is reached at much lower field values than for the Rh\(_2\)Ni compound, confirming the presence of a complex interaction pathway competing with the strong Ni\(^{II}\)–Ni\(^{II}\) coupling. The saturation could indicate the stabilization, with the field, of a complex magnetic state of the form reported in Figure 8.

![Figure 8. Spin orientation of the magnetic ions in the compound Cr\(_2\)Ni](image)

In this magnetic configuration the Ni ions are antiferromagnetically coupled and thus give no neat contribution to the magnetization, while each pair of Cr\(^{III}\) ions interacts with two oppositely oriented Ni\(^{II}\) centers, thus giving a null contribution to the energy of the system. In the same time, all Cr\(^{III}\) ions can orient with the field, thus minimizing the Zeeman contribution to the Hamiltonian and explaining the observed saturation value.

The Fe\(^{III}\)-containing material shows again a temperature dependence of the \( \chi T \) product (Figure 9) as a clear indication of a one-dimensional behavior with no appreciable three-dimensional long-range ordering. At high temperature the \( \chi T \) value (9.18 emu K/mol at 300 K) is slightly lower than expected for one Ni\(^{II}\) ion and two high spin \( S = 5/2 \) Fe\(^{III}\) ions per repeating unit.

Contrary to the Cr\(^{III}\) derivative, the \( \chi T \) curve decreases steadily on lowering the temperature, reaching a minimum at 32 K (\( \chi T \) being 8.65 emu K/mol). Then a marked increase of the susceptibility gives rise to a small peak at 10.5 K (\( \chi T \) being 8.8 emu K/mol) in \( H = 10 \) kOe. The peak is again typical of a ferrimagnetic system. A similar feature, at roughly the same temperature, was reported for the analogue containing the Mn\(^{II}\) ion\(^4\), where Zero-Field-Cooled and Field-Cooled measurements revealed no sign of irreversibility, thus further confirming the absence of long-range 3D ordering due to interchain interactions.
The magnetic behavior of the Ni derivative is dominated by the presence of strong Ni$^{II}$-Ni$^{II}$ antiferromagnetic next-nearest-neighbour couplings that becomes competitive with Cr$^{III}$-Ni$^{II}$ or Fe$^{III}$-Ni$^{II}$ ferromagnetic interactions. This behaviour has not been observed in the Co$^{II}$ derivatives which magnetic properties are reported following the same order I followed presenting the Ni$^{II}$ derivative. It’s important to point out that the Co$^{II}$ ion is well known to not follow the Curie behaviour and, as a consequence, the M$^{III}$$_2$Co compounds show some peculiar properties. As expected, the diamagnetic Rh$^{III}$ centers, [Rh$_2$Co(C$_2$O$_4$)$_6$] [DAMS]$_4$[DAMBA]$_2$.2H$_2$O is characterized only by weak magnetic interactions inside the chain, mainly attributable to uncoupled Co$^{II}$ centres. This is in itself an interesting output, since the octacoordinated geometry is very rare in Co$^{II}$ compounds and no report on the magnetic behaviour of the Co$^{II}$ ion in this environment is present in literature.

The magnetic behaviour of this compound is more resembling to that of the Rh$_2$Mn or the Rh$_2$Ni compounds, in fact, the $\chi T$ vs T value (figure 10) measured at room temperature (3.1 emu K mol$^{-1}$) is much higher than the one of the Ni derivative (1.14 emu K mol$^{-1}$) but closer to the one of the Mn$^{II}$ compound (4.33 emu K mol$^{-1}$).
Antiferromagnetic exchange interactions can be excluded by taking into account the magnetization curve as a function of field, which tends to saturate at a value in agreement with an effective $S=1/2$ and $g_{\text{ave}} = 4.3$ ($M = 2.1 \, \mu_B$ at 6 T and 2 K, inset of figure 10). Furthermore, these results suggest that the magnetic behaviour of this kind of octacoordinated Co$^{II}$ is more resembling to that of octahedral Co$^{II}$ (with largely unquenched orbital contribution) than to that of tetrahedral Co$^{II}$, characterized by an orbitally singlet ground state. The magnetic properties change dramatically by substitution of Rh$^{III}$ with Cr$^{III}$. The $\chi T$ vs T value for Cr$_2$Co derivative at room temperature (6.71 emu K mol$^{-1}$) coincides quite well with the sum of the values of $\chi T$ found for Rh$_2$Co (3.1 emu K mol$^{-1}$) and Cr$_2$Zn compounds (3.68 emu K mol$^{-1}$), suggesting the absence at this temperature of a magnetic interaction between adjacent paramagnetic centres such as Co$^{II}$ and Cr$^{III}$. In accordance the $\chi T$ curve (Figure 11) slowly decrease on cooling down to 200 K, in a way parallel with the decrease observed for the Rh$_2$Co derivative. The decrease of $\chi T$ should thus be attributed to single ion effects of Co$^{II}$ ions, at least down to 200 K, and that exchange coupling interactions are not effective in this temperature range. At lower temperatures, the plot of $(\chi T_{\text{Cr}_2\text{Co}} - \chi T_{\text{Rh}_2\text{Co}})$ vs T, which steadily increases with temperature, clearly testifies the presence of ferromagnetic interactions, which results in a $\chi T$ vs T curve passing through a quite sharp maximum at 4 K (7.9 emu K mol$^{-1}$).
Figure 11. Temperature dependence of $\chi T$ product for Cr$^{III}$Co$^{II}$ (left scale, full squares) and of $(\chi_{T_{C2CO}} - \chi_{T_{Rh2Co}})$ (right scale, empty circles). In the inset the field dependent magnetization at 2 K (upper curve) and 4.5 K (lower curve) for Cr$^{III}$Co$^{II}$ is reported.

The achievement of a ferromagnetic behaviour of the Cr$^{III}$/Co$^{II}$ chain is confirmed by the low temperature field dependent magnetization curves (inset of Figure 11), which attains a saturation value of 8 $\mu_B$, in agreement with what expected for a full “spin-up” configuration on the basis of the saturation values observed for Cr$_2$Zn and Rh$_2$Co derivatives. The presence of a ferromagnetic interaction between Cr$^{III}$ and Co$^{II}$ centers at low temperatures is in agreement with what reported for simple dinuclear and trinuclear cluster$^{23}$. It is however to be noticed that both the relatively low maximum value of $\chi T$ and the shape of the M vs H curve, attaining saturation only at quite high fields, points to exchange interactions weaker than those reported for other Cr$^{III}$-Co$^{II}$ mixed oxalates$^{23}$. This behaviour can also be due to the competing effects of weak antiferromagnetic interactions between Cr$^{III}$ ions, which were visible below 10 K in the Cr$_2$Zn derivative. The relative weakness of the exchange coupling interaction, coupled to the good isolation provided by the organic layer, responsible for the second order NLO activity, results in the absence of both the magnetic long range order and of the single-chain magnet behaviour.

Figure 12. Temperature dependence of $\chi T$ product at 1 KOe (full squares) and 10 KOe (empty triangles) for Fe$_2$Co. In the inset the field dependent magnetization at 2 K is reported.
Much more interesting is the magnetic behaviour of the Fe$_2$Co derivative which experimental value of $\chi T$ at room temperature is 9.8 emu K mol$^{-1}$, lower than that expected assuming the three spins to be uncoupled and considering the experimental values observed for Rh$_2$Co and Fe$_2$Zn. This suggests the presence of sizeable antiferromagnetic interactions, already visible at this temperature, as confirmed by the marked decrease of $\chi T$ by lowering temperature (Figure 12). This behaviour cannot be attributed to simple ligand field effects of Co$^{ll}$ centers, since the corresponding, isostructural, Rh$_2$Co derivative shows a less marked temperature dependence of $\chi T$ in the same range of temperatures. On further lowering the temperature $\chi T$ passes through a minimum at 30 K (8.3 emu K mol$^{-1}$) and then starts to increase again. This behaviour is reminiscent of a ferrimagnetic like structure, which indicates that antiferromagnetic interactions result in a non compensation of the spins and suggesting that they are active between Fe$^{lll}$ and Co$^{ll}$ ions. On further lowering the temperature a maximum in $\chi T$, which is field dependent due to saturation effects, is observed (9.8 emu K mol$^{-1}$ at 4.2 K for H $\leq$ 1 KOe). The antiparallel orientation of the spin on Co$^{ll}$ and Fe$^{lll}$ sub lattices due to the dominating antiferromagnetic interactions is confirmed by the field dependent magnetization curve recorded at 2 K (inset of Figure 12), which saturates at about 8 $\mu_B$. As a whole the observed behaviour is strongly resembling that observed for the Fe$_2$Mn derivative$^4$ and agrees with expectations of dominant antiferromagnetic interactions between Co$^{ll}$ and Fe$^{lll}$ mediated by oxalate bridges$^{24}$. The $ac$ susceptibility measured at zero field allows to rule out any long range order: indeed, the imaginary contribution, which shows up below 4 K, is frequency dependent and should thus be attributed to dynamic effects (Figure 13). The analysis of the frequency dependence of $\chi''$ maximum by the Arrhenius law, assuming that at the temperature of the maximum $\tau = (2\pi\nu)^{-1}$, yields as best fit values $\tau_0 = 8.6*10^{11}$ s and $\Delta E = 21.4$ K (inset of Figure 13). The physically reasonable values of $\tau_0$ and $\Delta E$, even if obtained in a somewhat restricted range of frequencies, lead to rule out the possibility that the system is a spin glass and suggest that Fe$_2$Co is behaving as a SCM at low temperature. It is however to be noted that the ratio between real ($\chi'$) and imaginary ($\chi''$) components of the susceptibility is very large, suggesting either a broad distribution of relaxation times, which would also explain the broadness of the observed maxima in $\chi''$ (Figure 12), or that only a fraction of the chains is showing slow relaxation of the magnetization$^{25}$. This may also explain the somehow small value of the barrier $\Delta E$ to the reversal of the magnetization, compared to the expectations based on static magnetic measurements. Indeed, in SCM this parameter is related to the strength of the exchange interaction by the relation $\Delta E = 4 J/kT^{26}$. Thus, the relatively small $\Delta E$ value
obtained here would point out a relatively weak magnetic interaction (ca. 5 K), in contrast with the $\chi T$ vs $T$ data, indicating sizeable exchange magnetic interactions are active between Fe$^{III}$ and Co$^{II}$ centres even at room temperature.

Figure 13. Temperature dependence of the in-phase (upper) and out-of phase (lower) magnetic susceptibility at different frequencies (5-25000 Hz). In the inset of the lower panel the corresponding Arrhenius plot with best fit line is reported.
2.2 Stabilization through p-dimethylaminobenzaldehyde of a new NLO active phase of [trans-4-(4-dimethylaminostyryl)-1-methylpiridinium] iodide

As already introduced in Chapter 1, the quadratic NLO effects of bulky materials are related to the molecular hyperpolarizability (\(\beta\)) of the chromophores as well as on their packing. In particular, a *condition si ne qua non* for a second order NLO response is the non-centrosymmetry of the crystal structure\(^{27,28,14b}\). However, an optimal orientation of the molecules, assumed as non-interacting, is also required to elicit highly efficient SHG.\(^{28b,29}\). On the other hand, less widely established are the effects of interchromophoric interactions on the overall NLO response.

Although engineering a non-centrosymmetric crystallization and a proper chromophore orientation is not an easy task, several approaches\(^{28a,30,9}\) have been suggested to fulfil these requirements such as the use of salts for which Coulombic interactions could overwhelm the unfavourable dipole-dipole interactions and allow an asymmetric assembly of polar ionic moieties has been suggested by Meredith\(^{28a}\) and successfully applied by Marder et al.\(^{9}\) who reported one of the most active (1000 times urea) second harmonic generator organic crystalline materials ever reported: [trans-4-(4-dimethylaminostyryl)-1-methylpyridininum][p-toluenesulfonate], [DAMS][p-TS], (also known as [DAST]). Since then, many studies concerning the combination of the [DAMS\(^+\)] cation with different counterions have been reported with the aim of finding new acentric crystalline compounds showing high SHG signal with a comparable intensity to that of DAST. Studied counterions are both organic, such the tosylate-like negative ions reported by Yang et al., or an inorganic negatively-charged scaffold as reported in the section 2.1.

During the optimization of the synthesis of the phases \(\text{M}^{\text{III}}_2\text{M}^{\text{II}}(\text{C}_2\text{O}_4)_6\) [DAMS]_4[DAMBA]_2·2H\(_2\)O (\(\text{M}^{\text{III}} = \text{Rh, Fe, Cr}; \text{M}^{\text{II}} = \text{Mn, Zn, Ni, Co}; \text{DAMBA} = p\)-N\((\text{CH}_3)_2\text{C}_6\text{H}_4\text{CHO})), a new highly NLO active co-crystal of [DAMS\(^+\)]I and DAMBA was obtained. Its electronic and optical properties are investigated by DFT and TDDFT calculations with the aim of better understand how they are related to the chromophores assembly.

2.2.1 Synthesis and characterization of [DAMSI] \(\frac{1}{3}\)[DAMBA] \(\frac{1}{2}\) \(\text{H}_2\text{O}\)

The best general synthetic way to obtain compounds of the family of mixed oxalates of formula \(\text{M}^{\text{III}}_2\text{M}^{\text{II}}(\text{C}_2\text{O}_4)_6\) [DAMS]_4[DAMBA]_2·2H\(_2\)O, reported in section 2.1, consists in a two step procedure with the formation of the intermediate phase \(\text{AM}^{\text{IV}}/\text{M}^{\text{III}}\) which is then converted into the desired compound by dissolution in \(\text{H}_2\text{O}\) and addition with DAMBA.
During the optimization of the synthetic procedure an unknown compound with an interesting SHG has often isolated. The X-Ray Powder Diffraction (XRPD) pattern is completely different from the ones reported for the mixed metal oxalate systems and the elemental analysis pointed out the lack of both M^{III} and M^{II}. In order to isolated the new material, the synthesis has been repeated without the M^{III} and M^{II} salts and the pure compound can be prepared by refluxing for 1 hour 30 minutes a MeOH/H_{2}O (1/1) solution of [DAMS]I /DAMBA in a 1/4 molar ratio. A lot of efforts have been spent to obtain crystals suitable for XRD analysis but the quality of the samples was always very poor and therefore the diffraction pattern quite scarce. Nevertheless, a structural model could be tentatively formulated and refined (crystallographic data reported in Table 4). The compound crystallizes in a pseudo-orthorhombic symmetry. However, the most reliable lattice is actually monoclinic, in the space group Cc, with two almost equivalent twinned subcomponents (due to β angle being very close to 90°). From the structure solution, the [DAMS\textsuperscript{+}] and I\textsuperscript{-} ions can be clearly identified, whereas uncertainties remain on the actual orientation of the included DAMBA, which presence is inferred from NMR data and from the analysis of the voids in the crystal structure. In fact, by comparison of the integral values of the \textsuperscript{1}H-NMR peaks, the ratio [DAMS\textsuperscript{+}]/DAMBA in the structure is found to be equal to about 1/0.3.

The [DAMS\textsuperscript{+}] chromophores stack in columns with a separation between their mean planes of ca. 3.4 Å, in agreement with what is typically found in other salts containing the same chromophore or some analogues\textsuperscript{3,4}. As usual, the stacking is accompanied by a shift of half a molecule along the direction of the intramolecular charge transfer axis. This produces an angle between the direction of the column and the [DAMS\textsuperscript{+}] mean plane of ca. 34°. Interestingly, two adjacent columns of [DAMS\textsuperscript{+}] are related by a glide plane (c), which produces a special coupling between the chromophores (see Figure 14) in a fishbone-like arrangement. Each molecule of [DAMS\textsuperscript{+}] is surrounded by the two stacked [DAMS\textsuperscript{+}] partners (in the typical J-aggregation mode) and two [DAMS\textsuperscript{+}] belonging to the mirror symmetric column, with interactions through the methyls of the dimethylamino groups (see Figure 14). The N-methyl groups, instead, are directed toward the anions which also are segregated in columns. Anions and cations form a layer in the (100) plane together with an apparently empty volume, very likely occupied by DAMBA (crystallographically disordered). Because of the C centering of the lattice, the next layer (occurring at ± a/2) is shifted by [0.0, 0.5, 0.5] and therefore along a axis each [DAMS\textsuperscript{+}] column is surrounded by I\textsuperscript{-} and DAMBA columns. The glide plane generates a
macroscopic polarity, because all $[\text{DAMS}^+]$ have the same dipole component along the $c$ axis, which is of course very important for the NLO properties.

### Table 4. Crystal data and structure refinement for $[\text{DAMSI}]^{\frac{1}{3}} [\text{DAMBA}]^{\frac{1}{2}} \text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>Empirical formula$^\text{(a)}$</th>
<th>$\text{C}<em>{16}\text{H}</em>{19}\text{IN}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight$^\text{(a)}$</td>
<td>366.2</td>
</tr>
<tr>
<td>Temperature</td>
<td>298(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, Cc</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 8.777(2)$ Å</td>
</tr>
<tr>
<td></td>
<td>$b = 34.912(7)$ Å</td>
</tr>
<tr>
<td></td>
<td>$c = 6.280(1)$ Å</td>
</tr>
<tr>
<td></td>
<td>$\beta = 90.459(2)$ °</td>
</tr>
<tr>
<td>Volume</td>
<td>1924(1) Å$^3$</td>
</tr>
<tr>
<td>$Z$, Calculated density$^\text{(a)}$</td>
<td>4, 1.264 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient$^\text{(a)}$</td>
<td>1.657 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$ $^\text{(a)}$</td>
<td>728</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.25 x 0.08 x 0.05 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.2 to 26.4 °</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>7486 / 3727</td>
</tr>
<tr>
<td>$R$(int)</td>
<td>0.0226</td>
</tr>
<tr>
<td>$R_\sigma$</td>
<td>0.0370</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.92, 0.79</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3727/ 2 / 58</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.15</td>
</tr>
<tr>
<td>Final R indices $[I&gt;2\sigma(I)]$</td>
<td>$R_1 = 0.0564$, $wR_2 = 0.1766$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.0696$, $wR_2 = 0.1859$</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.87 and -0.57 e.A$^{-3}$</td>
</tr>
</tbody>
</table>

$$R_{\text{int}} = \frac{\Sigma |F_o|^2 - |F_{\text{mean}}|^2}{\Sigma |F_o|^2}; \ R_\sigma = \Sigma \sigma(F_o)^2/\Sigma F_o^2; \ R_1 = \Sigma |F_o|^2 - |F_c|^2/\Sigma |F_o|^2; \ wR_2 = (\Sigma (F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$$

$[a]$ The disordered $p$-dimethylaminobenzaldehyde is not considered in the formula, in the weight, in the absorption coefficient and in the sum of electrons.
Figure 14. Left, a view of the layers formed in [DAMSI] $\frac{1}{3}$ [DAMBA] $\frac{1}{2}$ H$_2$O by [DAMS$^+$], I$^-$ and DAMBA (the latter is represented only by an aromatic ring which was included in the voids calculated from the refinement of a model including only the two ions). The central [DAMS$^+$] (in red) is stacked along a column with two other cations (in blue). Two molecules (purple and violet) belonging to the adjacent column (related with a glide plane) are somewhat close to the red cation. On the other side, there are I$^-$ anions and DAMBA. Right: a view along (0 0 1), showing the voids (in blue) available for DAMBA molecules in the crystal.

It is important to stress that the motif described above is different from the pure [DAMS]I$^{31}$, which is centrosymmetric and does not show stacking of the chromophores hence J aggregation, and from the one reported for the organic layer in to the $\text{M}^{[\text{III}]}_2\text{M}^{[\text{II}]}(\text{C}_2\text{O}_4)_6[\text{DAMS}]_4[\text{DAMBA}]_2\cdot\text{2H}_2\text{O}$, where the [DAMS$^+$] cations arrange as J-type aggregates. Furthermore, the fishbone-like motif obtained by a double column is also quite unique, at least for this kind of chromophores.

Interestingly, while slipped [DAMS$^+$] chromophores stacked in columns nicely reproduce the assembly pattern of classical J-type aggregates, the solid state electronic absorption spectrum (Figure 15) show a broad band centred at 490 nm and only a very weak shoulder at 550 nm which could not be used to establish the presence of J-aggregation.

Figure 15. UV-vis absorption spectrum of [DAMSI] $\frac{1}{3}$[DAMBA] $\frac{1}{2}$ H$_2$O in KBr

The non linear optical properties has been studied on powdered batches graded using standard sieves into sizes ranging from 20 to 210 µm and their SHG activities are measured by the Kurtz-Perry powder method at the non-resonant wavelength of 1907 nm. On the whole,
[DAMSI]$^{1/3}$[DAMBA]$^{1/2}$H$_2$O behaves as a phase-matchable material, its SHG efficiency increasing, with respect to the particle dimensions, up to a constant value. Under our experimental conditions, measurements on powders 105 to 210 µm in size indicate a SHG signal equal to that of DAST (SHG 1000 times that of urea$^9$) used as reference.

2.2.2 Theoretical investigation on [DAMSI]$^{1/3}$[DAMBA]$^{1/2}$H$_2$O

The theoretical investigation of the electronic and optical properties of this new compound has been performed by Simona Fantacci’s group at the University of Perugia. TDDFT calculations on realistic models of [DAMSI]$^{1/3}$[DAMBA]$^{1/2}$H$_2$O have been performed in order to unravel the relationship between its peculiar structural motif and the observed spectroscopical properties. According to the results of the single crystal X-ray analysis, [DAMS$^+$] aggregates have been considered as arranged in a fishbone-like structural motif where two adjacent columns of stacked [DAMS$^+$] chromophores are facing with the dimethylamino groups. The standalone [DAMS$^+$] optimized geometry is found in good agreement compared with available X-ray data obtained for several salts containing the [DAMS$^+$] cation$^{11}$. On the basis of these considerations, hybrid models based on calculated and X-ray data, where the [DAMS$^+$] optimized molecular structure are oriented along the same inertial axes found in the experimental arrangement have also been defined. The interchromophoric distance within the [DAMS$^+$] column, d$_z$, and the slippage along the intramolecular charge transfer axis x (d$_x$) are fixed at the average crystallographic value, which are respectively 3.5 and 5.0 Å. The α angle between the mean planes of two chromophores lying on two adjacent columns is kept at 70°, which is the average crystallographic angle, see figure 16. The smallest fishbone-like unit reproducing the essential features of the [DAMSI]$^{1/3}$[DAMBA]$^{1/2}$H$_2$O structure is therefore constituted by four [DAMS$^+$] chromophores arranged in two adjacent columns, hereafter labelled as 1. Notably, two [DAMS$^+$] chromophores stacked on one column of 1 correspond to the dimeric [DAMS$^+$] slipped configuration, whose calculated absorption spectrum nicely reproduces the typical features of J-aggregation. Then, the model has been extended considering eight [DAMS$^+$] chromophore units in the same fish-bone like arrangement, hereafter we call this model 2, and, since X-ray data suggest that the next layer of fishbone-like [DAMS$^+$] cations is shifted with respect to the first one. A different model, hereafter 3, is also considered; it is constituted by eight chromophores arranged in two couple of adjacent columns, with a displacement along the y axis between the two cationic layers of 3.0 Å, as shown in the X-ray packing (Figure 16).
Figure 16. Fishbone-like aggregate models 1 and 3, respectively constituted by four [DAMS\(^+\)] chromophores units arranged in two adjacent columns and by eight units arranged in two couple of adjacent columns. The interchromophoric distance \(d_z\) is 3.5 Å, the slippage distance along the x and y axes are 5.0 Å (\(d_x\)) and 3.0 Å (\(d_y\)), respectively, while the \(\alpha\) angle between the columns is 70°.

The counterion effect on the absorption spectra is simulated including negative charges in the TDDFT calculations on the monomer and dimer and fishbone like tetramer 1. It is quite a difficult task to evaluate the electric field originated by the crystal packing so the optical properties of the investigated species are considered mainly determined by the [DAMS\(^+\)] chromophores and their mutual interactions.

2.2.2.a Electronic and optical properties

A previous analysis of the TDDFT excitation eigenvectors for some dimeric [DAMS\(^+\)] chromophores aggregates\(^4\), shows that the absorption spectrum of the slipped conformation, corresponding to a J-type aggregation, is characterized by two interchromophoric transitions at low energy (I at 1.88 eV and II at 2.18 eV with oscillator strength of 0.037 and 0.123, respectively) followed by an intense charge-transfer transition (III at 2.77 eV) of intrachromophoric character, which corresponds to the monomeric one. Because of the increased number of chromophore units in model 1, an increased number of electronic transitions are identified in its calculated absorption spectrum, which are formally collected into three groups labeled as I, II, III depending on their character. In particular it’s possible to distinguish intrachromophoric and interchromophoric transitions, where the latter can involve chromophores stacked on the same columns (which hereafter are referred as “proper” interchromophoric transitions) or chromophores lying on two adjacent columns (which hereafter are referred as intercolumn transitions), see Figure 17.
Figure 17. Schematic representation of the molecular orbitals involved in transitions groups I (red), II (yellow) and III (cyan) for model 1

It is worth noting that this kind of transition represents a peculiar feature of the absorption spectrum of this new phase to be related to the unique stacking of [DAMS⁺] units in the fishbone-like motif. In table 6 the most relevant transitions (f > 0.02) of 1 have been summarized.

Group I transitions, S₁-S₁₀ in table 6, are assigned as charge-transfer interchromophoric excitations from molecular orbitals localized on the -N(Me)₂ donor group to states mainly localized on the methylpyridinium acceptor moiety of different [DAMS⁺] units of the same column, see figure 17. Within this group of interchromophore transitions, S₉, calculated at 2.46 eV with a high intensity (f=0.27), shows both an intrachromophoric contribution, responsible for its strong oscillator strength, and a partial “intercolumn” character due to the (12% H-1→L+3) contributions. Such intercolumn contribution is characteristic of the fishbone-like arrangement present in the [DAMSI]¹/₄[DAMBA]¹/₂H₂O phase, and is probably the origin of the spectral blue-shift observed in this phase with respect to the conventional J-aggregates (i.e. 504 nm vs. 569 nm).

Transitions S₁₁-S₁₃, group II, show intercolumn character involving essentially the following excitations: (H-3→L+2), (H-1→L+3), (H-2→L+3) and (H-3→L+1) in which the initial and final states orbitals are localized on different columns, see Figure 17.
Table 6. Excitation energy (E), oscillator strength (f) and composition of the lowest singlet excited states (Sn) with f > 0.02 for the fishbone 1 aggregate computed at the B3LYP(6-31G(d,p) level of theory

<table>
<thead>
<tr>
<th></th>
<th>E (eV)</th>
<th>wl (nm)</th>
<th>f</th>
<th>MOs</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_1</td>
<td>1.7028</td>
<td>728</td>
<td>0.0248</td>
<td>95%(H→L)</td>
</tr>
<tr>
<td>S_5</td>
<td>2.1305</td>
<td>582</td>
<td>0.0385</td>
<td>77%(H-1→L+1)+12%(H-2→L+1)</td>
</tr>
<tr>
<td>S_6</td>
<td>2.1885</td>
<td>566</td>
<td>0.0783</td>
<td>52%(H-2→L+2)+40%(H-1→L+2)</td>
</tr>
<tr>
<td>S_8</td>
<td>2.3643</td>
<td>524</td>
<td>0.0333</td>
<td>84%(H-1→L+3)+8%(H→L+3)+4%(H-3→L+3)</td>
</tr>
<tr>
<td>S_9</td>
<td>2.4593</td>
<td>504</td>
<td>0.2661</td>
<td>34%(H-3→L+3)+34%(H→L+3)+12%(H-1→L+3)</td>
</tr>
<tr>
<td>S_10</td>
<td>2.5757</td>
<td>481</td>
<td>0.0499</td>
<td>22%(H-2→L+2)+20%(H3→L+3)+17%(H-3→L+1)+17%(H-3→L+2)</td>
</tr>
<tr>
<td>S_11</td>
<td>2.6182</td>
<td>473</td>
<td>0.0533</td>
<td>46%(H-3→L+2)+18%(H-3→L+1)+9%(H-3→L+3) +5%(H→L+3)</td>
</tr>
<tr>
<td>S_12</td>
<td>2.6273</td>
<td>472</td>
<td>0.2313</td>
<td>29%(H-3→L+2)+19%(H-1→L+3)+16%(H-2→L+3) +10%(H-3→L+1)+6%(H-2→L+2)</td>
</tr>
<tr>
<td>S_13</td>
<td>2.6727</td>
<td>464</td>
<td>0.0542</td>
<td>90%(H-2→L+3)</td>
</tr>
<tr>
<td>S_15</td>
<td>2.7174</td>
<td>456</td>
<td>1.1366</td>
<td>23%(H-3→L+3)+20%(H-2→L+1)+12%(H→L+3) +5%(H-3→L)+5%(H-2→L+2)</td>
</tr>
<tr>
<td>S_16</td>
<td>2.9012</td>
<td>427</td>
<td>2.8467</td>
<td>19%(H-3→L)+12%(H-2→L+1)+11%(H-2→L+2) +9%(H-1→L+2)+6%(H-3→L+3)+6%(H→L+3)</td>
</tr>
</tbody>
</table>

\(S_{15}\) and \(S_{16}\) transitions of group III, involves two transitions in Table 6, are computed at high energies (i.e. 2.71 and 2.90 eV) with a very strong oscillator strength (1.14 and 2.85, respectively). These transitions are related to the main absorption band of the monomer, computed at 2.70 eV, and have essentially intrachromophoric character. However, transition \(S_{15}\) shows still a sizable contribution from an interchromophoric excitation (H-3→L+3), that reflects into a lower intensity and a red-shift with respect to \(S_{16}\) transition. This latter transition, of pure intrachromophoric character, corresponds to the absorption maximum of model 1 spectrum and results blue-shifted with respect to the absorption maximum of the experimental broad band.

