

## **An excursion in the second-order nonlinear optical properties of platinum complexes**

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*This excursion is dedicated to the memory of Professor Emeritus Renato Ugo, an exceptional scientist and professor with an unforgettable humanity, for his important involvement in the field of coordination compounds with second-order nonlinear optical properties.*

### **Abstract**

Electrooptical devices and optical communications need compounds with second-order nonlinear optical (NLO) properties as construction blocks. Typically, to show a large quadratic hyperpolarizability, a compound should be asymmetric, be characterized by a large variation between the dipole moments in the excited and ground states, and have low energy electronic transitions. For example, a large quadratic hyperpolarizability can be reached when an electron-donor moiety is linked by means of a  $\pi$ -conjugated spacer to an acceptor group.

In the field of second-order nonlinear optics, particularly attractive are coordination metal complexes because they are often characterized by low-energy and high-intensity intraligand (IL), ligand-to-metal (LM), and metal-to-ligand (ML) charge transfer (CT) electronic transitions, that can be regulated by the choice of the metal and ligands. Among them, platinum(II) complexes are captivating. During this excursion, we will see the quadratic hyperpolarizability of many of them.

After some basic NLO notions, the review presents various classes of NLO-active platinum compounds having mono- and bidentate nitrogen ligands (pyridine, bipyridine, phenanthroline), dithiolenes, cyclometalated ligands (imines, phenylpyridine, phenylbipyridine, and dipyritylbenzene), alkynyl ligands. It is shown how to regulate the quadratic hyperpolarizability with suitable ligands and how to photomodulate the NLO properties by means of a dithienylethene (DTE) moiety. Some examples of complexes with redox-switchable NLO properties are also given. Although the accent is on the quadratic hyperpolarizability measured in solution, it is also shown how some NLO-active platinum complexes can be nano-organized to afford thin films with nonlinear optical properties. The report is not comprehensive, but it allows to get into the field of NLO-active platinum compounds and to understand their potential.

**Keywords:** platinum(II) complexes, photochromism, quadratic hyperpolarizability, EFISH, optical switches

**Highlights:**

- Platinum compounds are very attractive for second-order nonlinear optics (NLO)
- Well-designed platinum compounds can present a large quadratic hyperpolarizability
- The NLO response of complexes can be photomodulated or redox-switched

**Contents**

1. Some basic second-order nonlinear optical notions .....	3
2. Pt(II) compounds with pyridine, bipyridine, or phenanthroline.....	6
3. Pt(II) compounds with dithiolene .....	10
4. Pt(II) compounds with cyclometalated imine .....	13
5. Pt(II) compounds with cyclometalated phenylpyridine .....	14
6. Pt(II) compounds with N <sup>^</sup> C <sup>^</sup> N-pincers.....	17

7. Pt(II) compounds with cyclometalated N <sup>^</sup> C <sup>^</sup> N dipyridylbenzene .....	19
8. Pt(II) compounds with cyclometalated N <sup>^</sup> N <sup>^</sup> C phenylbipyridine .....	28
9. Pt(II) dialkynyl compounds.....	31
10. Conclusion.....	37
11. Acknowledgment.....	39
12. References.....	39

### 1. Some basic second-order nonlinear optical notions

Nonlinear optics (NLO) is concerned with optical phenomena, in which an incident electromagnetic field and a compound interact affording electromagnetic fields with new frequency, phase, or other physical characteristics [1–3]. These optical phenomena depend on molecule or bulk material's polarizability. Some basic notions are given here, along with methodologies to measure the second-order NLO properties. Detailed information is reported elsewhere [1-23].

The induced polarization of a bulk material interacting with an electric field of very high power,  $\vec{E}$ , can be expressed by equation (1):

$$\vec{P} = \vec{P}_0 + \chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}^2 + \dots + \chi^{(n)} \vec{E}^n \quad (1)$$

in which  $\chi^{(1)}$  and  $\vec{P}_0$  are the linear polarizability and the intrinsic polarity, respectively, whereas  $\chi^{(2)}$ ,  $\chi^{(3)}$  and  $\chi^{(n)}$  tensors are the nonlinear polarizabilities and correspond to the 2<sup>nd</sup>, 3<sup>rd</sup> and n-order electrical susceptibilities.

For a molecule, equation (1) becomes equation (2):

$$\vec{P} = \mu_0 + \alpha \vec{E} + \beta \vec{E}^2 + \gamma \vec{E}^3 + \dots \quad (2)$$

in which the dipole moment in the ground state is  $\mu_0$ , whereas the linear polarizability, the quadratic hyperpolarizability and the cubic hyperpolarizability are  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively.  $\beta \vec{E}^2$

represents the generation of a frequency that is two times the incident one. In a centrosymmetric structure,  $\chi^{(2)}$  and  $\beta$  equal zero. A high  $\beta$  or  $\chi^{(2)}$  value corresponds to a high NLO activity.

For linear-shaped molecules in which the  $\beta$  value is controlled by only one charge-transfer transition along the z direction, Oudar provided the “two-level” model that allows calculation of  $\beta$  as a function of the charge transfer transition frequency ( $\nu_{eg}$ ), the incident radiation frequency ( $\nu_L$ ), the dipole moment of the transition ( $r_{eg}$ ) and the variation of the dipole moment between excited and ground states ( $\Delta\mu_{eg}$ ), according to equation (3) [24-25]:

$$\beta_{zzz} = \frac{3}{2h^2 c^2} \frac{\nu_{eg}^2 r_{eg}^2 \Delta\mu_{eg}}{(\nu_{eg}^2 - \nu_L^2)(\nu_{eg}^2 - 4\nu_L^2)} \quad (3)$$

In agreement with the two-level model, a molecule with low  $\nu_{eg}$  but large  $\Delta\mu_{eg}$  and  $r_{eg}$  values is expected to have a large  $\beta$  value. If a molecule is centrosymmetric,  $\Delta\mu_{eg}$  is zero and therefore  $\beta$  is null.

Thus, good quadratic hyperpolarizabilities values can be reached when an electron-donor moiety (D) is connected by means of a polarizable bridge to an electron-acceptor moiety (A). Coordination complexes, with the metallic center acting as donor or acceptor or bridge, are particularly appealing for second-order NLO. These are often characterized by low-energy and high-intensity transitions with charge transfer character [5-23, 26].

Multipolar systems, such as octupolar molecules, are also of interest from an NLO point of view, because it was shown that non dipolar structures may also be the origin of significant second harmonic generation [1-3, 10-15]. An advantage of octupolar molecules is that they have no net dipole moment, an advantage with respect to dipolar compounds which have to be aligned, parallel to an applied electric field, to be NLO-active. The prototypical example of an octupolar molecule is represented by 1,3,5-triamino-2,4,6-trinitrobenzene. Some efficient NLO-active octupolar molecules have a central

core characterized by an electron donor or acceptor behaviour to which three  $\pi$ -delocalized branches, containing acceptor or donor groups, are linked [15].

Experimentally, the quadratic hyperpolarizability of dipolar compounds can be determined in solution by the EFISH (Electric Field Induced Second Harmonic generation) technique [27], working with an incident wavelength  $\lambda$ , by means of equation (4):

$$\gamma_{\text{EFISH}} = (\mu\beta_{\lambda}/5kT) + \gamma(-2\omega; \omega, \omega, 0) \quad (4)$$

where  $\beta_{\lambda}$  corresponds to the projection of  $\beta_{\text{VEC}}$  (vectorial contribution of the tensor  $\beta$ ) along the  $\mu$  (dipole moment in the ground state) axis. The first term of the sum is the dipolar orientational contribution of the NLO response whereas the second term is the electronic cubic contribution, usually negligible for dipolar compounds. This technique gives the  $\mu\beta_{\lambda}$  product. In order to obtain  $\beta_{\lambda}$ ,  $\mu$  has to be determined (theoretically or experimentally with the Guggenheim technique [28]).

Another way to determine the quadratic hyperpolarizability in solution is the HRS (Hyper-Rayleigh Scattering, sometimes called Harmonic Light Scattering) technique [29-32], suitable for all compounds (dipolar or not). The dissolved molecule is irradiated with  $\lambda$  as incident wavelength, there is generation of the incoherently scattered second harmonic which gives  $\beta_{\text{x}}\beta$  as mean value. The components of the quadratic hyperpolarizability tensor are obtained by studying how the second harmonic generation (SHG) depends on the polarization.

Besides, the quadratic hyperpolarizability can be calculated by means of Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) methods or by the "Sum Over States" (SOS) approach [33-34].

From an applicative point of view, there is particular interest for compounds with values of  $\mu\beta$  larger than  $500 \times 10^{-48}$  esu, the value characteristic of Disperse Red One [*trans*-4,4'-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>NEt(CH<sub>2</sub>CH<sub>2</sub>OH)], which has been used in electrooptic polymeric poled films [35]. NLO-active compounds, soluble in a suitable solvent such as dichloromethane or chloroform, can be easily nano-organized in a polymeric matrix, such as poly(methyl methacrylate) or

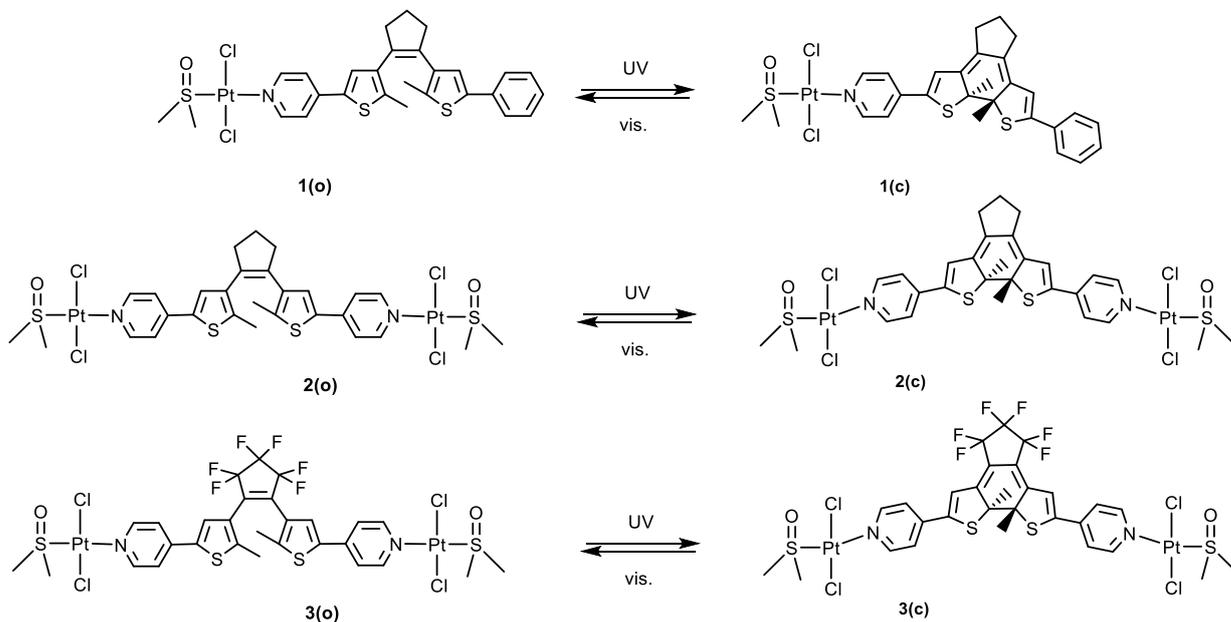
polystyrene, to afford thin films with nonlinear optical properties. It is usually necessary to orient dipolar molecules by corona wire poling to give NLO-active thin films with a given  $\chi^{(2)}$  value, whereas this strategy is not required for octupolar compounds [1-3].

In the last two decades, coordination complexes with second-order NLO properties have attracted increasing attention, often reaching an NLO response superior to that of the prototypal Disperse Red One, making them competitive materials with respect to organic chromophores [5-23]. Complexes with metals of groups 6 and 8-12 of the periodic table have been investigated with a variety of ligands. Particularly large quadratic hyperpolarizabilities have been reached with Ru, Ir, Pt, and Zn complexes. Although reviews have been dedicated to ruthenium [36-37], zinc [38], and iridium [39] complexes, to the best of our knowledge no review has appeared documenting the NLO properties of platinum complexes. This observation prompted us to write an overview on platinum-containing second-order NLO active complexes which is reported in the next sections. The aim is to focus on important aspects of each family of platinum complexes, therefore the review does not provide an exhaustive account of all NLO-active platinum compounds.

## **2. Pt(II) compounds with pyridine, bipyridine, or phenanthroline**

The EFISH technique put in evidence the augmentation of the  $\beta$  value of NMe<sub>2</sub>-Phenyl(CHCH)Pyridine upon coordination; the enhancement factor is controlled by the identity of the metallic center and of its ancillary ligands [16, 20]. For example, there is a two-fold and four-fold augmentation of  $\beta$ (EFISH) upon coordination to “W(CO)<sub>5</sub>” [40] and “*cis*-Ir(CO)<sub>2</sub>Cl” [41], respectively. The augmentation of  $\beta$  is controlled by an intraligand charge transfer transition that depends on the acidity of the metallic fragment that augments the  $\pi^*$  accepting behaviour of the pyridine moiety; the “two level” model [24-25] explains the resulting bathochromic shift of the ILCT transition with augmentation of  $\beta$ . It was observed that the  $\beta$  value of NMe<sub>2</sub>-Phenyl(CHCH)Pyridine doesn't change upon coordination to “*cis*-PtCl<sub>2</sub>”, as expected for the absence of ILCT red shift [42].

It is important pointing out that the control of the optical behaviour of molecules by an exterior stimulus is of great interest in order to develop new materials, notably for photonic communication and data processing [43-50]. In particular, the use of light, to control the NLO response of coordination compounds, is fascinating because it leads to all-optical molecular materials, in which light reads, writes, and stores the information [51]. In this context, an appealing photochrome is dithienylethene (DTE) because it presents thermal stability, high photoconversion, and because the open (o) and closed (c) isomers are characterized by a very different optical behaviour [52-53]. As a matter of fact, the passage from the open isomer to the closed one, and vice versa, is a tool to photomodulate the  $\pi$ -delocalization of the system [54]. In this context, the quadratic hyperpolarizability of various mono and bimetallic platinum(II) complexes bearing a pyridine ligand functionalized with a photoresponsive DTE moiety was studied by the density functional theory method (Figure 1) [55].

