

3.3 | Nonlinear Optical Properties

3.3.1. INTRODUCTION

It was with the advent of the laser in 1960 and the first observation of second-harmonic generation in quartz by P. Franken in 1961, that a period began in which the field of nonlinear optics has gained tremendous interest. Since then, several groups dealing with the theory, preparation and applications of nonlinear optical molecules and materials have appeared.¹ A major advantage of the use of photonics instead of electronics is the possibility to increase the speed of information processes such as photonic switching and optical computing,² which may have potential applications in communication and information technologies.³

Nonlinear optics (NLO) deals with the interaction of electromagnetic fields (light) with matter to generate new electromagnetic fields, altered with respect to phase, frequency, amplitude or other propagation characteristics from the incident field. One of the most intensively studied nonlinear optical phenomena and specifically the NLO property studied in the present Thesis, is second harmonic generation (SHG) or frequency doubling. By this process, near infrared laser light (frequency ω) can be converted by a nonlinear optical material to blue light (2ω). The resulting wavelength is half the incident wavelength and hence materials with this property will be able to store information with a higher density.



Scheme 29

From now on, the theory of second harmonic generation, the experimental techniques used to measure and a brief review of different molecular systems exhibiting second-order NLO responses will be revised.

3.3.1.1 Theory of Nonlinear Optics

The interaction of an electromagnetic field with matter induces its polarization. Indeed, in linear optics there is an instantaneous displacement (polarization) of the electron density of an atom by the electric field E . The displacement of the electron density away from the nucleus results in a charge separation (an induced dipole), with moment μ . With small fields, the strength of the applied field is proportional to the displacement of charge from the equilibrium position, and leads to the Equation 11, in which α is the linear polarizability of the molecule or atom. If the field oscillated with a frequency, then the induced polarization will have the same frequency and phase, if the response is instantaneous.

$$p = \mu + \alpha E \quad \text{Equation 11}$$

When a molecule is subject to laser light (i.e. a very high intensity electric field) the polarizability of the molecule may change driving it beyond the linear regime.

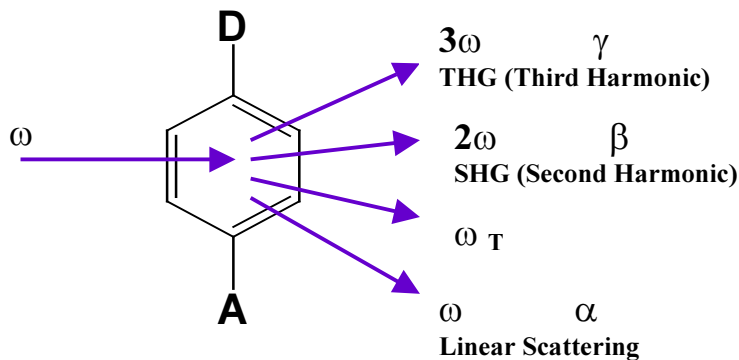


Figure 45. Linear and Nonlinear optical properties of a given material under high power fields (E).

Therefore, the new nonlinear molecular polarization P which is a function of the applied field, leads to the observation of nonlinear effects that can be expressed by Equation 12, where β = first molecular hyperpolarizability (second order effect), γ = second molecular hyperpolarizability (third order effect) and so on.⁴ Since α is much greater than β and γ , NLO was not commonly observed before the introduction of the laser and its associated large electric fields.

$$p = \mu + \alpha E + \beta E^2 + \gamma E^3 + \dots \quad \text{Equation 12}$$

The expression for the total bulk polarization of a material in the presence of an intense optical field is then given in Equation 13, where P_0 is the static dipole of the sample and $\chi^{(n)}$ is the nth order NLO susceptibility.

$$P = P_0 + \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots \quad \text{Equation 13}$$

Important to note is also the fact that for β or $\chi^{(2)}$ to be non zero, the molecules (or materials) need to be non-centrosymmetric or to have a special symmetry like octupolar molecules.

Molecular Hyperpolarizability

The strict theoretical calculation of the hyperpolarizability requires a “sum-over state” treatment and, therefore, the knowledge of: I) energy of all states, II) molecular dipole moment of each state and III) the transition moments between the states. However, in the case of a unidirectional charge-transfer transition, it can be simplified using a model introduced by Oudar and Chemla.⁵ This model considers only two levels for the molecule: the ground state g and the excited state e , between which a transition can occur in resonance with either the fundamental or second harmonic frequency of the incoming optical field (see Figure 46). On the other hand, it allows the prediction and estimation of the molecular second-order NLO response. Extrapolation to zero frequency allows the estimation of static hyperpolarizability (Equation 14). The first hyperpolarizability β can be expressed in either the cgs ($\text{cm}^4 \text{statvolt}^{-1} = \text{esu}$) or the SI ($\text{C m}^3 \text{V}^{-2}$) unit system. The conversion from the SI to the cgs system is given by the relationship: $10^{-50} \text{Cm}^3 \text{V}^{-2} = 2.694 \cdot 10^{-30} \text{esu}$.

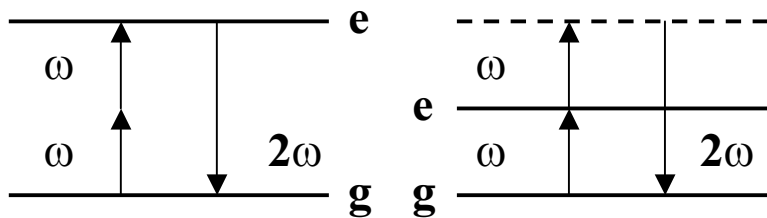


Figure 46. Schematic representation of the Oudar and Chemla model that considers exclusively two levels, the ground state g and the excited state e .

$$\beta_0 = \frac{3e^2 (r_{ge})^2 \Delta\mu_{ge}}{2(E_{ge})^2} \quad \text{Equation 14}$$

3.3.1.2 Experimental Techniques

Although β is a vectorial magnitude,⁶ sometimes it is expressed by a scalar quantity.⁷ This fact is important to be considered in experiments where the applied field points along a molecular axis and therefore, the hyperpolarizability in that direction will be the dominant component. Then, how does the experimental techniques used to measure NLO properties face up to treat it?. Here we will revise the two experimental techniques that were used in the present Thesis, which are: Electric Field Induced Second Harmonic Generation (EFISHG) and Hyper-Rayleigh Scattering (HRS) techniques.

*Electric Field Induced Second Harmonic Generation (EFISHG):*⁸ This experiment gives the projection of the β vector along the molecule dipole (μ) direction for non-ionic molecules with a permanent dipole moment. A strong direct current electric field is applied to the solution of interest in order to remove the orientational averaging caused by statistical alignment of molecular dipoles in the medium. The disadvantage of EFISHG is that it involves the application of a strong electric field to break the centrosymmetry of the solution in order to orient the molecules. Thus, it is limited to molecules having a dipole moment. Neither ionic species, nor molecules possessing octupolar charge distribution, or whose hyperpolarizability is noncollinear with their dipole moment can be studied by EFISHG. Moreover, in the case of the EFISHG technique, the value of β cannot be obtained independently of the dipole moment μ and the third-order polarizability γ . All these drawbacks are eliminated in the Hyper-Rayleigh Scattering technique.