The TDDFT analysis therefore allows to assign the transitions constituting the absorption spectrum of 1, that represents the basic unit model for the fishbone-like architecture of [DAMS^+] chromophores in [DAMSI]^{1/3}[DAMBA]^{1/2}H_2O.
In Figure 18, the computed spectra of monomeric [DAMS$^+$], dimeric slipped conformation and fishbone-like aggregates 1, 2 (four and eight units, respectively) and 3 (eight units arranged in two fishbone-like motifs) are compared. The calculated absorption spectrum of 1 shows a very intense transition at 2.90 eV of pure intrachromophoric character and a series of less intense hybrid and pure interchromophoric transitions, whose intensity should increase by increasing the number of the [DAMS$^+$] units. Some interchromophoric charge-transfer transitions at low energy (group I), involving stacked chromophores on the same column, can be recognize as the characteristic feature of the J-type aggregation. However, the fishbone-like architecture, where two adjacent columns of slipped chromophores are faced, gives rise to an additional series of unique transitions (group II), with interchromophoric charge-transfer character between chromophores lying on two adjacent columns. These intercolumn transitions, with an oscillator strength comparable to that of the typical J-band transitions, have energies lying in between the main absorption band and the typical J-band.

The absorption spectrum of model 2, is originated by the same groups of transitions in similar energy regions, computed for model 1. The main differences are a broadening of the absorption band towards lower energies and an intensification of the interchromophoric transitions in the 470-500 nm spectral region between the main absorption band and the typical J-peak, consistently with the experimental shape of the spectrum with a single broad band.

In order to evaluate the effect of the interaction among groups of different fishbone-like layers on the absorption spectrum, TDDFT calculations on model 3 as also been performed. The most evident effect of the presence of a second fishbone-like layer of [DAMS$^+$] chromophores, is to further broaden the main absorption band. Indeed, the analysis of the
TDDFT eigenvectors shows, besides the presence of interchromophoric (group I) and intrachromophoric (group III) character transitions, the presence of numerous transitions with intercolumn (group II) character involving chromophores stacked on all the four columns. Finally, we computed two transitions with intrachromophoric character (group III), very similar to those computed for 1, both in terms of energy and oscillator strength (2.91 and 2.94 eV with $f = 1.02$ and 3.05, respectively).

According to the computational results, the experimental spectrum reported in figure 15 can be regarded as the superposition of three characteristic bands with different character, i.e., in order of increasing energy, interchromophoric, intercolumn and intrachromophoric. The absorption spectrum of $[\text{DAMSI}]^{1/3}[\text{DAMBA}]^{1/2}\text{H}_2\text{O}$ still contains the typical absorption band of J-aggregates with interchromophoric character (group I) red-shifted with respect to the main intrachromophoric absorption band, (group III) of the monomeric $[\text{DAMS}^+]$, but the J-peak is somewhat hidden by the presence of various transitions with intercolumn character (group II) that fall in energy in between the two former bands. As for the investigated $[\text{DAMSI}^+]$ J-aggregates, these new intercolumn transitions are due to the splitting of HOMO and LUMO of the unique fishbone-like structural motif.

2.2.2. Non-linear optical properties

The geometrical relationships linking the molecular hyperpolarizability tensor ($\beta_{ijk}$) to the bulk susceptibility tensor ($\chi_{IJK}$) have been extensively studied by Zyss$^{14b}$ for all Kleinman allowed$^{32}$ crystal point groups. For the point group $m$, optimum phase-matched SHG effect is obtained when the angle between the monoclinic axis and the intra-molecular charge transfer axis is 35.3°. In $[\text{DAMSI}]^{1/3}[\text{DAMBA}]^{1/2}\text{H}_2\text{O}$, the angle is ca. 56°, which explains quite well the large SHG efficiency, but it also means that an even more intense signal could be expected if $[\text{DAMS}^+]$ cations were more properly oriented. It’s important to point out that the above estimation is based only on the molecular properties of $[\text{DAMS}^+]$, it ignores contribution from the other molecules in the structure (for example DAMBA) and it does not consider the perturbation produced by the intermolecular aggregation of $[\text{DAMS}^+]$, in particular the J-aggregation described above. However there is evidence that interchromophoric transitions, typical of J-type aggregation, produce enhanced NLO response$^{11}$ and this should hold also for this new specie.
2.3 Conclusions

In the field of multifunctional materials, the results reported in section 2.1 confirm that substitution of either $M^{II}$ or $M^{III}$ metal centres in this new class of multifunctional hybrid mixed metal oxalates based on the second-order NLO chromophore $[\text{DAMS}^+]_2$ does not alter the layered structure of these systems. In such crystalline network hydrogen bonds involving DAMBA and water molecules play a major role in stabilizing inorganic chains of metal oxalates and allow an efficient control of the segregation of layers of $[\text{DAMS}^+]$ chromophores self-organized in a head-to-tail disposition, forming NLO efficient J aggregates. This has the very important consequence of maintaining a strong SHG efficiency, which is provided by the organic layer, irrespectively of the metal ions employed. A tuning of the magnetic properties of these mixed metal oxalates by suitable substitution of metal ion centers was then systematically pursued since the first observation of the total absence of bi- and three-dimensional magnetic interactions in $\text{Mn}^{III}$ and $\text{Zn}^{II}$ derivatives.

In particular, new $\text{Ni}^{II}$ and $\text{Co}^{II}$ derivative have been obtained and fully characterized and, while the crystalline structure remains almost the same, the magnetic properties dramatically change (see Table 5).

Table 5. Summary of the nature of the exchange coupling interactions between metal ions of the chains in the different compounds of mixed metal oxalates with strong second order NLO activity reported up to now.

<table>
<thead>
<tr>
<th>$M^{III}$</th>
<th>$\text{Mn}^{II4}$</th>
<th>$\text{Ni}^{II}$</th>
<th>$\text{Co}^{II}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Rh}$</td>
<td>Negligible (Mn-Mn)</td>
<td>Antiferromagnetic (Ni-Ni)</td>
<td>Negligible (Co-Co)</td>
</tr>
<tr>
<td>$\text{Cr}$</td>
<td>Weakly ferromagnetic (Mn-Cr)</td>
<td>Ferromagnetic (Ni-Cr)</td>
<td>Ferromagnetic (Co-Cr)</td>
</tr>
<tr>
<td>$\text{Fe}$</td>
<td>Antiferromagnetic</td>
<td>Ferromagnetic (Ni-Fe)</td>
<td>Antiferromagnetic</td>
</tr>
</tbody>
</table>

The $\text{Ni}$-derivatives show a strong delocalization of the $\text{Ni}^{II}$ magnetic orbitals along the “stripes” and the magnetic behavior is dominated by the presence of strong Ni-Ni antiferromagnetic next-nearest-neighbor couplings. When $\text{Cr}^{III}$ or $\text{Fe}^{III}$ are substituted to the $\text{Rh}^{III}$ diamagnetic centers this interaction pathway becomes competitive with the ferromagnetic $M^{III}$-Ni$^{II}$ nearest-neighbor interactions, giving rise to a very intricate behavior. Things become more interesting if $\text{Co}^{II}$ is present in the structure, in fact, no exchange coupling interactions between $\text{Co}^{II}$ centers is observed not even in the $\text{Rh}_2\text{Co}$ compound, in similarity with $\text{Rh}_2\text{Mn}$ compound and at variance with $\text{Rh}_2\text{Ni}$ one. The $\text{Cr}_2\text{Co}$ compounds is
characterized by ferromagnetic $M^{\text{III}}$-$M^{\text{II}}$ interactions, as already observed for the corresponding Mn$^{\text{II}}$ and Ni$^{\text{II}}$ ones, while the Fe$_2$Co compound is characterized by a moderate antiferromagnetic interaction between Fe$^{\text{III}}$ and Co$^{\text{II}}$, resulting in a ferrimagnetic like structure. Its low temperature dynamic magnetic properties candidate this compound as an interesting example of oxalate-based SCM, a property which in this case is coupled to the strong second order NLO activity.

A new stable solid state form of [DAMS]I, showing a very large SHG has been synthesized and characterized. The co-crystallization of [DAMS]I and DAMBA leads to this structure characterized by an unusual packing. Beside highly affected by the disorder of DAMBA, the structure unequivocally show a new arrangement for [DAMS$^+$], never observed in other salts of this chromophore. The unusual packing (coupling in a fishbone fashion, two columns of stacked [DAMS$^+$]) contains anyway a J-type aggregation of the chromophores, but surprisingly this structural feature is not supported by the UV-vis absorption spectrum (which lacks of the typical narrow red-shifted band). By theoretical characterization three groups of transitions have been distinguished: (i) the interchromophoric, which involve [DAMS$^+$] stacked on the same columns (ii) the intercolumn, within chromophores lying on two adjacent columns, and (iii) the intrachromophoric, which occur within the single chromophores and which are related to the parent peak of the monomer [DAMS$^+$] spectrum.

The low-energy interchromophoric transitions of the [DAMS]I spectrum are responsible of the characteristic optical response of J-type aggregation. But, due to the unique fishbone structural motif, the J-band is hidden by intercolumn transitions lying in between the parent absorption band and the typical J-band, thus providing a unique broad feature. Analysis of the [DAMS$^+$] orientation tells us that the SHG signal could be even larger, if the chromophores were more appropriately oriented but these data reinforce the hypothesis that NLO activity is enhanced by the J-type aggregation of the chromophores.
The results lead to the following publications:

“Tuning the magnetic properties of a new family of hybrid mixed metal oxalates having 1D magnetic chains and layers of J aggregates of [DAMS+] producing superior SHG”
Cariati, E.; Macchi, R.; Tordin, E.; Ugo, R.; Bogani, L.; Caneschi, A.; Macchi, P.; Casati, N.; Sironi, A.
*Inorganica Chimica Acta*, **2008**, 361, 4004–4011

“Slow relaxation of the magnetization in NLO active layered mixed metal oxalate chains”
Cariati, E.; Ugo, R.; Santoro, G.; Tordin, E.; Sorace, L.; Caneschi, A.; Sironi, A.; Macchi, P.; Casati, N.
*Accepted by Inorganic Chemistry.*

“Stabilization through p-dimethylaminobenzaldehyde of a new NLO-active phase of [E-4-(4-dimethylaminostyryl)-1-methylpyridinium] iodide: synthesis, structural characterization and theoretical investigation of its electronic properties”
Nunzi, F., Fantacci, S., Cariati, E., Tordin, E., Casati, N., Macchi, P.
*J. Mater. Chem.*, **2010**, 20, 7652–7660
2.4 Experimental Section

2.4.1 Solid-state SHG by Kurtz–Perry measurements

The 1064 nm initial wavelength of a Nd:YAG pulsed laser beam is shifted to 1907 nm by stimulated scattering in a high-pressure hydrogen cell. A portion of this beam is directed on sample containing capillaries. The scattered radiation is collected by an elliptical mirror, filtered in order to select only the second-order contribution and recollected with a Hamamatsu R5108 photomultiplier tube. SHG efficiency is evaluated by taking as reference the SHG signal of DAST or urea.

2.4.2 X-ray powder diffraction analysis.

The powders of all phases analysed were gently ground in an agate mortar and then cautiously deposited in the hollow of an aluminium holder equipped with a zero background plate with the aid of glass slide. Diffraction data (Cu Kα, λ = 1.5418 Å) were collected on a vertical scan Philips PW1820 diffractometer with the generator operating at 40 kV and 40 mA. Intensities were measured in the range 5 < 2θ < 35°, typically with step scans 0.02° (10s/step).

2.4.3 X-ray diffraction measurements.

2.4.3.a structure of \([\text{Fe}_2\text{M}^{II}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}(\text{M}^{II} = \text{Ni}, \text{Co})\)

A crystal of \([\text{Fe}_2\text{M}^{II}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}\) is mounted on a glass fiber and collected on a Bruker SMART APEX 2 CCD area-detector diffractometer. Data collection was carried out in air at room temperature. Graphite-monochromatized Mo-Kα (λ = 0.71073 Å) radiation is used with the generator working at 50 kV and 30 mA. Orientation matrix is initially obtained from least-squares refinement on ca. 300 reflections measured in three different ω regions, in the range 0 < ω < 30°; cell parameters are eventually optimised on the position, determined after integration, of all reflections above 10 σ(I) level. 1080 frames, at 60 s per frame respectively, are collected with Δω = 0.5°. Sample-detector distance is set at 6 cm; an empirical absorption correction is applied (SADABS). The structure is refined starting from the known crystal structure of the Mn^{II} analogues (using SHELX97 within the WINGX suite of programs). Anisotropic temperature factors are assigned to all non-hydrogenic atoms. Hydrogen atoms are riding on their carbon atoms, though water hydrogens are not located and included in our solutions.
2.4.3.b Structure of [DAMSI]$_{1/3}$[DAMBA]$_{1/2}$H$_2$O

A deep purple needle like crystal (0.25 x 0.05 x 0.05 mm) is mounted on a glass fiber and collected on a Bruker APEXII CCD under a nitrogen stream. Graphite-monochromatized Mo Kα (λ=0.71073 Å) radiation is used with the generator working at 50 kV and 30 mA. 1080 frames, at 90 s per frame, are collected with Δω = 0.5° and integrated within the limits 0 < 2θ < 52° in the full sphere (ω scan method). Orientation matrix is initially obtained from least-squares refinement on ca. 200 reflections and cell parameters are optimized on the position, determined after integration, of all reflections above the 10 σ(I) level. Sample-detector distances are set at 6.0 cm; an empirical absorption correction is applied (SADABS)$^{36}$. The structure is solved by direct methods (using SIR97)$^{37}$ within the WINGX1.8 suite of programs$^{33}$, and on this solution all structures are subsequently refined with full-matrix least-squares (SHELX97)$^{32}$ on F$^2$; anisotropic temperature factors are tentatively assigned to all non hydrogen atoms, however the extended disorder of DAMBA and the presence of some twinning (twin law 1 0 0; 0 -1 0; 0 0 -1) severely affect the final model. For this reason, the DAMBA molecule is not refined, but a SQUEEZE procedure$^{38}$ is applied to remove from measured structure factors the electron density contribution of regions occupied by the disordered DAMBA. The voids calculated in the structure indicate the possible presence of DAMBA molecules, in agreement with the NMR data. Due to the instability of the refinement, some atoms are refined only isotropically. Although the structure is refined without restraints, some distances (especially the central C=C bonding of the [DAMS$^+$]) are certainly affected by the well known pedal motion of stilbene-like molecules$^{39}$. 

2.4.4 Magnetic measurements on [M$^{III}_2$M$^{II}$(C$_2$O$_4$)$_6$][DAMS]$\cdot$2DAMBA$\cdot$2H$_2$O (M$^{III}$ = Rh; Fe; Cr; M$^{II}$ = Ni; Co)

DC magnetic measurements are performed by using a Cryogenic S600 SQUID magnetometer operating between 2 and 300 K and with an applied field ranging from 0 to 6 T or with a QD MPMS working in the same range of temperature between 0 and 5 T. The latter instrument is also used to perform AC measurements at frequencies below 1 KHz in the temperature range 1.8 - 12 K. For higher frequencies (400-25000 Hz) and lower temperature (1.6-3.9 K) AC measurements have been performed using a home developed probe based on the Oxford Inst. MAGLAB platform$^{40}$. All the samples are prepared by grinding freshly filtered crystals and then wrapping the powder in a Teflon tape. Measurements are repeated also by pressing the sample in a pellet to check for possible orientation effects. Magnetic susceptibilities are
corrected for diamagnetism by using Pascal’s constants. The diamagnetic contributions of the sample holder and the Teflon tape are independently measured and subtracted.

2.4.5 Computational details of the theoretical investigation on [DAMSI]$_{1/3}$[DAMBA]$_{1/2}$H$_2$O

[DAMS$^+$] aggregates of different size are investigated using the geometry of the monomer optimized at BP86/DZP level of theory. All the calculations are performed with the Gaussian03 (G03) program package. For all [DAMS$^+$] aggregates the electronic excitation energies are calculated by TDDFT using the B3LYP exchange-correlation functional and a 6-31g(d,p) basis set for N, C and H atoms. The counteranions effect has been simulated using negative point charges placed in the X-ray $\Gamma$ positions. To simulate the absorption spectrum and to allow a direct comparison with the experimental data, the computed transition energies and oscillator strengths have been convoluted by Gaussian functions with a $\sigma$ of 0.2 eV. TDDFT methods using conventional exchange-correlation (XC) functionals can fail in calculating charge-transfer intra-molecular transitions and excitations in spatially separated systems so all the calculation has been made considering the lowest excited state of the [DAMS$^+$] monomer and dimer in the slipped configuration, at different level of calculations.
2.4.6 Synthesis and characterization of Phases $\text{A}^{\text{M}^{\text{II}}/\text{M}^{\text{III}}}$

Reaction

$$K_3[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]\cdot \text{XH}_2\text{O} + \text{M}^{\text{II}}\text{X} + [\text{DAMS}][\text{I}] \xrightarrow{\text{H}_2\text{O/CH}_3\text{OH 1:1}} \text{Phase A} \text{M}^{\text{II}}/\text{M}^{\text{III}}$$

Procedure

In a 100 mL two-necked flask [DAMS]I (183.2 mg, 0.50 mmol) is dissolved in 40 mL H$_2$O/CH$_3$OH (1:1). The solution is heated at 60 °C and 0.5 mmol $K_3[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]\cdot 4.5\text{H}_2\text{O}$ ($M = \text{Rh, Fe, Cr}$), prepared according to the literature$^{44}$, previously dissolved in 20 mL H$_2$O/CH$_3$OH (1:1), are added. The heating is turned off and 0.50mmol of M$^{\text{III}}$X ($M^{\text{II}}X = \text{NiCl}_2\cdot6\text{H}_2\text{O}$ or Co(NO$_3$)$_2\cdot6\text{H}_2\text{O}$) dissolved in CH$_3$OH (2–3 mL), are added to the still hot solution. A brownish-black precipitate, as phase A M$^{\text{II}}$/M$^{\text{III}}$, separated immediately. After 1h 30min of stirring at room temperature the solid is filtered, washed with few drops of H$_2$O/CH$_3$OH (1:1) and dried under vacuum.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Weight (mg)</th>
<th>N° of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_3[\text{Rh}(\text{C}_2\text{O}_4)_3]\cdot 4.5\text{H}_2\text{O}$</td>
<td>565.33</td>
<td>282.7</td>
<td>0.50</td>
</tr>
<tr>
<td>$K_3[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$</td>
<td>487.40</td>
<td>243.2</td>
<td>0.50</td>
</tr>
<tr>
<td>$K_3[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$</td>
<td>491.24</td>
<td>245.8</td>
<td>0.50</td>
</tr>
<tr>
<td>$\text{NiCl}_2\cdot 6\text{H}_2\text{O}$</td>
<td>237.7</td>
<td>123.6</td>
<td>0.50</td>
</tr>
<tr>
<td>$\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O}$</td>
<td>291.04</td>
<td>145.4</td>
<td>0.50</td>
</tr>
<tr>
<td>[DAMS]I</td>
<td>366.25</td>
<td>183.2</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Characterization of Ni-containing phases A

Elemental Analysis (experimental data)

<table>
<thead>
<tr>
<th>Compound</th>
<th>%C found(calc)$^a$</th>
<th>%H found(calc)$^a$</th>
<th>%N found(calc)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase A$^{\text{Rh}^{\text{III}}/\text{Ni}^{\text{II}}}$</td>
<td>40.20–41.30</td>
<td>3.87–3.98</td>
<td>4.83–4.92</td>
</tr>
<tr>
<td>Phase A$^{\text{Cr}^{\text{III}}/\text{Ni}^{\text{II}}}$</td>
<td>44.55–45.17</td>
<td>3.42–3.89</td>
<td>5.15–5.09</td>
</tr>
<tr>
<td>Phase A$^{\text{Fe}^{\text{III}}/\text{Ni}^{\text{II}}}$</td>
<td>44.17–44.99</td>
<td>3.52–3.99</td>
<td>5.13–5.14</td>
</tr>
</tbody>
</table>

$^a$ intervals are refered to a series of different preparations

XRPD : Isomorphs to Mn$^{\text{II}}$ and Zn$^{\text{II}}$ phases$^4$

Characterization of Co-containing phases A

XRPD: Found corresponding to the phases A $M^{\text{II}}/M^{\text{III}}$ ($M^{\text{III}} = \text{Rh, Cr}; M^{\text{II}} = \text{Zn, Mn}$) by comparison of XRPD pattern diffraction.
2.4.7 Synthesis and characterization of \([\text{M}^{\text{III}}_2\text{M}^{\text{II}}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}\) (\(\text{M}^{\text{III}} = \text{Rh}; \text{Fe}; \text{Cr}; \text{M}^{\text{II}} = \text{Ni}; \text{Co}\))

2.4.7.a Synthesis of \([\text{M}^{\text{III}}_2\text{Ni}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}\) \(\text{M}^{\text{III}} = \text{Rh}; \text{Fe}; \text{Cr}\)

**Reaction**

\[
\text{Phase ANi}/\text{M}^{\text{III}} + \text{DAMBA} \rightarrow [\text{M}^{\text{III}}_2\text{Ni}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}
\]

**Procedure**

In a 100 mL flask DAMBA (20.5 mg; 0.14 mmol) is added to the corresponding a phase ANi/M\(^{\text{III}}\) (80.0 mg), prepared as above-reported, dissolved in 70 mL of H\(_2\)O. The solution is heated under reflux for 1 h 30 min and then cooled at room temperature. On standing overnight, the formation of a greenish compound with a metallic luster is observed. After filtration, the compound is dried under vacuum.

**Characterization**

Chemical formula and elemental analysis:

<table>
<thead>
<tr>
<th>Compound</th>
<th>%C found(calc)</th>
<th>%H found(calc)</th>
<th>%N found(calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh}_2\text{Ni}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O})</td>
<td>54.13 (54.17)</td>
<td>5.00 (4.93)</td>
<td>6.85 (6.72)</td>
</tr>
<tr>
<td>([\text{Cr}_2\text{Ni}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O})</td>
<td>57.06 (56.95)</td>
<td>5.16 (5.19)</td>
<td>7.18 (7.06)</td>
</tr>
<tr>
<td>([\text{Fe}_2\text{Ni}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O})</td>
<td>56.54 (56.73)</td>
<td>5.08 (5.17)</td>
<td>7.10 (7.04)</td>
</tr>
</tbody>
</table>

**XRPD**

Isomorphs to the Mn\(^{\text{II}}\) and Zn\(^{\text{II}}\) derivatives reported by Cariati et al\(^4\).

**XRD**

Crystals of \([\text{Fe}_2\text{Ni}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}\), suitable for single crystal X-ray diffraction analysis are obtained by leaving the solution at room temperature for 3 days and the crystallographic data are reported in Table 1.
2.4.7.b Synthesis of $[\text{Rh}_2\text{Co(C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot\text{DAMBA}\cdot2\text{H}_2\text{O}$

**Reaction**

$$\text{H}_2\text{O}$$

Phase A$\text{Co/Rh} + \text{DAMBA} \rightarrow [\text{Rh}_2\text{Co(C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot\text{DAMBA}\cdot2\text{H}_2\text{O}$

**Procedure**

In a 100 mL flask DAMBA (80.0 mg; 0.55 mmol) is added to the corresponding a phase A$\text{Co/Rh}$ (80.0 mg), prepared as above-reported, dissolved in 70 mL of H2O. The solution is heated under reflux for 1 h 30 min and then cooled at room temperature. On standing overnight, the formation of a dark compound with a metallic luster is observed. After filtration, the compound is dried under vacuum.

**Characterization**

**Chemical formula and elemental analysis:**

<table>
<thead>
<tr>
<th>Compound</th>
<th>%C found (calc)</th>
<th>%H found (calc)</th>
<th>%N found (calc)</th>
<th>%Co found (calc)</th>
<th>%Rh found (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Rh}_2\text{Co(C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot\text{DAMBA}\cdot2\text{H}_2\text{O}$</td>
<td>54.13 (54.11)</td>
<td>5.00 (4.89)</td>
<td>6.85 (6.72)</td>
<td>2.91 (2.83)</td>
<td>9.69 (9.87)</td>
</tr>
</tbody>
</table>

**XRPD**

Isomorphs to the Mn$^{II}$ and Zn$^{II}$ derivatives reported by Cariati et al$^4$. 
2.4.7.c Synthesis of $[M^{III}_2Co(C_2O_4)_6][DAMS]_4\cdot2DAMBA\cdot2H_2O$ $M^{III} = Fe, Cr$

**Reaction**

\[
\text{Phase ACo/M}^{III} + \text{DAMBA} \quad \xrightarrow{H_2O:CH_3OH} \quad [M^{III}_2Co(C_2O_4)_6][DAMS]_4\cdot\text{DAMBA}_2\cdot2H_2O
\]

**Procedure**

In a 100 mL flask DAMBA (20.5 mg; 0.14 mmol) is added to the corresponding a phase A Co/M$^{III}$ (80.0 mg), prepared as above-reported, dissolved in 70 mL of a mixture 1:1 of H$_2$O:CH$_3$OH. The solution is heated under reflux for 1 h 30 min and then cooled at room temperature. On standing overnight, the formation of a dark compound with a metallic luster is observed. After filtration, the compound is dried under vacuum.

**Characterization**

Chemical formula and elemental analysis:

<table>
<thead>
<tr>
<th>Compound</th>
<th>%C found (calc)</th>
<th>%H found (calc)</th>
<th>%N found (calc)</th>
<th>%Co found (calc)</th>
<th>%M$^{III}$ found (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cr}_2\text{Co}(C_2O_4)_6][\text{DAMS}]_4\cdot\text{DAMBA}_2\cdot2H_2O$</td>
<td>57.06 (56.88)</td>
<td>5.16 (5.14)</td>
<td>7.18 (7.06)</td>
<td>3.05 (2.97)</td>
<td>5.36 (5.24)</td>
</tr>
<tr>
<td>$[\text{Fe}_2\text{Co}(C_2O_4)_6][\text{DAMS}]_4\cdot\text{DAMBA}_2\cdot2H_2O$</td>
<td>56.54 (56.67)</td>
<td>5.08 (5.13)</td>
<td>7.10 (7.03)</td>
<td>3.06 (2.96)</td>
<td>5.49 (5.61)</td>
</tr>
</tbody>
</table>

**XRPD**

Isomorphs to the Mn$^{II}$ and Zn$^{II}$ derivatives reported by Cariati et al$^4$.