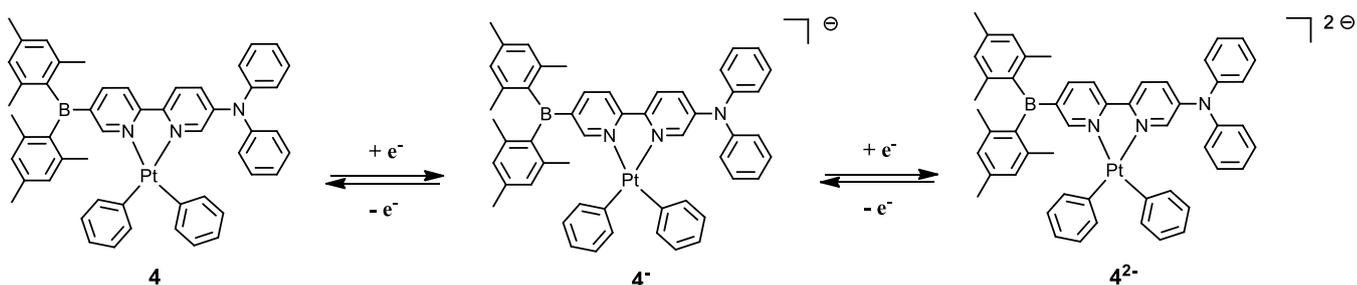


**Figure 1.** Mono and bimetallic pyridine platinum(II) complexes with a photo-switchable NLO response.

It turned out that the computed quadratic hyperpolarizability of complex **1** increases by a factor of

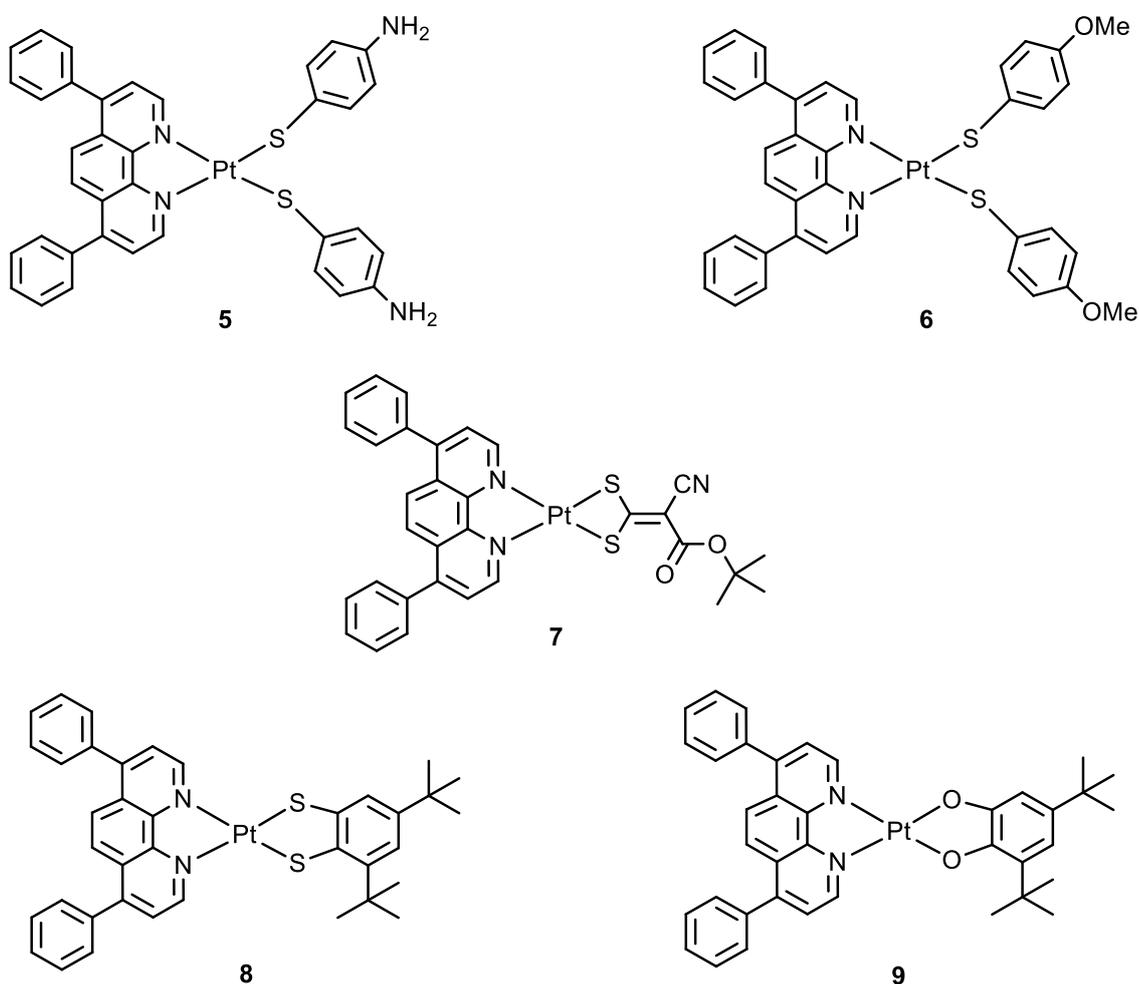
5.4 on going from the open to the close form ( $\beta_{\text{tot}} = 26.8 \times 10^{-30}$  and  $145 \times 10^{-30}$  esu for **1o** and **1c**, respectively) in agreement with an increase of the system delocalization. In the related bimetallic complex (**2**), a similar trend is observed although the quadratic hyperpolarizabilities are lower ( $\beta_{\text{tot}} = 12.4 \times 10^{-30}$  and  $46.6 \times 10^{-30}$  esu for **2o** and **2c**, respectively). Interestingly, substitution of the cyclopentene ring with a perfluorocyclopentene causes a decrease of the second-order NLO response ( $\beta_{\text{tot}} = 5.8 \times 10^{-30}$  and  $20.1 \times 10^{-30}$  esu for **3o** and **3c**, respectively). These results confirm that the introduction of a DTE moiety is an effective method to allow switching of the quadratic hyperpolarizability [55].

Besides, the second-order NLO response of a Pt(II) complex bearing a bipyridine, substituted with dimesitylboryl and diphenylamino groups, has been studied by density of states (DOS), and time-dependent DFT (TDDFT) calculations (Complex **4**, Figure 2) [56]. As a consequence of the enhanced  $\pi$  conjugation, this complex is stable toward reduction and display reversible reduction peaks, providing a model for redox switching of NLO responses. According to the calculations, there is a three-fold enhancement of the  $\beta_{\text{vec}}$  value of **4** upon formation of the one-electronic-reduced species **4<sup>-</sup>**. For the second one-electron-reduced process of complex **4**, two possible spin states (singlet state **14<sup>2-</sup>** and triplet state **34<sup>2-</sup>**) have been studied; it was found that the more stable (by 13.87 kcal/mol) singlet state has a  $\beta_{\text{vec}}$  value 3.8 times larger than that of the neutral form **4** whereas the value of **34<sup>2-</sup>** is huge ( $1349.4 \times 10^{-30}$  esu), being 286 times larger than the value of **4**. In this system, the reduction process affects the geometries resulting in a better conjugation in the bipyridine, compared to the neutral form, and thus heightens  $\beta_{\text{vec}}$  [56].



**Figure 2.** Structure of a bipyridine Pt(II) compound with a redox-switchable NLO response.

Besides, the quadratic hyperpolarizability of various square planar platinum(1,10-phenanthroline)(dithiolate) have been investigated, in dichloromethane solution, by EFISH with a 1.907  $\mu\text{m}$  incident wavelength (Figure 3) [57]. It was shown how a suitable design of the compounds, by variation of the thiolate ligands, is a way to optimize the NLO properties. The thiolate ligands play the role of electron-donors and contribute to the composition of the highest occupied molecular orbitals (HOMOs), which consist in a combination of the orbitals of the metal and thiolate, whereas the phenanthroline acts as electron-acceptor through the lowest unoccupied molecular orbitals (LUMOs), which are  $\pi^*$  orbitals. For this reason, the introduction of a donating unit on the thiolate ligands leads to an increase of  $\beta$ .



**Figure 3.** Structure of Pt(II) compounds with phenanthroline.

Thus the complex with two *p*-aminothiophenolate ligands (**5**) presents the greatest  $\mu\beta_{1.907}\text{EFISH}$  ( $-390 \times 10^{-48}$  esu where  $\mu = 10 \times 10^{-18}$  esu and  $\beta_{1.907}\text{EFISH} = -39 \times 10^{-30}$  esu), larger than that of the complex with two *p*-methoxythiophenolates (**6**;  $\mu\beta_{1.907}\text{EFISH} = -279 \times 10^{-48}$  esu,  $\mu = 9 \times 10^{-18}$  esu,  $\beta_{1.907}\text{EFISH} = -31 \times 10^{-30}$  esu), because the amino group is a stronger donor than the methoxy group. Complex **7** with a dithiolate bearing electron-withdrawing substituents has a lower NLO response ( $\mu\beta_{1.907}\text{EFISH} = -135 \times 10^{-48}$  esu,  $\mu = 9 \times 10^{-18}$  esu,  $\beta_{1.907}\text{EFISH} = -15 \times 10^{-30}$  esu). Interestingly, the quadratic hyperpolarizability decreases upon substitution of Pt(II) by Pd(II), in line with a diminution of the oscillator strength of the HOMO-LUMO transition. In this family, all compounds present negative  $\beta$  values, in accordance with a negative solvatochromism and with a diminution of  $\mu$  upon charge transfer ( $\Delta\mu_{eg} < 0$ ) [24-25].

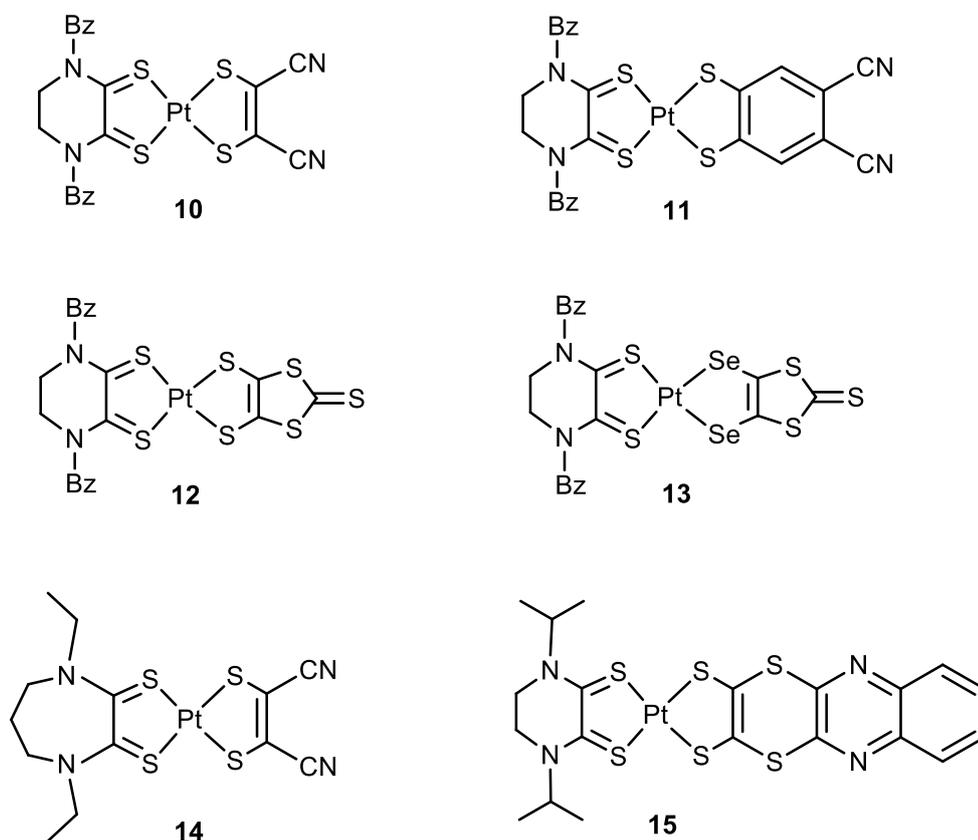
The related complex **8**, bearing the same phenanthroline but a chelating di-*t*-butylbenzenedithiolate, is characterized by a much higher NLO response ( $\mu\beta_{1.907}\text{EFISH} = -821 \times 10^{-48}$  esu, in dichloromethane) which increases even more upon substitution of the sulphur atoms by oxygen (complex **9**;  $\mu\beta_{1.907}\text{EFISH} = -1300 \times 10^{-48}$  esu) as expected for the red-shift of the HOMO (mixed platinum-thiolate or catecholate) – LUMO ( $\pi^*$  phenanthroline) transition [58].

### 3. Pt(II) compounds with dithiolene

Pt(II) compounds bearing two different dithiolenes ligands,  $[\text{R}_2(\text{C}_2\text{S}_2)\text{Pt}(\text{C}_2\text{S}_2)\text{R}'_2]$  where R and R' have different electron-withdrawing capability are fascinating for nonlinear optics. In these mixed-ligand dithiolenes platinum complexes, the dithiolato ligand acts as donor, contributing mainly to the HOMO whereas the dithione is the acceptor, contributing mainly to LUMOs; the HOMO-LUMO excitation is mediated by the platinum(II) center leading to interesting quadratic hyperpolarizabilities. The NLO potential of these mixed-ligand platinum complexes with dithione–

dithiolato ligands was well investigated by Deplano, through a systematic investigation of dithione and dithiolato ligands to understand the structure/property relationship useful to synthesize compounds with optimized properties. These complexes exhibit large negative quadratic hyperpolarizabilities, in line with their negative solvatochromism and negative  $\Delta\mu_{eg}$  [59].

For example, complex **10** (Figure 4), with a dibenzyl-piperazine-3,2-dithione and a maleonitrile-dithiolato ligands, dissolved in DMF, has a  $\mu\beta_{1,907}\text{EFISH}$  equal to  $-1950 \times 10^{-48}$  esu. A much lower value is obtained upon substitution of Pt with Pd ( $-1450 \times 10^{-48}$  esu) or Ni ( $-1436 \times 10^{-48}$  esu), due to a better mixing of the orbitals of the metal with those of the dithione and dithiolato ligands and to a larger oscillator strength for the Pt compound [60].



**Figure 4.** Pt(II) compounds with dithiolene.

The mixed-ligand dithiolene platinum complex (**11**) bearing the same dithione but a benzodithiolato ligand shows a stronger  $\mu\beta_{1,907}\text{EFISH}$  value ( $-3390 \times 10^{-48}$  esu), in line with a lower HOMO-LUMO distance with respect to **10** [61]. Complex **12**, with the same dithione but with a different dithiolato

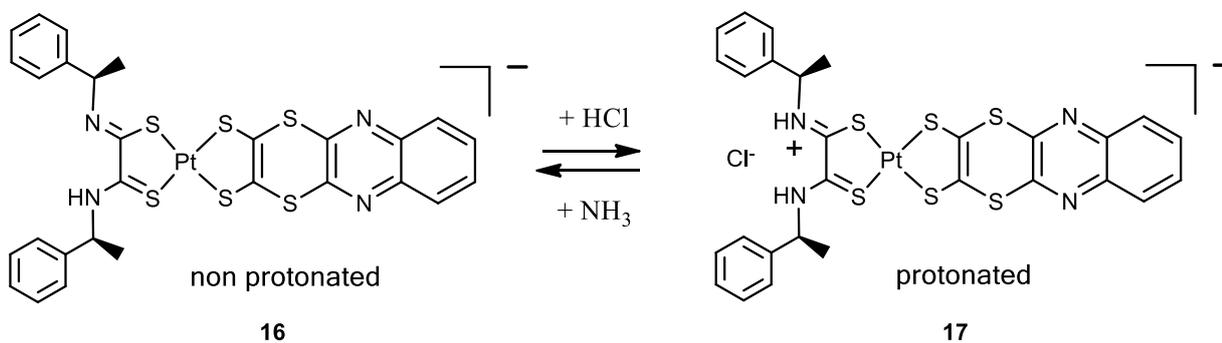
ligand is characterized by an even lower energy gap, and therefore an even stronger NLO response ( $\mu\beta_{1.907}\text{EFISH}$  value =  $-10000 \times 10^{-48}$  esu) [62]. A lower  $\mu\beta_{1.907}\text{EFISH}$  value ( $-4400 \times 10^{-48}$  esu) is obtained upon substitution of sulphur with selenium in the dithiolato ligand (complex **13**), despite the greater size and polarizability of selenium with respect to sulphur [63].

The effect of the nature of the acceptor dithione ligand was also investigated. Thus the mixed-ligand platinum complex with diethylperhydrodiazepine-dithione and the same dithiolate of complex **10** (complex **14**) was prepared. Its second-order NLO response ( $\mu\beta_{1.907}\text{EFISH}$  value =  $-1300 \times 10^{-48}$  esu) was lower than that observed for **10**, because the structure of these compounds tunes intensely their quadratic hyperpolarizability. In compounds **10** and **12**, the dithione torsion angle N–S– S'–N' is about  $2.7^\circ$  whereas it is about  $40^\circ$  in **14**. Thus the torsion angle of **14** is much higher than that of **10** and **12**, putting in evidence that the highest dithione torsion angle corresponds to the lowest oscillator strength and therefore to the lowest quadratic hyperpolarizability. The fascinating high quadratic hyperpolarizability of **12** is due to a low N–S– S'–N' angle and great dithiolate's  $\pi$  delocalization [64].