Hyper-Rayleigh Scattering (HRS): This newly developed technique was introduced by the group of Persoons in the early nineties.^{9,10,11} The two main advantages of HRS technique are: I) it can be used to measure isotropic samples either of noncentrosymmetric and even centrosymmetric molecules, and II) the hyperpolarizability β is determined independently of the dipole moment and it measures the average response along all directions. For these reasons, NLO molecules whose hyperpolarizability response may originate from octupolar charge distribution,¹² molecules where β is non-collinear to the dipole moment and ionic species¹³ can be studied using this technique.

For more detailed information about EFISHG and HRS techniques see Appendix 7.2 and 7.4.

3.3.1.3 Materials for Second Order Nonlinear Optics

Traditionally, materials exhibiting second order nonlinear optical behaviour were inorganic crystals, such as lithium niobate (LiNbO₃) and potassium dihydrogenphosphate (KDP). However, organic materials, such as organic crystals and polymers, have been shown to offer better nonlinear optical and physical properties, such as ultrafast response times, lower dielectric constants, better processability characteristics and a remarkable resistance to optical damage, when compared to inorganic materials.¹⁴ Moreover, the ease of modification of organic molecular structures makes it possible to synthesize tailor-made molecules whose

properties may be to fine-tuned at will. In a further step to develop molecular NLO research, metal organic species are being increasingly explored, partly because of the “added value” of metal centres with their incipient magnetic, electrochemical and stereochemical potentials.¹⁵ These systems will be briefly revised here by, grouping them into two categories: A) Push-Pull systems and B) Octupolar systems.

A) Push-Pull Systems

Donor-acceptor systems linked through a π -backbone are one of the most developed structures in the search for new compounds with efficient NLO responses. Indeed, as pointed out in the introduction, the Oudar and Chemla model¹⁶ suggests that molecules to exhibit interesting NLO properties must possess: a) excited electronic states close in energy to the ground state, b) large oscillator strengths for electronic transitions from ground and excited state, and c) a large difference between ground and excited state dipole moments (see Equation 14).¹⁷ Such requirements are best met by highly polarizable donor-acceptor dyads, showing charge transfer between electron-donating and electron-withdrawing groups. Typical examples of push-pull systems exhibiting remarkable NLO properties are the *p*-nitroaniline and 4-amino- β -nitroestirene molecules shown in Figure 47.

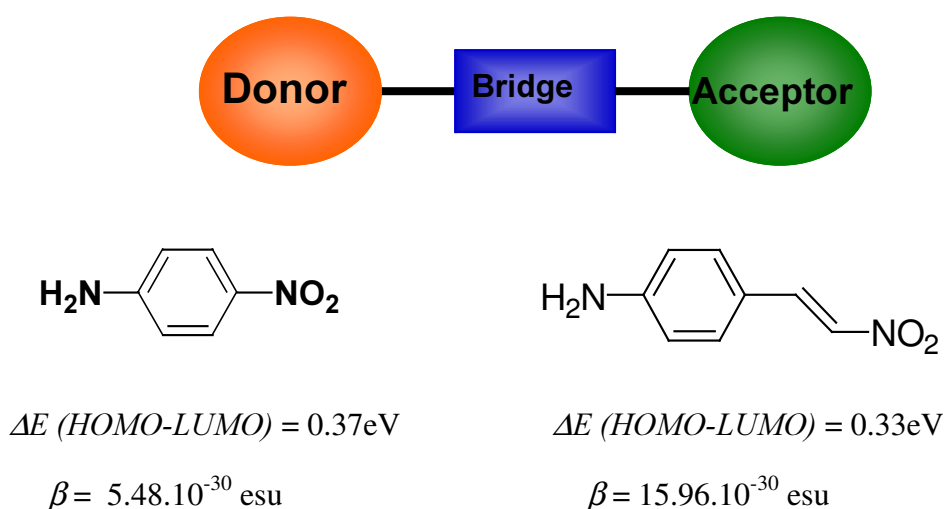


Figure 47. *Top:* Schematic representation of a model Donor-bridge-Acceptor (D- π -A) system with NLO properties. *Bottom:* dipolar *p*-nitroaniline and 4-amino- β -nitroestirene molecules with its energy difference between HOMO and LUMO orbitals and their corresponding β values.

Due to the interest of these systems, particular effort¹⁸ has been placed to find the optimum combination of bridge, acceptor and donor groups in a given molecular system to enhance its NLO response, especially with organic compounds that are easily substituted, and therefore can be chemically fine-tuned.¹⁹ Among the donor groups, dithiol,

dimethylamino or alcoxibenzene units are the most extensively used groups whereas nitro, cyano, and polycyano units are characteristic acceptor groups. The nature of the bridge has also been widely studied, paying especial attention to concepts such as bond-length alternation (BLA).²⁰ With this aim, polyenes, thiophenes, imines and aromatic systems have been commonly used. For instance, Prasad et.al.²¹ have studied the effect of the conjugation path of the bridge in 4-amino- β -nitroestirene derivatives showing that either the increment of the conjugation length nor the increment of the strength of the donor or acceptor units increase the NLO response (β) due to the decreasing of the energy difference between the HOMO and LUMO transition.

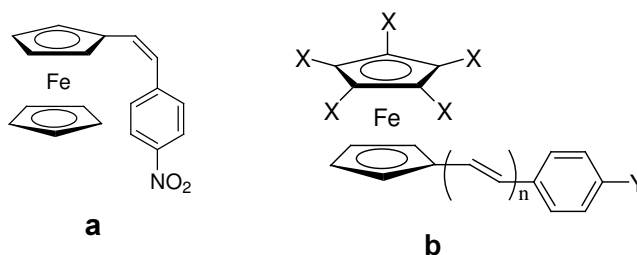
Organometallic Units

Since the pioneering work of Green et al.²² who reported the obtaining of a ferrocene derivative (Scheme30-a) with excellent NLO responses, there has been considerable interest for the use of metallocenes, especially ferrocene derivatives, as donor groups in NLO molecular materials.²³ The reasons for such interest are:²⁴

- i) metallocenes possess low energy metal-to-ligand (MLCT) and ligand-to-metal (LMCT) charge transfer excitations,
- ii) metallocenes have redox processes associated to the central atom, fact that can be used to tune its donor or acceptor capability,
- iii) metallocenes exhibit excited state with very low energy and dipolar moments that differ considerably from the fundamental one,

On the other side, the main inconvenient for the incorporation of metals in NLO systems lies in a decrease of its transparency. In fact, the presence of $d-d$ transitions of low energy originates the appearance of absorption bands in the visible region, compromising their functionality as its transparency decreases.