**XRD**

Crystals of $[\text{Fe}_2\text{Co}(C_2O_4)_6][\text{DAMS}]_4\cdot\text{DAMBA}_2\cdot2H_2O$, suitable for single crystal X-ray diffraction analysis are obtained by leaving the solution at room temperature for 3 days and the crystallographic data are reported in table 1.
2.4.8 Synthesis and characterization of [DAMSI] \( \frac{1}{3} \) [DAMBA] \( \frac{1}{2} \) H\(_2\)O

**Reaction**

[DAMSI]I + DAMBA $\xrightarrow{\text{H}_{2}\text{O} : \text{MeOH}}$ [DAMSI] \( \frac{1}{3} \) [DAMBA] \( \frac{1}{2} \) H\(_2\)O

**Procedure**

In a 150 mL flask [DAMSI]I (100,0 mg, 0.274 mmol) and \( p-\text{N(CH}_3\text{)}_2\text{C}_6\text{H}_4\text{CHO} \) (162.8 mg, 1,092 mmol) are dissolved in 90 mL of H\(_2\)O/CH\(_3\)OH (1/1) and heated under reflux for 1h 30min and then slowly cooled at room temperature. By reduction of the volume under vacuum, a red powder is obtained. After filtering, the compound is washed with diethylether to remove the excess of \( p-\text{N(CH}_3\text{)}_2\text{C}_6\text{H}_4\text{CHO} \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Weight (mg)</th>
<th>N° of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DAMSI]I</td>
<td>366.25</td>
<td>100</td>
<td>0.274</td>
</tr>
<tr>
<td>DAMBA</td>
<td>149.0</td>
<td>162.8</td>
<td>1.092</td>
</tr>
</tbody>
</table>

**Characterization**

\(^1\text{H-NMR (CD}_3\text{COCD}_3\text{), 400.1 MHz, 298 K):}\n
![1H-NMR spectrum](image)
<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Multiplicity (J, Hz)</th>
<th>Integral</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.74</td>
<td>s</td>
<td>0.30</td>
<td>H4a</td>
</tr>
<tr>
<td>8.80</td>
<td>d (6.8)</td>
<td>2.0</td>
<td>H7 H7'</td>
</tr>
<tr>
<td>8.16</td>
<td>d (6.8)</td>
<td>2.03</td>
<td>H6 H6'</td>
</tr>
<tr>
<td>7.97</td>
<td>d (16.0)</td>
<td>0.97</td>
<td>H5</td>
</tr>
<tr>
<td>7.72</td>
<td>d (8.9)</td>
<td>0.70</td>
<td>H3a H3'a</td>
</tr>
<tr>
<td>7.65</td>
<td>d (9.0)</td>
<td>1.93</td>
<td>H3 H3'</td>
</tr>
<tr>
<td>7.24</td>
<td>d (16.0)</td>
<td>0.96</td>
<td>1H, H4</td>
</tr>
<tr>
<td>6.83</td>
<td>m</td>
<td>2.64</td>
<td>H2 H2', H2a, H2'a</td>
</tr>
<tr>
<td>4.46</td>
<td>s</td>
<td>2.80</td>
<td>H8</td>
</tr>
<tr>
<td>3.12</td>
<td>s</td>
<td>1.89</td>
<td>H1a</td>
</tr>
<tr>
<td>3.09</td>
<td>s</td>
<td>5.40</td>
<td>H1</td>
</tr>
</tbody>
</table>

The ratio [DAMS\(^+\)]/DAMBA, inferred from the \(^1\)H NMR intensity picks, is about 1/0.3.

XRD: Single crystals of [DAMSI] \(^{1/3}\)[DAMBA] \(^{1/2}\) H\(_2\)O are obtained by slow evaporation of the solvent. The crystallographic data are reported in Table 5.
References


7 (a) E. Coronado; J.R. Galan-Mascaros; C. Marti-Gastaldo; *Crystengcomm* **2009**, 11, 2143; (b) E. Coronado; J.R. Mascaros; C. Marti-Gastaldo; *J. Am. Chem. Soc.*, **2008**, 130, 4987.

8 a) S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* 1968, **39**, 3798


Chapter 2

Chapter 2


34 Sheldrick, G. M. *SHELX97-Program for the refinement of Crystal Structure*, University of Göttingen, Germany, 1997.


36 G. M. Sheldrick, *SADABS v2.10*, University of Göttingen, Germany, 2003.


Chapter 3

NEW ORGANIC MOLECULES WITH INTERESTING SECOND ORDER NONLINEAR OPTICAL PROPERTIES
3.1 New class of highly stable second order NLO-active chromophores

The design and synthesis of new non linear optical (NLO) chromophores possessing high values of quadratic hyperpolarizabilities $\beta$ and characterized by chemical, photochemical and thermal stability are of great technology-driven interest in view of their integration into bulk materials for the preparation of photonic and optoelectronic devices. Stilbene and azobenzene based chromophores, having appropriate donor and acceptor groups, are well known NLO active molecules and have been already incorporated into electrooptic polymeric systems. However these molecules present several intrinsic drawbacks due to cis-trans photoisomerism around the C=C or N=N double bond and photorotamerism of the aromatic rings thus reducing the chromophore NLO activity or to the oxidation of isolated double bond that causes an interruption of the $\pi$-conjugation between the donor and the acceptor groups. These problems can be overcome if the double bond is included in a rigid polyaromatic system, which should ensure not only stability, but also highly electronic delocalization.

For that reason the study of the second order NLO properties, measured by the Electric Field Induced Second Harmonic generation (EFISH) technique, of 7-$N,N$-dibutylamino-2-azaphenanthrene (1) and 8-$N,N$-dibutylamino-2-azachrysene (2) has been performed. For comparison $N,N$-dimethyl-4-(pyridin-4-yl)aniline (3) and $N$-methyl-$N$-hexadecylamino stilbazole (4) (Figure 1), the corresponding non-anellated chromophores of 1 and 2 respectively, were also investigated. Finally cis-[Ir(CO)$_2$Cl] (Ir 1) and cis-[Ir(CO)$_2$Cl] (Ir 2) complexes and methylated salts have been studied in order to evaluate the modification of the chromophores electronic properties and their effect on the NLO activity.

![Figure 1. structure of the studied compounds 1, 2, 3, and 4](image-url)
3.1.1 Synthesis of the new chromophores, their [Ir(CO)$_2$Cl] complexes and methylated salts

1 and 2 have been reported as intermediates for the preparation of anellated emicyanine dyes and they have been synthesized by the group of Dr. Silvio Quici at Università degli Studi di Milano. 1 has been prepared in good yields by careful modification and optimization of the known procedure while for 2 a new procedure has been developed. A scheme of the synthesis is reported in Figure 2.

![Figure 2. Scheme of the synthesis of compounds 1 and 2](image)

(a) PPh$_3$, CCl$_4$, THF, 48 h, 95%; (b) PPh$_3$, heptane, reflux, 24 h, 82%; (c) 3-pyridinecarboxaldehyde, ’BuOK, dry MeOH, N$_2$, reflux, overnight, 82%; (d) 2-Me-THF, hv, 1.5 h, -15 °C, 46%; (e) isoquinoline-5-carbaldehyde, ’BuOK, dry MeOH, N$_2$, reflux, overnight, 82%; (f) THF, hv, 8 h, 17 °C, 33.5%;

3 has been obtained using a standard Suzuki coupling as reported in Figure 3 while 4 has been prepared as previously reported by Locatelli et al. Complexes Ir 1 and Ir 2 have been obtained by reaction of 1 and 2 with [Ir(CO)$_2$Cl]$_2$ The methyl pyridinium iodide salt of 2 (2 CH$_3$I) has been prepared by reaction with CH$_3$I following a standard procedure. The compounds has been characterized by $^1$H and $^{13}$C-NMR and Mass Spectroscopy.

![Figure 3. Synthesis of compound 3](image)

(g) aqueous Na$_2$CO$_3$, tetrakis(triphenylphosphine) palladium(0), THF, 80 °C, 18 h, 79%.
3.1.2 Non-linear optical characterization

The experimental electronic spectra are reported in Table 1, along with their \( \mu \beta_{\text{EFISH}} \) values measured with the EFISH technique and the theoretical or experimental \( \mu \) values of all compounds.

3 is characterized by a low value of \( \mu \beta_{\text{EFISH}} \) in CHCl\(_3\) due to the absence of a complete \( \pi \)-conjugation between the two aromatic rings. However this value increases drastically by a factor of 8.9, if the single bond is included into the polyaromatic scaffold of 1. A further increase of \( \beta \) by a factor of 1.4 is obtained upon coordination of 1 to the “Ir(CO)\(_2\)Cl” moiety which acts as an additive electron-acceptor group producing a red-shift of the ILCT transition (from 347 to 390 nm, Table 1) dominating the NLO response. Remarkably, an increase of the \( \pi \)-conjugation of the free ligand leads to a huge positive effect on the second order NLO response, with an enhancement factor of 4.4 on going from 1 to 2, reaching a \( \mu \beta_{\text{EFISH}} \) value much higher than that of the related stilbazole 4.

### Table 1. Experimental electronic spectra, \( \mu \beta_{\text{EFISH}} \) and \( \mu \) values of 1, 2 and related compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda ) (nm) ([\varepsilon \text{ (M}^{-1}\text{cm}^{-1})])^a</th>
<th>( \mu \beta_{\text{EFISH}} ) (x10(^{-48}) esu)(^a,b )</th>
<th>( \mu )(^c ) (( \mu )(^\text{theor} )) (x10(^{-18}) esu)</th>
<th>( \beta ) (x10(^{-30}) esu) |</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>278 [28626] 347 [14397]</td>
<td>430</td>
<td>3.5 (7.6)</td>
<td>123(^d) (56)(^e)</td>
</tr>
<tr>
<td>Ir 1</td>
<td>279 [35420] 390 [25670]</td>
<td>620</td>
<td>(16.2)</td>
<td>(38)(^e)</td>
</tr>
<tr>
<td>2</td>
<td>305 [41462] 361 [17179](^f)</td>
<td>1800</td>
<td>4.2 (8.0)</td>
<td>429(^d) (224)(^e)</td>
</tr>
<tr>
<td>Ir 2</td>
<td>272 [34541] 421 [12737]</td>
<td>-2310</td>
<td>(16.9)</td>
<td>(-137)(^e)</td>
</tr>
<tr>
<td>3</td>
<td>417 [46500] 506 [9160]</td>
<td>48</td>
<td>2.4</td>
<td>20(^d)</td>
</tr>
<tr>
<td>4</td>
<td>381(^6) 223(^6)</td>
<td>3.7(^6)</td>
<td>60(^6)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) In CHCl\(_3\) at 10\(^{-4}\) M with an incident radiation of 1.907 \( \mu \)m. \(^b\) The error on EFISH measurements is ± 10\%. \(^c\) Experimental \( \mu \) obtained by the Guggenheim method\(^10\) in CHCl\(_3\); the error is ± 1x10\(^{-18}\) esu. \(^d\) By using experimental \( \mu \). \(^e\) By using theoretical \( \mu \). \(^f\) There is a band tail a ca 400 nm
Surprisingly, contrarily to what was observed in the case of stilbazolium salts, methylation of the pyridine ring of 2 does not affect strongly the second order NLO response although there is a relevant red shift ($\Delta \lambda_{\text{max}} = 112$ nm) of the ILCT transition. This effect might be related to a different orientation of the dipole moment in the two salts, which determines the overall EFISH response.

Coordination of 2 to “Ir(CO)$_2$Cl” leads to a slight increase (enhancement factor = 1.2) of the absolute $\mu\beta_{\text{EFISH}}$ value which, unexpectedly, becomes negative. This behaviour is in contrast with that observed upon coordination of 4 to the same Ir(I) moiety where $\mu\beta_{\text{EFISH}}$ is enhanced but remains positive, being dominated by an ILCT transition. It is worth noting that the very high $\mu\beta_{\text{EFISH}}$ values of 1 and 2 are due to large $\beta$ values since their dipole moments are quite similar to that previously reported for 4. The absolute $\mu\beta_{\text{EFISH}}$ value of 1 and 2 decreases by increasing the concentration from $10^{-4}$M to $10^{-3}$M due to aggregation effects at the higher concentration and $\mu$ could not be determined experimentally at this concentration.

### 3.1.3 Stability of the new compounds determined by DSC measurements

In order to evaluate a possible application in electrooptic devices, where temperatures higher than 300°C are required to process, the thermal stability of 2 has been measured by Differential Scanning Calorimetry (DSC). The sample has been subjected to three reversible cycles of melting and crystallization with a heating rate of 5°C/min under nitrogen atmosphere. As it is evident from the DSC spectrum, the melting and the crystallization peaks show similar intensities within the three cycles thus indicating that there is neither sublimation nor partial decomposition of the product. The decomposition temperature of 434°C has been determined by further heating of the sample over its melting temperature (Figure 2).

![Figure 4. Differential Scanning Calorimetry (DSC) spectrum of 2.](image-url)
3.1.4 Theoretical calculations

In order to get insight on the peculiar second order NLO properties of the systems, DFT (Density Functional Theory) and Time Dependent DFT (TDDFT) computational studies on 1 and 2 have been carried out\textsuperscript{12} by the group of Simona Fantacci at University of Perugia.

3.1.4.a Electronic and optical properties

From the analysis of the electronic structure of 1 and 2 it emerges that the highest occupied orbitals (HOMOs) are of $\pi$ character and show similar energies and similar charge distribution apart from an increased delocalization due to the presence of four rings in 2. The 2 lowest unoccupied orbitals (LUMOs) of $\pi^*$ character are, on the other hand, the result of different carbon and nitrogen p orbitals combinations with respect to 1, which is reflected by their different energies (Figure 5). The 2 LUMO is at lower energy with respect to that of 1 as a consequence of the increased $\pi$-conjugation, leading to a 0.38 eV decrease of the 2 HOMO-LUMO gap.

![Figure 5. Schematic representation of frontier molecular orbitals of 1 and 2.](image)

The absorption spectra of both systems have been simulated by computing the lowest 20 singlet-singlet excitations. The agreement between theory and experiment is good (Figure 6), in particular, in the 1 case the theoretical spectrum reproduces all the features of the experimental absorption spectrum and only the lowest absorption band is computed slightly red-shifted by 0.16 eV. For 2, the calculated intensity distribution does only qualitatively compares with the experimental absorption bands, even though also in this case the computed transitions nicely fit with the main experimental features, see Figure 6.
The absorption spectrum of 1 is characterized by a low-energy band computed at 332 nm and one more intense at 277 nm, to be compared with the experimental absorption bands at 347 and 287 nm. The lowest transition is calculated as being a rather weak HOMO-LUMO excitation at 361 nm, of $\pi-\pi^*$ character. The transition giving rise to the band at 332 nm is essentially from the HOMO to the LUMO+1 and has charge-transfer character, going from the donor dibutylamino part of the ligand to the acceptor pyridine ring. The absorption band computed at 277 nm is constituted by two main transitions of global $\pi-\pi^*$ character. The experimental absorption spectrum of 2 has a quite similar shape with respect to that of 1, even though it is red-shifted and it shows the appearance of a band tail at ca.400 nm. The computed bands at 353 nm and 312 nm can be compared to the experimental absorption bands at 361 nm and 305 nm. The band at 353 nm is a charge-transfer transition essentially of HOMO-LUMO+1 character. The calculated weak lower energy transition at 392 nm with a charge transfer character, corresponds to the HOMO-LUMO transition, related to the low energy experimental feature and more intense than that of the 1 ligand, consistently with the experimental spectra.
3.1.4.\textit{b} Non-linear optical properties

To gain insight into the electronic transitions responsible of the observed quadratic hyperpolarizability $\beta$ of 1 and 2, a Sum Over States (SOS) analysis has been performed. The results, reported as insets of Figure 6, show in both cases a converged positive value in agreement with the experimental evidence. The ratio of the computed $\beta$ values of 1 and 2 is 2.2, which is in line with the experimental increase of the EFISH $\beta$ value observed passing from 1 to 2. This increase is mainly due to the red-shifted absorption spectrum of 2, related to the HOMO-LUMO gap decrease. Indeed, according to the two-level model\textsuperscript{13}, $\beta$ increases quadratically with decreasing the energy of the electronic transitions. From an in depth analysis of calculated SOS $\beta$ values, it appears that the largest contributions to $\beta$ are provided for both 1 and 2 by ILCT transitions. In particular, for 2 the lowest energy transition considerably contributes to the calculated $\beta$, while, for 1, such excited state has almost vanishing contribution to $\beta$, due to its higher energy and considerably lower transition dipole moment. Moreover, at higher energy the 314 nm transition is that mainly responsible for the converged higher $\beta$ value of 2 compared to 1, indeed the same state in 1 is characterized by a lower transition dipole moment.
3.2 Non-linear optical properties of $\pi$-delocalized perfluorinated systems

In the field of electrooptic materials, a strategy based on hydrogen bonding (HB)-driven self-assembly, among others, has already demonstrated its great potential for the design of transparent organic thin films with very high electrooptical responses\(^\text{14}\). Halogen bonding (XB)\(^\text{15}\), any noncovalent interaction involving halogens as electrophilic sites, is a rather new item in the supramolecular toolbox and shares numerous properties with the better known HB. The great potential of XB in the design of new and high-value functional materials and, for example in combination with significant molecular second order non linear optical properties, exploiting XB to the self-assembly of organic thin films for nonlinear optical (NLO) and optoelectronic applications\(^\text{16}\).

In collaboration with Prof. Resnati’s research group at Politecnico di Milano, the change in the second-order NLO response increasing the $\pi$-delocalization in fluorinated bi-arylic systems has been studied in order to evaluate the effect of the halogen bonding on the non-linear optical response. In a previous paper N,N-dimethyl-4-[(E)-2-(2,3,5,6-tetrafluoro-4-iodophenyl)vinyl]aniline (5), N,N-dimethyl-4-[(1E,3E)-4- (2,3,5,6-tetrafluoro-4-iodophenyl)buta-1,3-dien-1-yl]aniline (6) and N,N-dimethyl-4-[(1E,3E)-4- (2,3,5,6-tetrafluorophenyl)buta-1,3-dien-1-yl]aniline (7) (Figure 7) has been studied as new XB-based NLO-phores\(^\text{17}\).

![Figure 7. Chemical formula of the NLO-phores 5, 6 and 7](image)

Chromophores 5 and 6 possess terminal XB-donor and -acceptor groups and incorporate a conjugated $p$-electron spacer between electron-rich and electron-poor aromatics (push–pull effect), in analogy with most of the molecular materials for NLO applications\(^\text{18}\) while 7 is chosen as a reference compound, which lacks the I atom on the tetrafluorophenyl fragment and is not capable of XB. From the $\mu\beta$ value of the two chromophores in different solvents (see Table 2), measured with the EFISH technique\(^\text{5}\), it has been possible to show for the first time that both the value and the sign of second-order NLO responses in solution can be tuned thanks to solvent-chromophore XB. As a function of the ability of the solvent to behave as XB-acceptor, the NLO-phores under study give rise to $\mu\beta$ values ranging from $+192 \times 10^{-48}$ esu to $-465 \times 10^{-48}$ esu. Since no significant shift or intensity variation of the CT band, which
Chapter 3

dominates $\beta$, is observed by comparison of the UV-Vis spectra of 5,6 and 7 in DMF and CHCl$_3$, the sign inversion in $\mu\beta_\lambda$ must be due to a change in the direction of $\mu$ as a consequence of the simultaneous presence, in the halogen bonded complexes, of two competitive electron-donor sites, the intramolecular ($-\text{N(CH}_3)_2$) and the intermolecular ones (solvent), placed on either sides of the electron-acceptor iodoperfluorinated ring.

Table 2. Computed $\mu$, experimental $\mu\beta_{\text{EFISH}}$ and calculate $\beta_0$ values and CT bands of NLO-phores 5, 6 and 7 in CHCl$_3$ and DMF.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu$(D)</th>
<th>CHCl$_3$</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu\beta_{\text{EFISH}}$ ($\times 10^{-48}$ esu)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\mu\beta_{\text{EFISH}}$ ($\times 10^{-48}$ esu)</td>
</tr>
<tr>
<td>5</td>
<td>6.31</td>
<td>+124</td>
<td>382</td>
</tr>
<tr>
<td>6</td>
<td>7.25 (6.8)$^a$</td>
<td>+192</td>
<td>406</td>
</tr>
<tr>
<td>7</td>
<td>6.10</td>
<td>+173</td>
<td>392</td>
</tr>
</tbody>
</table>

$^a$ Experimental value in CHCl$_3$

$^b$ Measured at the concentration of $1\times 10^{-4}$M

Since the performances of these molecules are quite interesting, the study has been extended to a system more delocalized in order to improve its non linear optical properties.

In Figure 8 the chemical formula of N,N-dimethyl-4-(4-(2,3,5,6-tetrafluoro-4-iodostyryl) styryl)aniline (8) and N,N-dimethyl-4-(4-(2,3,5,6-tetrafluorostyryl)styryl)aniline (9) are reported and their NLO properties are summerized in Table 3.

![Figure 8. Chemical formula of compounds 8 and 9.](image)

Table 3. Experimental $\mu\beta_{\text{EFISH}}$, computed $\mu$ and calculated $\beta_0$ of NLO-phores 8 and 9.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu\beta_{\text{EFISH}}$ ($\times 10^{-48}$ esu)$^a$</th>
<th>$\mu$(D)</th>
<th>$\beta_0$ ($\times 10^{-30}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>+772</td>
<td>8.30</td>
<td>93</td>
</tr>
<tr>
<td>9</td>
<td>+816</td>
<td>7.44</td>
<td>110</td>
</tr>
</tbody>
</table>

$^a$ Measured at the concentration of $2\times 10^{-3}$M in CHCl$_3$. 

75
The μβ value are affected by a great experimental error and thus have to be confirmed by some additional EFISH measurements but they shows a large improvement if compared to the value obtained for the molecules 6 and 7. These values appear particularly interesting since, from the literature it is known that the μβ value of a system in which donor group (D) and acceptor group (A) are linked by double bonds is higher than the analog in which D and A are connected by aromatic rings. For example, Blanchard-Desce et al.\textsuperscript{19} reported for compounds 10 and 11 reported in Figure 9, a theoretical value of the first-order hyperpolarizability (β(0)) equal to $282 \times 10^{-30}$ esu and $162 \times 10^{-30}$ esu respectively.

![Chemical formula of the compounds 10 and 11.](image)

The polyenic chains seem to be the most efficient conjugated linker to get high β(0) however, for the systems under our investigation the opposite seems to be true, in fact 8 is characterized by a μβ value 4 times higher than the value obtained for 6. Dr. Alessandra Forni of the Università degli Studi di Milano is currently working on the theoretical calculations of the NLO properties of these systems in order to better understand the origin of this particular behavior.

These systems are particular appealing not only for the NLO properties but also for their emissive ones. In fact, the hydrogenated derivative 9 shows an intense photoluminescence quantum yield (PLQY) (89%\textsuperscript{1} in toluene and 77%\textsuperscript{a} in CHCl\textsubscript{3}). This strong emission is completely unexpected since the twisting intramolecular charge transfer (TICT) quenching process always occurs in push-pull molecules\textsuperscript{20}. Both these values are much higher than the PLQY of 14%\textsuperscript{a} measured for the iodine derivative 8 in which the heavy atom effect quenches the fluorescent emission.

According to the push-pull character of 9, an intense red shift of the maximum of the emission is observed increasing the polarity of the solvent (Figure 10). Polar solvents, in fact, stabilize the excited state, that has a charge transfer character, decreasing the HOMO-LUMO band gap and causing the red-shift of the emission.

\textsuperscript{1} $\lambda_{exc}=350$nm, compared to the standard quinine sulfate in 0.1M H\textsubscript{2}SO\textsubscript{4} solution
Several charge-transfer models are reported in literature but the one that might explain such huge red-shift is model is the formation of twisted intramolecular charge-transfer states (TICT)\textsuperscript{21}.

Further theoretical calculations have to be performed in order to confirm the TICT character of the excited state and to better understand the electronic properties of the compound.

A variation of the emissive properties has also been investigated in the solid state. 9 is characterized by a strong emission at 530nm and, by simple grinding, the emission maximum is shifted to 560nm while a parallel smaller shift is observed in the diffuse reflectance UV-Vis absorption spectra (Figure 11).

The grinding process doesn’t induce any structural modification. In fact, the XRPD patterns before and after grinding present the same peaks (Figure 12). A slight modification of the shape can be observed in the pattern of the grinded one in which the noise signal at low angle,
due the more amorphous character of the powder, appears. The signal at $\theta = 12.8$ is more intense in the spectrum of 9 before grinding, indicating the presence of crystallites characterized by a preferential orientation which is partially lost with the grinding process.

Figure 12. XRPD spectra of 9 before (top) and after (bottom) grinding.

In order to classify this behavior as piezochromism, powders of 9 have been subjected to high pressure (5000kg for 5 minutes) and the same variation of the luminescent properties has been observed. The XRPD analysis shows that, in this case, crystallites maintain a certain preferential orientation.
Moreover, the different photoluminescent behavior of 9 in crystalline and amorphous film has been investigated. A crystalline film has been prepared by casting of a dichloromethane solution of 9 on a glass slide while the amorphous one has been obtained by melting a crystalline film and then cooling it down in liquid nitrogen. The photoluminescence quantum yield measurements, performed by Dr. Chiara Botta of ISMAC, show a great difference of PLQY which are 61% for the crystalline and 1.6% for the amorphous. The very low intense emission of the amorphous film is due to a residual crystallinity as confirmed by the fluorescent emission spectra reported in Figure 14. The emission for both films is, in fact, centered at 530nm but for the amorphous one it is weaker and broader.

Figure 13. Overlay of the XRPD patterns of 9 before (black line) and after (red line) grinding and after pressing (green line).

Figure 14. Normalized emission spectra of the crystalline and amorphous films of 9 ($\lambda_{exc} = 365$nm).
3.3 Conclusions

The polyaromatic push-pull chromophores 1 and 2 seems to be particularly appealing because of their notable values of $\mu\beta_{\text{EFISH}}$ that are likely due to the absence of photorotamerism and photoisomerism processes operating in the corresponding compounds 3 and 4 respectively. The very high thermal stability, combined with the absence of isolated double bonds ensure the astonishingly high thermal stability, rendering 2 particularly appealing from an applicative point of view. Such molecule can constitute a springboard for the design of other NLO chromophores.

In addition, molecules 8 and 9 seem to be very appealing for their peculiar linear and non linear properties. Both 8 and 9 are, in fact, characterized by significant NLO properties which can be exploited in optoelectronics devices, while 9 has an impressive strong emission which is not quenched by TICT phenomena that always occur in push-pull molecules. A piezochromic behavior of the linear optical properties has been observed at the solid state. The grinding process induces the amorphization of powders of 9 and a shift at higher energies of the fluorescent emission.

Further studies have to be performed in order to better investigate this properties and, eventually, hypothesis an application as a sensor.

The results reported in section 3.1 have been published on Chemical Communication.

“Highly stable 7-$N$,$N$-Dibutylamino-2-azaphenanthrene and 8-$N$,$N$-dibutylamino-2-azachrysene as a new class of second order NLO-active chromophores”

3.4 Experimental section

3.4.1 EFISH techniques

Measurements of $\mu \beta_{\text{EFISH}}$, the products of the chromophore dipole moment ($\mu$) and the projection of $\beta_{\text{VEC}}$, the vector part of the molecular first-order hyperpolarizability $\beta$ tensor along the direction of $\mu$, were performed by the solution-phase DC EFISH generation method. EFISH measurements were carried out in CH$_2$Cl$_2$ solutions at a nonresonant fundamental wavelength of 1907 nm using a Q-switched, mode-locked Nd$^{3+}$:YAG laser [pulse durations of 15 ns (90 ns) at a 10 Hz repetition rate]. The 1064 nm initial wavelength was shifted to 1907 nm by a Raman shifter with a high-pressure H$_2$ cell. All the measurements have been performed in amylene stabilized CHCl$_3$.