A related platinum–dithiolene complex (**15**), bearing a quinoxaline-dithiolate and diisopropyl-piperazine-dithione as donor and acceptor ligands, respectively, also shows a significant  $\mu\beta_{1.907}\text{EFISH}$  value ( $-4280 \times 10^{-48}$  esu). As expected from the above presented dithiolene complexes, substitution of Pt by Ni ( $\mu\beta_{1.907}\text{EFISH}$  value =  $-1490 \times 10^{-48}$  esu) or Pd ( $\mu\beta_{1.907}\text{EFISH}$  value =  $-1970 \times 10^{-48}$  esu) leads to a lower response [65].

Besides, the anionic platinum(II) complex **16** (Figure 5) shows an interesting  $\mu\beta_{1.907}\text{EFISH}$  ( $-735 \times 10^{-48}$  esu), as  $\text{NBu}_4^+$  salt in  $\text{CHCl}_3$  solution. Remarkably, addition of HCl gives **17**, characterized by a four-fold NLO response ( $-2980 \times 10^{-48}$  esu). The dipole moment of **16** and **17** being  $12.6$  and  $3.9 \times 10^{-18}$  esu, respectively, the  $\beta_{1.907}\text{EFISH}$  value increases by a factor of 12 (complex **16**,  $60 \times 10^{-30}$  esu; complex **17**,  $735 \times 10^{-30}$  esu). Addition of  $\text{NH}_3$  to **17** gives back **16**. The quadratic hyperpolarizabilities have a negative sign, as expected for a negative  $\Delta\mu_{\text{eg}}$  and the negative solvatochromism of the involved transitions. Interestingly, **16** is deep blue and gives a red emission

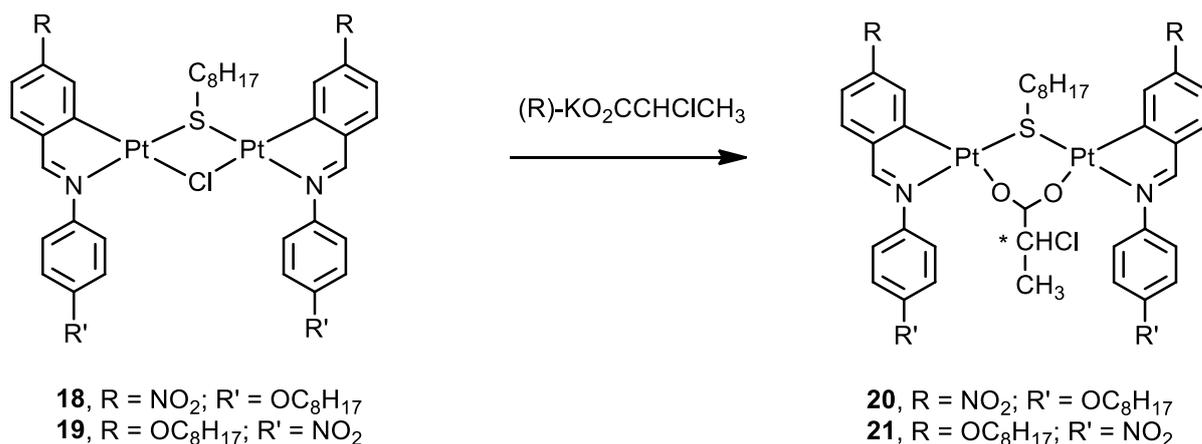
whereas **17** is green and emits in the green region. Therefore, this system is a fascinating multiresponse optical switch [43].



**Figure 5.** A fascinating platinum(II) optical switch.

#### 4. Pt(II) compounds with cyclometalated imine

An EFISH study of dimeric platinum complexes with mixed bridges (chloro-thiolato or thiolato-carboxylato) and two cyclometalated imine ligands has been accomplished in chloroform at 1.34  $\mu\text{m}$ . Complexes **18** and **20** (Figure 6) are characterized by  $\mu\beta_{1.907}\text{EFISH}$  equal to 454 and  $325 \times 10^{-48}$  esu, respectively, greater than the value of the related non-coordinated imine ( $158 \times 10^{-48}$  esu). Similarly, in the case of complexes **19** and **21** ( $\mu\beta_{1.907}\text{EFISH} = 513$  and  $590 \times 10^{-48}$  esu, respectively, compared to  $200 \times 10^{-48}$  esu for the free imine). However, this increase can be attributed to an augmentation of  $\mu$  upon formation of the dimers. Thus,  $\mu$  goes from 4.4 to 10.8 and  $12.5 \times 10^{-18}$  esu upon formation of **18** and **20** and from 5.7 to 9.5 and  $10 \times 10^{-18}$  esu upon formation of **19** and **21**. Therefore, although the imine moieties in the dimer have a *cisoid* disposition, which could lead to positive addition of the nonlinear effects from each moiety, it turned out that there is a decrease of the  $\beta$  value upon cyclometallation. It was suggested that, in these systems, the metal atom acts as an electron acceptor, through its bond with the iminic nitrogen, making the charge-transfer in the imine ligand more difficult and thus decreasing the quadratic hyperpolarizability. As a matter of fact there is a decrease of the intraligand charge transfer transition band wavelength of the imine upon formation of the platinum complexes. A similar effect is observed upon substitution of Pt with Pd [66].

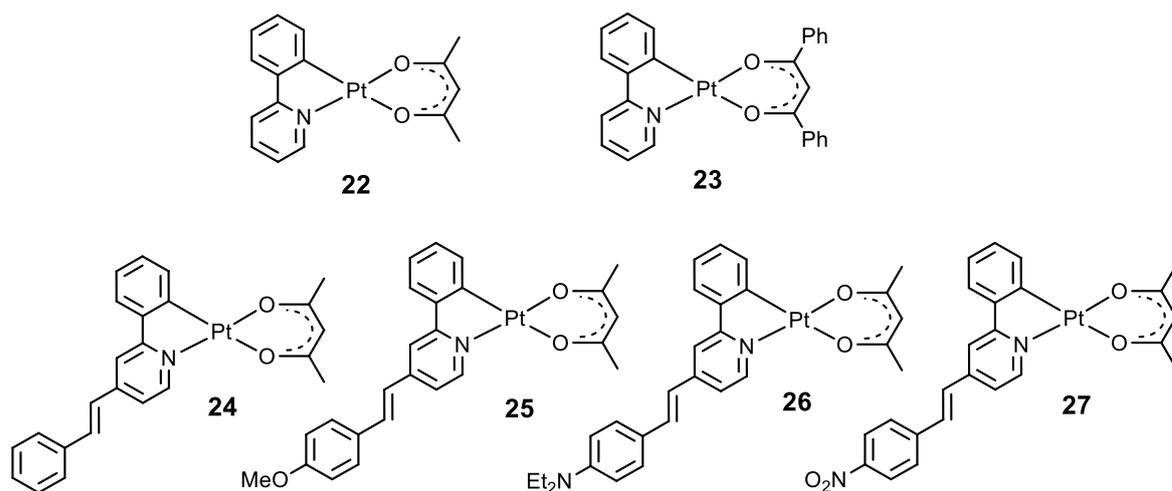


**Figure 6.** Pt(II) compounds with cyclometalated imine.

### 5. Pt(II) compounds with cyclometalated phenylpyridine

Luminescent coordination compounds with good quadratic hyperpolarizabilities are interesting multifunctional molecular materials [39, 67-71]. For this reason, the quadratic hyperpolarizabilities of luminescent Pt(II) compounds, with a  $\beta$ -diketonate and a cyclometalated 2-phenylpyridine, were studied by the EFISH method in chloroform. Complex **22** (Figure 7), with the acetylacetonate ligand, has a good  $\mu\beta_{1.907}\text{EFISH}$  ( $-535 \times 10^{-48}$  esu with  $\mu = 4 \times 10^{-18}$  esu and  $\beta_{1.907}\text{EFISH} = -134 \times 10^{-30}$  esu). With a more  $\pi$ -delocalized  $\beta$ -diketonate (complex **23**), there is not a significant change of  $\mu$  but there is an increase of  $\beta_{1.907}\text{EFISH}$  ( $-193 \times 10^{-30}$  esu), in line with the lower polarizability of methyl with respect to phenyl. These high  $\beta_{1.907}\text{EFISH}$  have been attributed to ILCT transitions of the 2-phenylpyridine. It is worth pointing out that the relatively low  $\beta_{1.907}\text{EFISH}$  ( $35 \times 10^{-30}$  esu) of the non-coordinated 2-phenylpyridine increases by a factor of 4-5 upon cyclometallation, showing the importance of platinum [72].

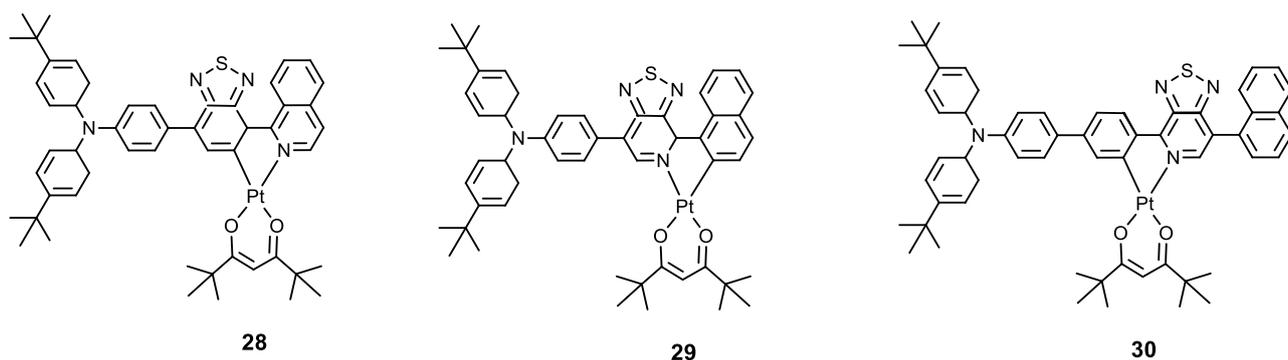
Following this report, a study was carried out on the influence of the functionalization of the cyclometalated 2-phenylpyridine. Some 4-styryl-2-phenylpyridines, bearing in *para* position R groups of different donor or acceptor ability, were prepared along with the related Pt(II) complexes (**24**, **25**, **26**, **27** for R = H, OMe, NEt<sub>2</sub>, NO<sub>2</sub>, respectively; Figure 7) [73].



**Figure 7.** Pt(II) compounds with cyclometalated phenylpyridines.

All these complexes have a positive value of  $\mu\beta_{1.907}\text{EFISH}$ , as expected for a positive  $\Delta\mu_{\text{eg}}$ , in contrast with the parent complex **22**. This difference can be explained because the first hyperpolarizability  $\beta$ , determined with the EFISH method, is the projection of  $\beta_{\text{VEC}}$  (the  $\beta$  tensor's vectorial component) along the  $\mu$  axis. For complex **22**,  $\beta$  is controlled by charge transfer from the phenyl ring to pyridine. On the contrary, in complex **24**, the quadratic hyperpolarizability is controlled by charge transfer along the styryl group. By increasing the donor power of R ( $\text{NEt}_2 > \text{OMe} > \text{H} > \text{NO}_2$ ), the  $\mu\beta_{1.907}\text{EFISH}$  values increase, essentially caused by an augmentation of  $\mu$  ( $\mu\beta_{1.907}\text{EFISH} = 620, 1060, 1330$  and  $1790 \times 10^{-48}$  esu where  $\mu = 4.5, 6.2, 7.2,$  and  $13.0 \times 10^{-48}$  esu for **27, 24, 25,** and **26**, respectively). The  $\mu\beta_{1.907}\text{EFISH}$  value of complex **25** is four-fold that of the non-coordinated phenylpyridine, confirming the important role of cyclometallation on the NLO activity. Interestingly, dispersion and orientation of **26** in poly(methyl methacrylate) gives a film characterized by a good ( $\chi_{33}^{(2)} = 5.62$  pm/V) and relatively stable ( $\chi_{33}^{(2)} = 2.8$  pm/V after 3 months) second harmonic generation (SHG) response [73], higher than that observed for related Ir(III) compounds [74] but slightly lower than that observed for NMe<sub>2</sub>-methylstilbazolium ( $\chi_{33}^{(2)} = 10.6$  pm/V) [75] or ferrocene-quinoxaline Y-shaped chromophores ( $\chi_{33}^{(2)} = 10.6$  pm/V) [76-77].

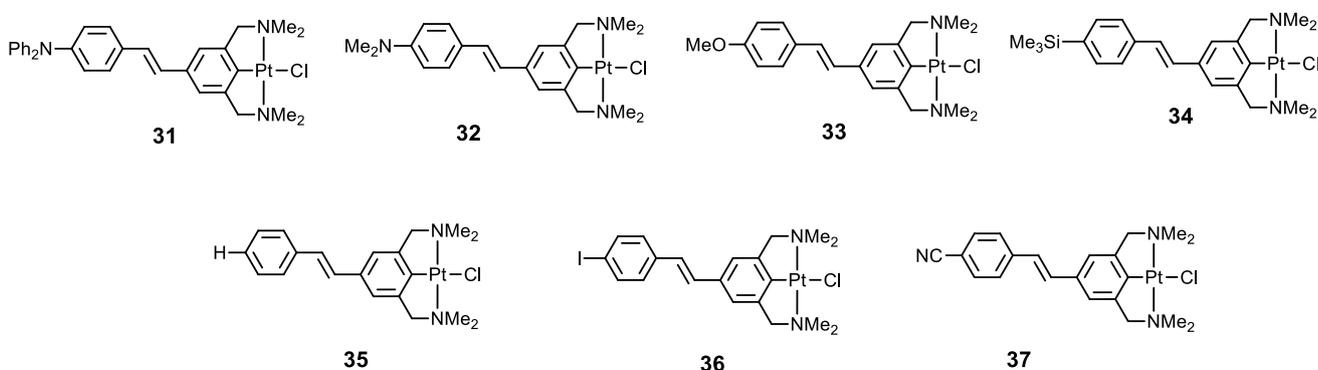
Recently, the first hyperpolarizability of various cyclometalated platinum(II) acetylacetonate complexes (**28-30**) bearing an isomeric donor-acceptor conjugation framework phenylpyridine ligand (Figure 8) have been studied by the density functional theory method [78]. In the case of complex **29**, coordination with the strong electron donating ability of triphenylamine and the electron-withdrawing capacity of the [1,2,5]thiadiazolo[3,4-c]pyridine unit produces the highest first hyperpolarizability ( $\beta_{\text{tot}} = 329 \times 10^{-30}$  esu). Complexes **28** and **30** are characterized by a lower NLO response ( $\beta_{\text{tot}} = 145 \times 10^{-30}$  and  $55 \times 10^{-30}$  esu, respectively). Remarkably, good to large  $\beta_{\text{tot}}$  contrasts were observed for these isomeric Pt(II) complexes upon redox process. The first hyperpolarizability is enhanced for the three complexes after the oxidation reaction, while it is slightly decreased by the reduction process, except for complex **30**. In the case of complex **28**, the oxidized species has a  $\beta_{\text{tot}}$  of  $7346 \times 10^{-30}$  esu, 51 times larger compared to the related neutral complex. On the other side, the one-electron reduction induces a slight diminution of the NLO response by 2.5 times, putting in evidence that complex **28** is characterized by a two-state switching NLO effect. In the case of complexes **29** and **30**, the one-electron oxidation leads to an increase of  $\beta_{\text{tot}}$  by a factor of 3.3 and 168, respectively). Complex **30**, characterized by the highest on/off ratio using an oxidation stimulus, appears as a promising candidate for efficient redox-triggered NLO switches [78].