Due to the inherent interest to include a metallocene unit as donor groups in NLO molecular systems, several authors have been systematically exploring the molecular hyperpolarizabilities of ferrocene π -bridge compounds, such as those shown in Scheme 30. For instance, the series of compounds schematically represented in Scheme 30b exhibit hyperpolarizability values between $66 \cdot 10^{-30}$ and $4 \cdot 10^{-30}$ esu depending either on the nature of the ferrocene and acceptor groups and/or the number of unsaturated bonds present in the bridge.²⁵ The authors have shown that the introduction of methyl groups in the ferrocene units leads to an increase of the β value whereas the extension of conjugation between both, the donor and acceptor units, leads also to an increase of β . Finally *cis* isomers have been shown to usually exhibit lower β values than their corresponding *trans* isomers.



Scheme 30

B) Octupolar Systems

In addition to “push-pull” dipolar molecules, more recently there has been increasing interest for octupolar molecules exhibiting NLO responses.²⁶ These are nondipolar species whose second-order NLO response is related to multidirectional charge transfer excitations, rather than to dipolar unidirectional excitations. Therefore, the first hyperpolarizability for such molecules cannot be described by the two-level model. In fact, the molecular hyperpolarizability, can be reduced into two irreducible components, $\beta_{J=3}$ (dipolar part) and $\beta_{J=1}$ (octupolar part). For molecules belonging to octupolar space groups such as D_3 , D_{3h} , T_d , C_{3v} , and C_2 , the vector part of β is cancelled out and only the octupolar contribution of β remains. A characteristic example of a trigonal octupolar (D_3 or D_{3h}) chromophore and their related octupolar charge distribution are shown in Figure 48. The main advantage of octupolar molecules belonging to planar T_d , D_{3h} or C_{3v} and non planar D_3 or C_2 symmetry groups when compared to dipolar push-pull systems lies on an easier noncentrosymmetric arrangement as well as in the improvement of the balance between transparency and second order NLO signal.^{27,28}

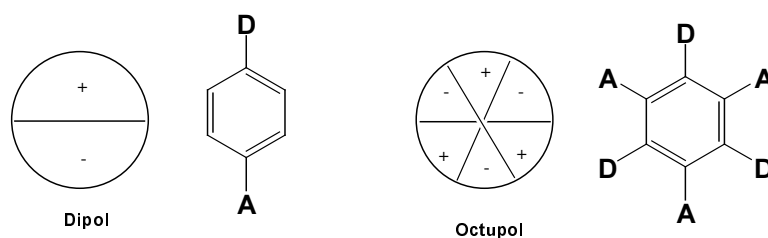


Figure 48. Dipolar vs. Octupolar charge distribution in characteristic dipolar and octupolar systems.

The absence of dipole moment in such structures precludes the exploitation of the EFISHG techniques to measure their NLO response in solution. For this reason, the development of octupolar systems for NLO have experienced a great enhancement since the discovery of the HRS technique, which does not require a poling dipolar electric field.¹ In this order, research on octupolar structures has recently focused on organic molecules with

¹ An increasing number of two- and three-dimensional (2D and 3D) octupolar molecules have appeared in the literature with the development of the Hyper Raleigh Scattering technique (see Chapter 7.3). Wolff, J. J.; Wortmann, R. *J. Prakt. Chem.* **1998**, *340*, 99.

threefold symmetry such as triamino or trinitrobenzenes derivatives,²⁹ crystal violet cation,³⁰ trisubstituted amines or cyanine salts.³¹ For instance, TATB (1,3,5-triamino-2,4,6-trinitrobenzene) has been studied theoretically and experimentally by Bredas *et al.*³² (see Figure 49a). A more extended systems is the crystal violet, which consists of a trigonal conjugated cationic dye with electronic charge transfer from the amino donor groups to an electron deficient sp^2 carbon, with a β value of $150 \cdot 10^{-30}$ esu (Figure 49b). Organometallic and coordination molecules have also attracted the attention of both physicists and chemists since a wide range of metals with different oxidation states, as well as a large choice of ligands and geometries, may be obtained.³³ In addition, bipyridyl ligands are also excellent building blocks for the construction of octupolar metal complexes like $[M(\text{bpy})_3]^{n+}$ of D_3 symmetry for which hyperpolarizability values between 200 and $500 \cdot 10^{-30}$ esu have been found.ⁱⁱ