3.4.2 Theoretical calculations on 7-N,N-dibutylamino-2-azaphenanthrene (1) and 8-N,N-dibutylamino-2-azachrysene (2)

The DFT and TDDFT studies have been carried out by means of Gaussian 03 (G03) program package. The molecular structures of 1, 2, Ir 1 and Ir 2 have been optimized in CHCl$_3$ using B3LYP exchange-correlation functional, a 6-31G* basis set for C, H and N and Lanl2DZ basis set with related pseudo-potentials for Ir and Cl. The solvation effects have been included by means of a Polarizable Continuum Model (PCM) as implemented in G03. The geometry optimization of 1 and 2 provides very similar molecular structures characterized by planarity of the azaphenanthrene and azachrysene and similar CC and CN bond distances. The N(Butyl)$_2$ moiety goes out of the plane of the anellated rings by ca. 6° for both species, with the two butyl groups oriented in opposite directions. Similar dipole moments both in vacuo, 5.2 and 5.6 D, and in CHCl$_3$ solution, 7.6 and 8.0 D, for 1 and 2, respectively have been calculated. The optimized Ir 1 and Ir 2 are square planar complexes with the 1 and 2 twisted with respect to the square planar coordination plane, by 54° and 65°, respectively.

3.4.3 XRPD measurements on N,N-dimethyl-4-(4-(2,3,5,6-tetrafluorostyryl)styryl)aniline (9)

The X-ray powder diffraction data was measured with PANalytical X’Pert PRO diffractometer in Bragg–Brentano geometry using Johansson monochromator ($\alpha_1$ setup) to produce pure CuK$\alpha_1$ radiation (1.5406 Å; 45kV, 30mA) and step–scan technique in 20 range of 5.000–55.239°. The data was collected by X’Celerator detector in continuous scanning mode with a step size of 0.003° and step time of 192s. Programmable divergence slit (PDS) was used in automatic mode to set irradiated length on sample to 10mm together with 10mm.
incident beam mask. Soller slits of 0.02° rad. were used on both incident and diffracted beam sides together with anti-scatter slits (4° and 13 mm, respectively). Before further analyses, the diffraction data were converted from automatic slit mode (ADS) to a fixed slit mode (FDS) data by the tools implemented in Highscore Plus v. 2.2c software package. Hand-ground powder samples were prepared on a silicon-made zero-background holder using petrolatum jelly as an adhesive.
References


Chapter 4

CORONA-POLING OF HOST-GUEST
PMMA-DAST FILM
In the last two decades organic and hybrid inorganic–organic nanostructured materials based on molecular second order non linear optical (NLO) chromophores characterized by a large quadratic hyperpolarizability (β) have been investigated for their potential application in various electro-optical devices such as optical waveguides or frequency modulators\(^1\). In order to be useful for technological applications, these materials must possess not only a satisfactory macroscopic second order susceptibility ($\chi^{(2)}$) but also attributes such as chemical stability, easy preparation and processability together with long term stability of their electrooptical properties. Large $\chi^{(2)}$ values can be obtained starting from molecular second order NLO chromophores as building blocks by engineering their organization in a non centrosymmetric way. To reach this goal various strategies have been proposed such as stepwise construction of multilayers\(^2\), Langmuir–Blodgett films\(^3\), self-assembly in layered crystalline structures\(^4\) or in films\(^5\), chirality to induce acentric crystalline structures\(^6\), ordered inclusion in 1D or 2D host structures\(^7\) and electrical poling of composite polymeric films based on molecular second order NLO chromophores\(^8\).

The latter one seems the most interesting because it combines the mechanic properties and the processability of polymeric materials with the possibility of drive a noncentrosimmetric arrangement of chromophore through electrical poling to form thin films of composite hybrid materials useful for optical-optical or electro-optical applications\(^9\). However, this process suffers of few disadvantages, such as the easy decay of the electrooptical properties due to orientational relaxation of the aligned NLO chromophores and, often, of scattering losses originated by inhomogeneities of the film\(^10\). In particular, the electric field poling process is usually applied to polymers mixed with neutral second order NLO chromophores since ionic chromophores may produce, under the effect of the directional strong electric field, an opposite diffusion of cations and anions towards the surface of the film.
4.1 Poling

A versatile and inexpensive technique, in order to obtain films containing oriented NLO-phores, is the Poling.

![Figure 1. The Poling process on dipolar molecules. The dipole moments of the molecules are randomly oriented when the electric field $(E_p)$ is not applied. At high temperatures ($T_g$) and under a strong electric field dipoles can be orientate along its direction.](image)

In the pristine film, prepared by spin-coating or casting, the dipole moments, $\mu_0$, of the chromophores are randomly oriented but when a strong static electric field, called Poling field $E_p$, is applied on the film, a torcent moment is induced on the dipoles which are forced to align parallel to the Poling field (the common direction is indicated with $z$) (Figure 1). In order to facilitate the rotation of the dipoles, the temperature $T$ of the system is increased till the glass transition temperature of the polymer, $T_g$. When the system reaches the equilibrium, keeping $E_p$ on, it is cooled down to room temperature freezing the orientation of the chromophores inside the polymeric matrix. After that, the Poling field can be turned off\textsuperscript{11,12,13}. The time necessary to reach the equilibrium depends from different factors as: $E_p$, $\mu_0$, $T$, $T_g$ and it can be from few minutes to many hours, depending on the capacity of the matrix to hold and block the molecules with their new orientation.

There are three different static electric field Poling techniques: \textit{Contact} (electrode) \textit{Poling}; \textit{Corona Poling} and \textit{Wire Poling}. In Contact Poling, the static electric field is applied to two coplanar electrodes and the polymeric film is between them (Figure 2).

![Figure 2. Contact Poling](image)

With this configuration it is not possible to apply a strong electric field because the dielectric breakdown potential of the air or of the film can be easily reached, leading to burnings or damages on the film and a loss of transparency. On the contrary, for both Corona and Wire Poling, the electric field is applied between a wire (positively charged) and a planar electrode,
1 cm far each from the other. The electrons, normally present in the atmosphere, are accelerated to the anode and they ionize the molecules in the gas phase. These ions migrate to the cathode and deposit on the sample surface. The applied electric field can be calculated assuming that the potential difference, around 10 KV, is applied between the surface of the polymeric film, which is 1 mm thick, and the support. In this case, high electric fields of about $10^7$ V/m can be reached. Otherwise, if we consider a system as the one shown in Figures 3 and 4 in which the electrode is a thin ITO (Indium Tin Oxide) layer, the potential difference is applied directly on the polymeric film and the applied field is around $3 \times 10^8$ V/m.

![Figure 3. Corona Needle Poling](image)

In Corona Needle Poling a needle perpendicular to the film surface is used as the anode. The field lines goes from the point of the needle to the other electrode and the film is subjected to a non-homogeneous electric field with the maximum intensity close to the needle, Figure 3. In Wire Poling technique the applied electric field is more uniform because two positively charged wires, parallel to the support, work as the anode (Figure 4).

![Figure 4. Wire Poling](image)

In both conformations the film’s surface can be damaged by the ionized particles formed in the free space between the electrodes and usually degradation increase with temperature. In order to prevent damages, the Poling treatment can be performed in nitrogen atmosphere or a layer of a sacrificial material can be deposited on the film surface and then removed after Poling.

The main critical experimental factors in the Poling techniques are the applied potential difference and the working temperature. Both factors need to be optimized for each sample in order to have i) the maximum orientation of the active molecules, ii) prevent the deterioration of the optical qualities of the film, iii) avoid damages or losses of chromophores by sublimation. A typical potential value reported in several papers is 5 KV with discharge current never above to $2 \pm 4 \mu A^{13,14,15}$ and temperatures close to the $T_g$ of the polymer.
Temperatures higher than the $T_g$ cause the increase of the thermal agitation in the system and induce a partial loss of the orientation achieved with the Poling. Moreover, the electric conductivity of the matrix increases with consequent decrease of the effective charge deposited on the sample surface. Also the air conductivity increases and some discharge phenomena between the two electrodes can be observed with consequent film damages.

4.2 Evaluation of the order parameter

Push–pull molecules have a high anisotropy that allows to monitor a small variation of their orientation by the absorption spectrum of the film\textsuperscript{12}. This is possible because the transition responsible of the absorption in the visible region of the spectrum is a charge transfer between the donor and the acceptor groups whose transition dipole moment $\mu_{ij}$ is orientated along the main axes of the molecules. The probability of a molecular transition between the ground and the excited is defined as:

$$P_{ij} \propto \left| \mu_{ij} \cdot \vec{E} \right|^2$$  \hspace{1cm} \text{Eq. (1)}$$

and when a polarized radiation hits a molecules, it has zero probability to be absorbed if its polarization, $\vec{E}$, is perpendicular to the main axis of the molecule. For that reason, in a polymer containing aligned chromophores, the absorbance changes a lot if the incident radiation is parallel or perpendicular to Poling axis.

Experimental evidences showed that the absorbance of a polymeric film during the Poling process, at first, decreases and then increases in the next few days after the treatment; the first effect is due to the orientation and the second effect is due to the relaxation of the matrix\textsuperscript{13,16}.

This phenomenon can be related to the order parameter $\phi$:

$$\phi = \frac{A_{\|} - A_{\perp}}{A_{\|} + 2A_{\perp}} = 1 - \frac{A_{\perp}}{A_0}$$  \hspace{1cm} \text{Eq. (2)}$$

where $A_{\|}$ and $A_{\perp}$ are the absorbances measured with a polarized incident light respectively parallel and perpendicular to the Poling electric field direction. $A_0$ is the absorbance of the isotropic system and it is calculated as:

$$A_0 = \frac{A_{\|} + 2A_{\perp}}{3}$$  \hspace{1cm} \text{Eq. (3)}$$
The order parameter can assume values ranging between, 0, for an isotropic media, and 1, for a media with all the chromophores aligned. The order parameter can be determined also using not polarized light, in fact, the method proposed in Eq. (2) for its estimation is not able to discriminate between polar order and axial order but it is a good way to evaluate the performances of a Poling treatment just considering two simple parameters such as the absorption before Poling \( A_0 \) and the after Poling \( A_\perp \). However, this parameter doesn’t consider in the degradation of the chromophores that occurs during the Poling treatment. For this reason it is better to use \( A_0 \) of spectra of the film after a thermal recover carried out at a temperature above the \( T_g \). This treatment brings again the system in a disordered situation and, if the film had been damaged during the Poling treatment, the absorbance value will be lower than the one of the pristine film. On the hand a polarized light absorbance measurement can be performed by changing the incident angle on the sample. This technique is called PAS (Polarized Absorption Spectroscopy).

### 4.3 Maker fringes

Since 1970 the determination of the nonlinear optical (NLO) coefficients associated with second-harmonic generation (SHG) has been performed almost exclusively by the Maker fringe technique. The method is based on the analysis of the intensity of the SHG signal transmitted by a NLO material while the incident angle of the light is changed. The set up of the instrument was fully described by Jerphagnon and Kurtz (JK) in the 1970 then revised and refined by Herman and Hayden (HH) in the 1995. This last revision is the logical consequence to the increase of its application to new materials, in fact, over the years this technique has been applied to inorganic and organic crystals and organic polymers. However, some of the original assumptions made in the derivations by JK were applicable to the transparent crystals of the day, but not uniformly applicable to all material classes currently under investigation. Many of the second-order NLO organic materials under investigation today, such as liquid crystals, Langmuir–Blodgett films, poled polymers, and organic crystals, are absorbing at the wavelength of the typical SHG experiment and exhibit a fair degree of anisotropy. The technique revised by HH allows a resolution for birefringence material and another one for media that absorbs the ground radiation or the generated doubled one; it includes the multiple reflection effect inside the material.

Maker fringes are defined as oscillations of the second harmonic generation (SHG) intensity as a function of the transmitted pump-beam angle of incidence. They have often been used as to comparatively measure the second-order susceptibility of nonlinear optical materials with
respect to reference samples. The standards must have good second order NLO properties, low absorbance, good conducibility and high damage level. The standards used are: ADP (ammonium dihydrogen phosphate NH\(_4\)H\(_2\)PO\(_4\)), KDP (potassium dihydrogen phosphate KH\(_2\)PO\(_4\)), LiNbO\(_3\) (lithium niobate) and quartz for the visible and near infrared. The quartz is, at the moment, the best one, even though it’s not the most NLO active standard, because it has high thermal stability and low cost.

In order to measure the Maker fringes, a sample is typically rotated around a particular crystalline axis while a polarized pump beam illuminates a spot on the sample. The SHG fringes are continuously produced as long as the sample is rotated and the second order NL properties can be calculated by the diffraction pattern of the SHG and the pump radiation. These calculations are possible only knowing the linear optical properties such as the refraction index and the extinction coefficient, according with the Fresnel and Lambert–Beer Laws.

HH demonstration describes the Maker fringes formation starting from the Maxwell equation for the incident radiation and for the doubled one. The continuity conditions are imposed for every interface crossed (see Figure 8, air–film NLO, film NLO–substrate, substrate–air) and the incident angle is varied. The result gives the power of the SH signal as a function of the angle.

![Figure 8](image-url)

Figure 8. Scheme of the SHG of a three-layer system (air/NL film /substrate) q and k are the wave vectors respectively in air and in the NL film. The subscript 1 is referred to the incident radiation while the subscript 2 is for the double-frequency radiation. The superscript r is referred to the reflected radiation. L is the thickness of the NL film.\(^{18,21}\).


**4.4 Stable and long-lasting SHG of oriented nanocrystal of DAST in PMMA**

Recently some interesting attempts have been made to move from molecular second order NLO chromophores to acentric NLO active nanocrystals as building blocks of composite polymers. For example, the systems [DAZOP][MnPS₃] (where [DAZOP⁺] is the 4-[2(4-dimethylaminophenyl)azo]-1-methyl pyridinium cation) has been reported to form ordered nanoparticles in the solid phase of a polymer matrix²². It was also shown that acentric NLO active nanocrystals, obtained by the reprecipitation technique, can behave as large second order NLO chromophores, characterized by a very high dipole moment, which can be oriented by a strong directional electric field when dispersed into a liquid host²³. The orientation process is accompanied by a significant increase of the second harmonic generation which is, however, totally transient due to the high mobility of the dipolar NLO active nanocrystals in the dispersion²⁴. In fact, few seconds after switching off the electric field the SHG relaxes back close to zero. The only reported example of a long lasting anisotropic orientation of NLO active ionic nanocrystals concerns the use of a magnetic field. In fact, nanocrystals of the second order NLO ionic chromophore [trans-N,N-dimethylamino-N’-methylstilbazolium][p-toluenesulfonate] (DAST)⁴c, first prepared by the reprecipitation technique and then suspended in laurylacrylate, produce, by UV-induced polymerization in the presence of a directional magnetic field, a composite polymeric film characterized by a stable in time SHG²⁵.

Since the intensity of a coherent second harmonic signal given by an assembly of N chromophores, in an excitation volume smaller than the wavelength, increases as $N^2$ multiplied by an efficiency factor which depends on the relative orientation of the chromophores²⁶, the main goal is to achieve a synergy through appropriate packing modes of the chromophores, in order to increase the SHG intensity per unit volume. Therefore, the *in situ* growth by electrical poling, followed by careful thermal annealing, of oriented dipolar acentric nanocrystals of DAST starting from a pristine film of DAST dispersed in poly(methyl methacrylate) (PMMA) has been investigated.
4.4.1 Preparation and characterization of the PMMA/chromophores film

Thin films are obtained by spin-coating of a 4% solution of DAST in CHCl$_3$/MeOH containing the PMMA (see experimental section). In Figure 9 are reported the UV-Vis spectra of DAST dissolved in methanol and chloroform, of the pristine film and at the solid state. The absorption spectra in methanol and chloroform of DAMSI have also been measured and compared to the ones of DAST. Both compounds present the typical internal charge transfer broad band at 475nm when dissolved in CH$_3$OH, suggesting that both salts are completely dissolved and the isolated cation [DAMS$^+$] is present in solution. Otherwise, in CHCl$_3$ the maximum for DAMSI is at 500 nm and for DAST at 490 nm as a consequence of the presence of ion pairs in this non-polar solvent.

![DAST and [DAMS]I](image)

The UV-Vis spectra of the pristine film is only characterized by charge transfer broad band of DAST centered at 450 nm, so quite blue shifted when compared with that of DAST dissolved in MeOH (475 nm) or in CHCl$_3$ (490 nm). Moreover, it differs from the spectrum of the DAST in KBr lacking of the narrow red shifted band at 580 nm which is the fingerprint of the J type organization of the [DAMS$^+$] chromophores within the crystalline structure.

Moreover, acentric crystals of DAST are not present in the pristine film as confirmed by the GIXRD (Grazing Incident X ray diffraction) analysis (Figure 10). Therefore we can hypothesis the presence of a mesophase corresponding to unknown nanostructures (called nanoseeds) not yet organized as in crystals of DAST.

![UV-Vis spectra](image)

Figure 9. Electronic absorption spectra: (1) DAST in CHCl$_3$; (2) DAST in MeOH; (3) pristine PMMA (4% DAST) film, (4) DAST in KBr.
4.4.2 Corona-poling at a temperature close to the glass transition temperature ($T_g$) of PMMA

The pristine film is heated under corona poling at 8 kV and a SHG signal is obtained almost instantaneously (Figure 11). The SHG signal increased by increasing the temperature from 25°C to about 32°C but then decreased down to zero above 40°C. Such behavior can be probably related to an increased of thermal agitation of the PMMA matrix which introduces some thermal disorder of the DAST nanoseeds in competition with the initial ordering produced by the electric poling process. However, a further increase of the temperature up to 90°C lead again to an increase of the SHG signal, as expected for a higher mobility and thus an easier orientation of the ions under the electric field when reaching the glass transition temperature $T_g$ of PMMA (86.5°C as determined by differential scanning calorimetry)\textsuperscript{27}. Keeping the electric field at 8 kV but gradually decreasing the temperature, the SHG signal remains almost constant. However, turning off the electric field, at around 35°C the SHG signal of the poled film fall to a much lower value although not to zero.

![Graph](image)

Figure 10. GIXRD analysis of a pristine film of DAST in PMMA.

![Graph](image)

Figure 11. Thermal treatment under electric poling (8 kV) of the PMMA film blended with DAST (4%). T is always kept lower than the $T_g$ of PMMA.
The electronic absorption spectrum after poling is similar to that of the pristine film but with a slightly lower value of the absorbance (Figure 12). It appears that the structure of the nanoseeds of DAST is maintained under the poling process, and that they can be oriented along an electric field as it occurs for molecular dipolar species.\textsuperscript{28}

**Figure 12.** UV-Vis spectra of film before (red line) and after (blue line) poling at \( T < T_g \).

### 4.4.3 Thermal annealing of the poled film

The poled film is then gradually heated up, in the absence of a directional electric field, to 140°C, a temperature much higher than the glass transition temperature of PMMA. At the same time its SHG is monitored (Figure 13). Despite the absence of a strong directional electric field, a strong increase of the SHG is observed, which reached a plateau after two hours of thermal treatment. Interestingly, during the subsequent cooling process the SHG response of the final film remains stable. It is also long lasting in fact it is quite unchanged after 6 months.

**Figure 13.** Complete treatment performed on the DAST film: poling followed by thermal annealing in the absence of electric field up to ca 140°C and subsequent cooling.

The extremely intense and very stable SHG of the film would suggest a relevant thermal effect on the structure of the still oriented nanoseeds of DAST that is confirmed by the electronic absorption spectrum of film (Figure 14) which shows two bands, one broad
centered at 490 nm and one red shifted and narrower at 545 nm, which closely reminds to that of crystalline DAST in KBr (Figure 14) and of a DAST single crystal as reported in the literature\(^{29}\).

This spectroscopic evidence would suggest that, by effect of the controlled thermal annealing, the nanoseeds of DAST aggregate into new ordered structures in which the narrow absorption band at 545 nm, typical of the ordered J-aggregates of [DAMS\(^+\)] in the acentric crystalline structure of DAST, is present\(^4\).

![Figure 14. Electronic absorption spectra: (1) pristine film, (2) poled and thermally annealed film, (3) DAST in KBr; (4) just thermally annealed film](image)

The poling treatment of the film seems to be a necessary condition in order to produce a film containing these oriented species of crystalline DAST. In fact, when the thermal annealing was carried out on a new pristine film (without any pre-poling treatment) the SHG of the film is much lower as it is for the intensity of the J-aggregates band in the UV-Vis spectrum (Figure 14).

### 4.4.4 Characterization of the crystalline species in the film

The presence of oriented crystalline specie has been investigated by X-ray diffraction both in grazing incidence 2 theta-scan mode and in omega/2theta-scan mode. The same peaks, over an amorphous background, typical of crystalline DAST were observed for both samples with a higher degree of crystallinity for the poled & annealed film (Figure 15a, profile 1 and 2, respectively). The amorphous background signal can be due either to the PMMA matrix or to an uncompleted aggregation into these crystalline species of the original nanoseeds of DAST. Omega/2theta-scan of the poled & annealed (profile 3 in Figure 15) showed a strong preferential orientation of the crystalline grains in the direction perpendicular to the film surface mostly for the reflection family (0 0 2n) of the monoclinic DAST phase indexed, after background subtraction, for the poled & annealed film in Figure 15b in agreement with literature data\(^{4c}\).
The aggregation effect due to the combination of electrical poling and annealing to produce oriented crystalline species of DAST is very clear in Figure 15, which compares the GIXRD (Figure 16a) or the omega/2theta-scan profiles (Figure 16b) of the poled and annealed film with that of the pristine film, which does not show evidence of the presence of crystalline species of the original nanoseeds of DAST.

Omega/2theta-scan of poled and annealed film (profile 3 in Fig.16a) showed a strong preferential orientation of the crystalline grains in the direction perpendicular to the film surface (fig.16b).

Transmission electron microscopy (TEM) showed the size of the crystalline species in the range expected for nanocrystals of DAST (about 100 nm or less) for both the films. TEM images are not of high quality probably due to the instability of the PMMA polymer under the electronic beam; however the difference in size, shape and type of aggregation, due to the preliminary electrical poling treatment, is pretty clear for the 2 systems. For the poled & annealed film the nanocrystals of DAST are well separated and with a rather homogeneous
distribution (Figure 17a), while for the just thermally annealed film disordered aggregates of nanodomains of DAST (the dark stains in Figure 17b) are formed.

Figure 17. TEM images of poled and annealed film (a) and just annealed film (b) (scale 500nm).

4.4.5 Maker fringe measurement

The Maker fringe are defined as oscillations of the second harmonic generation intensity as a function of the transmitted pump-beam angle of incidence and its shape gives information about the presence of ordered domains in the system. The comparison of the SHG, by the Maker fringe technique, of films poled & annealed and just annealed films (Figure 18) indicates the absence of oriented crystalline species of DAST when the original nanoseeds have not been previously oriented by electrical poling. In fact, the SHG of the just annealed film is not only much lower than that of the poled & annealed one, but it shows a very low dependence of the SHG from the incident angle with a not null signal at zero degree\textsuperscript{30}. On the other hand, the poled & annealed film shows an intense incident-angle dependent SHG with a NLO coefficient\textsuperscript{31} $d_{33}$ of 5.3 pm/V, a significant value for a film containing a low amount of NLO-phore (Figure 18). Also this film shows a not null SHG signal at zero degrees suggesting the parallel presence of oriented and disordered crystalline species.

It must be pointed out that a rigorous control of the heating ramp is required to obtain film poled & annealed film since a fast temperature increase produces a SHG signal which is not dependent on the angle of the incident radiation, similar to that of the just annealed film. Moreover, with the purpose of increase the number of oriented nanocrystals, another film has been thermally treated while the poling electric field was on. The result is, unfortunately, a
degradation of the chromophores due to the combination of the strong electric field (8.5 kV) and the high temperature (140°C).

Figure 18. Normalized SHG response, measured with the Maker fringe technique, of the poled and thermally annealed film showing the typical shape arising from a $C_{\infty v}$ system (solid line) and of the just thermally annealed film (dashed line).
4.4.6 Conclusions

The evidences reported lead to the following conclusions:

- The pristine PMMA film obtained by spin-coating is an isotropic dispersion of a not yet crystalline mesophase of DAST called nanoseeds.

- These nanoseeds behave as traditional dipolar molecular second order NLO chromophores because they can be oriented by a strong directional electric field (with consequent increase of the SHG), with the difference that, by switching off the electric field, the SHG decrease quickly but not to zero. By further controlled thermal annealing up to 140°C, in the absence of the poling electric field, an unexpected controlled growth of nanocrystals of DAST, some of which oriented, occurs with parallel significant increase of the SHG which does not decrease when cooling to room temperature.

- The pre-orientation of the nanoseeds is the key-point of this strategy, in fact, when the thermal annealing is performed without electrical poling pre-treatment of the pristine film, nanocrystals of DAST are formed, but they are randomly distributed. The nanodomains are not oriented and the SHG of the film is negligible.

- The strong electric field and thermal annealing must not be applied at the same time, otherwise the film surface would be damaged.

This *in situ* growth technique is a new very elegant way to produce nanocrystalline film inside a polymeric matrix and it could be an alternative choice to the currently used reprecipitation technique in which nanocrystals are growth, then dispersed in a liquid host and only in a second time anisotropically oriented by an electric field. For what concerns the DAST, the film obtain with the *in situ* growth technique has a stable and long lasting SHG while, with the other orientation technique, the SHG disappear as soon as the field is turned off $^{23}$.

This work has been published on the Journal of Material Chemistry:

“Stable SHG from in situ grown oriented nanocrystals of [(E)-N,N-dimethylamino-N’-methylstilbazolium][p-toluenesulfonate] in a PMMA film”


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4.5 Experimental section

4.5.1 Experimental set-up

The apparatus for the measure is assembled on an optic desk using different optical elements in order to create a versatile set-up, suitable for all the possible experimental working conditions. The instrumental set-up allows to carry out the Poling of polymeric materials or sol-gel matrix and, at the same time, verify the orientation of the molecules by the in-situ measurement of the SHG. Moreover, the second order NLO properties of the material may be determined using the Maker fringes technique. This measurement requires the use of a reference, as quartz, and the determination of some parameters such as the refractive index, the extinction coefficients and the thickness of the film. The thickness and the refractive index of the film were calculated using the ellipsometric technique while the extinction coefficient is calculated by the absorption spectra.

The measurement apparatus consists of a laser, a power attenuator system, a main optic line, a reference line, the apparatus box where Poling, SHG in-situ and Maker fringes measurements are carried out and the apparatus for the acquisition and the evaluation of the data.

4.5.1.a Laser, power attenuator and main optic line

The laser is a Nd: YAG Q-switched (Giants, G790-20) purchased from Quanta System that emits pulses with a frequency of 10 Hz at a wavelength of 1064 nm. The pulses have energy of 500 mJ and approximately 7 ns long. The beam diameter is about 1 cm. The laser power unit and the pumping lamps system are cooled by water. The temperature is kept of 20°C with a variation of ±0.2°C which is, although small, responsible for a variation of ± 3% on the power emitted, which in terms of second harmonic becomes ± 9%. The attenuation system is necessary to decrease to few mJ the energy of the pulses and at the same time to provide linearly polarized radiation.

With reference to Figure 19, two thin-film linear polarisers (TFP) and two foils of delay $\lambda/2$ are used. The polarisers let the $p$ polarized radiation pass while the $s$ polarized radiation is reflected on a screen which is able to absorb it. Adjusting the orientation of the first $\lambda/2$ foil the polarization of the $p$ light is rotated so the first TFP transmits only the $p$ component. The second pair of $\lambda/2$ and TFP works only as an attenuation system for $p$ polarized radiation. The $\lambda/2$ are placed on a goniometric support: a 45° variation of the angle corresponds to a rotation of the propagation plan of the light of 90°. The attenuation system has a maximum of transmission when the polarization is not rotated and a minimum when it is rotated by 90°.
Figure 19. Schematic representation of the apparatus of measurement. The laser system and the attenuation of the power are on the top, the main optical line is on the bottom left side and the reference line is on the right. $\lambda/2$ delay plate are written as $\lambda/2$. The optics indicated with TFP are thin film polarizers operating in reflection, they let pass the $p$ polarization and reflect the $s$ polarization. BS is a beam-splitter optimized for radiation at 1064nm. O.D. is an Optical Density.

After the attenuation system a red filter is placed in order to cut any radiation at 532 nm from the laser. The main optic line is optimized in terms of polarization, the power and the focusing of the fundamental radiation for each experiment carried out in the apparatus box. A $\lambda/2$ foil allows us to choose the polarization. The radiation’s power is an essential parameter: it must be low to avoid burning or damaging of the samples or to blind the detector, but, at the same time, high enough to generate the second harmonic signal even in samples with modest NLO properties.