**Figure 8.** Platinum(II) complexes for redox-triggered NLO switches.

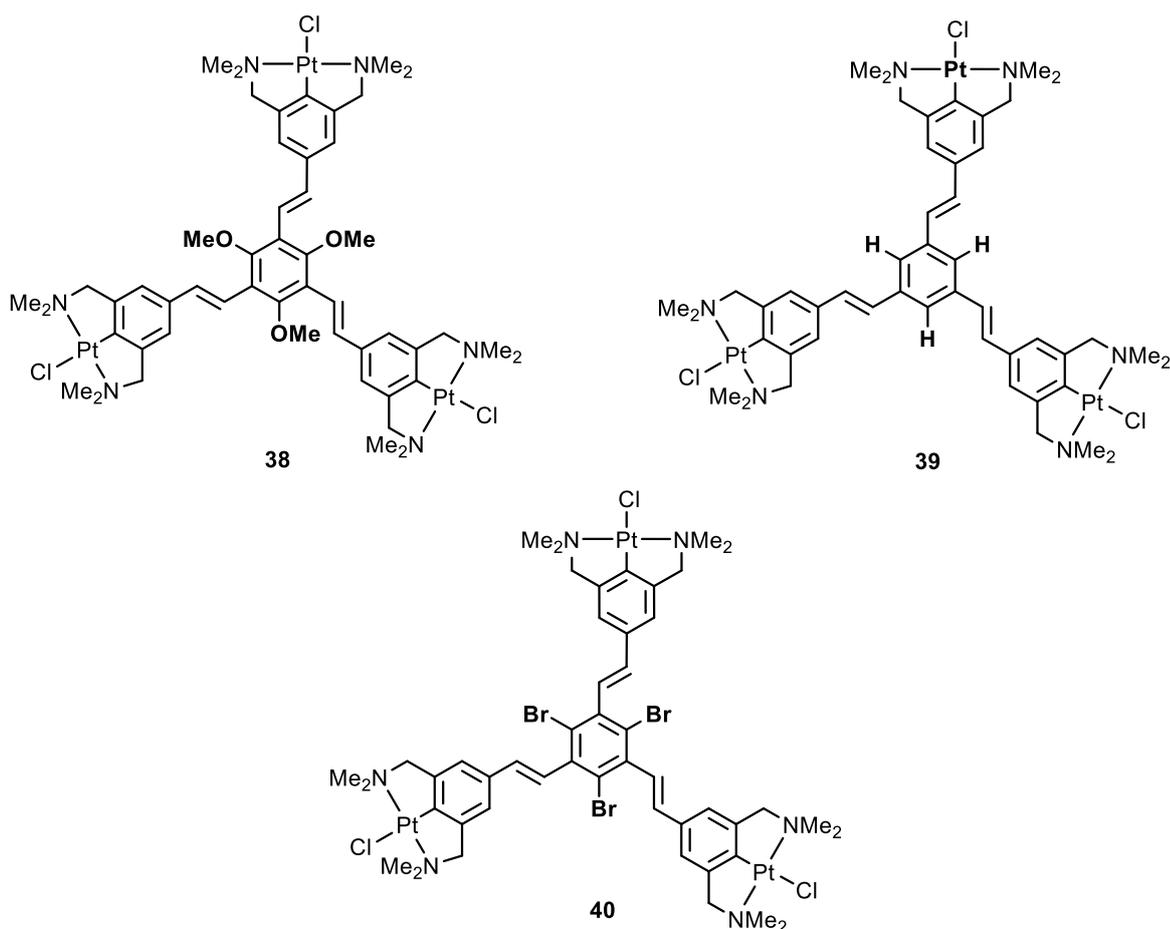
## 6. Pt(II) compounds with N<sup>^</sup>C<sup>^</sup>N-pincers

Various Pt(II) compounds of the type [PtCl([Ph(CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>-2,6-R-4)] (where R = *trans*-CHCHPh-R'-4' and R' = N(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (**31**), N(CH<sub>3</sub>)<sub>2</sub> (**32**), OCH<sub>3</sub> (**33**), Si(CH<sub>3</sub>)<sub>3</sub> (**34**), H (**35**), I (**36**), CN (**37**) (Figure 9) were investigated in dichloromethane with an incident wavelength of 0.8 μm by the HRS method which gives the β<sub>zzz</sub> contribution of the hyperpolarizability's tensor (z represents the charge transfer direction). The β<sub>zzz</sub> value (1106 (**31**), 667 (**32**), 164 (**33**), 270 (**34**), 272 (**35**), 1324 (**36**), 940 (**37**) × 10<sup>-30</sup> esu) goes from 164 to 1324 × 10<sup>-30</sup> esu. The best responses are obtained for complexes **31** and **36**, which bears the N(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and I moiety, respectively, in agreement with the fact that they have the largest absorption coefficient and therefore the largest oscillator strength. In the case of **36**, the large value can also be attributed to the high polarizability of iodine which leads to a large Δμ<sub>eg</sub>. In this family of complexes, the PtCl moiety acts as donor, and interestingly, a good NLO response is observed for both donor or acceptor R' groups, in line with TD-DFT calculations that indicate that the HOMO–LUMO gap diminishes on going from **35** (with R'=H) to **32** (with the electron-donor R', N(CH<sub>3</sub>)<sub>2</sub>) or **37** (with the electron-acceptor R', CN). In **37**, the HOMO is essentially centered on the Pt moiety and the LUMO on nitrile, whereas in **32** the HOMO is localized on Pt and N(CH<sub>3</sub>)<sub>2</sub> with LUMOs on the central ethylene bridge [79]. Interestingly, in related 4,4'-substituted benzylidene aniline platinum complexes, it was shown that the Pt-pincer moiety can behave as a strong acceptor inductively and as a strong donor mesomerically [80].



**Figure 9.** Pt(II) compounds with stilbenoid N<sup>^</sup>C<sup>^</sup>N-pincers.

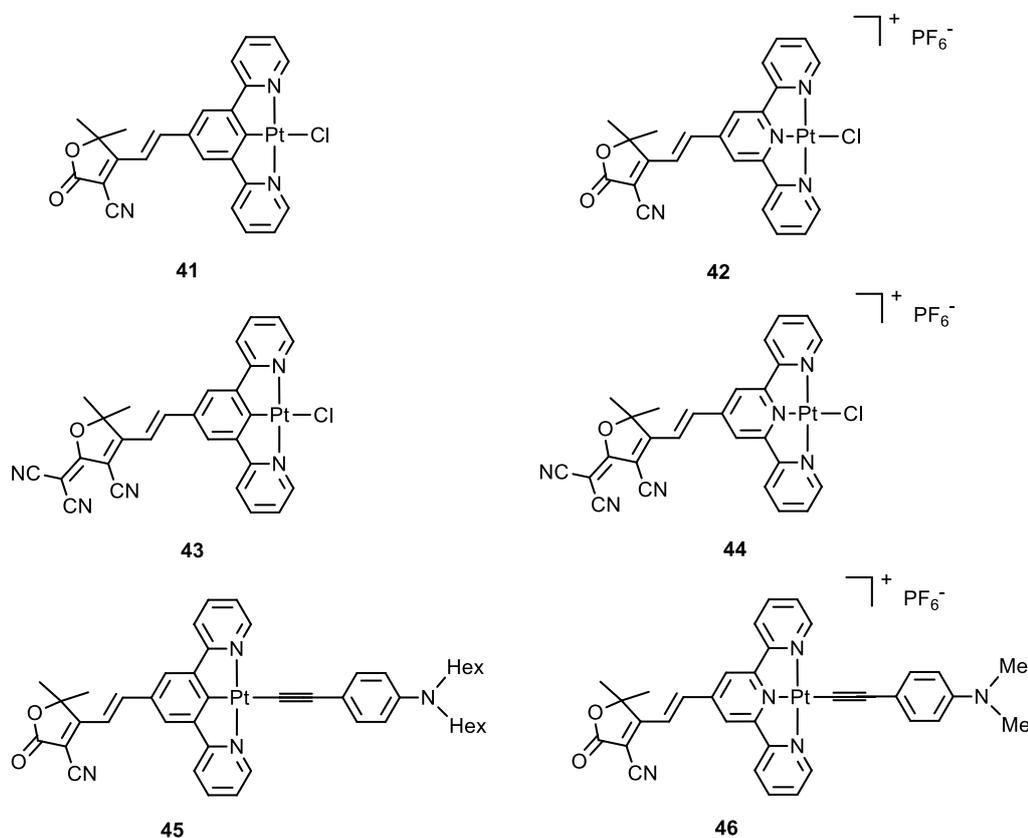
As reported in Section 1, NLO-active octupolar molecules represent an interesting class of materials [15, 81-83]. Thus, the significant NLO properties of the above reported dipolar N<sup>+</sup>C<sup>-</sup>N<sup>-</sup>-pincer Pt(II) compounds led to the synthesis of related octupolar Pt(II) compounds (**38-40**, Figure 10). The  $\beta_{0.8\text{HRS}}$  values, measured in dichloromethane, are 430 (R = OMe; **38**), 870 (R = H, **39**) and 183 (R = Br, **40**)  $\times 10^{-30}$  esu, the corresponding non-zero hyperpolarizability tensor  $\beta_{xxx}$  being 700, 1410 and 300  $\times 10^{-30}$  esu. It is worth pointing out that complex **39**, which does not have a donating or accepting substituent on the central phenyl, has the highest second-order NLO response, in agreement with the fact the NLO activity of these octupolar complexes is controlled by dispersion and not by charge transfer [84].



**Figure 10.** Octupolar N<sup>+</sup>C<sup>-</sup>N<sup>-</sup>-pincer Pt(II) compounds.

## 7. Pt(II) compounds with cyclometalated N<sup>^</sup>C<sup>^</sup>N dipyridylbenzene

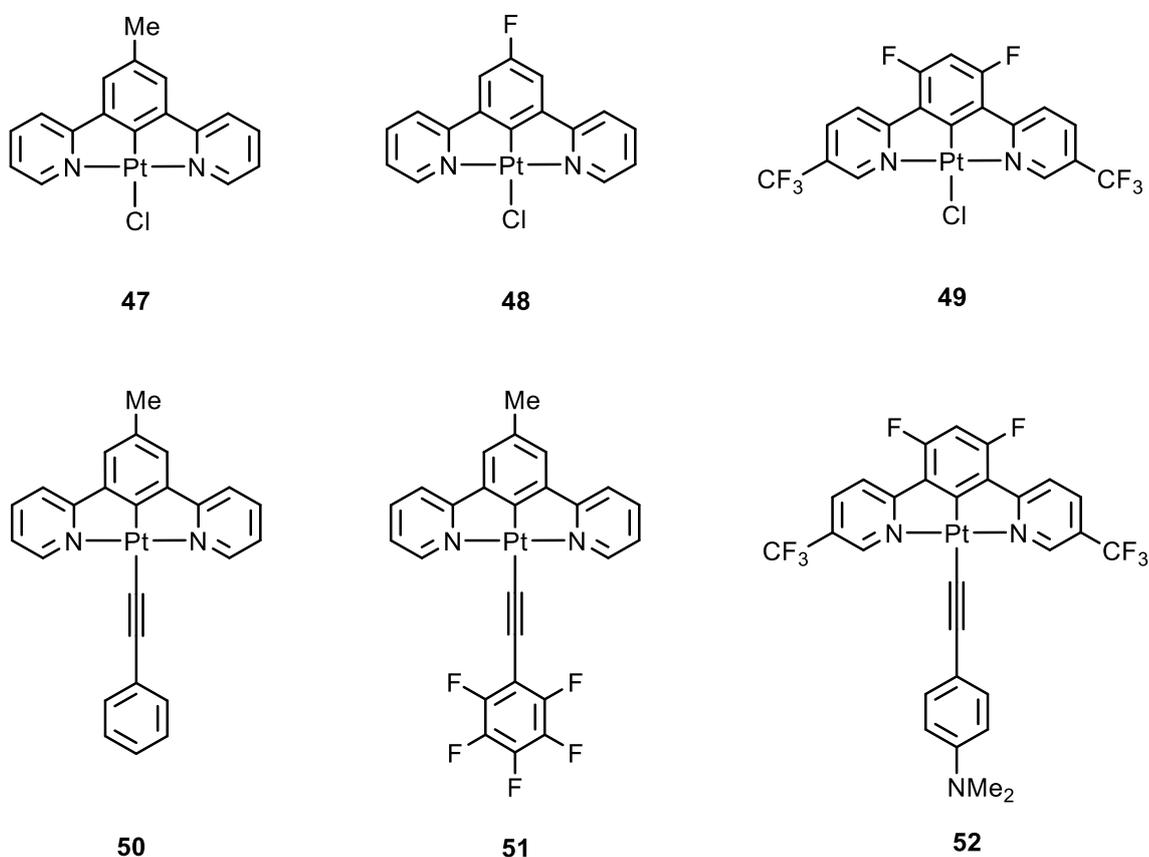
A HRS study, in DMF at 1.064  $\mu\text{m}$ , has been carried out on Pt(II) compounds with a cyclometalated dipyridylbenzene and a chloride (**41** and **43**, Figure 11) or arylacetylide ligand (**45**). It turned out that these complexes are characterized by large quadratic hyperpolarizabilities ( $\beta_{zzz} = 1160$  (**41**),  $1460$  (**43**),  $610$  (**45**)  $\times 10^{-30}$  esu), the highest value being obtained in the case of compound **43** with an electronwithdrawing unit on the cyclometalated ligand. Substitution of chloride by arylacetylide causes a significant decrease of  $\beta_{zzz}$  (compare **41** and **45**), probably because  $\Delta\mu_{eg}$  is lower with acetylide than with chloride. Remarkably, complexes **41** and **43** present a much higher quadratic hyperpolarizability than the related terpyridine complexes (**42** and **44**) which have a  $\beta_{zzz}$  value of  $66$  and  $430 \times 10^{-30}$  esu, respectively. The increase is much less pronounced in the presence of dimethylamino arylacetylide instead of chloride, complex **46** showing a  $\beta_{zzz}$  of  $540 \times 10^{-30}$  esu, lower than the value of **45** [85].



**Figure 11.** Pt(II) compounds with cyclometalated dipyridylbenzene ligands investigated by the HRS

method.

Pt(II) compounds with a cyclometalated dipyriddybenzene constitute an interesting family of multifunctional materials since they show remarkable luminescent [86-90] and NLO [85] properties. To better understand the influence of the cyclometalated ligand's substituents and of the ancillary ligands on the electronic origin and control of the quadratic hyperpolarizabilities, a series of complexes was investigated (for example, complexes **47-52** presented in Figure 12) in DMF at 1.907  $\mu\text{m}$  by EFISH and HRS techniques, and by TD-DFT calculations [91].