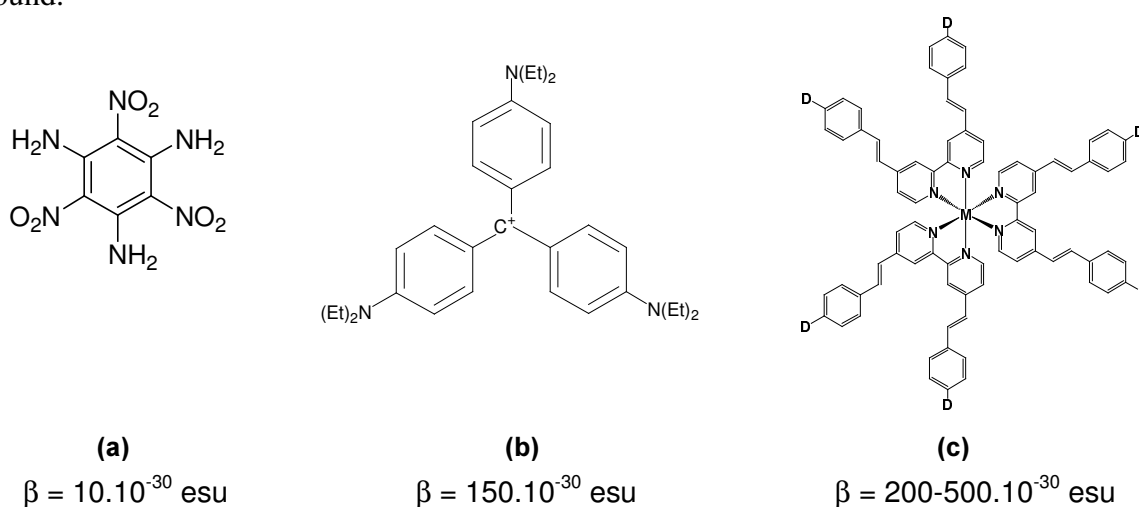


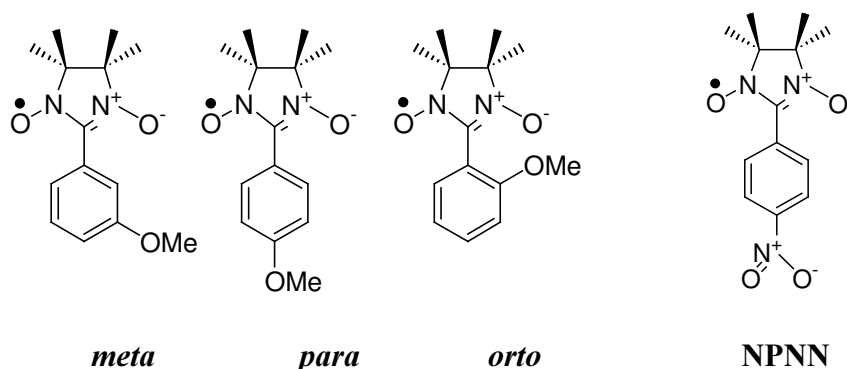
Figure 49. Hyperpolarizability values for (a) 1,3,5-triamino-2,4,6-trinitrobenzene (b) Crystal Violet (c) 4,4'-Di(alkenyl)-2,2'-bipyridines bearing π -donor substituents and corresponding octahedral complexes which exhibit NLO responses.

3.3.1.4 Open-Shell Systems in NLO

Up to now, most attempts to discover new molecular chromophores having large second-order hyperpolarizabilities have been largely focused on closed-shell organic species. On the contrary, the investigation and development of NLO materials having open-shell electronic structures is in its early stage. As pointed out by Marks *et al.*³⁴ there is, in fact, recent evidence that species having open-shell electronic states, such as organic radicals,³⁵ or transition metal complexes with paramagnetic centres³⁶ may exhibit very large second-order hyperpolarizabilities in comparison with analogous closed-shell systems. It is seen that the larger second-order nonlinearity of systems having open-shell electronic states, as compared to those having analogous closed-shell structures, are a consequence of accessible lower-lying charge-transfer electronic states. These results pointed out the possibility of using

ⁱⁱ However, a special precaution have to be taken into account due to the presence of some overestimated values caused by some two-photon excited luminescence.

purely organic free radicals as molecules with large second order NLO (SONLO) activities since their open-shell electronic states permit to expect the presence of accessible low-lying charge transfer electronic states enhancing the β values. However, as far as we know, only a few examples of organic open-shell species showing second-order hyperpolarizabilities have been up to now described, mostly due to the low persistency and the high chemical and thermal instability of these species (see Scheme 31).³⁷ Compounds of the family α -nitronyl-nitroxide (NIT) shown in Scheme 31 cannot be measured by the EFISHG technique because of its low stability in solution.³⁸ The NLO properties for these compounds have been measured by the Kurtz Powder technique³⁹ and very low and irreproducible SHG values have been obtained. On the other hand, the radical *p*-nitrophenyl α -nitronyl-nitroxide (NPNN) (see Scheme 31) seemed to be more stable in solution making possible to measure its NLO response with the EFISHG technique. Such measurements gave a β value of $6.24 \cdot 10^{-30}$ esu, being the first organic open-shell compound with NLO responses and magnetic properties in solid state.^{37a}



Scheme 31

3.3.2 RESULTS

In this chapter, the capability of polychlorotriphenylmethyl monoradicals to generate non linear optical responses, either as octupolar materials or as a component of a *push-pull* system connected to a ferrocene group, have been analysed and the corresponding hyperpolarizability values measured using two different techniques; Hyper-Rayleigh Scattering (HRS) and Electric Field Induced Second Harmonic Generation (EFISHG). The HRS measurements have been performed in collaboration with the Centre de Physique Moléculaire Optique et Hertzienne of Bordeaux under the supervision of Dr. E. Freysz in collaboration with Dr. J.-F. Létard and the EFISHG measurements have been performed at the Instituto de Ciencia de Materials de Aragón (CSIC) under the supervision of Prof. R. Alcalá.

3.3.2.1 PTM Radicals as Octupolar Systems

Initially, the NLO octupolar response of polychlorinated triphenylmethyl radicals **30-35**, **12** and **15**, which were synthesized following the methodology previously described,⁴⁰ were studied. Molecular nonlinear optical coefficients of radicals **30-35**, **12** and **15** were determined in methylene chloride solution at room temperature using the HRS technique and irradiating with a laser light at 1064nm. The resulting quadratic hyperpolarizability β values, shown in figure 50, were derived from the intensity $I_{2\omega}$ of the incoherent scattered light at 532nm according to equation 15,

$$I_{2\omega} / (I_{\omega}^0)^2 = G(N_s \beta_s^2 + N_c \beta_c^2) e^{-N_c \sigma_{2\omega} l} \quad \text{Equation 15}$$

where I_{ω}^0 is the incident laser intensity and G is a constant relative to the collection and quantum efficiencies. The subscripts s and c denote solvent and molecule, respectively, while N is the number density of each component, $\sigma_{2\omega}$ is the molecular cross section at the harmonic frequency and l is the effective optical path length. The macroscopic value β for all the compounds were calibrated against methylene chloride ($\beta=0.43 \cdot 10^{-30}$ esu). For more information see Appendix 7.3.