The power is quantitatively regulated with a series of generic filters with different optical density (OD) and a convergent lens with focal length of 400mm that focuses the radiation on the sample.

4.5.1.b Reference optical line

The purpose of the reference line is to monitor the fluctuations of the power of fundamental radiation emitted by the laser. In such a way it’s possible to distinguish if a variation of the detected SHG is actually due to the sample or if it’s just a consequence of a variation of the radiation’s power. The fluctuations can be of two types: the short term fluctuations, which are mainly due to the cooling cycle of the laser and have period of about 62 s, and the long-term
fluctuations, occurring within one hour after the laser is turned on and they are observed when the working conditions are reached.

The reference beam is generated from the main laser radiation after it passes through a beam-splitter optimized for the radiation at 1064nm. After selecting the polarization with a $\lambda/2$ foil placed on a goniometric support, the radiation interacts with the reference crystal (KDP) that is kept at constant temperature and properly oriented in the direction of phase matching\textsuperscript{20}. The radiation outcoming from the crystal contains both the fundamental and the double frequency radiation and, thanks to the IR filter, the fundamental at 1064nm is cut off. The radiation at 532 nm passes through a polarizing beam-splitter cube, which reflects at 90° the $s$ component while the $p$ component passes through, see Figure 20. The double-frequency $p$-polarized radiation is focused by a lens, with focal of 400 mm, on a photodiode with active area of 1 mm\textsuperscript{2} (Figure 21).

![Figure 20](image)

**Figure 20.** Schematic representation of a Polarizing Beam-splitter Cube, the radiation $p$ polarized is transmitted and the radiation $s$ polarized is reflected to 90°. The behaviour of the polarizers TFP is similar.

As shown in Figure 19, in front of the phototube there is also an interference filter that stops any residual of the fundamental radiation. The signal generated by the double-frequency radiation on the photodiode is acquired with an oscilloscope Tektronix TDS 3032 and used to normalize the signal of the sample that comes out from the measurement box.

![Figure 21](image)

**Figure 21.** Photodiode.

The reference line can also be used for the measurement on the quartz with the Maker fringe technique. In this way the measurements on the quartz and on the sample are carried out simultaneously and quickly.
4.5.1.c Measurement Box

The measurement box is a Plexiglas box 50 cm high, 32 cm long and 32 cm wide (Figure 22). The sample can be placed into the box through a door on the front and an hose connects the box with the nitrogen line. The fundamental radiation enters into the box through a window of amorphous silica.

The box contains an aluminium plate of 10 cm long, 6 cm high and 1 cm wide (Figure 23), that works as sample holder and Poling site. The plate is located on a goniometric support which allows to rotate the sample keeping it perpendicular to the optical desk. The rotation is used during the measurement of the Maker fringe.

Parallel to the plate there are two platinum wires 100 μm thick, 1 cm far from each other and also from the plate, in a typical Wire Poling configuration. The wires are connected to a positive potential while the plate has no charge. The Poling field is supplied by a TREK 610E generator that can reach 10 KV as maximum value. The generator, also, controls the maximum current that passes between the wires and the plate, set at 40 μA and an increase of that current lead to an automatic decrease of the potential applied, preventing any possible electrical discharges between the wires and the plate. The generator also has an exit-potential control systems with a fixed potential value 2000 times smaller than the real applied potential, this output is connected to the Tektronix oscilloscope and allows us to monitoring the potential during the measurement.

Figure 22. Measurement box
The plate contains two heating elements specially designed to reach a maximum temperature of 300°C. A temperature regulation system (Gefran 800) measures the temperature of the plate with a platinum thermal-resistance of 100 Ω, (PT100) with a triple-wire system that keeps the temperature ± 0.1°C. The plate has a slit approximately 3 cm long and 0.3 cm wide in which the fundamental radiation passes and hits the sample, so the second harmonic generation can be measured during Poling. The polymeric samples are placed on the plate with the film up, so the fundamental radiation first hits the substrate and then the NLO film. The signal generated by the NLO material passes through an interferometric filter and a polarizing cube beam-splitter before reaching the detector. The filter allows to pass only the radiation at 532 nm and the beam-splitter selects the polarization of the radiation that we want to detect. The double-frequency radiation is detected by a phototube Hamamatsu C3860 with gallium arsenide cathode, which works between 185 and 900 nm wavelength. The device contains a circuit for the supply of the high potential for the operation of dynodes and requires an external power supply of 1.5V.

4.5.1.d Detection of the signal and acquisition of the data

The measurement of the signals is based on the oscilloscope Tektronix TDS 3032 which has 4 measuring channels with time resolution of 2 ns. It is used to detect the signal emitted by the photodiode at the end of the reference line and by the photomultiplier in the measurement box. The oscilloscope is used to obtain average values. The acquisition data is carried out using two programs written in LabView, one for the Poling measures and the monitoring of the in-situ SHG, the other for the Maker fringes measurement. The programs calculates the value of the power of the duplicate radiation $P_{2\omega}$. 

Figure 23. Measurement Box, view of the aluminium plate. The sample stands on the plate, the area where the Poling is applied is delimited by the rectangular window obtained with the Teflon mask. The platinum wire is kept tensioned by two ceramic supports.
4.5.2 Film preparation

Thin films containing 4 wt% of DAST were obtained by spin-coating, with a Cookson Electronic Company P-6708D Spincoater, on an ordinary glass plate (thickness 0.5 mm) working at these parameters of spinning (RPM 1 : 1000; ramp 1 : 1 s, time 1 : 3 s; RPM 2 : 2500; ramp 2 : 1 s, time 2 : 60 s; RPM 3 : 3000; ramp 3 : 5 s, time 3 : 60 s) from few drops of a 3 ml of a CHCl₃–CH₃OH (2/1 vol.) solution containing 375 mg of PMMA and 15 mg of DAST. The film thickness was about 1.2 mm, measured with an α-step stylus profilometer.
References


Chapter 4


Chapter 4


Chapter 5

NEW MOLECULES WITH NLO PROPERTIES AND INTRIGUING EMISSIVE PROPERTIES
5.1 A simple push-pull chromophore as a highly efficient crystallization induced emissive material

As extensively discussed in the Chapter 1, on the basis of the Oudar’s model, the molecular non-linear second order properties are strictly related to the difference between the dipole moments of the excited and fundamental states. From this point of view, push-pull molecules are the most interesting kind of chromophores, because an internal charge transfer is usually followed by a big variation of the dipole moments. In collaboration with Prof. Dario Pasini of Università di Pavia, the NLO properties of the new class of push-pull molecules reported in Figure 1 have been studied and the results are reported in Table 1.

![Chemical formula of studied compounds.](image)

n = 0 (1), 1 (2) and 2 (3)

Figure 1. Chemical formula of studied compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CHCl₃ μβ (x10⁻⁴⁸ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
</tr>
<tr>
<td>2</td>
<td>172</td>
</tr>
<tr>
<td>3</td>
<td>293</td>
</tr>
</tbody>
</table>

Table 1. μβ values measured with the EFISH technique in 10⁻³M CHCl₃ solutions.

μβ values of 10⁻³M chloroform solution are measured with the EFISH technique and, as expected, the increase of the delocalization leads to an increase of μβ value of the systems. Despite the not appealing NLO properties of these compounds, an interesting behaviour of the emissive properties has been observed for 4-dimethylamino-2-benzylidene malonic acid dimethyl ester (1). In fact, crystals of 1 are characterised by an intense blue emission which is quenched in solution and in the amorphous phase.

Solid-state luminogens have been subject of great interest because high tech applications of light emitting materials very often require their use in the condensed phase (for example thin films in the fabrication of OLEDs). However, very often, luminogenic molecules are highly
emissive in dilute solutions but they become weakly or even non emissive in the solid state\(^3\); a phenomenon known as aggregation-caused-quenching (ACQ). The development of luminogens more efficiently emitting in the solid state than in solution has recently aroused much interest since the pioneering works of Tang and co-workers who first proposed the concept of aggregation-induced-emission (AIE)\(^4\): molecules non emissive in solution show strong light emission in the condensed phase. To explain the AIE behavior different mechanisms (i.e. restriction of intramolecular rotation (RIR), formation of J aggregates, intramolecular planarization, inhibition of photoisomerization and photocyclization) have been suggested\(^5\). Even more intriguing are some non emissive molecules which are induced to emit by crystallization but not amorphization; a behavior which has been defined as crystallization-induced-emission (CIE)\(^6\). CIE is particularly relevant since crystalline films usually exhibit higher charge carrier mobility than their amorphous counterpart.

### 5.1.1 Synthesis and characterization

1 has been synthesized by the group of Prof Dario Pasini following the procedure reported by Desimoni et al.\(^1\) An equimolar amount of dimethylamino benzaldehyde and dimethyl malonate within a catalytic amount of piperidinium acetate are dissolved in 20 mL of benzene and refluxed overnight with a Dean-Stark apparatus. The solvent is evaporated to give a yellow oil which is crystallized upon treatment with diisopropyl ether. The solid is filtered to give pure 1 in a good yield.

### 5.1.2 Photophysical characterization

1 shows in dilute toluene solution a very weak emission centered at 440 nm with a photoluminescence (PL) quantum yield (QY) of less than 0.1%. This hardly discernible emission shows, in agreement with the dipolar push-pull molecular structure, a solvatochromic behavior moving from toluene to acetonitrile (475 nm) (Figure 2). However, no relevant variations are observed both in the emission intensity and in the absorption by varying the solvent polarity (Figure 2). Despite the extremely weak emission in solution, its crystalline powders are characterized by an intense blue emission at around 480 nm (see Figure 3) for which a PLQY of 14% has been measured, while for a single crystal the PLQY has been found to be 24%.

To gain more information on the PL behavior of 1 its emission in dilute EPA (diethylether:pentane:ethanol with volume ratio 5:5:2) has been measured. While at room temperature the emission is hardly discernible, a quite strong emission peaked at 445 nm
appears by quickly cooling the solution at 77 K (Figure 3). Such strong emission in frozen solution is not related to the formation of aggregates at the cryogenic temperature since it was observed even when working at concentrations as low as $10^{-6}$ M. It appears more probable that in solution the molecular conformation becomes quite rigid at low temperatures as in the crystalline state producing a RIR behavior. The blue shifted and broadened spectrum of the frozen solution, with respect to the crystal, might be related to the more distorted conformation and the higher conformational disorder of the molecules obtained by quickly freezing the solution in liquid nitrogen.

![Absorption and Emission Spectra](image)

Figure 2. Absorption (solid lines) and emission (dashed lines, $\lambda_{exc} = 350$nm) spectra of 1 in different solvents.

![Photoluminescence](image)

Figure 3. Photoluminescence of 1 as crystalline powder (solid line) and EPA frozen solutions (dotted line), excited at 363 nm.
5.1.3 Restriction of intramolecular rotation (RIR) as cause of the emission intensity

The evidence of a RIR process is obtained by combined emission and $^1$H NMR experiments working in THF solution at different temperatures (Figure 4). The easy rotation of the aryl moiety around its own main axis leads to sharp NMR peaks and no sizable emission for temperatures above 200K. However, when the temperature is lowered down to about 166-167 K the $^1$H NMR signal of H$_b$ (see Figure 5 for the assignment) at 7.4 ppm becomes very broad and a parallel sharp increase of the emission intensity is observed. Evidence for a hindered intramolecular rotation around the aryl main axis was also gained by $^{13}$C NMR spectra of I in THF solution and as a crystalline solid (Figure 4). The CH carbon resonances of the aryl moiety at 130 and 110 ppm effectively split, in solution at low temperature and in the crystalline state at room temperature, as a consequence of the reduced local symmetry imposed by the restricted rotation.

![Figure 4](image)

Figure 4. Top left: Temperature dependence of PL intensity of I in THF solution and in crystalline and amorphous films. The arrow is at 166.5 K. The PL Intensity is normalized to one at low temperatures for the three samples. Top right: chemical formula of I with assigned protons. Bottom left: Middle: 400 MHz $^1$H NMR spectra of I in THF solution at different temperatures. Bottom right: A: 400 MHz $^{13}$C NMR spectrum of I in THF solution at r.t. and B: at 166K; C: 500 MHz $^{13}$C NMR spectrum of crystalline powder of I at r.t.
The effect of the matrix rigidity the on the fluorescent emission has also been demonstrated by the measurements of the photoluminescent quantum yields of 1 in solvent with different viscosity (see Table 2). In the more viscous PEG, the rotational movements are hindered and an increase of the PLQY is observed.

Table 2. PLQY of 1 in tetrahydrofuran (THF), diethylene glycol (DEG) and polyethylene glycol (PEG). Coumarine 503 in MeOH has been used as standard.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity (cP)</th>
<th>PLQY</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>0.48</td>
<td>&lt;0.1%</td>
</tr>
<tr>
<td>DEG</td>
<td>35.7</td>
<td>0.30%</td>
</tr>
<tr>
<td>PEG (MW 400)</td>
<td>90</td>
<td>2.6%</td>
</tr>
</tbody>
</table>

5.1.4 The relation between crystalline order and fluorescence

In order to check whether enhanced emission in the solid state is strictly related to the crystal structure of 1, this latter was determined by single crystal X-ray diffraction. The crystal packing (see Figure 4) shows only weak $\pi-\pi$ stacking interactions even if aromatic rings and polar substituents are clearly segregated and there is little room for internal motions of the aryl groups.

Figure 5. Crystal packing of 1 (down the c axis) highlighting the aromatic/polar/methyl segregation leading to a ‘layered’ structure

An amorphous film of 1 was prepared by heating a crystalline film, prepared by spin casting on a quartz substrate a solution of 1 in CH$_2$Cl$_2$, at 90°C, which is above the melting point of 1 (86.5-87°C), and by quickly cooling the melted film in a dry ice/acetone bath. The reduced cristallinity of the ‘amorphous’ film was confirmed by XRPD analysis, although it turned into its crystalline phase within two weeks at room temperature. The emission properties of the amorphous and crystalline films are quite different, as evidenced by the fluorescence.
microscopy images reported in Figure 6. At room temperature the crystalline film displays a bright blue emission (PLQY of 11%) peaked at 470 nm, while the amorphous one shows a very weak blue-greenish emission (PLQY of less than 1%) peaked at 495 nm (see Figure 6e). Interestingly, while the emission of the crystalline film shows a modest (2.8 fold) enhancement from 300 to 80K, a much higher (17 fold) enhancement is observed for the amorphous film (see also Figure 2 and ESI), whose PL peak shifts to 510 nm at 90K.

Figure 6. Fluorescence (a,c) and Optical (b,d) microscopy images of a crystalline (a,b) and amorphous (c,d) film. Bar is 5 μm long. PL spectra of 1 crystalline and amorphous films at 90K and 300K, excited at 363 nm (d). The spectra are normalized to the same intensity at low temperatures.

Another evidence of the relation between crystalline order and fluorescent emission is the enhancement of the emission intensity in methanol solution when an increasing amount of a non solvent, such as water is added. The emission intensity is very low until the water content in the mixture is lower than 50% but it greatly increases with a slightly blue shift when the water amount is about 50% (Figure 7). Because of the presence of the non solvent water, molecules of 1 can aggregate in aqueous methanol mixtures with increased water contents. In accordance, the emission intensity of 1 changes dramatically, while its absorption spectrum remained similar independently from the water amount. When the water content is increased up to 70% a large decrease and a small red shift of the emission was observed (Figure t). As already reported for other CIE molecules, this behavior seems to be due to a structural change of the nanoaggregates of 1 formed by the addition of different amounts of water to the methanol solution. At relatively low water content (50%) the molecules of 1 can slowly aggregate into pseudo-crystalline nanoclusters characterized by more intense emissive properties. By increasing the water content, such nanoclusters possess a more amorphous character due to the abrupt aggregation process with parallel strong decrease of the emission intensity.
The effects of the aggregation phenomena have also been investigated varying the amount of 1 in nujol. 1 dissolves in nujol at very low concentration and, as a consequence, both its absorption and emission spectra are those reported for 1 in solution, with an extremely weak fluorescent emission. By increasing the concentration, the solubility of 1 gradually decreases. In agreement we observed the decrease of the main absorption band and the increase of two components one at 320nm and the other at 430 nm. At very high amount the absorption spectrum of 1 in nujol is very similar to the one in measured in KBr. In parallel, a high increase of the intensity is observed in the emission spectrum.

Figure 7. PL spectra of 1 in MeOH/water mixtures with increasing water content. The concentration of 1 is constant for all the solutions and equal to 7.7μM.

Figure 8. Absorption (solid lines) and emission (dashed lines) of 1 in nujol. The concentration of 1 increases going from black to grey.
5.1.5 Acidochromic behavior

In the attempt to develop a stimuli-responsive functional material exploiting the CIE behavior of 1 we examined whether the PL of an aqueous suspension of 1, similarly to what has been previously observed for siloles\(^7\), could be turned “on” and “off” by favoring aggregation or deaggregation respectively. In aqueous media insoluble 1 forms crystalline aggregates and emits (Figure 10 a,d). However, by addition of HCl to the suspension the soluble protonated form of 1 is obtained. As a result, the emission of the transparent solution is quenched (Figure 10 b,e). The original blue emission can be restored by addition of NH\(_3\) which transforms the salt back to its neutral form which aggregates making the mixture turbid but emissive (Figure 10 c,f). Very interestingly, we have observed that a similar “on-off” of the emission can be obtained by a reversible uptake of HCl via a gas-solid reaction. In fact the blue emission of a crystalline film of 1 can be completely quenched upon exposure to vapors of concentrated aqueous HCl for few minutes. In parallel the yellow color of the film turns into white, in agreement with a reduced push-pull character of the system due to protonation (Figure 10 g-j). The fluorescence and the original color of the film can be recovered either in one night at ambient condition or by exposure to ammonia vapors for few minutes (Figure 8 k) indicating a possible application of the material as sensor for volatile acids and bases.
Figure 10. Acidichromic switch of 1 suspended in water (a,d) with addition of HCl (b,e) and subsequent addition of NH₃(c,f). Cast film of 1 before (g,i) and after (h,j) exposure to acid vapors. The bottom pictures show the solutions and the film excited by UV lamp. PL spectra (k) of the pristine film (blue line), after acid vapor exposure (black line) and after 5 min NH₃ vapor exposure (green line), excited at 350 nm.
5.2 Emissive properties of perylene tetracarboxylic diimide - POSS (Polyhedral Oligomeric Silsesquioxanes) hybrid materials

The continuously growing interest around materials characterized by emitting and non linear optical properties (NLO) is justified by their numerous electronic and photonic applications in the field of material science, such as, for instance, modulation of optical signals, microfabrication, sensing and medical imaging. For applications in optical devices, materials have to possess not only significant molecular response, but also attributes like chemical, photochemical and thermal resistance, must be easy to produce and process and with long term optical stability. In this field, a particular interest has devoted towards inorganic-organic hybrid systems, which offer the possibility to combine the properties of the organic component with those of the inorganic scaffold thanks to synergetic effect between the two systems with the aim to optimize the performance of the material.

In the field of optics and electronics, the synthesis of hybrid materials containing the POSS (Polyhedral Oligomeric Silsesquioxanes) has attracted a lot of attention in the last years. For example, Choi and Huang reported a series of polyaromatic substituted POSS with peculiar photoluminescent and charge transport abilities. Moreover, Imae reported the synthesis of another photoluminescent POSS compound having a carbazolebased substituent in which the presence of the POSS core doesn’t affect the electronic properties typical of the carbazole species.

The role of the photoluminescent compound is crucial in the fabrication of devices and it must be characterized by high chemical and photochemical stability, molar absorptivity and fluorescence quantum yield. In this regard, one of the most intriguing organic dyes is the perylene tetracarboxylic diimide as both bulky material and molecular compound. In particular, at the solid state is one of the quite few examples of n-type semiconductor, in comparison to the more common p-type counterpart in organic semiconductors. This property has been widely exploited in various optoelectronics devices, i.e. thin-film transistors, photovoltaics, liquid crystals and light-emitting diodes. On the other hand, due to its high thermal and photostability, perylene tetracarboxylic diimide molecules have also attracted increasing interest in fabrication of single-molecule devices such as fluorescence switches, sensors, molecular wires, and transistors. Like most of the fluorophores reported in literature, Aggregation-Caused Quenching, ACQ, phenomenon (see section 5.1) has been observed in perylene-diimide-molecules at the solid state. Since the ACQ phenomenon is mainly due to π-π interaction between perylene rings, the quenching of the emission can be
avoided by modification of the substituents of the biimide nitrogen with more steric hindered organic or inorganic frameworks\textsuperscript{20}.

With the aim of avoid the aggregation phenomena typical of the peylene-like structure and the ACQ phenomenon, that very often hampers the development of efficient solid state emitters, a new perylene diimide- POSS (Polyhedral Oligomeric Silsesquioxanes) hybrid materials (Figure 11) has been prepared and characterized in order to evaluate whether or not the aggregation phenomenon is prevented.

![Chemical formula of the studied compounds.](image)

5.2.1 Synthesis and characterization of the hybrid materials

The synthesis of these new molecules has been performed by the group of Dr. Elena Lucenti at Università degli Studi di Milano and it is extensively reported in Michele Scarpellini’s PhD thesis. In Figure 10, 11 and 12 are summarized the most important steps of the synthesis. Asymmetrically substituted perylene bisimides are generally obtained in a multistep procedure (Figure 5.1)\textsuperscript{21}. First, symmetrically substituted perylene bisimides (4) are partially saponificated into the potassium salt by reaction with KOH in tert-butanol, and subsequent treatment with acid. The obtained monoimide monoanhydride compound can be reacted with an amine to form the non-symmetrically substituted bisimide (Figure 10).
Figure 10. Synthesis of asymmetrically substituted perylene bisimides 5a and 6a that are the precursor for the synthesis of 5 and 6.

Two different typologies of POSS have been used for the preparation of these inorganic-organic derivatives. The first is the incompletely condensed [(c-C<sub>6</sub>H<sub>11</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub>] or Cy<sub>7</sub>T<sub>7</sub>(OH)<sub>3</sub> (the one reported in Figure 11) while the second is the completely condensed [(c-C<sub>6</sub>H<sub>11</sub>)<sub>7</sub>(CH=CH<sub>2</sub>)Si<sub>7</sub>O<sub>12</sub>] or Cy<sub>7</sub>VyT<sub>8</sub> (the one reported in Figure 12).

5 has been synthesized by the corner capping, performed in dry toluene and in the presence of para-toluensulfonic acid as a catalyst, between incompletely condensate silsesquioxane Cy<sub>7</sub>T<sub>7</sub>(OH)<sub>3</sub> and the perylene derivative bearing the Si(OMe)<sub>3</sub> moiety. This latter has been prepared by silylation of the allyl group of 5a, performed by HSi(OMe)<sub>3</sub> and Karstedt catalyst (Figure 11)
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The second organic-inorganic hybrid compound 6 has been prepared by Heck coupling between the derivative 6a and the completely condensed POSS Cy7VyT8. The latter one has been obtained of the uncomplete condensate POSS used in the synthesis of 5 and the vinyltrichlorosilane in triethylamine (Figure 12).

![Chemical structure of compound 6](image)

**Figure 12. Synthetic of the compound 6**

All the pure compounds have been fully characterized by NMR, Mass spectroscopy and elemental analysis.

### 5.2.2 Spectroscopic properties

The absorption spectra of 5 and 6 show three pronounced peaks (in the range of 450-525 nm) and a shoulder around 425 nm. The fluorescence spectrum depicts the same peak structure in a mirror image of the absorption (Figure 13). These are the typical spectra of every molecule containing the perylene diimide backbone which always dominates the absorption and emission spectra shape and it is not affected by the presence of different substituents on the diimide nitrogens.
Figure 13. Absorption (solid line) and emission (dashed line) spectra ($\lambda_{exc} = 489$nm) of 5 in CHCl$_3$

On the other hand it has been observed that different substituents on the perilene diimide core affect the photoluminescence quantum yield (PLQY). Since the emission spectra of the perylene-like molecules is so typical, only another perylene-like molecule can be used as standard for the determination of the PLQY and, for this reason, compound 4 with QY in CHCl$_3$ close 100%$^{18b}$ has been chosen. PLQYs of 73% for 5 and 90% for 6, both in chloroform, have been measured. The presence of the POSS-fragment induces a slight decrease of the PLQY of the perylene moiety without altering the shape of the absorption and emission spectra.

Measurements of the emissive properties in solution at different concentrations and at the solid state are currently under investigation in order to understand whether the presence of the silsesquioxanes prevents the ACQ phenomenon.
5.3 A new pyrene derivative as NLO and fluorescence switch

The current interest in miniaturizing the components of electronics down to the molecular level is a major driving force in the research of new chromogenic systems\(^\text{22}\). These molecular systems are sensitive to external perturbations of both “physical” (heat, light, pressure or electric field) and “chemical” (complexing agents or pH variations) nature. These perturbations induce structural molecular transformations that are often reversible; by interrupting the perturbation or applying a different one, the initial state and colour can be restored. Chromogenism is classified according to the nature of the external perturbation: “thermochromism”, if it is favoured by heating, “photochromism”, if it is promoted by light, “piezochromism”, if caused by a mechanical force, “electrochromism”, if stimulated by an electric field and “acidichromism”, if pH variations are responsible for colouration-decolouration processes. These materials have been receiving increasing attention because they can be used to improve display and optical storage technology and can be employed as signal transducers between the microscopic and macroscopic worlds\(^\text{23}\).

In the last years, large interest has been focused on the emissive properties of different polycyclic aromatic hydrocarbons and in particular pyrene and pyene-like molecules. This compounds may have an important role in the field of photochemistry and photophysics since they may act as sensitive fluorescent probes that can undergo changes in their spectral making them useful for a wide range of applications such as monitoring the degree of polymerization, radiation cure technology, and photocurable coatings\(^\text{24}\). Moreover, since pyrene and other selected polycyclic aromatic hydrocarbons (PAH) exhibit absorption and/or emission spectral shifts that depend on the dielectric and dipolar properties of their local environment, they are extensively used for probing local polarity, even in biological systems\(^\text{25}\).

Despite the great interest about the emissive properties of pyrene and pyrene-like molecules, in literature there are no studies about NLO properties of this class of compounds. For that reason, the linear and non-linear optical properties of (2-pyren-1-yl-vinyl) pyridine (7) have been investigated and in particular their variation after exposition to acidic and basic vapors.
5.3.1 Synthesis and characterization

Compound 7 has been synthesized by the group of Dr. Elena Lucenti at Università degli Studi di Milano and it is extensively reported in Michele Scarpellini’s PhD thesis. It is obtain in good yield by Heck coupling of 1-bromopyrene and 4-vinylpyridine in dicyclohexylmethylamine for 24 hours (Figure 11). The pure compound has been fully characterized by NMR, mass spectroscopy and elemental analysis.

Figure 11. Synthetic path of the molecule 7.

5.3.2 Linear and non-linear optical characterization

Compound 7 is fluorescent in both solid state and solution, in particular the solid is characterized by a green emission (maximum at 516 nm) that turns light blue (maximum at 440 nm) when it is dissolved in chloroform (see Figure 12).

The emission in solution is quite intense with a PLQY, in toluene solution, of 64%, measured using coumarine 503 dissolved in methanol as standard.

The NLO measurements have been performed using the EFISH techniques and the $\mu\beta$ values of solution of 7 in CHCl$_3$ at different concentration are reported in Table 3.
Table 3. $\mu\beta$ values of CHCl$_3$ solution of 7 at different concentrations.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>$\mu\beta$ ($\times 10^{-48}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3}$</td>
<td>203</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>2200</td>
</tr>
<tr>
<td>$5 \times 10^{-5}$</td>
<td>2660</td>
</tr>
</tbody>
</table>

Decreasing the concentration an increase of the $\mu\beta$ values is observed indicating the possible formation of centrosymmetric aggregates. The aggregation is also supported by the variation of the shape of the emission spectra of 7 in CHCl$_3$ solution at different concentrations (Figure 12). It’s worth nothing that, the most significant variation is observed moving from a $10^{-3}$M solution to a $10^{-4}$M one which are also the critical concentrations for the variation of the NLO response. However, no change is observed in the UV-Vis spectra (Figure 13) which show almost the same shape ranging from $7 \times 10^{-4}$M to $10^{-5}$M solutions.