**Figure 12.** Pt(II) compounds with cyclometalated dipyriddybenzene studied by the EFISH method.

Their  $\mu\beta_{1.907}\text{EFISH}$  is negative, in line with a diminution of  $\mu$  upon excitation. With chloride as ancillary ligand, the absolute value of  $\beta_{1.907}\text{EFISH}$  for the complex with F on the phenyl (**48**,  $\beta_{1.907}\text{EFISH} = -177 \times 10^{-30}$  esu;  $\mu = 6 \times 10^{-18}$  esu) is almost four-fold the value obtained for the

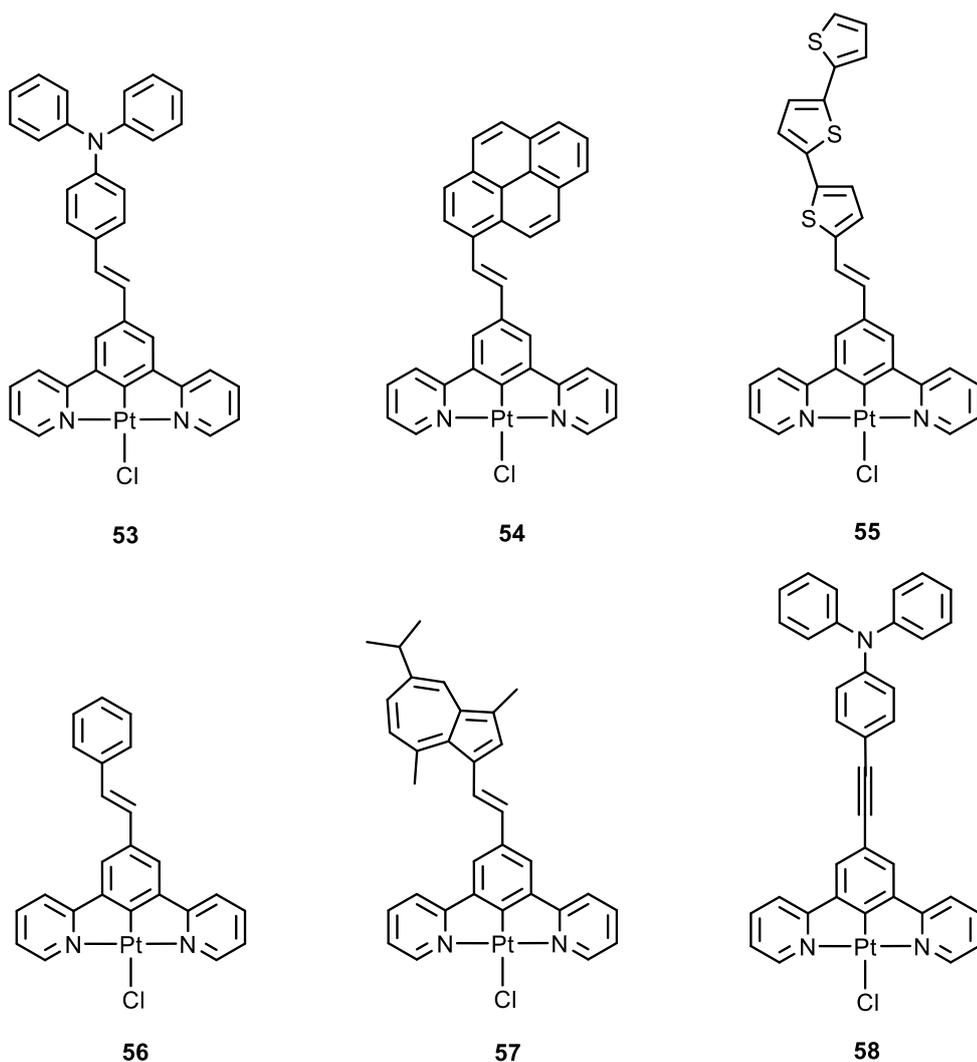
compound with CH<sub>3</sub> (**47**,  $\beta_{1.907}\text{EFISH} = -47 \times 10^{-30}$  esu;  $\mu = 10.2 \times 10^{-18}$  esu), in accordance with a stronger charge-transfer process. Complex **49**, with two fluorine atoms on the metalated benzene and two CF<sub>3</sub> groups on the pyridine rings, has a slightly higher value of  $\beta_{1.907}\text{EFISH}$  ( $-188 \times 10^{-30}$  esu) and a much larger dipole moment ( $\mu = 13.1 \times 10^{-18}$  esu) leading to a very large  $\mu\beta_{1.907}\text{EFISH}$  ( $-2470 \times 10^{-48}$  esu). The introduction of acceptor groups on the N<sup>^</sup>C<sup>^</sup>N ligand causes an augmentation of its accepting power, as confirmed by a diminution of the LUMO orbitals energy, allowing an easier MLCT from the Pt center, therefore consenting an augmentation of the first hyperpolarizability. Interestingly, introduction of CF<sub>3</sub> groups on the pyridine rings constitutes a way to augment  $\mu$  and therefore the  $\mu\beta_{1.907}\text{EFISH}$  values. Replacement of Cl in compound **47** by a phenylalkynyl (**50**;  $\beta_{1.907}\text{EFISH} = -296 \times 10^{-30}$  esu), leads to a six-fold augmentation of the first hyperpolarizability, caused by an augmentation of the charge transfer from the metal–phenylalkynyl fragment and a diminution of the HOMO–LUMO distance. The charge transfer from the phenylalkynyl to the cyclometalated ligand corresponds to the HOMO–LUMO transition.

An augmentation of the acetylide's accepting ability does not affect significantly  $\mu\beta_{1.907}\text{EFISH}$ , as evidenced upon comparison of **50** (with phenylacetylide;  $\mu\beta_{1.907}\text{EFISH} = -2190 \times 10^{-48}$  esu) and **51** (with pentafluorophenylacetylide;  $\mu\beta_{1.907}\text{EFISH} = -2290 \times 10^{-48}$  esu), because the diminution of the quadratic hyperpolarizability in **51** ( $\beta_{1.907}\text{EFISH} = -180 \times 10^{-30}$  esu) is shielded by an augmentation of  $\mu$  ( $12.7 \times 10^{-18}$  esu). In complex **52**, with a NMe<sub>2</sub> group on the phenylacetylide ligand, the HOMO is localized on the phenylalkynyl and the LUMO on the cyclometalated ligand, leading to a facile HOMO–LUMO transition and to the greatest  $\beta_{1.907}\text{EFISH}$  value ( $-470 \times 10^{-30}$  esu), keeping a high  $\mu\beta_{1.907}\text{EFISH}$  ( $-2020 \times 10^{-48}$  esu) although the dipole moment is much lower ( $\mu = 4.3 \times 10^{-18}$  esu).

An HLS investigation confirmed that complexes **47**, **48** and **51** present a large first hyperpolarizability, that is not due to the low dipolar contribution but to the high octupolar involvement [91], as reported in the case of some Ln(III)  $\beta$ -diketonates [92], Ir(III) and Pt(II) compounds [93], and bipyridyl iridium(III) compounds [94]. However, in the case of complex **52**, the

dipolar component is relatively high (51%) as expected for the strong charge transfer from the NMe<sub>2</sub>Ph-alkynyl ligand to the cyclometalated one.

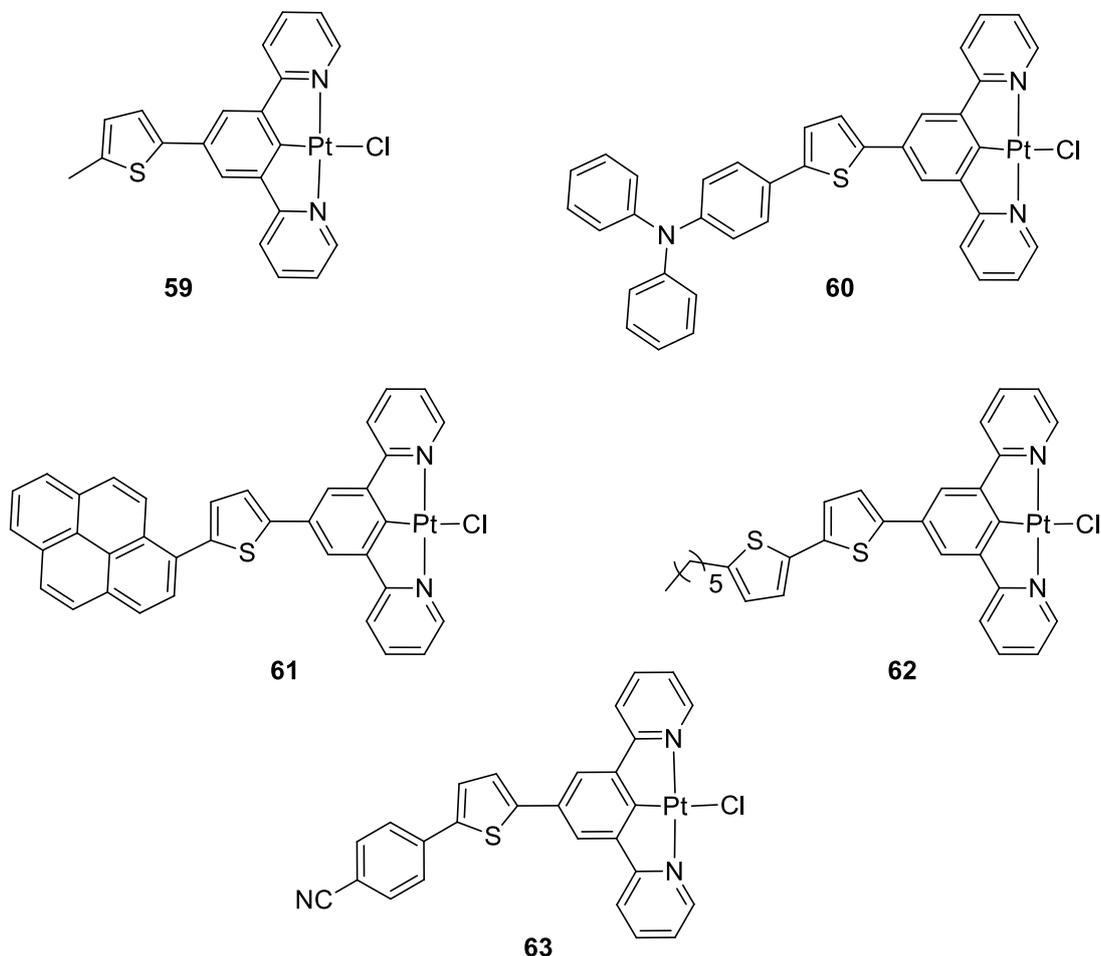
It is known that the  $\mu\beta_{1.907}\text{EFISH}$  of 5-(*p*-Ph<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHCH)-1,3-dipyridylbenzene ( $230 \times 10^{-48}$  esu where  $\mu = 3.6 \times 10^{-18}$  esu) is increased upon methylation, due to an 8-fold enhancement of  $\mu$  [45]. As expected from the intensification of the quadratic hyperpolarizability of phenylpyridines by cyclometallation to a Pt center [72-73], the  $\mu\beta_{1.907}\text{EFISH}$  of 5-(*p*-Ph<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHCH)-1,3-dipyridylbenzene can also be increased upon formation of complex **53** (Figure 13;  $\mu\beta_{1.907}\text{EFISH} = -880 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -82 \times 10^{-30}$  esu and  $\mu = 10.7 \times 10^{-18}$  esu) [95], by means of an augmentation of the first hyperpolarizability and dipole moment. The sign of  $\beta_{1.907}\text{EFISH}$  becomes negative, as expected for a diminution of  $\mu$  upon excitation [40]. In this complex, the quadratic hyperpolarizability can be attributed to the charge transfer from the Pt center to the N<sup>^</sup>C<sup>^</sup>N ligand, shielded by the ILCT [91]. The highest occupied molecular orbital of **53** is localized on Pt *d*<sub>yz</sub> and on the  $\pi$ -delocalized phenyl system, whereas pyridyl moieties are involved in the LUMO and LUMO+1, in accordance with two opposite sign contributions to the NLO behaviour, as observed for related complexes, with the negative contribution giving the global quadratic hyperpolarizability sign. Similarly a large  $\mu\beta_{1.907}\text{EFISH}$  has been observed for compounds **54** ( $\mu\beta_{1.907}\text{EFISH} = -820 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -87 \times 10^{-30}$  esu and  $\mu = 9.4 \times 10^{-18}$  esu) [95], **55** ( $\mu\beta_{1.907}\text{EFISH} = -1260 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -133 \times 10^{-30}$  esu and  $\mu = 9.5 \times 10^{-18}$  esu) [95], **56** ( $\mu\beta_{1.907}\text{EFISH} = -660 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -69 \times 10^{-30}$  esu and  $\mu = 9.5 \times 10^{-18}$  esu) [96], and **57** ( $\mu\beta_{1.907}\text{EFISH} = -1540 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -115 \times 10^{-30}$  esu and  $\mu = 13.4 \times 10^{-18}$  esu) [97], much higher than that found for **47** (Figure 12). Thus, substitution of the methyl in **47** by a polarizable  $\pi$ -delocalized vinyl fragment causes a great intensification of the NLO activity.



**Figure 13.** Pt(II) compounds with cyclometalated  $\pi$ -delocalized dipyritylbenzene.

The best quadratic hyperpolarizabilities are reached with the highly  $\pi$ -delocalized terthiophene (**55**) and guaiazulene (**57**) moieties, higher than that measured for a guaiazulene linked to a squaraine bearing an electron-acceptor group ( $\mu\beta_{1.907}\text{EFISH} = -420 \times 10^{-48}$  esu) [98]. Interestingly, complex **58** is also characterized by a good response ( $\mu\beta_{1.907}\text{EFISH} = -764 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -69 \times 10^{-30}$  esu and  $\mu = 11 \times 10^{-18}$  esu) [96]. Thus, the use of an ethylene bond, to link the cyclometalated phenyl ring and the triphenyl amino moiety, instead of a triple bond (compare complexes **53** and **58**), does not influence significantly the nonlinear optical behaviour of these compounds. This is in contrast with organic molecules where substitution of an ethylenic linker with a triple bond causes a strong reduction of the NLO activity [99].

The quadratic hyperpolarizabilities of a series of Pt(II) compounds functionalized with various thiophene fragments on the dipyriddybenzene were also investigated by the EFISH method (Figure 14 [97]).