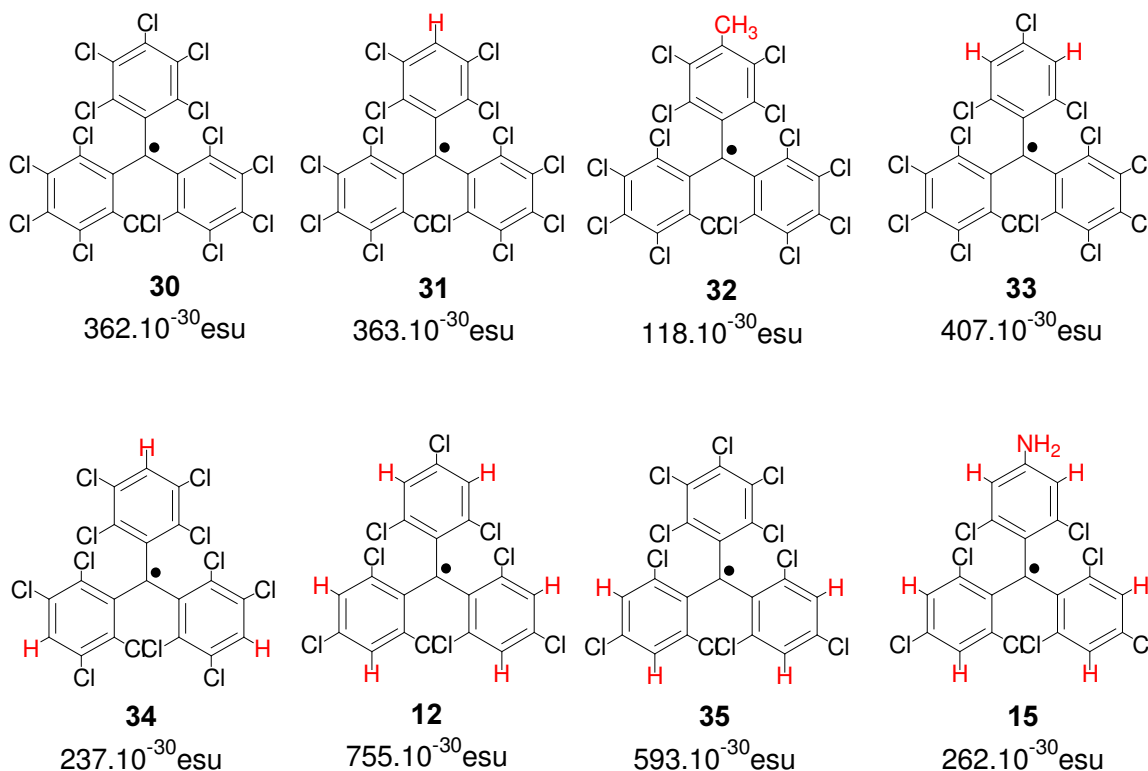


Figure 50. Hyperpolarizability β values for radicals **30-35**, **12** and **15**.

Data reported in Figure 50 show that radicals **30-35**, **12** and **15** exhibit relatively high NLO responses, with β values ranging from 118.10^{-30} to 755.10^{-30} esu. This fact is not surprising since this family of radicals is structurally very similar to the octupolar symmetry of crystal violet, which exhibits a large β value. In fact, both types of compounds have the general formula $Ar^1Ar^2Ar^3Z$, where Z is an sp^2 hybridized atom – a C^+ in crystal violet and C^- in triphenylmethyl radicals- and Ar^i denotes an aromatic group with polarizable substituents (NEt_2 in the crystal violet and chlorine atoms in the radicals).⁴¹ Moreover, the considerably large β values obtained point out to an enhancement of the second-order NLO (SONLO) activities according to their open-shell electronic states.^{42,43} (Papers VI and VIII). However, it is not possible not to extract any irrefutable conclusion about the influence of their open-shell character on their NLO responses since a closer look to radicals **30-35**, **12** and **15** reveals they are composed of three individual building blocks (three aryl groups), each one having a SONLO contribution by themselves. More precisely, 1,3,5-trichlorobenzene (TCB) and pentachlorobenzene (PCB) compounds have an octupolar component and belong, respectively, to D_{3h} (pure octupolar system) and C_{2v} (with dipolar and octupolar contributions) group of symmetry. For this reason, polychlorinated triphenylmethyl radicals give access to individual pure octupolar molecules, constituted itself with individual octupolar blocks, for which the term of "Super-Octupolar" systems was coined. If an octupolar synergistic effect takes place, this would greatly contribute to enhance the SONLO responses of this type of materials, together with their open-shell character.

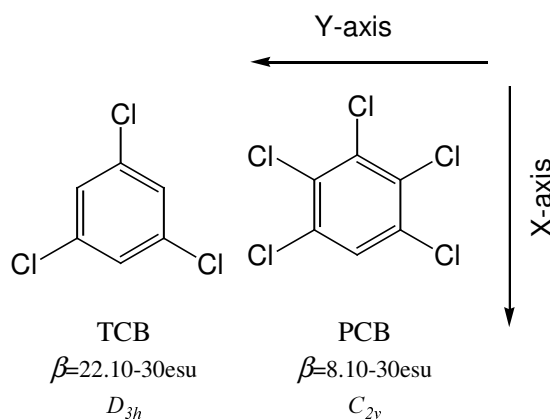


Figure 51. Schematic representation of prototypical noncentrosymmetric planar D_{3h} and C_{2v} symmetry aromatic charge-transfer molecules. (a) TCB: Octupolar system for which $\beta_{J=1} = 0$, $\beta_{J=3} \neq 0$, and $\beta_{xxx} = -\beta_{yyy}$ and (b) PCB: multipolar system for which $\beta_{J=1} \neq 0$, $\beta_{J=3} \neq 0$ and $\beta_{xxx} > -\beta_{yyy}$

To give more insight to the relationship between the electronic configuration and the NLO responses of polychlorotriphenylmethyl radicals, cyclic voltammetric studies of radicals **30-35**, **12** and **15** in methylene chloride using 0,1M nBu_4NPF_6 as electrolyte were performed and analysed. Electrochemical data is collected in Table 10. Interestingly, the representation of the hyperpolarizability β value in front of the reduction or oxidation redox

potentials of radicals **30-35** **12** and **15** yields a linear dependence (see Figure 52). Indeed, as the oxidation potential decreases, the hyperpolarizability β value increases whereas on the contrary, the easier to reduce the lower results β . As an example, the representation of the oxidation potential in front of the β value for radicals **30-35** **12** and **15** is shown in Figure 52. This is an indication that the orbital involved in the redox phenomena, is the same for both the oxidation and the reduction, consequently this orbital must correspond to the SOMO, where the single unpaired electron resides (see Paper VIII).

Table 10. Electrochemical data in methylene chloride, 0,1M $n\text{Bu}_4\text{NPF}_6$ as electrolyte and Ag/AgCl as reference electrode.

Compound	30	31	32	33	34	12	35	15
$E_{1/2 \text{ ox}}$	1.680	1.689	--- ^a	1.558	1.713	1.340	1.441	0.500
$E_{1/2 \text{ red}}$	-0.130	-0.149	-0.219	-0.231	-0.228	-0.520	-0.360	-0.770