![Figure 12. Normalized spectra of CHCl$_3$ solution of 7 at different concentration.](image)

![Figure 13. UV-Vis spectra of CHCl$_3$ solutions of 7 at different concentrations.](image)
5.3.2 Acidochromism

In order to investigate a possible application of 7 as pH sensor, the variation of its linear and NLO properties after exposition to HCl and NH₃ vapors has been studied (Figure 14).

![Figure 14. Protonation and deprotonation reaction of molecules 7 and 8.](image)

By exposition of a small amount of 7 to HCl vapor, a change in color from yellow to dark orange is observed and the fluorescent emission shifts to higher energies from green to red, with a maximum centered at 615nm, as reported in Figure 15.

![Figure 15. Emission spectra of 7 (λ_{exc}=378nm) and 8 (λ_{exc}=400nm) at the solid state.](image)

The same happens in CHCl₃ solution, in fact, in both absorption and emission spectra a redshift of the main peak is observed (Figure 16 and 17).
Moreover, the emission of 8 is not only red shifted compared to the one of 7 but it is also quenched, in fact, in CHCl₃ solution, a PLQY of 19% has been obtained using the quinine sulphate in 0.1M H₂SO₄ as standard.

The NLO properties are also affected by the protonation and the μβ value measured with the EFISH technique is 3 times lower and not anymore dependent by the concentration (Table 4).

Table 4. μβ values of CHCl₃ solution of 8 at different concentrations.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>μβ (*10⁻¹⁸ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2 10⁻⁴</td>
<td>414</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>525</td>
</tr>
</tbody>
</table>
5.4 Conclusions

Unusual fluorescent behavior has been investigated and confirmed for different classes of materials. The CIE behavior of the molecule 4-dimethylamino-2-benzylidene malonic acid dimethyl ester has been investigated and confirmed. The emission intensity has been shown to be temperature dependent in solution, amorphous and crystalline films and it is controlled by a RIR process. In fact, by lowering the temperature a strong increase of the emission intensity occurs only when (solution and amorphous film) intramolecular rotations are allowed at room temperature so that the very low emission is due to non-radiative relaxation processes favoured by the molecular torsional mobility\textsuperscript{26}. Thanks to combined emission and \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopies, the rotation around the aryl main axis has been identified as the origin of such non-radiative relaxation processes. The PL behavior of such relatively simple push-pull aromatic molecular structure is quite unusual since crystallization of aromatic molecules usually red-shifts emission spectra and decreases emission intensity due to easy molecular \(\pi-\pi\) stacking which weakens the emission by a fast migration of the excitation towards non emissive sites\textsuperscript{27}. However, the XRD crystal structure indicates the presence of only weak \(\pi-\pi\) stacking interactions which are therefore unable to produce an emission quenching in the crystalline phase. The emissiveacidochromism of \textsuperscript{1} in aqueous solution or as crystalline film has also been studied, enabling the material to function as chemosensor.

With the aim of prevent aggregation and ACQ phenomena, the introduction of steric hindered groups on the luminophore structure has been investigated on a perylene tetracarboxylic diimides bonded to a polyhedral oligomeric silsesquioxanes. The results show that the presence of the POSS substituent on the perylene diimide backbone affects the efficiency of the radiative decay of the excited states, in fact, a slight decrease of the PLQY has been observed for both \textsuperscript{5} and \textsuperscript{6} in comparison to the POSS-free molecule \textsuperscript{4}. The fluorescence behavior at different concentrations and the measurements of the PLQY at the solid state are currently under investigation.

The switch by protonation-deprotonation reaction of both linear and non linear optical properties of 1-vinylpyridine pyrene has been studied. The non protonated form, in fact, shows a high value of \(\mu_\beta\) and a quite strong fluorescence at 450nm in solution while the protonated one is characterized by lower NLO properties and a less intense fluorescent emission at 550nm. A concentration effect on the NLO properties has been observed for the not protonated form which \(\mu_\beta\) value at high concentration is lowered by the formation of centrosymmetric aggregates. Such aggregation effect is not observed in the protoned form.\u201d
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5.5 Experimental section

5.5.1 EFISH measurements

Measurements of $\mu \beta_{1907}$, the products of the chromophore dipole moment ($\mu$) and the projection of $\beta_{VEC}$, the vector part of the molecular first-order hyperpolarizability $\beta$ tensor along the direction of $\mu$, were performed by the solution-phase DC EFISH generation method. EFISH measurements were carried out in CH$_2$Cl$_2$ solutions at a nonresonant fundamental wavelength of 1907 nm using a Q-switched, mode-locked Nd$^{3+}$:YAG laser (pulse durations of 15 ns (90 ns) at a 10 Hz repetition rate). The 1064 nm initial wavelength was shifted to 1907 nm by a Raman shifter with a high-pressure H$_2$ cell. All the measurements have been performed in amylene stabilized CHCl$_3$.

5.5.2 Fluorescence Spectroscopy

PL measurements are obtained with a SPEX 270 M monochromator equipped with a N$_2$ cooled charge-coupled device exciting either with a monochromated Xe lamp or an Ar$^+$ laser. The spectra are corrected for the instrument response. Low temperature measurements are obtained with a double chamber Oxford DN1704 variable temperature cryostat equipped with a thermocouple. PLQY for solutions are obtained by using coumarin 503 as reference. PL QY for solid state materials is carried out using a home-made integrating sphere according to the procedure reported elsewhere$^{29}$. Microscopy Fluorescence images are collected with a Nikon Eclipse TE2000-U inverted confocal microscope by exciting with a 100 W Hg lamp with 330-380 nm band-pass excitation filter.

5.5.3 NMR Spectroscopy

$^1$H and $^{13}$C NMR spectra were acquired with a Bruker Avance DRX 400 and DRX 500 spectrometers.

5.5.4 Single crystal data collection, structure solution and refinement

A crystal sample of dimensions 0.19 $\times$ 0.04 $\times$ 0.04 mm was mounted on a glass fiber in air and collected at RT on a Bruker AXS APEX2 CCD area-detector diffractometer. Graphite-monochromatized Mo-K$\alpha$ ($\lambda = 0.71073$ Å) radiation was used with the generator working at 50 kV and 35 mA. Orientation matrix were initially obtained from least-squares refinement on ca. 300 reflections measured in three different $\omega$ regions, in the range $0 < \theta < 23^\circ$; cell parameters were optimised on the position, determined after integration, of 14246 reflections. The intensity data were collected within the limits $0 < 2\theta < 52^\circ$ in the full sphere ($\omega$ scan...
method), with sample-detector distance fixed at 6.0 cm; 1440 frames (50 s per frame; $\Delta \omega = 0.5^\circ$) were collected; the first 60 frames were recollected to have a monitoring of crystal decay, which was not observed; an empirical absorption correction was applied (SADABS$^{30}$). A total of 14246 reflections were collected (2739 unique, $R_{\text{int}} = 0.0560$ with $R_{\text{int}} = \Sigma|F_o^2 - F_{\text{mean}}^2| / \Sigma F_o^2$; $R_\sigma = \Sigma \sigma(F_o^2)/\Sigma F_o^2$; $R_\sigma = 0.0351$). The structure was solved by direct methods (SIR97)$^{31}$ and refined with full-matrix least squares (SHELX97)$^{32}$ on $F^2$ on the basis of 2739 independent reflection; anisotropic temperature factors were assigned to all non-hydrogenic atoms. Hydrogens were riding on their carbon atoms, though whenever possible, they have been freely refined.

Crystal data for 1: C$_{14}$H$_{17}$NO$_4$, Mr = 263.29, monoclinic, space group P2$_1$/c (No. 14), $a = 13.179(3)$, $b = 7.241(2)$, $c = 15.270(4)$ Å, $\beta = 101.58(1)^\circ$, $V = 1427.5(6)$ Å$^3$, $Z = 4$, $D_c = 1.225$ g cm$^{-3}$, $T = 293(2)$ K, crystal size = 0.19 × 0.04 × 0.04 mm$^3$, $\mu = 0.09$, Mo K$\alpha$ radiation, $\lambda = 0.71073$ Å. Refinement of 176 parameters on 2739 independent reflections out of 14246 measured reflections ($R_{\text{int}} = 0.0560$, $R_s = 0.0351$, 20 max = 56.0$^\circ$) led to $R_1 = 0.0547$ (I > 2$s$(I)), w$R_2 = 0.1743$ (all data), and $S = 1.043$, with the largest peak and hole of 0.22 and -0.25 e Å$^{-3}$. 
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Chapter 6

SYNTHESES AND CHARACTERIZATION OF Cu(I) COMPLEXES FOR THE PHOTORELEASE OF THE BIOACTIVE MOLECULES CS₂
Small molecules such as NO, CO and H₂S have attracted a lot interest in the last years for their use in medicinal applications. In fact, it has been demonstrated that they act as cell signaling agents and accelerate the immune response. Interestingly, these same molecules have acute toxic effects at higher dosage.

Inflammation is a common physiological response of the immune system to several diseases or injuries that, in sensitive tissues, can result in irreparable structural defects. Undesired/uncontrolled up-regulation of the immune system is the cause of autoimmune diseases, such as irritable bowel diseases (IBDs) and psoriasis, which are characterized by localized inflammation that has no positive physiological need and is debilitating to the patient. Nuclear factor-κB (NF-κB) is a member of a broad group of signaling proteins that signals immune system up-regulation, causing the initial stages of inflammation. Therefore, NF-κB represents a possible target for anti-inflammatory drug candidates. Recent interest in the suppression of NF-κB pathways has led to the discovery of several common molecule classes as direct inhibitors. One class of drug, N,N-dialkyldithiocarbamates (R₂NCS₂⁻)³, show promise in alleviating several inflammation diseases including IBD⁴, uveoretinitis⁵ and Rheumatoid arthritis.

Carbon disulfide has been found to be a major metabolite of orally administered dithiocarbamates (R₂NCS₂⁻)⁶ and it has been hypothesized to be the active metabolite of compounds containing dithiocarbamate functionality⁷. Masuda and Nakayama, demonstrated that carbon disulfide protects as well as, or better than, Et₂NCS₂⁻ against organ damage caused by small molecule poisons like CHCl₃, CCl₄, CCl₂=CH₂, acetaminophen, etc in rodent models⁸. More recently, Lai demonstrated that both CS₂ and R₂NCS₂⁻ inhibit the NF-κB pathway, suggesting CS₂ could be an effective anti-inflammatory target⁷. Since systemic exposure to free CS₂ has been demonstrated to be linked to a series of maladies including depression, cerebral atrophy and memory loss⁹, the in-situ photochemical release of CS₂ is a promising strategy for a controlled delivery mechanism that has never been studied under physiological conditions.

One possible way is the acid catalyzed elimination of CS₂ from dithiocarbonate compound which is generally too fast to allow reasonably controlled delivery. An alternative approach could be the use a physiologically inert metal complex that, upon irradiation with visible or near-infrared (NIR) light, releases CS₂.

The only example of metal complex with a photolabile CS₂ moiety reported till now is the [(PPh₃)₂Cu(i-dto)Cu(PPh₃)₂] (1), i-dto = 1,1- dithiooxalate¹⁰. The authors suggest that the photolysis causes the homolytic cleavage of the C-C bond giving, at first, metal bound CS₂.
and CO$_2$ radical anion fragments and, at the end, [(PPh$_3$)$_2$Cu(μ-Cl)$_2$Cu(PPh$_3$)], CO$_2$ and CS$_2$ as photoproducts (Figure 1). However, they failed to provide evidence of this mechanism with the exception of the isolated complex [(PPh$_3$)$_2$Cu(μ-Cl)$_2$Cu(PPh$_3$)] which has been characterized by XRPD. Moreover, the presence of the bridging chloride atoms in the photoproduct supports the hypothesis that an alternative mechanism, maybe solvent-mediated, can lead to the products.

\[ \text{Figure 1. Observed photochemical reaction of } [(\text{PPh}_3)_2\text{Cu}(\mu-\text{dto})\text{Cu(PPh}_3)_2]\text{, } \text{C}_2\text{S}_2\text{O}_2^{2-} = 1,1\text{-dithiooxalate} \]

During the 7 months period I spend at the University of California Santa Barbara in Prof. P. C. Ford’s laboratories, I worked on the a project about the photogeneration of CS$_2$ that implied the study of the photodegradation of the known compound reported in Figure 1 and the synthesis of new Cu(I) complexes.

**6.1 Photochemical degradation of [(Ph$_3$P)$_2$Cu(i-dto)Cu(PPh$_3$)$_2$] (1)**

Since the photochemistry of [(PPh$_3$)$_2$Cu(i-dto)Cu(PPh$_3$)$_2$] received limited attention, the photolysis of this complex has been followed by UV-Vis spectroscopy in order to better understand the mechanism of its decomposition.

Strauch et al., in their original paper, performed the photolysis using unfiltered sunlight whose UV component is known to causes the homolytic cleavage of C-X bond of most organohalides including the solvent used that was CH$_2$Cl$_2$. In order to avoid the formation of radical species in the system, which could be very dangerous for leaving cells, the photolysis of a 5x10$^{-5}$M solution of 1 in both dichloromethane and tetrachloroethylene (PCE), has been performed with 450±40nm light from a filtered Hg arc lamp. The UV-Visible spectrum of 1 before photolysis is characterized by a band centered at 260nm, related to a triphenyl phosphine centered transition, and by a band at 447nm that is a metal-to-ligand charge transfer (MLCT) as confirmed by theoretical calculations (Figure 2, top).
During the photolysis, a decrease of the intensity of the band at 447nm has been observed while the peak at 260nm is retained supporting a mechanism that doesn’t involve the Cu-phosphines center (Figure 2, bottom).

Figure 2. Spectra of 1 in CH$_2$Cl$_2$ (top) and the decrease of the intensity of the band at 447nm during the photolysis (bottom).

The same behavior has been observed in the more oxidizing solvent tetrachloroethylene (PCE) with the only difference that the MLCT is shifted to 458nm. The photoreaction quantum yields have been measured using K$_3$[Fe(C$_2$O$_4$)$_3$] in 0.1M H$_2$SO$_4$ as actinometer and the values (reported in Table 1) are very low, even in the presence of the more oxidizing PCE, and are oxygen independent.
Table 1. Photoreaction quantum yields of 1 in CH₂Cl₂ and perchloroethylene (PCE)

<table>
<thead>
<tr>
<th></th>
<th>DCM</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>0.06%</td>
<td>0.7%</td>
</tr>
<tr>
<td>Air</td>
<td>0.04%</td>
<td>0.6%</td>
</tr>
</tbody>
</table>

The amount of the (eventually) generated CS₂ is too low in both the solvents and its measurements is impossible either using the common spectroscopic techniques, such as IR or UV-Vis spectroscopy, and using specific reagents capable of react only with CS₂. Experiments at higher concentrations have also been performed but the increase of the amount of 1 slows down the reaction velocity and it's impossible to observe a relevant variation of the band at 447 nm in a reasonable time.

Since the photogeneration of a bigger amount of CS₂ seems to be impossible, the reaction has been performed in a chlorine-free solvent in order to, at least, confirm the proposed mechanism. Therefore the photolysis has been performed, maintaining the same experimentally conditions, on a 7x10⁻⁵ M solution of 1 in toluene and, surprisingly, the same variation in the UV-Vis spectra has been observed (Figure 3).

The photoreaction quantum yield has been measured using K₃[Fe(C₂O₆)₃] in 0.1M H₂SO₄ as actinometer and it is equal to 0.11% (in both air and argon atmosphere).

This evidence suggests that the mechanism of this reaction is much more complicated of the one that the authors proposed in their original paper and a deeper investigation is necessary in order to understand whether or not CS₂ is photogenarated and the role of the solvents.
6.2 Synthesis of new Cu(I) complexes containing a CS\textsubscript{2} moiety

6.2.1 Synthesis and characterization [Cu(dmp)(PPh\textsubscript{3})(tBuOOC-CS\textsubscript{2})]

The synthesis of new Cu(I) complexes has also been investigated in order to prepare compound with a more photolabile CS\textsubscript{2} moiety able to undergo photolysis at higher wavelength than the compound 1. As source of CS\textsubscript{2} both the 1,1-dithiooxalate [O\textsubscript{2}C-CS\textsubscript{2}\textsuperscript{2-}] (2) as bipotassium salt and its ter-butyl ester derivative [tBuOOC-CS\textsubscript{2}\textsuperscript{2-}] (3) as benzyltriphenylphosphonium salt, have been used and the more electron acceptor 2,9-dimethyl-1,10-phenanthroline (dmp, 4) has been chosen as ancillary ligand instead of the thiphenylphenanthrolines (see Figure 4).

![Chemical formula of the ligands](image)

Figure 4. Chemical formula of the ligands 1,1-dithiooxalate (2), O-\textit{t}-butyl-1,1-dithiooxalate ester (3) and 2,9-dimethyl-1,10-phenanthroline (4)

A lot of efforts have been spent trying to obtain a new complex by mixing together (in different solvent and conditions) the CS\textsubscript{2}-based ligand, the dmp and the [Cu(CH\textsubscript{3}CN)\textsubscript{4}][PF\textsubscript{6}]\textsuperscript{12} as source of Cu(I), but most of the time the extremely thermodynamic stable complex [Cu\textsuperscript{I}(dmp)\textsubscript{2}][PF\textsubscript{6}] has been obtain.

A different synthetic path has been hypothesized starting from the complex [(PPh\textsubscript{3})\textsubscript{2}Cu(tBuOOC-CS\textsubscript{2})] (5) (Figure 5) prepared by Dr. David Zigler adapting a synthetic procedure reported in literature\textsuperscript{13} (see experimental section). An equimolar amount of 5 and dmp has been dissolved in dichloromethane and kept at low temperature in order to exchange the two phosphines bonded to the Cu(I) in 5 with the 2,9-dimethylphenanthroline without obtaining the undesired Cu(I) bis-phenanthroline complex. Surprisingly, only one PPh\textsubscript{3} has been exchanged and the monodentate dithiooxalate ester complex [Cu(dmp)(PPh\textsubscript{3})(tBuOOC-CS\textsubscript{2})] (6) has been isolated as long orange needle suitable for XRD analysis.

6 is one of the rare example of tetrahedral Cu(I) complex with three different ligands. Its structure is reported in Figure 6 while its crystallographic data are summarized in Table 2.
Figure 5. Chemical formula of [(PPh$_3$)$_2$Cu(tBuOOC-CS$_2$)](5) and [Cu(dmp)(PPh$_3$)(tBuOOC-CS$_2$)](6)

Table 2. Crystallographic data of [Cu(dmp)(PPh$_3$)(tBuOOC-CS$_2$)] $\cdot$ CH$_2$Cl$_2$ (6 $\cdot$ CH$_2$Cl$_2$).

<table>
<thead>
<tr>
<th>Compound empirical formula</th>
<th>C$<em>{39}$H$</em>{38}$Cl$_2$CuN$_2$O$_2$PS$_2$</th>
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<tr>
<td>Symmetry</td>
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<tr>
<td>Morphology</td>
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<td>$T$ (K)</td>
<td>150(2)</td>
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<td>Space group</td>
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<td>Crystal dimension (mm)</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>$S$ $^a$</td>
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</tr>
<tr>
<td>$R$ $^a$</td>
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</tr>
<tr>
<td>$R$(w) $^a$</td>
<td>0.1335$^b$</td>
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</tbody>
</table>

$^a$ Refinement of $F^2$ against all reflections. The weighted $R$-factor $R$(w) and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors, etc., and is not relevant to the choice of reflections for refinement. $^b$ Weighting factor $(w) = [s^2(F_o^2)+0.0500P]^2+0.0000P]^{-1}$ where $P$=($F_o^2$+$2F_c^2$)/3. $^c$ Weighting factor $(w) = [s^2(F_o^2)+0.0686P]^2+0.0000P]^{-1}$ where $P$=($F_o^2$+$2F_c^2$)/3.
Figure 6. Crystal structure of 6·CH₂Cl₂ showing 50% thermal ellipsoids (T = 150 K). Hydrogen atoms and phenyl rings have been omitted for clarity.

Table 3. Selected interatomic distances for the compounds [BzPPh₃⁺][tBuOOC-CS₂⁻], [(PPh₃)₂Cu(tBuOOC-CS₂⁻)] (5) and [Cu(dmp) (PPh₃) (tBuOOC-CS₂⁻)]·CH₂Cl₂ (6)

<table>
<thead>
<tr>
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<th>C–S (Å)</th>
<th>Cu–S (Å)</th>
<th>Cu–P (Å)</th>
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<tbody>
<tr>
<td>[PPh₃Bz] [ 3 ]</td>
<td>1.666</td>
<td>1.659</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.682</td>
<td>2.4928</td>
<td>2.2727(10)</td>
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</tr>
<tr>
<td>6</td>
<td>1.656</td>
<td>2.3096</td>
<td>2.2253(11)</td>
</tr>
<tr>
<td></td>
<td>1.686</td>
<td>3.771</td>
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</table>

The C–S distances 1.656(3) and 1.686(3) Å for the C=S and C–S, respectively are only modestly different than those seen for the η² precursor 5 or the free ligand [BzPPh₃⁺] [3]. However, the Cu–S distance at 2.3096(11) Å is considerably shorter than in 5 perhaps as the result of backbonding from Cu(I) into the dmp acceptor that would make the copper center more electro-positive. The Cu–P distance is also shorter, 2.2253(11) Å.
6.2.2 Synthesis a new tricoordinated Cu(I) complex containing the perthiocarboxylato ligand [tBuOOC-CS₃⁻]

The exchange reaction seems to be a possible way so the synthesis of a compound, analog to 5, but with two acetonitrile molecules (more labile ligand) instead of the two phosphines has been tried by reaction of [Cu(CH₃CN)₄][PF₆] and 3 (as [BzPPh₃⁺] salt). After many days at low temperature, a dark powder has been obtained and the presence of the Cu(II) has been hypothesized since both the powder and solutions in different solvents are air stable.

In fact, the same product (as confirmed by UV-Vis spectroscopy in CH₂Cl₂ solution) has been isolated by biphasic reaction under argon of aqueous CuBr₂ with 2.1 equivalents of [BzPPh₃⁺][3] in CH₂Cl₂ that doesn’t lead to the formation of a complex of the [tBuOOC-CS₂⁻] (3) but to a complex of the unexpected perthiocarboxylato ligand [tBuOOC-CS₃⁻]. The crude [BzPPh₃⁺][CuBr(tBuOOC-CS₃⁻)] (7) salt is isolated and then repeatedly washed with tetrahydrofuran in order to separate the dark pink product 7 and the by-product [BzPPh₃⁺]Br.

Crystals of 7 suitable for a XRD diffraction analysis are growth by slow diffusion of diethylether into a concentrated THF solution of the compound. Chemical and crystal structures are reported in Figure 7 while the crystallographic information is summarized in Table 4.

![Chemical and crystallographic structure of 7.](image)
Table 4. Crystallographic data of [BzPh3][BrCu(S$_3$C-COOtBu)] · 0.5 THF (7-THF)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
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<td>Formula</td>
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</tr>
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<td>$F_w$</td>
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</tr>
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</tr>
<tr>
<td>Space group</td>
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<td></td>
<td>$b = 9.2736(19)$ Å</td>
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<td></td>
<td>$c = 38.513(8)$ Å</td>
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<tr>
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<td>Unique reflections</td>
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<td>1.587$^c$</td>
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<tr>
<td>$R^a$</td>
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</tr>
<tr>
<td>$R$(w)$^a$</td>
<td>0.2032$^c$</td>
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</table>

$^a$ Refinement of $F^2$ against all reflections. The weighted $R$-factor $R$(w) and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors, etc. and is not relevant to the choice of reflections for refinement. $^b$ Weighting factor (w) = [$s^2(F_o^2) + (0.0500P)^2 + 0.0000P]^{-1}$ where $P$ = ($F_o^2 + 2F_c^2$)/3. $^c$ Weighting factor (w) = [$s^2(F_o^2) + (0.0686P)^2 + 0.0000P]^{-1}$ where $P$ = ($F_o^2 + 2F_c^2$)/3.

Remarkably, this structure displays a 3-coordinated Cu(I) with distorted trigonal planar coordination geometry in which the S–Cu–S angle is 99.33(9)$^\circ$ and the bromide is centered between the bound S atoms, with S–Cu–Br $\approx$ 130$^\circ$. The coordination sphere of the copper atoms in 7 is not complete and its air-stability cannot be explained on the basis of the crystalline structure in fact the coordination environment of Cu(I) (Figure 8) shows no other ligands, including cations and solvent, within a normal distance for coordination. The shortest distance between two copper atoms is 8.785 Å and the closest non-bonded atoms, phenyl hydrogens, are 2.96 to 3.90 Å distant.
6.2.2.a The mechanism

The mechanism of this reaction involves oxidation of the ligand and reduction of Cu(II) to Cu(I) with the extra sulfur of the perthio ligand coming from the excess of 3 and its pathway can only be hypothesized on the basis of few evidences. For what concerns the per-thio ligand, from preliminary electrochemical measurements, it seems that [tBuOOC-CS₂] can be readily oxidized to the disulfide RC(=S)SSC(=S)R\textsuperscript{14}, however, the source of the oxidizing equivalents is unknown since an insufficient amount of Cu(II) is present in solution and, even if the reaction is carried out under argon, the possible role of spurious O\textsubscript{2} cannot be ruled out. Any attempt to repeat the synthesis using CuSO\textsubscript{4} or Cu(OAc)\textsubscript{2} did not result in analogous products suggesting that the bromide plays an important role in the mechanism and that Cu(II) does not directly oxidize [tBuOOC-CS₂\textsuperscript{+}] . It is also known that, in solution, CuBr\textsubscript{2} is in equilibrium with CuBr and Br\textsubscript{2} so this might be the source of the Cu(I)\textsuperscript{15}. A possible scheme of the pathway that leads to 7 is reported in Figure 9.

Figure 8. Crystal packing illustration of 7·0.5THF showing the distances between the central copper and its closest neighbors (Å)
6.2.3.b Spectroscopic properties

7 is quite soluble in most of the common solvents and its THF solution displays two broad and prominent bands at 358 nm (3730 M$^{-1}$cm$^{-1}$) and 512 nm (3420 M$^{-1}$cm$^{-1}$) with a low energy tailing at 720 nm (shoulder, 27 M$^{-1}$cm$^{-1}$).

Figure 10. UV-Vis spectra of 7 in THF.
In order to better understand the electronic properties of $7$, DFT calculation has been performed by Dr. Alexi Iretski of the Lake Superior State University. Figure 11 displays the calculated frontier orbitals for this anion. The HOMO ($-4.72$ eV) and the LUMO ($3.14$) are primarily ligand $\pi^*$ in character with regard to the perthiocarboxylato ligand with the HOMO indicating some contribution from the bromide lone pair perpendicular to the plane of the ring. The HOMO-1 and HOMO-2 are largely bromide lone pairs while HOMO-3, -4 and -5 are largely metal ligand bonding orbitals. The lowest lying singlet electronic excited states of $7$ and its theoretical electronic absorption spectrum are calculated using time-dependent DFT at the B3LYP/6-31G* level. This TD-DFT calculation predicted the absorption bands at 646 nm [(HOMO-1, 83%) $\rightarrow$ LUMO, or XLCT (where X is Br and L is the perthiocarboxylate ligand, and CT is charge transfer)]; at 499 nm [(HOMO-5, 89%) $\rightarrow$ LUMO, or largely MLCT]; overlapping transitions at 426 nm [(HOMO-3, 65%) $\rightarrow$ LUMO, largely $\sigma_{CuBr}$ to $\pi^*_L$ CT] and at 409 nm [(HOMO-6, 89%) $\rightarrow$ LUMO, or $\pi_L$ $\rightarrow$ $\pi^*_L$ ligand localized ]; and 356 nm [(HOMO-7, 68%) $\rightarrow$ LUMO, or largely $d_{Cu},\sigma_L$ $\rightarrow$ $\pi^*_L$].

Figure 11. Pictorial representations of the LUMO, HOMO and HOMO-1 through HOMO-7 for $7$ as calculated by DFT at the B3LYP/6-31G* level of theory.
Figure 12 is reported the DFT predicted electronic absorption spectrum of 7 in vacuum overlaid with the experimental spectrum measured in CH₂Cl₂. For the strongest transitions predicted at about 356 and ca. 426 nm respectively (in vacuum), the calculated oscillator strengths \( f^{\text{calc}} \) are almost twice than the experimental \( f^{\text{exp}} \) values calculated from the product of \( \varepsilon_{\text{max}} \) and the full width at half maximum (in cm⁻¹).