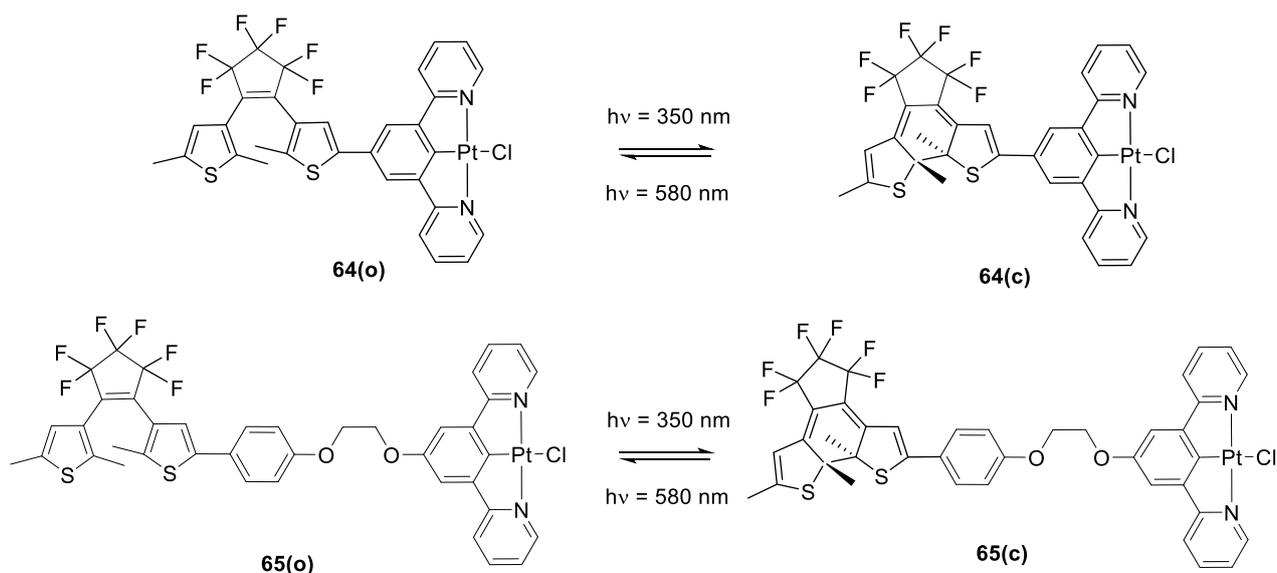


**Figure 14.** Pt(II) compounds with cyclometalated dipyriddybenzene functionalized with thiophene moieties.

The simplest compound with CH<sub>3</sub> on the thiophene (**59**) presents already a significant  $\mu\beta_{1.907}\text{EFISH}$  ( $-520 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -50 \times 10^{-30}$  esu and  $\mu = 10.5 \times 10^{-18}$  esu), which usually increases upon substitution of the methyl group with a polarizable  $\pi$ -delocalized moiety (**60**:  $\mu\beta_{1.907}\text{EFISH} = -498 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -46 \times 10^{-30}$  esu and  $\mu = 10.8 \times 10^{-18}$  esu; **61**:  $\mu\beta_{1.907}\text{EFISH} = -1078 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -109 \times 10^{-30}$  esu and  $\mu = 9.9 \times 10^{-18}$  esu; **62**:  $\mu\beta_{1.907}\text{EFISH} = -945 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -91 \times 10^{-30}$  esu and  $\mu = 10.4 \times 10^{-18}$  esu; **63**:

$\mu\beta_{1.907}\text{EFISH} = -570 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -116 \times 10^{-30}$  esu and  $\mu = 4.9 \times 10^{-18}$  esu). In this series, the absolute value of  $\beta_{1.907}\text{EFISH}$  increases in the order **59** = **60** < **62** < **61** < **63**, due to an augmentation of the polarizability caused by an increased delocalization of the LUMOs. As a matter of fact, complexes **59** and **60** are characterized by the lowest quadratic hyperpolarizabilities because their lowest unoccupied molecular orbital is centered on the cyclometallated Pt moiety only. Complexes **61** and **63** have LUMOs much more delocalized than the others of the series, leading to the largest quadratic hyperpolarizabilities. Thus, to have a large  $\beta_{1.907}\text{EFISH}$ , there must not be confinement of the charge transfer on the cyclometalated pyridine rings. As a matter of fact, substitution of the ethylene bond in the 5-(*p*-Ph<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHCH)-1,3-dipyridylbenzene ligand (**53**) by a thiophene (**60**) leads to a decrease of  $\beta_{1.907}\text{EFISH}$  because of the diminution of the LUMO's delocalization. With the pyrene complexes, there is no decrease of the quadratic hyperpolarizability on going from **54** (with the double bond) to **61** (with thiophene) since in both cases there is delocalization of the lowest unoccupied molecular orbitals on the pyrene moiety. Therefore, delocalization of the LUMO not only on the pyridines but also on the moiety in position 5 of the 1,3-dipyridylbenzene ligand appears crucial to improve the NLO activity of the Pt(II) family [97].

As above reported, dithienylethene (DTE) is a useful tool to photomodulate the NLO response of coordination compounds [51-55]. For this reason, an EFISH investigation was accomplished on two photochromic platinum(II) complexes (**64** and **65**, Figure 15), in which the phenyl of the dipyritylbenzene ligand bears a DTE moiety [100].



**Figure 15.** NLO switches created with photochromic Pt(II) compounds with dipyridylbenzene.

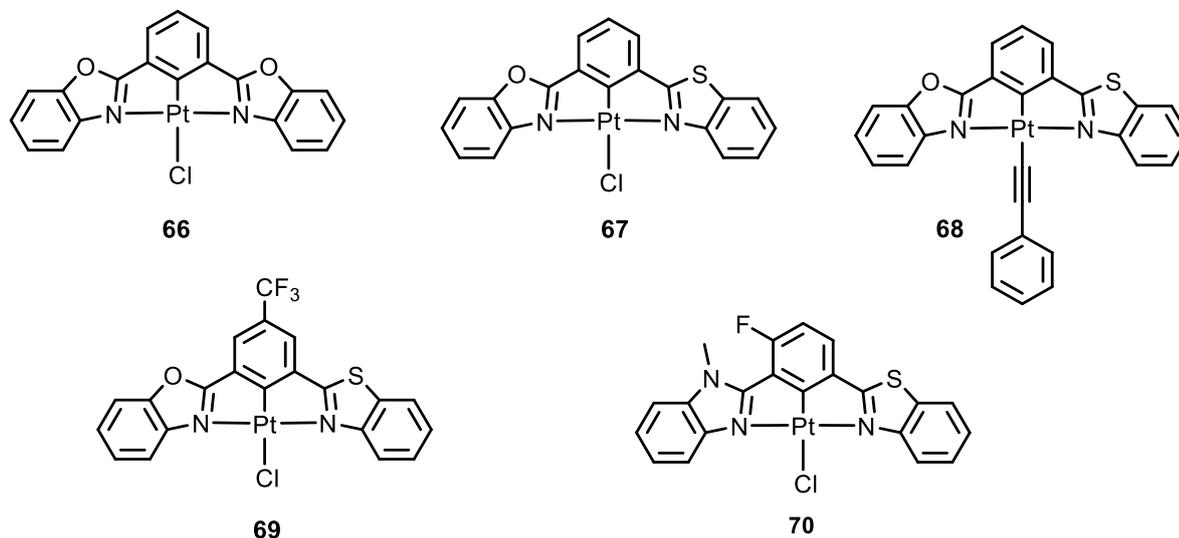
In **64**, the DTE unit is linked to the phenyl whereas, in **65**, there is a nonconjugated linker between the phenyl and the DTE unit. Therefore their investigation can show the effect of a linker on the photomodulation of the NLO behaviour.

Compound **64(o)** is characterized by a  $\mu\beta_{1.907}\text{EFISH}$  ( $-510 \times 10^{-48}$  esu with  $\mu = 8.9 \times 10^{-18}$  esu) rather comparable to the value of **59**, putting in evidence that the perfluorocyclopentene unit has almost no influence. Irradiation of **64(o)**, dissolved in dichloromethane, with a wavelength of 350 nm, leads to ring closure with formation of **64(c)**, characterized by a much higher  $\mu\beta_{1.907}\text{EFISH}$  ( $-1450 \times 10^{-48}$  esu with  $\mu = 7.1 \times 10^{-18}$  esu), as expected due to augmentation of  $\pi$ -delocalization and to diminution of HOMO–LUMO gap. Similarly, the second-order NLO response of **65(o)** ( $\mu\beta_{1.907}\text{EFISH} = -575 \times 10^{-48}$  esu with  $\mu = 15.4 \times 10^{-18}$  esu) increases upon formation of **65(c)** ( $\mu\beta_{1.907}\text{EFISH} = -1476 \times 10^{-48}$  esu with  $\mu = 8.9 \times 10^{-18}$  esu), although the DTE unit is separated from the phenyl by the ethylene glycol bridge. The NLO switch observed for **65** was unexpected because in the closed form of the dithienylethene unit there is no  $\pi$ -conjugation with the phenyl of the cyclometalated ligand. Remarkably, dispersion of **64** in a polystyrene matrix leads to a film which second harmonic generation (SHG) can be reversibly photoswitched [100]. Interestingly, it was observed that

polystyrene has a better ability than poly(methyl methacrylate) to maintain the orientation of the dipolar molecules. As a matter of fact, the SHG signal of films in poly(methyl methacrylate) progressively fades due to a rapid loss of orientation of the NLO-active dipolar molecules, perhaps due to the  $\beta$  transition of poly(methyl methacrylate), which has been attributed to rotation of the ester side group. Polystyrene gives a much better stability of the NLO response [100].

Another family of N<sup>^</sup>C<sup>^</sup>N derivatives are luminescent platinum(II) compounds with cyclometalated bis(heteroazolyl)benzene. Thus, substitution of pyridines in dipyriddybenzene with benzimidazolyl, benzoxazolyl or benzothiazolyl moieties leads to highly phosphorescent complexes [101-106]. This family was also investigated for its second-order NLO properties [107]. An EFISH study was accomplished on Pt(II) complexes with cyclometalated bis(benzoxazolyl)benzene (**66**, Figure 16), (benzoxazolyl)(benzothiazolyl)benzene (**67-69**), and (methylbenzimidazol-2-yl)(benzothiazolyl)benzene (**70**), dissolved in DMF. Complex **66** presents a  $\mu\beta_{1.907}\text{EFISH}$  value ( $-550 \times 10^{-48}$  esu where  $\beta_{1.907}\text{EFISH} = -65 \times 10^{-30}$  esu and  $\mu = 8.5 \times 10^{-18}$  esu) slightly larger than the value of the compound with dipyriddybenzene (**47**,  $\mu\beta_{1.907}\text{EFISH} = -480 \times 10^{-48}$  esu) due to a higher  $\beta_{1.907}\text{EFISH}$  value (by a factor of 1.4). Replacement of a benzoxazolyl unit with a benzothiazolyl (**67**) lowers the LUMO, because of the lower electronegativity of sulphur with respect to oxygen, and therefore leads to an increase of the quadratic hyperpolarizability ( $\mu\beta_{1.907}\text{EFISH} = -660 \times 10^{-48}$  esu;  $\beta_{1.907}\text{EFISH} = -76 \times 10^{-30}$  esu;  $\mu = 8.6 \times 10^{-18}$  esu). Addition of the electron-acceptor CF<sub>3</sub> group on the cyclometalated phenyl ring (**69**) leads to a large enhancement of  $\beta_{1.907}\text{EFISH}$  ( $-178 \times 10^{-30}$  esu) but  $\mu\beta_{1.907}\text{EFISH}$  ( $-670 \times 10^{-48}$  esu) remains similar because of a significant  $\mu$  reduction ( $\mu = 3.8 \times 10^{-18}$  esu). As above reported, exchange of Cl with phenylalkynyl leads to an increase of the NLO activity of cyclometalated dipyriddybenzene Pt(II) compounds. Similarly, the quadratic hyperpolarizability is multiplied by two on moving from **67** to **68** ( $\mu\beta_{1.907}\text{EFISH} = -850 \times 10^{-48}$  esu;  $\beta_{1.907}\text{EFISH} = -145 \times 10^{-30}$  esu;  $\mu = 5.9 \times 10^{-18}$  esu), due to a lower HOMO–LUMO distance with an augmentation of the charge transfer from the Pt–phenylacetylide fragment to the N<sup>^</sup>C<sup>^</sup>N ligand.

Compound **70**, with cyclometalated (methylbenzimidazol-2-yl)(benzothiazolyl)benzene, has a much higher dipole moment, leading to a higher  $\mu\beta_{1.907\text{EFISH}}$  value ( $-950 \times 10^{-48}$  esu where  $\beta_{1.907\text{EFISH}} = -87 \times 10^{-30}$  esu and  $\mu = 10.9 \times 10^{-18}$  esu).

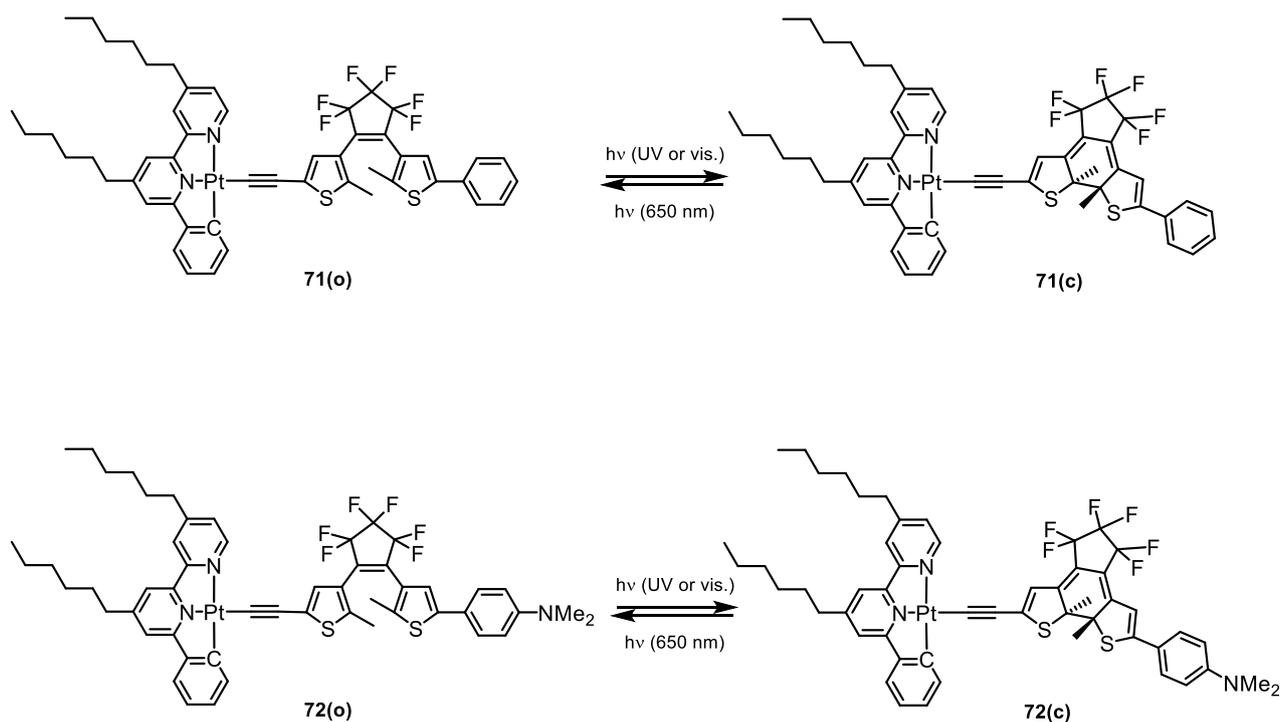


**Figure 16.** Pt(II) compounds with cyclometalated bis(heteroazoly)benzene.

### 8. Pt(II) compounds with cyclometalated N<sup>N</sup>C phenylbipyridine

As reported in section 7, cyclometalated N<sup>C</sup>N Pt(II) compounds are fascinating multifunctional materials characterized by remarkable luminescent and NLO properties. In these complexes, the use of an acetylide ancillary ligand represents a route for improving the NLO activity. These observations were a springboard for the investigation of related cyclometalated N<sup>N</sup>C Pt(II) compounds with an acetylide ancillary ligand [108-109]. A dithienylethene (DTE) unit was introduced in the acetylide ligand for NLO photomodulation.

Thus, an EFISH investigation was accomplished, in CH<sub>2</sub>Cl<sub>2</sub> solution, on two photochromic cyclometalated phenylbipyridine platinum(II) complexes with an acetylide DTE ancillary ligand bearing a phenyl (**71**) or dimethylaminophenyl (**72**) group (Figure 17) [108].