^a Not detected

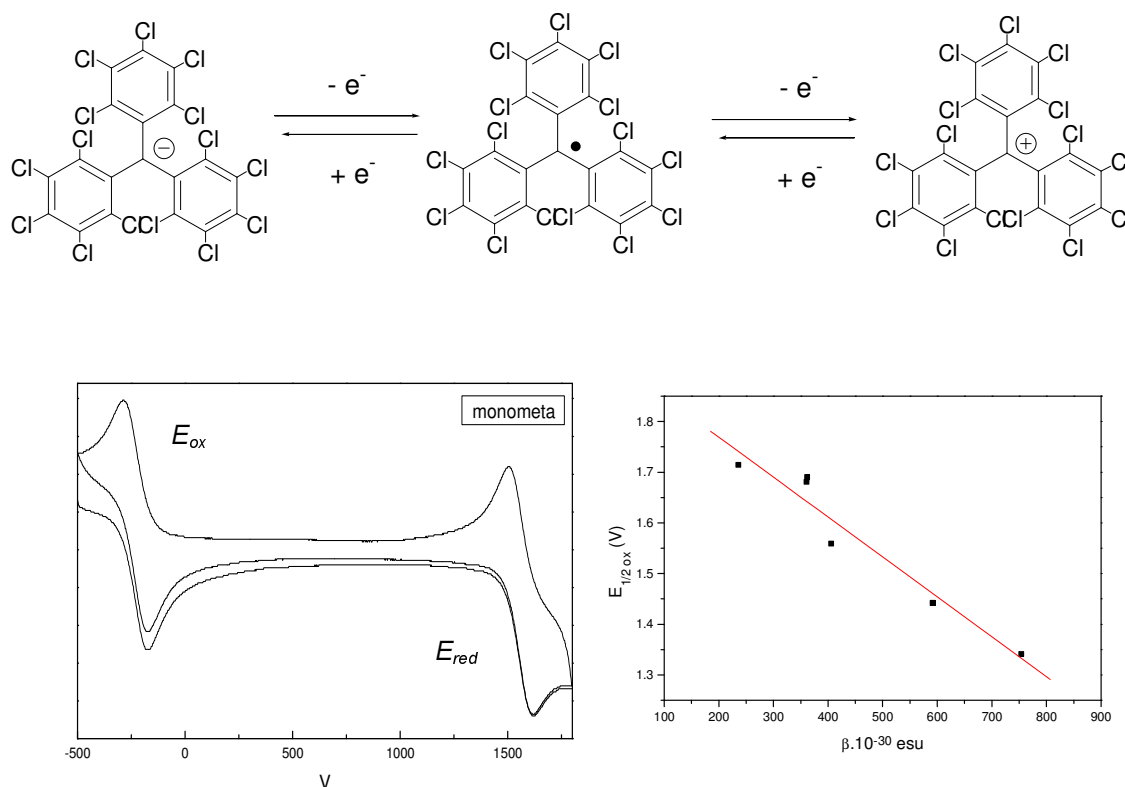


Figure 52. a) Cyclic voltammety of radical **33** b) Linear relationship between the redox potentials and the NLO response for a series of polychlorotriphenylmethyl radicals.

Theoretical Model

Under our experimental conditions (Appendix 7.3), the input laser beam is polarized along the X axis although it propagates along the Z axis. Therefore, the measured β_c^2 values obtained for any molecular symmetry are given by Equation 16:

$$\beta_c^2 = \beta_{xxx}^2 + \beta_{zxx}^2 \quad \text{Equation 16}$$

where β_{xxx}^2 and β_{zxx}^2 depend of different contributions of β_{ijk} where i, j, k are defined in the *molecular frame* (Appendix 7.3.2.3). Therefore, our experimental measurements only give access to two independent coefficients β_{xxx}^2 and β_{zxx}^2 , which depend of different components of $\beta_{ijk}^{(2)}$. Clearly, from Hyper-Rayleigh measurements it is almost impossible to deduce all the components of the molecular hyperpolarizability $\beta_{ijk}^{(2)}$ for a complex symmetry since many of the components result to be nonzero.

On the other side, radicals **30-35**, **12** and **15** belong to two different groups of symmetry, either D_3 (**30**, **34** and **12**) or C_2 (**31-33**, **35** and **15**), which must show more than two no null β coefficients. For instance, molecules belonging to the C_2 group of symmetry must have four independent $\beta^{(2)}$ (i.e. $\beta_{yyy}^{(2)}$, $\beta_{xyz}^{(2)}$, $\beta_{zzy}^{(2)}$, $\beta_{yyx}^{(2)}$) coefficients. Therefore unless some simplifications about the molecular symmetry are made, no useful information can be deduced from HRS experiments. Indeed, the situation is greatly simplified, if one consider the molecule as planar, belonging therefore to the C_{2v} group of symmetry, where only the $\beta_{xxx}^{(2)}$, $\beta_{xyy}^{(2)}$ coefficients remain no null. Further simplification is obtained for molecules that instead of D_3 belongs to D_{3h} group symmetry since in these cases $\beta_{xxx}^{(2)} = -\beta_{xyy}^{(2)}$. Such approximation, although seems to be somehow crude has already been proposed and justified for the analysis of the data of the crystal violet analogous, known to belong to D_3 and C_2 group symmetries.⁴⁴ This simplification seems to be also realistic for the polychlorinated triphenylmethyl radicals family on the basis of their X-ray structure, from where it can be consider that the β_z components remain negligible in regard to other β in-plane components. For C_{2v} and D_{3h} molecules, the averaged hyperpolarizability is given by Equations 17 and 18, respectively:

$$\beta_c^2 = \beta_{xyy}^2 (31(1 + \beta_{xxx}/\beta_{xyy})^2/210 + 4(3 - \beta_{xxx}/\beta_{xyy})^2/210) \quad \text{Equation 17}$$

$$\beta_c^2 = 32 \beta_{xxx}^2/105 \quad \text{Equation 18}$$

Under our experimental HRS conditions,⁴⁵ it can be seen from Equations 17 and 18 that β_c^2 for D_{3h} molecules only depends on β_{xxx}^2 (Equation 18) whereas for C_{2v} molecules it depends on two molecular β_{xxx} and β_{xyy} components. The relation between the averaged β_c^2 and the two molecular β_{xxx} , β_{xyy} components for planar molecules belonging either to C_{2v} and D_{3h} symmetry groups is shown in Figure 53. For our experiments, the β_{xxx}/β_{xyy} ratio of purely octupolar compound (D_{3h} symmetry group) is equal to -1. Therefore, in the later case, β_c^2 is predicted to either increase or decrease depending on the sign and the amplitude of the β_{xxx}/β_{xyy} ratio. It is interesting to compare such properties gathering the compounds in two

series. One series of radicals containing two (or three) octupolar building blocks derived from PCB, radicals **30-33**, while the other series of radicals, **34-35**, **12** and **15** which have two (or three) of such blocks derived from TCB. Concerning the first series, the experimental β_c value of the purely octupolar compound **30** ($362 \cdot 10^{-30}$ esu) is similar to **31**, larger than **32** ($118 \cdot 10^{-30}$ esu) and lower than **33** ($407 \cdot 10^{-30}$ esu). This well confirms that for a series of C_2 molecules the β_c value may also either decrease or increase, as predicted by Figure 53 (Paper VI and VIII).

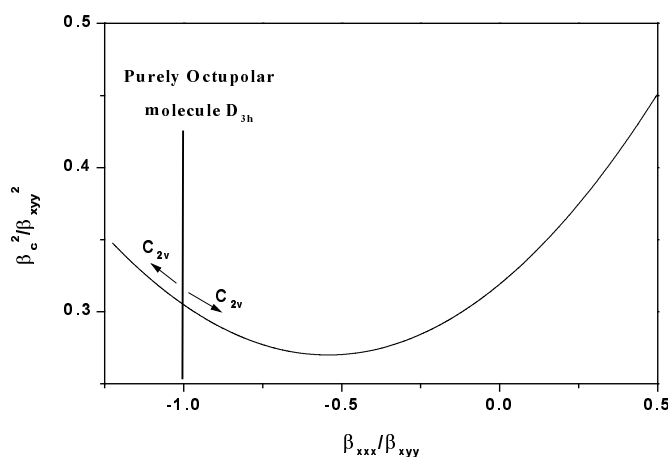


Figure 53. Relationship between the macroscopic β and the β_{xxx} and β_{yyy} components for planar molecule belonging either to C_{2v} or D_{3h} symmetry groups. Under our experimental HRS conditions, the β_{xxx}/β_{yyy} ratio of purely octupolar compound (D_{3h}) is equals -1 .