Unfortunately, correction for solvation using SM8 solvation model to evaluate solvent effect on calculated spectra are not possible due to lack of parameterization for Cu atoms.
6.3 Conclusions

The photogeneration of CS$_2$ from Cu(I) complexes containing a CS$_2$ moiety has been investigated starting from the study of the photophysical properties of the compound 1. By performing the photolysis in a chlorine free, it has been demonstrate that the mechanism of the reaction is different from the one proposed by Strauch et al. The photogenaration of CS$_2$ (if it is generated) is not even possible since the photoreaction quantum yield is extremely low in all the tested solvents.

In addition, two new Cu(I) complexes containing a CS$_2$ moiety have been isolated. By exchange reaction of [Cu(PPh$_3$)$_2$(tBuOOC-CS$_2$)] with 2,9-dimethyl-1,10-phenanthroline, orange long needles of [Cu(dmp)(PPh$_3$)(tBuOOC-CS$_2$)] (6) has been obtained. This is a rare example of tetracoordinated Cu$^I$ complex with three different ligands. Moreover, by addiction of [BzPPh$_3$][tBuOOC-CS$_2$] dissolved in dichloromethane on a water solution of Cu$^{II}$Br$_2$, the unpredictable formation of the air stable threecoordinated Cu$^I$ complex [Cu(tBuOOC-CS$_3$)(Br)] [PPh$_3$Bz] (7) is observed. The role of the bromide is crucial since compound analog to 7 cannot be isolated working with Cu(II) salts different from CuBr$_2$. Theoretical calculations also show that the band at lower energy in the absorption spectra is a XLCT (where X = Br).

Further study has to be performed in order to determine the stability and photoreactivity of both 6 and 7 in solution and whether or not CS$_2$ is photogenerated.
6.4 Experimental section

6.4.1 XRD

The solid state structures of the new series of molecules were determined using standard procedures. A Bruker 3-axis platform diffractometer was used to measure reflections for crystals using Mo Kα radiation selected with a graphite monochromator (λ = 0.71070 Å) and detected via SMART 1000 CCD. Crystal structures were solved with SHELXS-97 using experimental parameters listed in Table 2,3,4 and 5 and refined using SHELXL-97. Hydrogens were empirically placed using a constrained geometric arrangement based on energy minimized distances.

6.4.2 Spectroscopic characterization

Electronic absorption spectra were measured in spectroscopic grade solvent using a Varian-Cary UV-2401PC double beam UV-Vis spectrophotometer. Infrared spectra were measured in solid KBr using a Mattson FTIR at 2 cm⁻¹ resolution and averaging 32 scans. NMR spectra (¹H- and ¹³C) were measured in deuterated solvent on either a 200 MHz Varian MERCURY Vx or 500 MHz Varian UNITY INNOVA instrument. Mass spectrometry was performed either with a Micromass Q-ToF using a standard electrospray source (acetonitrile) or with a modified Q-ToF instrument using a nanospray source (THF). Source, cone and impact chamber potentials were optimized to decrease ion fragmentation. Theoretical mass spectra were determined for specific ions using the isotopic distribution calculator in ChemDraw Ultra Suite of programs.
6.4.3 Synthesis of the compounds

6.4.3.a Synthesis of potassium 1,1-dithiooxalate \([O_2C-CS_2], K_2[2]\)\(^{17}\)

**Reaction**

\[
\begin{align*}
\text{Na}_2\text{S} + \text{H}_2\text{SO}_4 & \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S} \\
\text{H}_2\text{S} + 2 \text{KOH} & \rightarrow \text{K}_2\text{S} + 2\text{H}_2\text{O} \\
\text{Cl}_3\text{CCOOH} + 2 \text{K}_2\text{S} & \rightarrow \text{K}_2[O_2\text{C-CS}_2] + 2 \text{KCl} + \text{HCl}
\end{align*}
\]

**Procedure**

Potassium hydroxide (2.50 g, 40.1 mmol) is dissolved in 20 mL of deoxygenated ethanol under argon flow. Half of the KOH solution is removed via syringe and H₂S is bubbled through the remaining 10 mL. The H₂S is generated in a separate flask by slowly dripping 6M H₂SO₄ (ca. 10 mL) via dropping funnel onto 34.0 g of Na₂S·9H₂O (141 mmol) with constant flow of argon. Excess H₂S is collected using a bubbler charged with a saturated Fe₂(SO₄)₃ solution. The H₂S generator is removed and the remaining KOH solution is added. After purging with argon for 30 min, the K₂S solution is heated to ca. 40 °C and 1.09 g of 1,1,1-trichloracetic acid (6.68 mmol) in ca. 10 mL of ethanol is slowly added via dropping funnel while maintaining the temperature below 65 °C. The reaction is heated at gentle reflux for 30 min, cooled till room temperature and then vacuum filtered. The resulting yellow solid is rinsed with 3x 30 mL of absolute ethanol and dried \textit{in vacuo} to give 2.53 g of a mixture of K₂[2] and KCl. The salt mixture can be enriched in K₂[2] by precipitating KCl from a saturated aqueous solution with methanol at low temperature. Carbon analysis reveals 5.14% of carbon content, indicating 42.4% K₂(i-dto) by mass, therefore a 72% synthetic yield.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Weight (g)</th>
<th>N° of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S·9H₂O</td>
<td>240</td>
<td>34.0</td>
<td>141</td>
</tr>
<tr>
<td>KOH</td>
<td>56.1</td>
<td>2.50</td>
<td>40.1</td>
</tr>
<tr>
<td>Cl₃CCOOH</td>
<td>163.35</td>
<td>1.09</td>
<td>6.68</td>
</tr>
</tbody>
</table>

**Characterization**

\(^{13}\)C-NMR (D₂O): \(\delta = 259\text{ppm }(-\text{CS}_2), 181\text{ ppm }(-\text{CO}_2^-)\)

UV-Vis (pH 12 KOH solution): \(\lambda_{\text{max}} = 335\text{nm}; \varepsilon = 15000 \text{ M}^{-1}\text{cm}^{-1}\).

FTIR (KBr pellet): \(\nu = 1583(\text{vs}), 1374(\text{vs}), 1020(\text{vs}), 772(s), 754(\text{vs}) \text{ cm}^{-1}\).
6.4.3.b Synthesis of [CuCl(PPh\textsubscript{3})\textsuperscript{3}]\textsuperscript{18}

Reaction

\[ \text{CuCl} + 3 \text{PPh}_3 \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{CuCl(PPh}_3)_3] \]

Procedure

To a stirring suspension of 2.00 g of CuCl (20.2 mmol) in 60 mL of CH\textsubscript{2}Cl\textsubscript{2} is added 15.9 g of PPh\textsubscript{3} (60.6 mmol). The CuCl and PPh\textsubscript{3} slowly co-dissolve. The reaction is heated at gentle reflux for 1 hour, giving a large quantity of white precipitate which is isolated by removal of the solvent under reduced pressure. The crude white solid is then added to 1.4 L of hot absolute ethanol. Not the entire solid dissolves with heating and stirring, but the super saturated hot ethanolic layer was easily decanted from the remaining solids. Tapping of the cool solution caused copious amounts of large plate like crystals to rain out of solution. The crystals were collected by vacuum filtration and were rinsed with 30 mL of ethanol and dried \textit{in vacuo} to give 13.6 g of [CuCl(PPh\textsubscript{3})\textsubscript{3}] (76% yield) as a fluffy white crystalline solid.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Weight (g)</th>
<th>N° of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl</td>
<td>98.7</td>
<td>2.0</td>
<td>20.2</td>
</tr>
<tr>
<td>PPh\textsubscript{3}</td>
<td>262.3</td>
<td>15.9</td>
<td>60.6</td>
</tr>
</tbody>
</table>
6.4.3.c Synthesis of [(Ph₃P)₂Cu(i-dto)Cu(PPh₃)]²⁻(1)

**Reaction**

\[
[CuCl(PPh₃)₃] + K₂\left[\begin{array}{c}
\text{S} \\
\text{S} \\
\text{O}
\end{array}\right] \xrightarrow{\text{water / CH₂Cl₂}} \text{water / CH₂Cl₂}
\]

**Procedure**

0.514 g of 42% pure K₂[2] (1.10 mmol) are dissolved in 40 mL of water and added dropwise to a vigorously stirring solution of [CuCl(PPh₃)₃] (2.0 g, 2.30 mmol) dissolved in 20 mL of CH₂Cl₂. After 20 min, the organic phase is separated from the aqueous phase, which is washed with 3 x 10 mL of CH₂Cl₂. The combined organic fractions are filtered and reduced in volume to ca. 20 mL. An equal volume of isopropyl alcohol is added and dichloromethane is removed under reduced pressure. The solution is then, chilled to induce crystal formation and a dark brown solid is isolated. 1.15 g of pure 1 are obtained by double recrystallization of the crude solid from CH₂Cl₂/isopropanol (0.90 mmol, 45% yield).

**Characterization**

**UV-Vis** (CH₂Cl₂ solution): \(\lambda_{\text{max}} = 447 \text{ nm (}\varepsilon = 11300 \text{ M}^{-1} \text{cm}^{-1})\), 260 nm (\(\varepsilon = 40000 \text{ M}^{-1} \text{cm}^{-1}\))

**FTIR** (KBr pellet): \(\nu = 3050(\text{m}), 1970(\text{w}), 1902(\text{w}), 1830(\text{w}), 1682(\text{w}), 1581(\text{vs}), 1567(\text{m}), 1478(\text{s}), 1433(\text{vs}), 1329(\text{m}), 1183(\text{w}), 1158(\text{w}), 1093(\text{m}), 1076(\text{vs}), 1026(\text{w}), 997(\text{w}), 741(\text{s}), 694(\text{vs}), 505(\text{bs}) \text{ cm}^{-1}\).
6.4.3.d Synthesis of [BzPh₃P][tBuOOC-CS₂] ([BzPPh₃][3])¹³

Reaction

\[ \text{S} + \text{N(Et)}_3 + \text{Cl} \rightarrow \underset{\text{DMF}}{\text{+ [BzPPh₃]Cl}} \rightarrow \underset{\text{DMF} / \text{CH₃OH}}{\text{BzPPh₃}} \]

Procedure

Sulfur (1.92 g, 60.0 mmol) and 12.5 mL of triethylamine (90.0 mmol) are stirred in 30 mL of deoxygenated dimethylformamide for ca. 50 min. O-t-butyl-2-chloroacetate (4.52 g, 30.0 mmol) is added in one portion to the dark green solution, turning it deep orange. The temperature of the reaction is kept at 20-30 °C using a water bath for 2 hours. Precipitated [NHEt₃]Cl is separated by vacuum filtration and rinsed with 2 x 5 mL of DMF. The filtrate is added to 11.7 g of [BzPPh₃]Cl (30.0 mmol) dissolved in 30 mL of MeOH. Crude [BzPPh₃][3] is precipitated by slow addition of 80 mL of water over ca. 50 min. After filtration, the crude [BzPh₃P][3] is suspended in 200 mL of diethyl ether in order to remove the excess of DMF and water. The salt [BzPPh₃][3], recrystallized twice from CH₂Cl₂/i-PrOH, is isolated as 5.24 g of dark orange crystals (9.87 mmol, 33 % yield).

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Weight (g)</th>
<th>N° of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>32</td>
<td>1.92</td>
<td>60.0</td>
</tr>
<tr>
<td>N(Et)₃</td>
<td>101.19</td>
<td>9.08 (12.5mL, d=0.726 g/mL)</td>
<td>90.0</td>
</tr>
<tr>
<td>Cl-CHCOOtBu</td>
<td>150.7</td>
<td>4.52</td>
<td>30.0</td>
</tr>
<tr>
<td>[BzPPh₃]Cl</td>
<td>388.87</td>
<td>11.7</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Characterization

¹H-NMR (CD₂Cl₂): δ = 6.98-7.82 (20H, m, Ar), 4.89 (2H, d, ²J_H-H = 14.2), 1.41 (9H, s) ppm

¹³C-NMR (CD₂Cl₂): δ = 246.3 (CS₂), 170.4 (CO₂), 127-136 (multi. C_Ar), 117.6 (P-CH₂-Ph, ¹J_CP = 88 Hz), 80.1 (C_Bu), 28.1 (Me_Bu) ppm.

UV-Vis (MeOH solution): λ_max = 343nm (ε = 14600 M⁻¹cm⁻¹), 267 nm (ε = 4280 M⁻¹cm⁻¹).

FTIR (KBr pellet): ν = 2986(w), 2921(w), 2881(w), 3051(w), 3017(w), 1691(C=O, vs), 1586(m), 1483(m), 1455(m), 1438(s), 1366(m), 1267(m), 1253(m), 1168(s), 1154(m), 1110(s), 1043(vs), 1001(m), 995(m), 850(m), 835(m), 803(m), 780(m), 752(m), 747(s), 718(m), 697(s), 689(s), 578(m), 512(s), 505(s), 495(s) cm⁻¹.
XRD: Crystals of [BzPh₃P][3] suitable for XRD analysis are isolated after slow diffusion of i-PrOH into a CH₂Cl₂ solution at low temperature. Crystallographyc information are reported in Table 5.

Table 5. Crystallographic data of the compounds [BzPPh₃][3] and 5

<table>
<thead>
<tr>
<th></th>
<th>[BzPPh₃][3]</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₃₁H₃₁O₂PS₂</td>
<td>C₄₂H₃₉CuO₂P₂S₂</td>
</tr>
<tr>
<td>Fw</td>
<td>530.65</td>
<td>765.33</td>
</tr>
<tr>
<td>Symmetry</td>
<td>Orthorhombic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Morphology</td>
<td>Orange block</td>
<td>Orange plate</td>
</tr>
<tr>
<td>Space group</td>
<td>Fdd2</td>
<td>Pı</td>
</tr>
<tr>
<td>T (K)</td>
<td>293(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>Crystal dimension (mm)</td>
<td>0.3 x 0.3 x 0.2</td>
<td>0.3 x 0.15 x 0.08</td>
</tr>
<tr>
<td>Unit cell dimentions</td>
<td>a = 52.853(3) Å</td>
<td>a = 10.262(2) Å</td>
</tr>
<tr>
<td></td>
<td>b = 13.0849(8) Å</td>
<td>b = 13.096(3) Å</td>
</tr>
<tr>
<td></td>
<td>c = 16.6948(10) Å</td>
<td>c = 14.625(3) Å</td>
</tr>
<tr>
<td>Unit-cell volume (Å³)</td>
<td>11545.8(12)</td>
<td>1855.2(6)</td>
</tr>
<tr>
<td>Z</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td>μ (cm⁻¹)</td>
<td>2.65</td>
<td>8.23</td>
</tr>
<tr>
<td>Total reflections</td>
<td>16494</td>
<td>13778</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>5490</td>
<td>7026</td>
</tr>
<tr>
<td>Reflections [I &gt; 2σ(I)]</td>
<td>4392</td>
<td>4777</td>
</tr>
<tr>
<td>S²</td>
<td>1.18⁰</td>
<td>1.029⁰</td>
</tr>
<tr>
<td>R</td>
<td>0.0460⁰</td>
<td>0.0476⁰</td>
</tr>
<tr>
<td>R(w)</td>
<td>0.1036⁰</td>
<td>0.1000⁰</td>
</tr>
</tbody>
</table>

*Refinement of F² against all reflections. The weighted R-factor R(w) and goodness of fit S are based on F²; conventional R-factors R are based on F, with F set to zero for negative F². The threshold expression of F² > 2σ(F²) is used only for calculating R-factors, etc., and is not relevant to the choice of reflections for refinement. Weighting factor (w) = [s²(Fo²)+0.0500P]⁻¹ where P=(Fo²+2Fc²)/3. Weighting factor (w) = [s²(Fo²)+0.0686P]⁻¹ where P=(Fo²+2Fc²)/3.
6.4.3.e Synthesis of \([\text{Cu}(\text{PPh}_3)_2(t\text{BuOOC-}CS_2)]\) (5)

### Reaction

\[
[\text{CuCl}(\text{PPh}_3)_3] + [\text{BzPh}_3\text{P}][3] \rightarrow \text{CH}_2\text{Cl}_2
\]

### Procedure

In a 100 mL beaker, 0.89 g of \([\text{CuCl}(\text{PPh}_3)_3]\) (1.0 mmol) are dissolved in 20 mL of \(\text{CH}_2\text{Cl}_2\) and 0.53 g of \([\text{BzPh}_3\text{P}][3]\) (1.0 mmol) in 30 mL of \(\text{CH}_2\text{Cl}_2\) are added dropwise over 5 min. The dark reaction mixture is stirred in the dark for 1 hour before evaporate all the solvent. The residue is recrystallized twice from \(\text{CH}_2\text{Cl}_2/i\text{-PrOH}\) at \(-20\) °C. 0.64 g of pale brown needles of 5 (0.84 mmol, 84%) are isolated.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Weight (g)</th>
<th>No. of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{CuCl}(\text{PPh}_3)_3])</td>
<td>885.6</td>
<td>0.89</td>
<td>1.0</td>
</tr>
<tr>
<td>([\text{BzPh}_3\text{P}][3])</td>
<td>530.68</td>
<td>0.53</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Characterization

\(^1\text{H-NMR (CD}_2\text{Cl}_2\):} \quad \delta = 7.1-7.4 (30H, m), 1.43 ppm (9H, s). FTIR (KBr): \(v = 2982(\text{w}), 2935(\text{w}), 3054(\text{w}), 1703(\text{C=O, vs}), 1478(\text{s}), 1432(\text{vs}), 1389(\text{m}), 1365(\text{m}), 1253(\text{b,vs}), 1156(\text{b,vs}), 1092(\text{s}), 1077(\text{s}), 1052(\text{s}), 1018(\text{s}), 997(\text{m}), 843(\text{m}), 811(\text{m}), 744(\text{vs}), 694(\text{vs}), 527(\text{m}), 516(\text{s}), 501(\text{s}) \text{ cm}^{-1}.

\(\text{UV-Vis (CH}_2\text{Cl}_2 \text{ solution):} \quad \lambda_{\text{max}} = 400\text{nm (shoulder, } \varepsilon = 3000 \text{ M}^{-1}\text{cm}^{-1})\), 364nm (\(\varepsilon = 5230 \text{ M}^{-1}\text{cm}^{-1})\), 265 nm (\(\varepsilon = 23100 \text{ M}^{-1}\text{cm}^{-1})\).

\(\text{XRD:} \quad \text{Crystals of 5 suitable for XRD analysis are isolated after slow diffusion of } i\text{-PrOH into a CH}_2\text{Cl}_2 \text{ concentrated solution at room temperature. Crystallography information are reported in Table 5.}\)
6.4.3.3 Synthesis of [Cu(dmp)(PPh$_3$)(tBuOOC-CS$_2$)] (6)

**Procedure**

A deoxygenated solution of 5 (0.20 g, 0.26 mmol) in minimal CH$_2$Cl$_2$ is charged with 0.055g of 2,9-dimethyl-1,10-phenanthroline (0.26 mmol), also in a minimal amount of deaerated CH$_2$Cl$_2$. The reaction is kept for 3 days at 5 °C and then most of the solvent is removed under argon flow and diethyl ether is layered on the reaction concentrate to give small orange crystals after 3 days at −20 °C. After filtration 0.11 g of air-sensitive, bright yellow microcrystals of 6 are isolated (0.16 mmol, 62 % yield).

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Weight (mg)</th>
<th>N° of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>765.12</td>
<td>200</td>
<td>0.26</td>
</tr>
<tr>
<td>2,9-dimethyl-1,10-phenanthroline</td>
<td>208</td>
<td>55</td>
<td>0.26</td>
</tr>
</tbody>
</table>

**Characterization**

Chemical formula and elemental analysis: CuC$_{38}$H$_{36}$N$_2$O$_2$PS$_2$

Experimental (calculated) : C 63.6 (64.2)% ; H 5.13 (5.10)%; N 4.03 (3.94)%.

FTIR (KBr): $v = 2981$(w), 2931(w), 3056(w), 3005(w), 1695(C=O, s), 1652(m), 1616(m), 1588(m), 1558(m), 1538(m), 1506(m), 1498(m), 1478(w), 1456(m), 1434(s), 1366(s), 1275(b,s), 1254(b,s), 1165(b,s), 1151(m), 1092(m), 1066(s), 1038(m), 988(s), 860(m), 842(m), 742(s), 731(m), 695(s), 522(s), 503(m), 491(m) cm$^{-1}$

XRD Crystals of 6 suitable for XRD analysis are isolated after slow diffusion of diethylether into the reaction mixture at −20 °C. The crystals readily lost the CH$_2$Cl$_2$ of crystallization, so they are carefully kept at low temperature. Crystallographic information are reported in Table 2 and 3.
6.4.3.3 Synthesis of [Cu(tBuOOC-CS$_3$)(Br)] [Bz PPh$_3$] (7)

Reaction

\[
\text{CuBr}_2 + [\text{BzPPh}_3][3] \rightarrow \text{Water} / \text{CH}_2\text{Cl}_2
\]

Procedure

Under argon flow a solution of 0.40 g of [BzPh$_3$P][3] (0.75 mmol, 2.1 eq) in ca. 10 mL dichloromethane is added slowly to a stirring deaerated solution of 0.080 g of CuBr$_2$ (0.36 mmol) in a minimal amount of water (ca. 3 mL). The aqueous phase is removed after 30 min of stirring and the organic layer is concentrated \textit{in vacuo}. The resulting violet solid is washed with 3 x 1 mL of THF and gravity filtered through a glass wool packed Pasteur pipette to extract 7. Red needles are obtained from slow diffusion of diethyl ether into the combined THF washing solutions. 0.16 g of 7 ·0.5THF are isolated after recrystallization from Et$_2$O / THF mixture. (0.21 mmol, 60% yield).

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Weight (mg)</th>
<th>N° of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBr$_2$</td>
<td>225.34</td>
<td>80</td>
<td>0.36</td>
</tr>
<tr>
<td>[BzPh$_3$P][3]</td>
<td>530.68</td>
<td>400</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Characterization

Chemical formula and elemental analysis: CuC$_{33}$H$_{35}$BrO$_{2.5}$PS$_3$

Experimental (calculated) : C 53.5 (53.4)% ; H 4.45 (4.75)%.

ESI(−)-MS (CH$_3$CN or THF): \(m/z\) (rel. peak height) = 350.81(77), 351.83(9.6), 352.81(100), 353.81(13), 354.81(51), 355.83(5.7), 356.82(7.1);

FTIR (KBr): \(v = 2980\text{(m)}, 2918\text{(m)}, 2836 \text{(m)}, 3056\text{(w)}, 1717\text{(b,s)}, 1586\text{(m)}, 1492\text{(m)}, 1482\text{(m)}, 1454\text{(m)}, 1436\text{(s)}, 1392\text{(m)}, 1368\text{(m)}, 1255\text{(b,s)}, 1151\text{(b,s)}, 1111\text{(s)}, 1074\text{(b,s)}, 1031\text{(w)}, 996\text{(m)}, 921\text{(w)}, 866\text{(w)}, 836\text{(m)}, 787\text{(m)}, 743\text{(m)}, 717\text{(m)}, 700\text{(m)}, 688\text{(s)}, 582\text{(m)}, 558\text{(m)}, 510\text{(s)}, 499\text{(m)}, 446\text{(w)}.

UV-Vis (THF solution): \(\lambda_{\text{max}} = 358\text{nm} (\varepsilon = 3730 \text{ M}^{-1}\text{cm}^{-1}), 512\text{nm} (\varepsilon = 3420 \text{ M}^{-1}\text{cm}^{-1}), 720\text{nm} \text{ (shoulder, } \varepsilon = 27 \text{ M}^{-1}\text{cm}^{-1})\) nm.

XRD: X-ray quality crystals are obtained from slow diffusion of Et$_2$O into a THF solution of 7 at low temperature. Crystallographic information are reported in Table 4.
References


Chapter 7

GENERAL CONCLUSIONS
In the last years, inorganic–organic hybrid crystalline materials with interesting electrical, magnetic and non-linear optical (NLO) properties have attracted the attention of the material science community. Particular interest was focused on the appealing polyfunctional hybrids, whose macroscopic functionalities can be due to cooperative effects between the two moieties (organic and inorganic). Within this wide new field, the coupling of magnetic and non-linear optical properties seems to be quite attractive, and yet largely unexplored. In particular, although some magnetic materials displaying efficient second harmonic generation (SHG) properties have been reported, systems in which the magnetic properties can be easily and rationally tuned, without affecting the SHG efficiency, are still rare.

In this regard, Cariati et al. reported the synthesis as well as the structural, magnetic and photophysical characterization of a new promising family of magnetic and second-order NLO isostructural layered hybrid materials of general formula \([\text{M}^{\text{III}}_2\text{M}^{\text{II}}(\text{C}_2\text{O}_4)_6][\text{DAMS}]_4\cdot2\text{DAMBA}\cdot2\text{H}_2\text{O}\), where \(\text{M}^{\text{III}} = \text{Rh, Fe, Cr; M}^{\text{II}} = \text{Mn, Zn, [DAMS]}^+\) is trans-4-(4-dimethylaminostyryl)-1-methylpyridinium and DAMBA is p-dimethylaminobenzaldehyde. This class of materials possesses some important features: it segregates [DAMS⁺] chromophores in layers of J-aggregates (densely packed domains of chromophores characterized by a peculiar visible absorption band narrower and red-shifted with respect to the parent monomeric chromophore) while mixed metal oxalate chains are present as stripes of complex layers of M³⁺ and M²⁺ cations. These can be properly chosen to produce specific magnetic behaviours, in fact examples containing antiferro-, ferro-, and ferri-magnetic interactions (mediated by oxalato bridges) have been obtained by coupling proper M³⁺ and M²⁺ ions. The variety of magnetic properties does not influence the very high SHG efficiency, measured by the Kurtz-Perry method at 1907 nm non-resonant wavelength, which is for all compounds of the same order of magnitude of \(\text{[trans-N,N-dimethylamino-}N'-\text{methylstilbazoliu}m][p\text{-toluensulfonate]}\) (DAST), one of the most active (1000 times that of the standard urea) organic crystalline materials ever reported. In view of the tunability of the magnetic properties we decided to extend our investigation studying the Ni²⁺ and Co²⁺ members of this class of hybrid mixed oxalates. Indeed, based on the structures of the Mn²⁺ and Zn²⁺ compounds of this class, the oxalates should form a cubic anti-prism coordination sphere around Ni²⁺ or Co²⁺ that only very rarely affords octa-coordination with traditional organic ligands. In addition, the magnetic behaviour of Ni²⁺ chains is particularly interesting as the magnetic orbitals of this metal are usually very delocalized along the chains, producing unexpectedly strong magnetic interactions while the Co²⁺ chains are usually characterized by a
strong anisotropy which can lead to a peculiar magnetic behaviour. The best general synthetic way to obtain compounds of the family of mixed oxalates consists in a two step procedure.

\[
[DAMS]I + K_3^{III}(C_2O_4)_3 + M^{II}X \xrightarrow{H_2O/MeOH \text{ r.t.}} \text{Phase (M}^{III}/M^{II})
\]

A similar strategy to obtain the M^{II} = Ni, Co analogous compounds using, as M^{II}X, NiCl_2 and Co(NO_3)_2·6H_2O has been successfully applied. [M^{III}M^{II}(C_2O_4)_6][DAMS]_4·2DAMBA·2H_2O derivatives of Co and Ni are isostructural with the Mn and Zn members of the family and possess the same SHG properties.