**Figure 17.** NLO switch based on photochromic Pt(II) compounds with cyclometalated phenylbipyridine.

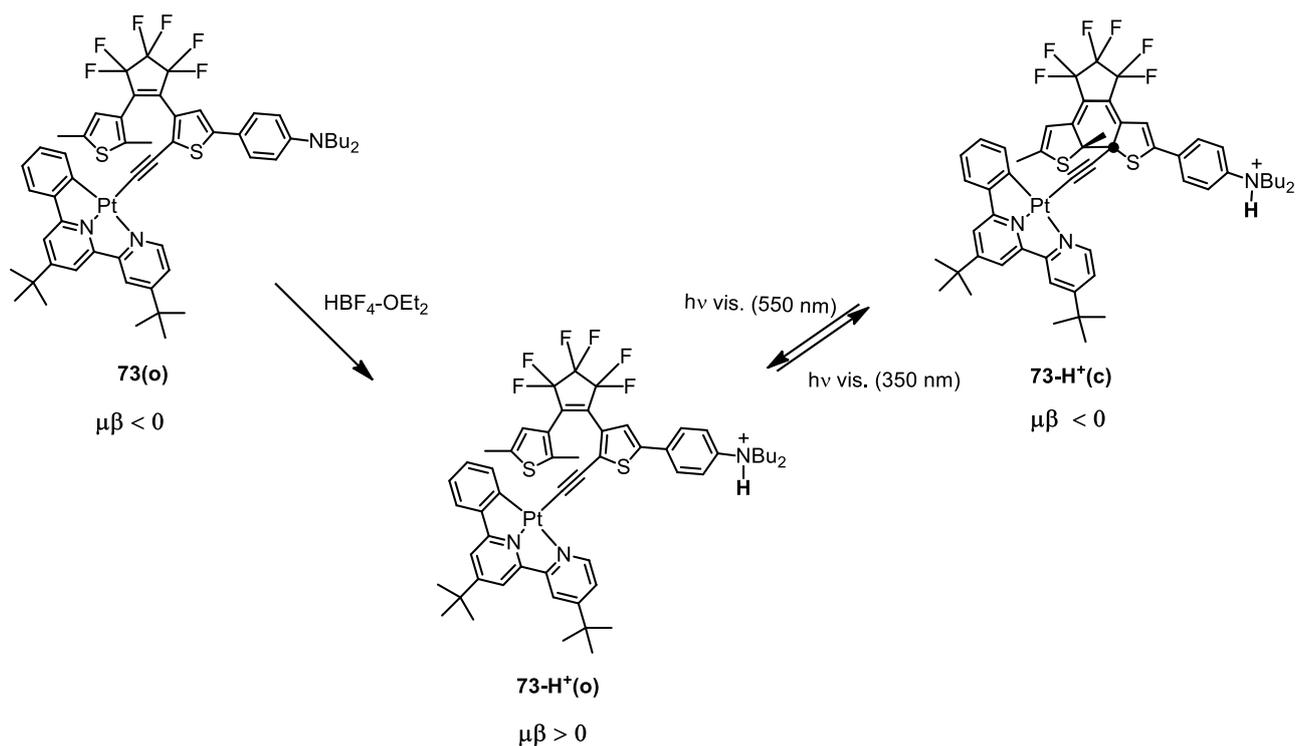
These complexes present a negative value of  $\mu\beta_{1.907}\text{EFISH}$ , in both the open and closed isomer of the DTE moiety, in line with a decrease of  $\mu$  upon excitation. This is in agreement with a quadratic hyperpolarizability dominated by a charge transfer from the Pt–alkynyl unit to the cyclometalated ligand, as confirmed by TD-DFT calculations.

The  $\mu\beta_{1.907}\text{EFISH}$  value of **71(o)** is weak ( $-180 \times 10^{-48}$  esu where  $\beta_{1.907}\text{EFISH} = -11 \times 10^{-30}$  esu and  $\mu = 15.7 \times 10^{-18}$  esu) but it increases drastically after UV irradiation which gives the closed form **71(c)** ( $-1150 \times 10^{-48}$  esu where  $\beta_{1.907}\text{EFISH} = -61 \times 10^{-30}$  esu and  $\mu = 18.7 \times 10^{-18}$  esu). The 6-fold enhancement of  $\beta_{1.907}\text{EFISH}$  is due to the highly delocalized  $\pi$ -electron system with the closed DTE which causes a significant decrease of the HOMO–LUMO distance. With the donor dimethylamino unit (**72**), the increase of the quadratic hyperpolarizability is much higher (12-fold enhancement). As a matter of fact, the  $\mu\beta_{1.907}\text{EFISH}$  value of **72(o)** is weak ( $-220 \times 10^{-48}$  esu where  $\beta_{1.907}\text{EFISH} = -19 \times 10^{-30}$  esu and  $\mu = 11.3 \times 10^{-18}$  esu) and it strongly increases upon formation of **72(c)** ( $-2635 \times 10^{-$

<sup>48</sup> esu where  $\beta_{1.907\text{EFISH}} = -214 \times 10^{-30}$  esu and  $\mu = 12.3 \times 10^{-18}$  esu). Remarkably, the quadratic hyperpolarizability of **72(c)** is 3.5 times larger than that of **71(c)**, a behavior that is due to an augmentation of charge transfer distance and therefore of  $\Delta\mu_{\text{eg}}$  [108].

Nano-organization of both complexes in poly(methyl methacrylate) affords NLO-active films. The second harmonic generation (SHG) response of the film based on **71(o)** is relatively low ( $\chi_{33}^{(2)}$ ,  $\chi_{31}^{(2)}$ , and  $\chi_{15}^{(2)} = 0.16, 0.10,$  and  $0.07$  pm/V, respectively) but increases significantly upon formation of **71(c)** ( $\chi_{33}^{(2)}$ ,  $\chi_{31}^{(2)}$ , and  $\chi_{15}^{(2)} = 0.32, 0.20,$  and  $0.08$  pm/V, respectively). Similarly, in the case of the film prepared with the complex bearing the NMe<sub>2</sub> electron donor group (**72(o)**:  $\chi_{33}^{(2)}$ ,  $\chi_{31}^{(2)}$ , and  $\chi_{15}^{(2)} = 0.58, 0.40,$  and  $0.12$  pm/V, respectively); **72(c)**:  $\chi_{33}^{(2)}$ ,  $\chi_{31}^{(2)}$ , and  $\chi_{15}^{(2)} = 0.70, 0.70,$  and  $0.13$  pm/V, respectively). Remarkably, it is possible to switch their SHG response by interaction with a suitable electromagnetic radiation [108].

Another kind of Pt(II) compound functionalized with DTE (**73(o)**, Figure 18) was investigated by EFISH in dichloromethane [109]. In contrast to **72**, where the platinum acetylide and dialkylaminophenyl units are on opposite thiophene rings of DTE (Figure 17), in **73**, the platinum acetylide and dialkylaminophenyl units are both on one DTE thiophene leading to a highly  $\pi$ -delocalized acetylide in the open isomer. Therefore, as expected, **73(o)** presents a significant negative  $\mu\beta_{1.907\text{EFISH}}$  value ( $-496 \times 10^{-48}$  esu) which is stable upon irradiation because closure of DTE doesn't take place. Treatment with HBF<sub>4</sub>-OEt<sub>2</sub> leads to protonation with formation of **73H<sup>+</sup>(o)** characterized by a large positive  $\mu\beta_{1.907\text{EFISH}}$  value ( $690 \times 10^{-48}$  esu), as expected for a drastic change of the electronic structure. Irradiation of **73H<sup>+</sup>(o)**, for 5 min at 350 nm, readily gives the closed isomer **73H<sup>+</sup>(c)** which presents a large negative  $\mu\beta_{1.907\text{EFISH}}$  value ( $-925 \times 10^{-48}$  esu), due to a new conjugated pathway centered on DTE (Figure 18). Complex **73** is of great interest because its protonation followed by irradiation with UV light allows a sequential double NLO switch with a change of the  $\mu\beta_{1.907\text{EFISH}}$  value sign at each step.

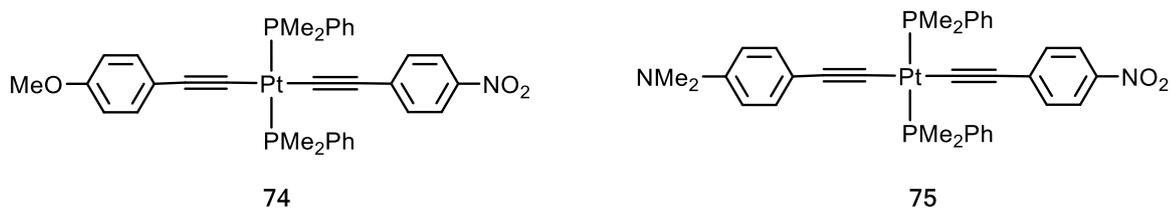


**Figure 18.** Sequential double NLO switch based on photochromic Pt(II) compounds with cyclometalated phenylbipyridine.

## 9. Pt(II) dialkynyl compounds

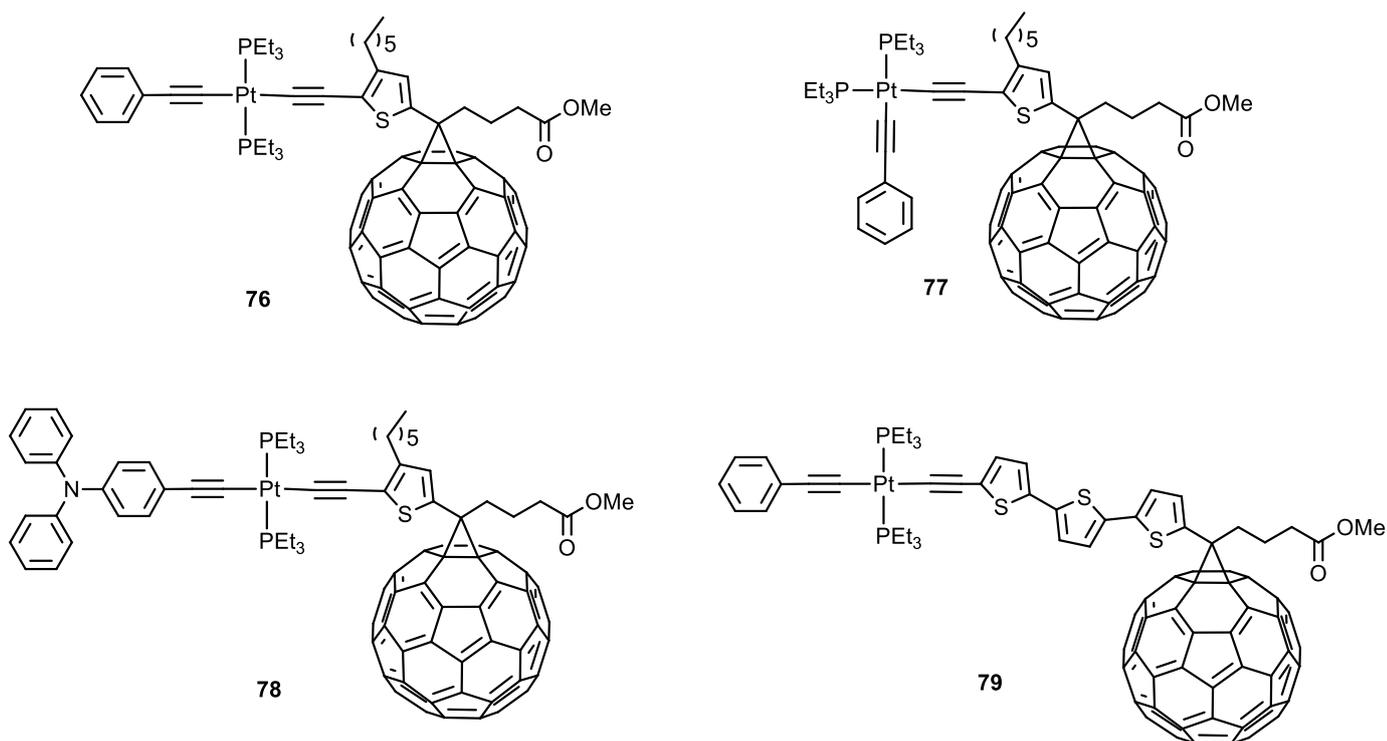
The great potential of unsymmetrical Pt bis(acetylide) for second-order nonlinear optics was reported in 1997, showing that Pt is an efficient element to prepare conjugated chains for NLO materials thanks to  $d\pi$ - $p\pi$  interactions [110]. A platinum(II) bis(dimethylphenylphosphine) moiety was used to bridge a donor phenylethyne and an acceptor nitrophenylethyne in a *trans* coordination arrangement (Figure 19). Donor groups of different strength were chosen (**74**, donor = OMe; **75**, donor = NMe<sub>2</sub>). The quadratic hyperpolarizability of these compounds was obtained with the EFISH technique, in chloroform solution at 1.064  $\mu\text{m}$ . The rather good  $\mu\beta_{1.064}\text{EFISH}$  value of **74** ( $310 \times 10^{-48}$  esu where  $\beta_{1.064}\text{EFISH} = 62 \times 10^{-30}$  esu and  $\mu = 5.0 \times 10^{-18}$  esu) doubles upon substitution of OMe with NMe<sub>2</sub> (for **75**,  $\mu\beta_{1.064}\text{EFISH} = 670 \times 10^{-48}$  esu,  $\beta_{1.064}\text{EFISH} = 126 \times 10^{-30}$  esu, and  $\mu = 5.3 \times 10^{-18}$  esu), in line with the greater donor strength of the dimethylamino group. This pioneering work

shows how platinum can be a key bridge between a donor and an acceptor moiety to obtain large quadratic hyperpolarizabilities. Interestingly, a poly(methyl methacrylate) film containing a complex similar to **74**, but with triphenylphosphine instead of dimethylphenylphosphine ancillary ligands, afforded a large second harmonic generation response ( $\chi_{33}^{(2)} = 4.6 \text{ pm/V}$ ) [111]. The NLO response doubled by using ferrocene instead of methoxyphenyl as donor group reaching a SHG response ( $\chi_{33}^{(2)} = 9.2 \text{ pm/V}$ ) closer to that of Disperse Red One ( $\chi_{33}^{(2)} = 16.7 \text{ pm/V}$ ) [111].



**Figure 19.** Pt(II) dialkynyl complexes.

It is known that fullerene  $C_{60}$  has a large polarizability and strong acceptor properties [112-113] and therefore it represents an appealing building block for NLO systems [114-115]. An interesting NLO investigation was carried out by EFISH, at  $1.907 \mu\text{m}$  in dimethylformamide, on donor–bridge–acceptor (D- $\pi$ -A) systems (Figure 20) in which the fullerene (A) is linked to an acetylide thienyl unit by means of a cyclopropane ( $\pi$ ) and then connected to a Pt acetylide moiety (D) [116].