3.3.2.2 PTM radicals in Push-Pull systems. *Tuning the NLO Response.*

Up to now, we have shown that polychlorotriphenylmethyl radicals are octupolar systems that exhibit relatively high hyperpolarizability values. From now on, we will revise the NLO response of a PTM radical with a given symmetry on the transition from an octupolar to a dipolar (or push-pull) system. Moreover, once the dipolar system is obtained, we will also study the possibility of tuning the NLO responses playing with the nature of the donor, acceptor or bridging units. With this aim, the series of radicals shown in Figure 54 were studied and analysed. All compounds have been prepared and characterized as described in Chapter 2 or more in detail in the Experimental Part (Chapter 5). All hyperpolarizability β values were measured using the HRS techniques and methylene chloride as a solvent (Appendix 7.3).

It is important to emphasise that these studies were faced up following a four-step approach:

Step I (Octupolarity): Initially, the hyperpolarizability response of triphenylmethyl radicals **30** (Series A) and **12** (Series B), exhibiting pure octupolar D_3 symmetry, were measured. These two radicals differ in the number of chlorines atoms per phenyl ring, five and three

chlorine atoms for radicals **30** and **12**, respectively. The different number of chlorines atoms leads to different NLO responses. Thus, an hyperpolarizability response of 362.10^{-30} for **30** and 755.10^{-30} esu for radical **12**, were obtained. Such values have already been rationalized in the precedent section and are expected also to influence the NLO response of their derivatives contemplated in Series A and B.

Step II (Breaking the symmetry): The introduction of an external unit such as a methyl (Serie A) or an amino (Serie B) group directly connected to the octupolar system reduces the symmetry from D_3 to C_2 , and hence, a huge decrease of the hyperpolarizability value is expected. This is the case. In the case of Series A, the introduction of a methyl group reduces the hyperpolarizability value β from 362.10^{-30} esu for radical **30** to 118.10^{-30} esu for radical **32**. For Series B, the introduction of the amino group in one the phenyl rings originates that the hyperpolarizability value β decreases from 755.10^{-30} esu for radical **12** to 262.10^{-30} esu for radical **15**.

Step III (Push-Pull system): The introduction of a donor unit such as bromobenzene (serie A) or a ferrocene unit (Serie B) connected through an isomerizable bridge to the radical species, leads to the formation of the new dipolar *push-pull* compounds **3** and **38**. In the case of series A, the introduction of a vinylene bridge connected to a bromophenyl group leads to an increase of NLO response, although if a better donor unit, such as the ferrocene group, is introduced (**1**) the NLO response increases up to 803.10^{-30} esu. The introduction of an imine bridge in series B also leads to an increase of the hyperpolarizability value although not so pronounced, shifting from 262.10^{-30} esu for radical **15** to 288.10^{-30} esu for radical **3**. The considerably smaller increase of the hyperpolarizability response for radicals involved in series B may be tentatively assigned to the lower electron delocalization through the molecule for the imine bridge.

Step IV (Chemical Tuning): The introduction of a nonamethyl ferrocene donor group is expected to enhance the NLO response of this type of molecular materials. This was the case. The transition from the ferrocene-imino derivative **3** to the nonamethyl derivative **4** in series B, entails an increase of the hyperpolarizability value from 288.10^{-30} to 596.10^{-30} esu. Unfortunately, at the moment of writing the present Thesis, the lack of the hyperpolarizability value for the permethylated radical **2**, prevent us from extracting any conclusion although according with to the trends previously described, such radical is expected to present the highest β value for this family of radicals. Further experiments are currently underway to obtain such experimental value.

Finally, from the results shown in Figure 54 it is worth to mark the divergence in the experimental hyperpolarizability values found for the *cis-5* and *trans-3* radicals. Unexpectedly, the *cis-5* isomer presents a higher hyperpolarizability value than the related *trans-3* isomer, fact that may be rationalized in terms of a higher electronic delocalisation for isomer *cis-5*. To give more insight into such divergences, the NLO response of radicals *cis-5* and *trans-3* was measured using the EFISHG technique. All experiments were carried out in methylene chloride irradiating at 1907nm (for more information see Appendix 7.3).

Surprisingly, the hyperpolarizability values for both radicals were $\beta = 12 \cdot 10^{-30}$ esu. Moreover, an examination of the data shows a marked discrepancy between β_{HRS} and β_{EFISHG} values. The β_{HRS} values are considerably larger than their corresponding β_{EFISHG} values (Paper V).⁴⁶