In the Ni^{II} derivatives, the delocalization of Ni^{II} magnetic orbitals along the inorganic “stripes” of the crystalline network produces strong next-nearest-neighbour magnetic interactions, otherwise absent in the chains of compounds containing the Mn^{II} ions. Such interactions, when in the presence of magnetic M^{III} ions such as Cr^{III} or Fe^{III}, give rise to an interesting and complex magnetic behaviour possibly due to an almost perfect compensation between nearest-neighbour and next-nearest-neighbour interactions along the chain. The magnetic behaviour of the Co^{II} members of the family is dominated by a large orbital contribution of Co^{II} ions and the high spin octacoordinated Co^{II} centers behave similarly to the hexacoordinated Co^{II} ones. The presence of magnetic M^{III} centres introduces ferromagnetic M^{III}-M^{II} interactions which are particularly interesting if the metal is Fe^{III}. Fe_2Co compound, in fact, is characterized by a moderate antiferromagnetic interaction between Fe^{III} and Co^{II}, resulting in a ferrimagnetic like structure. Its low temperature dynamic magnetic properties candidate this compound as the second oxalate-based Single Chain Magnets (SCM) reported up to date, a property which in this case is coupled to the strong second order NLO activity.

During the optimization of the synthetic procedure of the above reported hybrid mixed metal oxalates, some new compounds have been isolated which, all but one, revealed of no particular interest being centrosymmetric and, consequently, SHG inactive. We then focused our attention on the only active species which, by XRPD and elemental analysis, proved to be different from members of the [M^{III}M^{II}(C_2O_4)_6][DAMS]_4·2DAMBA·2H_2O family. Elemental analysis evidenced that this compound was lacking both M^{III} and M^{II} and, on the other side ^1H NMR indicated a [DAMS^+]/DAMBA ratio equal to 1/0.3. We then found that the pure material, with an SHG efficiency of the same order of magnitude of DAST measured by the Kurtz-Perry method at 1907 nm non-resonant wavelength, could be prepared by refluxing for
1 hour 30 minutes a MeOH/H$_2$O (1/1) solution of [DAMS]I and DAMBA. Crystals of the compound were analysed by single crystal X-ray diffraction. Despite several attempts, the quality of the samples was always very poor and therefore the diffraction pattern quite scarce. Nevertheless, a structural model corresponding to [DAMS]I-[DAMBA]$_x$ could be tentatively formulated and refined. The compound crystallizes in a pseudo-orthorhombic system. However, the most reliable lattice is monoclinic, in the space group Cc. From the structure solution, we could clearly identify the [DAMS$^+$] and I$^-$ ions, whereas some uncertainty remains on the actual orientation of the included DAMBA.

The [DAMS$^+$] molecules form column in which the units are organized in J aggregates. Interestingly, in the structure of the NLO active phase two adjacent columns of [DAMS$^+$] are related by a glide plane, which produces a special coupling between the chromophores in a fishbone-like arrangement. In this way, each molecule of [DAMS$^+$] is surrounded by the two stacked [DAMS$^+$] partners and by two [DAMS$^+$] belonging to the mirror symmetric column, with interactions through the methyls of the dimethyl ammino groups (Figure 1). Surprisingly, the solid state UV-vis absorption spectrum of this species lacks of the characteristic band of J aggregates (Figure 2). The TD-DFT analysis allowed us to investigate all the various contributions of the transitions to the absorption spectrum of fishbone-like [DAMS$^+$] aggregates. As expected on the basis of a previous study on J-type [DAMS$^+$] aggregation, the calculated absorption spectrum shows some interchromophoric charge-transfer transitions at low energy. However, the fishbone-like architecture, where two columns of slipped NLO-phores are faced, gives rise to an additional series of transitions, associated with interchromophoric charge-transfer transitions between NLO-phores on adjacent columns. These intercolumns-chromophoric transitions, with an oscillator strength comparable to that of the
typical J-band transitions, have energies lying in between the main adsorption band and the typical J-band, so that the overall shape of the absorption spectrum of this species is a broad band centred at ca. 530 nm, that slightly decrease in intensity up to 650 nm. So the characteristic J aggregates band is completely covered by the band of the intercolumn chromophoric transition as observed experimentally.

Not only crystalline systems are interesting for NLO application. Films containing molecular NLO-phores, in fact, can be used in various electro-optical devices such as optical waveguides or frequency modulators. Electrical poling of molecular NLO-phores dispersed in a polymeric matrix is one of the strategies to build NLO composite materials starting from NLO-phores with large quadratic hyperpolarizabilities (β). In the poling process the initial random arrangement of the dipolar chromophores is broken to generate asymmetry by aligning them with a strong directional electric field. However, such dipole orientation suffers the outcome of an easy decay of the electro-optical properties such as SHG due to orientational relaxation in the polymeric matrix. We have however prepared by the poling procedure poly(methyl methacrylate) (PMMA) films blended with DAST with a significant SHG stable for at least six months. The composite PMMA films containing 4wt% of DAST were obtained by spin-coating from CHCl₃/CH₃OH (2/1) solutions on ordinary cover glass substrates. The electronic absorption spectrum of the pristine hybrid film showed the typical internal charge transfer corresponding to a broad band centred at 450 nm, quite blue shifted with respect to that of DAST dissolved in MeOH, centred at 475 nm, or in CHCl₃, at 490 nm. The absence in the electronic spectrum of a sharp absorption at higher wavelength, typical of J aggregation of [DAMS⁺] NLO-phores within the crystalline structure of bulk DAST, would suggest the absence of micro-crystals of DAST, while the higher energy of the internal charge-transfer band with respect to DAST dissolved in MeOH or CHCl₃, would suggest the presence of nanostructures such as nano-seeds not yet organized as nano-crystals of DAST. Films were heated at T<Tg (70°C) under corona poling at 8kV and then, in the absence of electric poling, heated at T>Tg (120°C). The SHG response showed an unexpected gradual increase reaching a plateau after 2 hours and remained almost constant during the cooling process (Figure 3). In addiction the SH signal checked six months after the thermal treatment was unchanged. The UV-Vis spectrum shows the typical narrow, low energy exciton absorption band arising from J aggregates type disposition of the chromophore. This spectrum closely resembles that of crystalline DAST in KBr.
Remarkably, the poling process induces initially the orientation of the sub-nano seeds of DAST which are successively transformed into nano-crystals by the thermal treatment but still maintaining the orientation. The formation of nano-crystals of DAST of less than 100 nm is supported by TEM and GIXRD evidences. The electro–optic $d_{33}$ coefficient of the resulting film was measured by the Maker fringe method and equal to 5.3 pm/V. A rigorous control of the heating ramp is required to avoid undesirable thermal disorientation: under a fast temperature increase up to 120°C the SH signal is poorly angle dependent resembling that of a powdered system in which nano-seeds are randomly oriented. Surprisingly, when DAST/PMMA films are deposited on ITO (indium tin oxide) instead of glass slides, not only the film is less sensitive to the fast increase of the temperature, but also self-ordered nano-seeds are obtained by heating without electric field poling (as evidenced by the Maker fringes in the Figure 4).

In collaboration with the group of professor Dario Pasini of Università di Pavia, linear and nonlinear optical properties of molecules 1, 2 and 3 has been studied and the $\mu\beta$ value obtained with the EFISH technique are reported in the table below. As expected, an increase of the delocalization leads to an increase of the non-linear optical response of the system.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu\beta$ ($\times 10^{48}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120 ± 40%</td>
</tr>
<tr>
<td>2</td>
<td>172 ± 77%</td>
</tr>
<tr>
<td>3</td>
<td>293 ± 33%</td>
</tr>
</tbody>
</table>

In collaboration with the group of professor Dario Pasini of Università di Pavia, linear and nonlinear optical properties of molecules 1, 2 and 3 has been studied and the $\mu\beta$ value obtained with the EFISH technique are reported in the table below. As expected, an increase of the delocalization leads to an increase of the non-linear optical response of the system.
Of particular interest is also the unusual luminescence emission of \( 1 \) which is characterized by a strong fluorescence in the solid state while it’s not emissive in solution. This effect is totally different from the one observed in common luminophores that are highly emissive in their dilute solutions but become weakly luminescent in the solid state or when fabricated into thin films. The aggregate formation quenches light emission and for that reason the term Aggregation-Caused Quenching (ACQ) was introduced. However it has been found that non-emissive organic molecules are induced to emit efficiently by aggregate formation, a behavior known as Aggregation-Induced Emission (AIE). Even more intriguing are some non emissive molecules which are induced to emit by crystallization but not amorphization; a behavior which has been defined as crystallization-induced-emission (CIE).

\( 1 \) shows in dilute toluene solution a very weak emission centered at 440 nm with a photoluminescence (PL) quantum yield (QY) of less than 0.1\%. This hardly discernible emission shows, in agreement with the dipolar push-pull molecular structure, a solvatochromic behavior moving from toluene to acetonitrile (475 nm). Despite the extremely weak emission in solution, crystalline powders of \( 1 \) are characterized by an intense blue emission at around 480 nm (see Figure 5) for which a PL QY of 14\% has been measured, while for a single crystal the PL QY has been found to be 24\%. In dilute EPA (diethylether : pentane : ethanol 5:5:2) solution of \( 1 \) that shows at room temperature an hardly discernible emission while a quite strong emission peaked at 445 nm is observed at 77 K. This change in the emission intensity cannot be explained with the formation of aggregates since we worked at concentrations as low as \( 10^{-6} \) M. It is rather more probable that the molecular conformation has rigidified at low temperature and in the crystalline state. To confirm that crystallization is the exclusive morphology leading to enhanced emission in the solid state, crystalline and amorphous films of \( 1 \) has been prepared. At room temperature the crystalline film displays a bright emission (PLQY of 11\%) peaked at 470 nm, while the amorphous one shows a very weak emission (PLQY of less than 1\%) peaked at 495 nm. In addition, the emission of the crystalline film shows a modest (2.8 fold) enhancement from 300 to 80 K, a much higher (17 fold) enhancement is observed for the PL intensity of the amorphous film, whose peak shifts to 510
nm at 90 K. Another evidence of the relation between crystalline order and fluorescent emission is the enhancement of the emission intensity in methanol solution when an increasing amount of a non solvent, such as water is added. The emission intensity is very low until the water content in the mixture is lower than 50% but it greatly increases with a slightly blue shift when the water amount is about 50%. Because of the presence of the non solvent water, molecules of 1 can aggregate in aqueous methanol mixtures with increased water contents. In accordance, the emission intensity of 1 changes dramatically, while its absorption spectrum remained similar independently from the water amount. When the water content is increased up to 70% a large decrease and a small red shift of the emission was observed. As already reported for other CIE molecules, this behavior seems to be due to a structural change of the nanoaggregates of 1 formed by the addition of different amounts of water to the methanol solution. At relatively low water content (50%) the molecules of 1 can slowly aggregate into pseudo-crystalline nanoclusters characterized by more intense emissive properties. By increasing the water content, such nanoclusters possess a more amorphous character due to the abrupt aggregation process with parallel strong decrease of the emission intensity. The behavior of 1 in presence of acid and basis was also studied in order to verify if the PL can be turned “on” and “off” by external stimuli. In aqueous media the insoluble 1 forms crystalline aggregates and emits. However, by addition of HCl to the suspension, the soluble protonated form of 1 is obtained and the fluorescence of the transparent solution is quenched. The original blue emission can be restored by addition of NH3 which transforms the salt back to its neutral aggregated form. A reversible change of the emission can be observed also by exposition of crystalline films to vapors of HCl and NH3. This behavior indicates a possible application of the material as sensor for volatile acids and bases.

During a 7 months research period spent at UCSB (University of California, Santa Barbara) in Prof. Ford’s laboratories the synthesis and the photophysical / photochemical characterization of CuI compounds that release the bioactive molecule CS2 as a photoproduct has been studied. Carbon disulfide is interesting for physiological application because it inhibits the pathway of the Nuclear factor-κB (NF-κB), a member of a broad group of proteins that signals immune system up-regulation, causing the initial stages of inflammation. This evidence suggests that CS2 could be an effective anti-inflammatory target. The only example of a metal complex with a photolabile CS2 moiety is \([(PPh_3)_2Cu(i-dto)Cu(PPh_3)_2]\) (i-dto = 1,1-dithiooxalate) which produces \([(PPh_3)_2Cu(\mu Cl)_2Cu(PPh_3)\], CO2 and CS2 as photoproducts. (Figure 6).
It has been suggested that, even though not experimentally proven, the photolysis causes homolytic cleavage of the C-C bond giving metal bound \( \text{CS}_2^- \) and \( \text{CO}_2^- \) radical anion fragments.

The synthesis of new Cu\(^{\text{I}}\) compounds containing a photolabile \( \text{CS}_2 \) moiety was investigated. By exchange reaction of \([\text{Cu}(\text{PPh}_3)_2(\text{i-dto tBu})]\) with 2,9-dimethyl-1,10-phenanthroline, orange long needles of \([\text{Cu}(\text{dmp})(\text{PPh}_3)(\text{tBuOOC-CS}_2^-)]\) (4) has been obtained. This is a rare example of tetracoordinated Cu\(^{\text{I}}\) complex with three different ligands which structure is reported in Figure 7.

Moreover, by addition of \([\text{BrPPh}_3][\text{tBuOOC-CS}_2^-]\) dissolved in dichloromethane on a water solution of Cu\(^{\text{II}}\)Br\(_2\), the unpredictable formation of the air stable tricoordinated Cu\(^{\text{I}}\) complex \([\text{Cu}(\text{tBuOOC-CS}_3^-)(\text{Br})][\text{PPh}_3\text{Bz}]\) (5) is observed (Figure 7). The role of the bromide is crucial since compound analog to 7 cannot be isolated working with Cu(II) salts different from CuBr\(_2\). Theoretical calculations also show that the band at lower energy in the absorption spectra is a XLCT (where X = Br).

Further study has to be performed in order to determine the stability and photoreactivity of both 6 and 7 in solution and whether or not \( \text{CS}_2 \) is photogenerated.
Appendix: Determination of the dipole moment

Theoretical outline

An induced dipole moment ($\mu_{\text{ind}}$) can be generated in non-polar molecules after application of an electric field $E$. The relationship between $\mu_{\text{ind}}$ and $E$ is:

$$\mu_{\text{ind}} = \alpha E$$

where the proportionality constant $\alpha$ is the polarizability of the molecule. Clausius-Mosotti equation correlates the dielectric constant of the material, $\varepsilon$, to $\alpha$ as reported below:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4}{3} \pi z \alpha$$

where $z$ is the number of molecules for unity of volume. The adimensional quantity $(\varepsilon - 1)/(\varepsilon + 2)$ is called volume polarization.

The molar polarization, $P$, can be defined as:

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot Mv = \frac{4}{3} \pi z v M \alpha = \frac{4}{3} \pi N_a \alpha$$

where $M$ is the molecular weight of the substance, $v$ is its specific volume and $N_a$ is the Avogadro’s number.

For a polar molecule, with dipole moment $\mu_0$, the classic Debye treatment shows that the effective polarizability is given by $\alpha + \frac{\mu_0^2}{3kT}$, where $k$ is the Boltzmann’s constant. Therefore, for polar substances, the molar polarization is:

$$P = \frac{4}{3} \pi N_a \left( \alpha + \frac{\mu_0^2}{3kT} \right) = dP + \mu P = \varepsilon P + A P + \mu P$$

The first term $\frac{4}{3} \pi N_a \alpha$ is the polarization of the molecule when there is no permanent dipole orientation; it is correlated to the reciprocal moving of charged species thanks to the effect of the applied electric field. This component is called distortion polarization $dP$.

The second term $\frac{4}{3} \pi N_a \frac{\mu_0}{3kT}$ represents the contribution to the molecular polarization, given by the orientation of the dipoles with respect to the electric field and therefore it is known as orientation polarization $\mu P$. The term of the distortion polarization contains two different contributions. The first is correlated to the displacement of electrons and nuclei and it is mainly attributed to the displacement of the electrons, in fact they have a lower mass with respect to the mass of the nuclei: this is known as electronic polarization, $\varepsilon P$. Moreover, if a
molecule contains polar bonds, the atoms, with different effective charges, move reciprocally thanks to the effect of the electric field. This charge displacement produces an induced dipole and it’s contribute to the polarization is called *atomic polarization*, \( \alpha P \).

The electronic polarization, \( \varepsilon P \), can be correlated to the molar refraction at the infinite wavelength \( R_{\infty} \), defined by the following relation (where \( d \) indicates the substance density):

\[
\varepsilon P = [R_{\infty}] = \frac{(n_{\infty}^2 - 1)}{(n_{\infty}^2 + 2)} \cdot \frac{M}{d} = \frac{(n_{\infty}^2 - 1)}{(n_{\infty}^2 + 2)} \cdot Mv
\]

The atomic polarization, \( \alpha P \), is more difficult to estimate, but fortunately, the relative contribution is low, *ca. 5-10%* of \( \varepsilon P \) and it can be ignored. \( \varepsilon P \), in general is determined by the refraction index \( n_0 \) for the D row of sodium, is slightly higher than the value \( n_\infty \), extrapolated at infinite wavelength. In fact, the Debye equation is valid only for polar molecules that are enough distant and therefore cannot mutually influence their orientation in the presence of electric field; therefore, this equation could be applied only for substances at gaseous state and when the pressure is very low. However, the method can be simplified and applications to a relatively diluted solution of polar compounds in non-polar solvents. This simplification is based on the assumption that, when the concentration of polar substances decreases, the interaction between the dipoles also decreases until the limit value zero when the concentration is zero. As a consequence, it’s possible to obtain a molar polarization without error due to the interaction between dipoles, determining the molar polarization of the polar compound at finite values of concentration in an apolar solvent and extrapolating the results at the relative value of concentration equal to zero.

For a system constituted by more components, the polarization can be calculated as:

\[
P = \frac{\varepsilon - 1}{\varepsilon + 2} v\sum M_if_i = \sum P_if_i
\]

where \( v \) is the specific volume of the solution (equal to the reciprocal of density), \( M_i \) is the molecular weight of the \( i \) component and \( f_i \) is its molar fraction in the mixture.

For two components the relation is:

\[
P = P_1f_1 + P_2f_2
\]

When the component 1 is an apolar solvent, it is possible to assume that its polarization is not influenced by the presence of the solute. Therefore, \( P_1 \) is constant when \( f_2 \) changes. Consequently \( P \) values, determined by the measurements of the dielectric constant and densities of a series of solutions at known concentration of the component 2 in the component 1, allow to get the effective value of \( P_2 \) at different concentrations, because the \( P_1 \) value can
be obtained by the relative measures, carried out on the pure 1 component. The limit value \( P_{2\omega} \), determined when the concentration of the solute 2 tends to zero, represents the molar polarization of the solute, referred to the conditions in which the Debye equation is valid.

Generally, it is possible to use the measurements of the refraction index of the solutions (dielectric constant and densities of these solutions have been determined), to estimate the contribution of the distortion polarization (it must be subtracted). Carrying out the measurement also for the pure solvent, it is possible to obtain the molar refraction of the solute, using a similar expression, reported for polarization:

\[
R = Rf_1 + R_2 f_2 = \frac{(n^2 - 1)}{(n^2 + 2)} \cdot \nu (M_1 f_1 + M_2 f_2)
\]

The dipole moment value, \( \mu_0 \), can be obtained by the Debye equation from the orientation polarization value.

**Guggenheim’s method for the dipole moment determination of a substance in solution**

The method, proposed by Guggenheim (based on the theoretical approach described before) for the dipole moment calculation of a solute molecule in an apolar solvent, allows to a not-accurate determination of the solution densities.

The expressions, reported in the previous chapter for \( P \) and \( R \) in the case of a system with two components, can be written according to the relation reported below:

\[
\frac{\varepsilon - 1}{\varepsilon + 2} \cdot V = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \cdot V_1 f_1 + \left( \frac{\nu P_2}{\varepsilon} + \frac{\mu P_2}{\nu} \right)
\]

\[
\frac{(n^2 - 1)}{(n^2 + 2)} \cdot V = \frac{(n^2 - 1)}{(n^2 + 2)} \cdot V_1 f_1 + \frac{\nu P_2 f_2}{\varepsilon}
\]

By subtraction of the second equation from the first, it is possible to obtain:

\[
\left( \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{(n^2 - 1)}{(n^2 + 2)} \right) \cdot V = \left( \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{(n^2 - 1)}{(n^2 + 2)} \right) \cdot V_1 f_1 + \left( \frac{\nu P_2}{\varepsilon} + \frac{\mu P_2}{\nu} \right) f_2
\]

Because \( V = V_1 f_1 + V_2 f_2 \), where \( V_2 \) is the effective molar volume of the solute and so \( V_1 f_1 = V - V_2 f_2 \), we have:

\[
\left( \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{(n^2 - 1)}{(n^2 + 2)} \right) \cdot (V - V_2 f_2) = \left( \frac{\nu P_2}{\varepsilon} + \frac{\mu P_2}{\nu} \right) f_2
\]
Appendix

\[
\left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2}\right)V_1 \text{ is the atomic polarization } A_P_1 \text{ of the solvent.}
\]

If the atomic polarizations of the different compounds are proportional to their molecular volume, the atomic polarization of the solute is given by:

\[
A_P_2 = \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{n_2^2 - 1}{n_2^2 + 2}\right)V_2
\]

Introducing this hypothetical atomic polarization, the previous equation becomes:

\[
\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{(n^2 - 1)}{(n^2 + 2)}\right)V = \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{(n_1^2 - 1)}{(n_1^2 + 2)}\right)V + \left(\varepsilon A_P_2 + \varepsilon A_P_2^* + \varepsilon \mu P_2\right)f_2
\]

Dividing the first and the second member of this equation by \(V\) and changing the concentration \(c\) of the solute (in moles for volume units) with \(f_2/V\), the next relation is obtained:

\[
\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{(n^2 - 1)}{(n^2 + 2)}\right) = \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{(n_1^2 - 1)}{(n_1^2 + 2)}\right) + \left(\varepsilon A_P_2 + \varepsilon A_P_2^* + \varepsilon \mu P_2\right)c
\]

or, defining \(D = \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{n_2^2 - 1}{n_2^2 + 2}\right)\), it’s possible to write:

\[
D = D_1 + \left(\varepsilon A_P_2 + \varepsilon A_P_2^* + \varepsilon \mu P_2\right)c
\]

Therefore, reporting in a graph \(D\) values versus \(c\), the intercept at \(c=0\) is \(D_1\) and the slope is \((\varepsilon A_P_2 - \varepsilon A_P_2^* + \varepsilon \mu P_2)\), that is \((\varepsilon A_P_2 - \varepsilon A_P_2^* + 4\pi N_a \mu^2/9kT)\). Moreover, if the approximation that the atomic polarization value is proportional to the molecular volume is accepted, it is possible to write \(A_P_2 = \varepsilon A_P_2^*\) and so:

\[
\mu P_2 = \frac{4\pi N_a \mu^2}{9kT} = \lim_{c \to 0} \left(\frac{\partial D}{\partial c}\right)
\]

Because the solutions are prepared by weighing, it’s very simple to define the concentration of the solute by its ponderal fraction \(w_2\), correlated to \(c\) by the relation \(c = w_2/M_2\). Consequently the quantity \(D\) can be expressed in the following form:

\[
D = D_1 + \left(\varepsilon A_P_2 + \varepsilon A_P_2^* + \varepsilon \mu P_2\right)w_2
\]
Reporting in graph $D$ versus $w_2$, the slope is given by $(\lambda P - \lambda P^* + \mu P)/M^2$, or, assuming that $\lambda P = \lambda P^*$,

$$\mu P_2 = M_2 \nu_1 = \lim_{w_2 \to 0} \left( \frac{\partial D}{\partial w_2} \right)$$

In this way, it is possible to determine the dipole moment value of the solute without knowing the densities of the used solutions. Moreover, because $\partial D/\partial w_2$ can be written in the form:

$$\frac{\partial D}{\partial w_2} = \frac{3}{(\varepsilon + 2) \partial \varepsilon}{\partial w_2} - \frac{3}{(n^2 + 2)^2} \partial n^2$$

an alternative method provides for the determination of the limit values for $w \to 0$ of $\partial \varepsilon/\partial w_2$ and $\partial n^2/\partial w_2$. Because $\varepsilon$ and $n^2$ variations vs $w_2$ can be expressed by a power series of $w_2$ according to the following equations:

$$\varepsilon = \varepsilon_1 + a w_2 + a w_2^2 + \ldots$$

$$n^2 = n_1^2 + a w_2 + a w_2^2 + \ldots$$

it is possible to write, using only the first term of the series:

$$\mu P_2 = \frac{3M_2 \nu_1 a}{(\varepsilon_1 + 1)^2} - \frac{3M_2 \nu_1 v}{(n_1^2 + 2)^2}$$

Another simplification can be obtained by the observation that, for a polar solute, $v$ is usually much lower than $a$, and so there is not a significant error if the second term is written as $3M_2 \nu_1 v/(a_1^2 + 2)^2$ and not as $3M_2 \nu_1 v/(n_1^2 + 2)^2$ and in this case the equation becomes:

$$\mu P_2 = \frac{3M_2 \nu_1 (a - v)}{(\varepsilon_1 + 1)^2} = \frac{3M_2}{d_1 (\varepsilon_1 + 2)^2} (a - v)$$

where $d_1$ is the density of the solvent.

Therefore, the main steps for the measurement of the dipole moments of a compound with the Guggenheim’s method are:

1. preparation of solutions with known ponderal fraction of the compounds in an appropriate solvent of low polarity;
2. know dielectric constant and refraction index measurements for every solutions as described in this paragraph;
3. determination of $\alpha$ and $v$ coefficients by linear regression, applied to $\varepsilon$ and $n_2$ values as function of the ponderal fraction of the solute;
Appendix

4. determination of the orientation polarization of the solute $\mu P^2$ by the equations and approximations reported before;

5. determination of the dipole moment value by this relation:

$$\mu(D) = \frac{9kT}{4\pi N_a} \cdot \sqrt{\mu P^2 T} = 0.012813 \cdot \sqrt{\mu P^2 T}$$

where $D$ indicates Debye unity, that is unity of measure of the dipole moment equal to $10^{-48}$ esu x cm.

Experimental determination of the dipole moment

Preparation of solutions

For the determination of the dipole moment of each compound, five solutions have been prepared in CHCl$_3$ (99,9% HPLC grade, Sigma Aldrich) with ponderal fraction of solute in the range $4 \times 10^{-4}$ and $3 \times 10^{-3}$, determined by weighing of solute and solvent through an analytical balance with reading even 0,1mg.

Dielectric constant determination

This determination has been carried out by capacity C measurements through a dipolemeter of model WTW DM01 with a cell DFL 2.

The instrument sensibility for the determination of the dielectric constant $\varepsilon$ (expressed as $\Delta\varepsilon/\varepsilon$) is equal to $10^{-5}$ at the frequency of 2,0 MHz. The cell for measure has been maintained during the reading at a constant temperature (25°C) by a water circulation thermostat. For each solution the measure of the capacity C has been carried out after 15 min at constant temperature. Capacity C and constant dielectric $\varepsilon$ are correlated by this linear equation:

$$\varepsilon = a + bC$$

where $a$ and $b$ values depend on reading scale used for the measure. To determine $a$ and $b$, every experiment has been preceded by the determination of capacity values for three pure solvents, having well-known constant dielectric values and in range of reading scale used for the measure of the solutions. In particular, the reference solvents are CHCl$_3$ (the same solvent used for the preparation of solutions), C$_6$H$_5$Cl and AcOEt (at 25°C, respectively $\varepsilon = 4,72$; 5,621; 6,02). Each time the relative capacity values have been used to draw the calibration line of the instrument. By this line and by the measurements of the solutions capacity, it is possible to obtain $a$ and $b$ values, used for $\varepsilon$ determination.
Refraction index determination

The refraction index of the solutions has been determined by a Pulfrich Zeiss PR2 refractometer, using a Na lamp as source. By a series of filters it is possible to select a monochromatic radiation, emitted from the lamp at 589.3 nm (D line).

The refraction index values have been obtained, measuring the deviation angle $\gamma$ of the incident luminous beam on the prism of measurements containing solution. This angle is correlated to the refraction index of solution $n_\lambda$ (where $\lambda$ is the wavelength used for the measure) in the following way:

$$n_\lambda = \sqrt{N_\lambda^2 - \cos \gamma \cdot \sqrt{N_\lambda^2 - (\cos \gamma)^2}}$$

where $N_\lambda$ is the refraction index of the prism of measure at the wavelength $\lambda$. Here for the prism of measure, at 589.3 nm, $N_\lambda$ is 1.740704. Also in this case the measurements have been carried out at 25°C and the temperature has been maintained constant by a water circulation thermostat. Each reading has been carried out after 15 min of thermostatation.

References

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