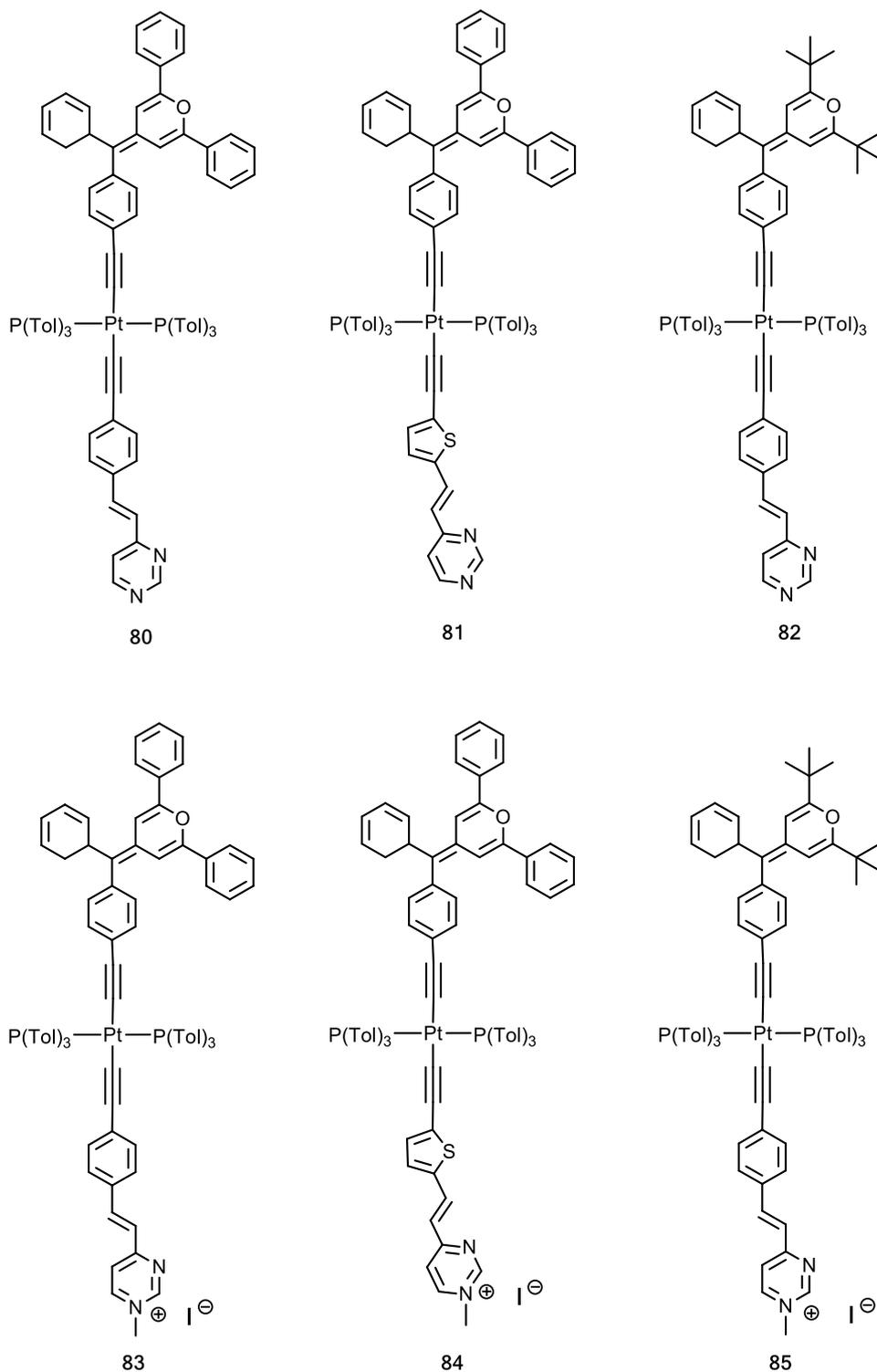
**Figure 20.** Platinum(II) dialkynyl complexes with fullerene.

Complex **76** presents a huge  $\mu\beta_{1.907}\text{EFISH}$  ( $-3100 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -534 \times 10^{-30}$  esu and  $\mu = 5.8 \times 10^{-18}$  esu), much higher (factor of 9) than that of a related compound with a trimethylsilyl unit instead of the (phenylacetylide) $\text{Pt}(\text{PEt}_3)_2$  moiety ( $\mu\beta_{1.907}\text{EFISH}$  value  $-350 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -83 \times 10^{-30}$  esu and  $\mu = 4.2 \times 10^{-18}$  esu), because of an augmentation of  $\mu$  and  $\beta_{1.907}\text{EFISH}$ . A similar huge response is reached with the *cis* isomer **77** ( $\mu\beta_{1.907}\text{EFISH} = -3200 \times 10^{-48}$  esu), as a consequence of a larger  $\mu$  ( $13.3 \times 10^{-18}$  esu) although the  $\beta_{1.907}\text{EFISH}$  is lower ( $-241 \times 10^{-30}$  esu) because the “*push-pull*” system is less efficient when the two alkynyl fragments are in *cis* position. A slightly lower  $\mu\beta_{1.907}\text{EFISH}$  value ( $-2700 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -458 \times 10^{-30}$  esu and  $\mu = 5.9 \times 10^{-18}$  esu) is obtained upon introduction of a diphenylamino group on the phenyl ring (complex **78**), probably because the measured NLO activity has negative and positive contributions caused by different charge transfer transitions. Replacement of thiophene (**76**) by

terthiophene (**79**) leads to a similar huge NLO response ( $\mu\beta_{1.907}\text{EFISH}$  value =  $-3200 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -627 \times 10^{-30}$  esu and  $\mu = 5.1 \times 10^{-18}$  esu). In these complexes, there is complete delocalization of the HOMO and HOMO-1 on the platinum acetylide terthiophene or thienyl moieties whereas LUMO and LUMO+1 are fullerene-centered orbitals, with charge transfer from the acetylide terthiophene or thienyl moiety to  $\text{C}_{60}$ .

Dispersion and orientation of the fullerene platinum bis(acetylide) complexes **76** and **78** in a polymeric matrix, afforded thin films with interesting NLO properties. In poly(methyl methacrylate), a two-fold SHG signal was observed for **78** with respect to **76**. Replacement of poly(methyl methacrylate) by polystyrene, for **78**, gives a further two-fold enhancement of SHG. Although  $\chi_{33}^{(2)}$  is not high (0.5 pm/V), the result shows how important is the nature of the polymer, influencing the stability of the NLO chromophores orientation [116].

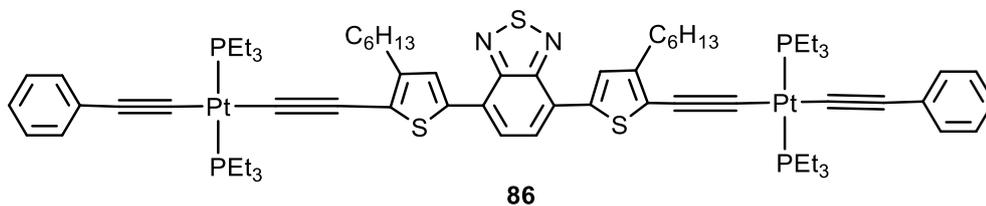
The quadratic hyperpolarizabilities of another family of Pt(II) diacetylide compounds (**80-85**, Figure 21), dissolved in chloroform, were studied by EFISH [117]. Complexes **80-82** incorporate pyranilidene as donor, diazine ring as acceptor, and thienylvinyl or styryl as linker between the Pt dialkynyl moiety and the accepting group. They present a fair  $\mu\beta_{1.907}\text{EFISH}$  value (260, 170 and  $390 \times 10^{-48}$  esu for **80**, **81** and **82**, respectively) which increases drastically upon methylation of the diazine ring ( $\mu\beta_{1.907}\text{EFISH}$  value = 2000, 3600,  $3600 \times 10^{-48}$  esu, for **83**, **84** and **85**, respectively), in line with an augmentation of the power of the acceptor unit. The positive sign of the  $\mu\beta_{1.907}\text{EFISH}$  values indicates that there is an augmentation of  $\mu$  upon excitation ( $\Delta\mu_{\text{eg}} > 0$ ). It is worth pointing out that substitution of phenyl with  $\text{C}(\text{CH}_3)_3$  on the pyranilidene moieties (**82** vs **80**, and **85** vs **83**) enhances significantly the NLO response. There is localization of the HOMOs on the pyranilidene unit whereas the LUMOs are localized on the diazine fragment. There is no significant participation of the Pt 6d orbitals in the transitions at low-energy since they lie far from the HOMO–LUMO region [117].



**Figure 21.** Platinum(II) dialkynyl complexes with pyran-ylidene.

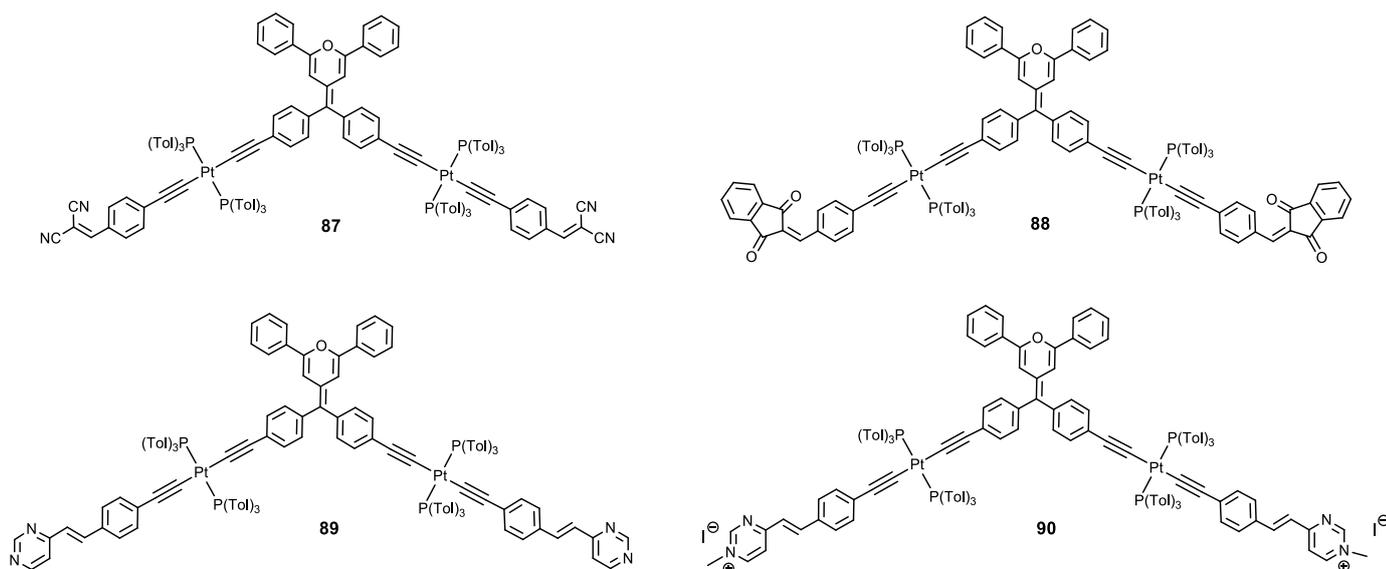
Interestingly, the dinuclear Pt(II) species **86** (Figure 22), in which two platinum bis(acetylide) moieties are linked by a benzothiadiazole unit, presents a significant  $\mu\beta_{1.907}\text{EFISH}$  ( $-520 \times 10^{-48}$  esu, where  $\beta_{1.907}\text{EFISH} = -151 \times 10^{-30}$  esu and  $\mu = 3.4 \times 10^{-18}$  esu) in  $\text{CH}_2\text{Cl}_2$  solution [118]. In this

complex, the HOMOs correspond to platinum orbitals mixed with benzothiadiazole and thiophene orbitals whereas there is localization of the LUMO on the benzothiadiazole only.



**Figure 22.** Dinuclear platinum(II) dialkynyl complex.

Recently, various Donor-( $\pi$ -Pt- $\pi$ -Acceptor)<sub>2</sub> V-shaped dinuclear platinum(II) dialkynyl complexes bearing a diphenylpyranylidene ligand as a pro-aromatic donor group and different electron-acceptor moieties (malononitrile, indane-1,3-dione, pyrimidine and pyrimidinium) separated by Pt bis-acetylide fragments have been synthesized, and their second-order NLO properties have been determined by using the EFISH generation technique. All complexes display positive  $\mu\beta_{1.907}$ EFISH, the second-order NLO responses being easily modulated by the nature of the end-capped electron-acceptor group ( $\mu\beta_{1.907}$ EFISH =  $830 \times 10^{-48}$ ,  $1100 \times 10^{-48}$ ,  $600 \times 10^{-48}$  and  $3300 \times 10^{-48}$  esu, for complexes **87**, **88**, **89**, and **90** respectively). Remarkably, complex **90** bearing a pyrimidinium moiety displays the highest NLO response among all the complexes of this series, in agreement with the strong charge transfer occurring in its lowest excited state. Its NLO response is almost twice as high as that of the related mononuclear complex **83** (Figure 21), which has been confirmed both experimentally and theoretically (TD-DFT studies). Clearly, a V-shaped design, when coupled to strong electron-withdrawing groups such as pyrimidinium, leads to significant NLO responses [119].



**Figure 23.** V-shaped dinuclear platinum(II) dialkynyl complexes.

## 10. Conclusion

This excursion in the second-order NLO properties of various platinum compounds affords a better understanding of the molecular design-NLO behaviour relationship and shows the appealing future of these coordination compounds in the NLO field. Many of the investigated platinum(II) complexes present a  $\mu\beta_{1,907}\text{EFISH}$  value much higher than the value of DR1 ( $500 \times 10^{-48}$  esu), a *push-pull* organic compound that found application in electrooptic films, and similar or even higher than the value of the best NLO-active metal complexes.

Thus, in (phenanthroline)(dithiolate) platinum compounds, where the thiolate ligands play the role of electron-donors whereas the phenanthroline acts as electron-acceptor, functionalization of thiolates with a donor unit leads to an augmentation of the first hyperpolarizability; the presence of a chelating dithiolate or catecholate allows to reach  $\mu\beta_{1,907}\text{EFISH}$  twice that of DR1. The highest second-order NLO properties ( $\mu\beta_{1,907}\text{EFISH} = -10000 \times 10^{-48}$  esu) have been obtained with platinum complexes bearing dithione–dithiolato ligands; in this fascinating family, the dithiolato ligand acts as donor, contributing mainly to the HOMO whereas the dithione is the acceptor, contributing mainly to the LUMO; the platinum atom acts as mediator for the HOMO-LUMO excitation.

Large quadratic hyperpolarizabilities have also been reached for platinum(II) complexes bearing cyclometalated phenylpyridines, N<sup>^</sup>C<sup>^</sup>N pincers, dipyritylbenzene, and N<sup>^</sup>N<sup>^</sup>C phenylbipyridine. In the case of platinum(II) complexes with a cyclometalated dipyritylbenzene, it was shown that the introduction of acceptor groups on the N<sup>^</sup>C<sup>^</sup>N ligand causes an augmentation of its accepting power, as confirmed by a diminution of the LUMO orbitals energy, allowing an easier MLCT from the Pt center, therefore consenting an increase of the second-order NLO properties; besides, the introduction of CF<sub>3</sub> groups on the pyridine rings causes an augmentation of  $\mu$  and therefore of  $\mu\beta_{1.907}\text{EFISH}$ .

Platinum(II) dialkynyl complexes represent another appealing NLO-active family, where the metal can act as an efficient bridge between a donor moiety and an acceptor unit. The introduction of a fullerene acceptor moiety leads to huge  $\mu\beta_{1.907}\text{EFISH}$  values ( $-3200 \times 10^{-48}$  esu). Similar values can be reached with well designed Donor-( $\pi$ -Pt- $\pi$ -Acceptor)<sub>2</sub> V-shaped dinuclear platinum(II) dialkynyl complexes bearing a strong electron-withdrawing group such as pyrimidinium.

Many of the investigated NLO-active platinum(II) complexes are highly luminescent, an aspect of particular interest for the design of multifunctional materials. Another fascinating characteristic is that their NLO properties can be controlled by an exterior stimulus, of great importance for photonic communication and data processing. For example, an efficient NLO switch controlled by acid/base external stimulus has been developed with a mixed-ligand dithiolene platinum complex. Also, it was shown how the introduction of a dithienylethene moiety is an elegant way to design platinum compounds which quadratic hyperpolarizabilities can be controlled and modulated by light. Platinum complexes with a redox-switchable NLO response are also very promising.

Most NLO studies have been carried out in solution. A few platinum(II) complexes have been nano-organized in polymeric films, affording an NLO-active material. The best second harmonic generation response was obtained for a poly(methyl methacrylate) film based on a Pt(II) dialkynyl compound having ferrocene as donor group. Preliminary studies put in evidence that the nature of the

polymeric matrix has a strong influence on the stability of some dipolar NLO chromophores orientation and therefore on the stability of the NLO response, polystyrene being superior with respect to poly(methyl methacrylate). Remarkably, it was shown how the NLO properties of films based on cyclometalated phenylbipyridine Pt(II) compounds, having an alkynyl ancillary ligand functionalized with a dithienylethene, can be easily photomodulated by a suitable radiation.

Up to now the great potential of platinum(II) complexes for nonlinear optics was put in evidence. Now, work should be devoted to study their nano-organization in polymeric films with the aim of reaching stable and large second harmonic generation.

## 11. Acknowledgment

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**Conflicts of interest**

There are no conflicts to declare.