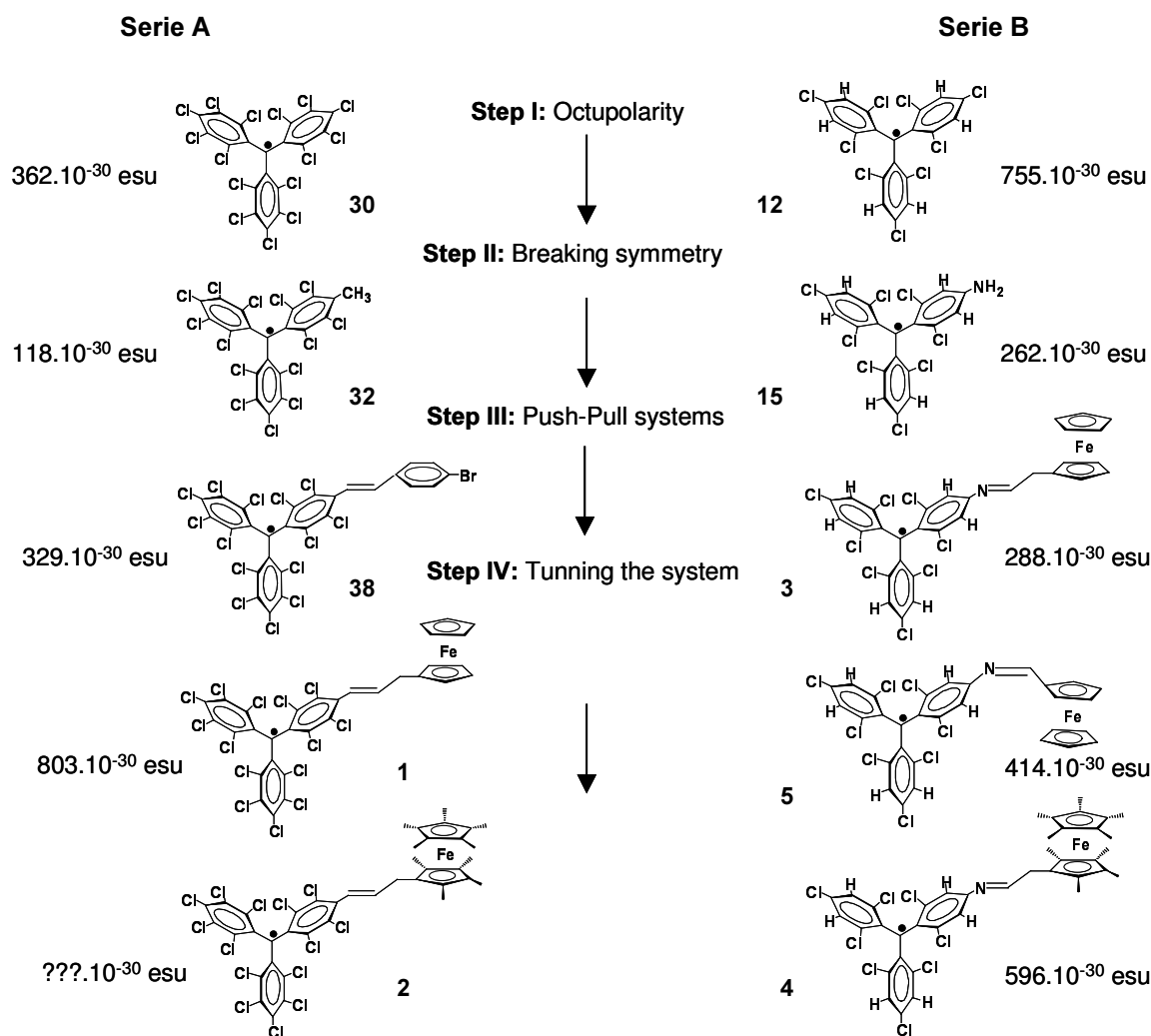


Figure 54. Tunability of Donor- π -Acceptor systems based in polychlorotriphenylmethyl radical connected to a ferrocene or other units.

Molecular Orbital Calculations

To give more insight into the electronic behaviour of ferrocene-(π -bridge)-PTM radical systems, ab initio calculations that allow us to evaluate the structural and electronic

properties of this family of radicals were done. These calculations were performed by Prof. J. Novoa at the University of Barcelona.⁴⁷ It has to be also emphasized that these calculations are highly demanding (CPU time) due to the complexity and large number of atoms, reason why only radicals **3-5** were studied.

The electronic structure of these radicals is a consequence of the shape and energy distribution of the highest occupied HOMO and the semi-occupied SOMO orbitals. As an example, the shape of these orbitals for radical **4** is shown in Figure 55.

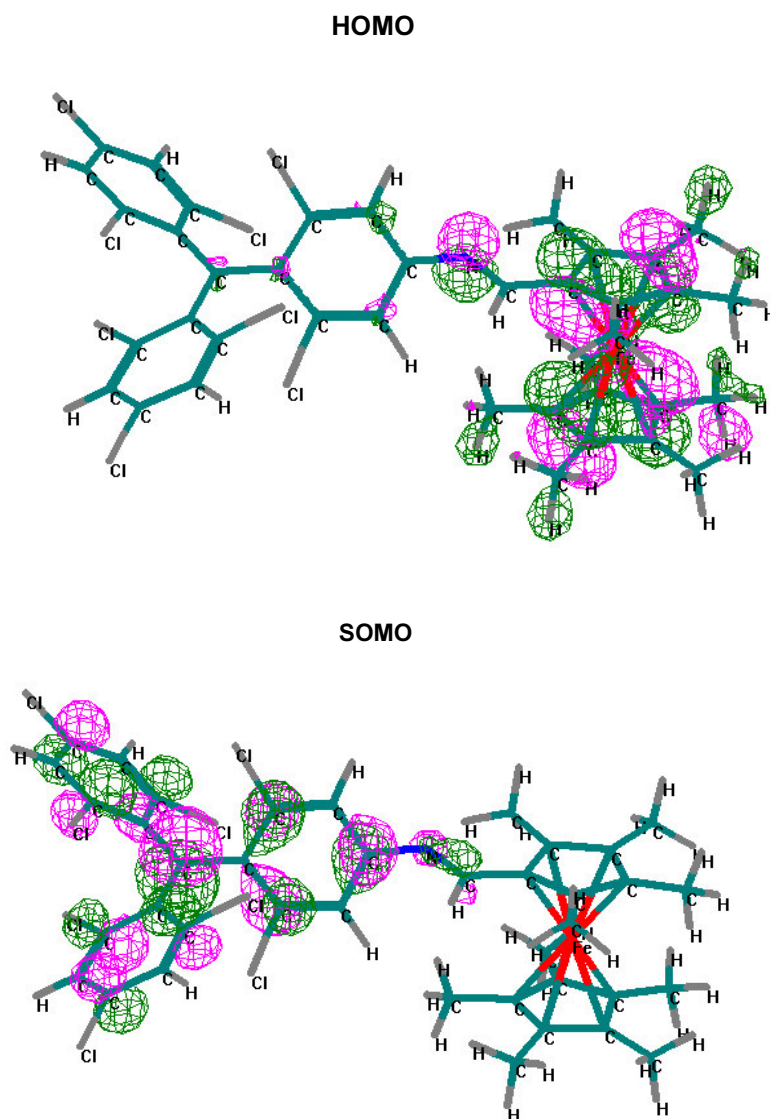


Figure 55. HOMO and SOMO orbitals for compound **4**

The energy of the two orbitals is $2 \times (-0.22)$ Hartrees, and -0.20 Hartrees respectively. The single occupied molecular orbital (SOMO) is mostly placed on the central carbon atom of the trichlorotriphenylmethyl unit, with a small contribution on the six-membered ring attached to the C=N group, and also on the C=N group. Below the SOMO one finds two

degenerated HOMO orbitals placed on the Fe atom of the ferrocene unit with a small contribution on the C=N unit. So we see that the SOMO orbital and the HOMO orbital have similar energies and share a common spatial region.

Moreover, it has also been shown that the decrease of the SOMO-HOMO energy separation lowers the energy of the first excited state and increases the degree of charge transfer.⁴⁸ From the perspective of nonlinear optics, this fact induces a larger molecular hyperpolarizability⁴⁹ according to the two state approximation model of Oudar and Chemla. This fact makes these Push-pull compounds good candidates to present non-linear optical properties, as experimentally demonstrated.

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43. As it has already been pointed out in Chapter 2, the radical forms of polychlorotriphenylmethyl radicals are obtained from a three steps procedure. Step I) is the synthesis of the trichlorotriphenylmethane precursor. Step II) consist in a deprotonation reaction and Step III) the subsequent oxidation to yield the radical species.
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