

Review

Porphyrins for Second Order Nonlinear Optics (NLO): An Intriguing History §

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§ This review is particularly dedicated to Prof. Renato Ugo on the occasion of his 80th birthday, whose contribution has been fundamental in this research field.

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Abstract: This short review outlines the main results obtained by our research group over the last 15 years in the field of porphyrins and metal porphyrins for second order nonlinear optics (NLO). This overview aims to provide a general framework of the key factors which affect the second order NLO response of porphyrin chromophores. The pivotal role of the porphyrin ring as π -conjugated linker, the nature of the metal center, the substitution pattern which features the geometrical arrangement of donor and acceptor substituents in the different classes of porphyrin NLO-phores, as well as the aggregation phenomena and the role of solvents are addressed in detail.

Keywords: Nonlinear optics; porphyrins; push–pull chromophores

1. Introduction

The expression nonlinear optics (NLO) defines the optical phenomena caused by the interaction of a strong oscillating electromagnetic field (such as the one associated with an intense and coherent laser light) with molecules or bulk materials, with emission of new electromagnetic fields (i.e., new light) that differ from the incident ones in frequency, in phase or in other optical properties.

When a laser beam interacts with a molecule, the perturbation (the total polarization) is expressed by Equation (1):

$$P_i = P_i + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots \quad (1)$$

where P_i is the dipole moment induced by the perturbing optical field E which polarizes the electronic charge. α_{ij} is the linear polarizability, while β_{ijk} and γ_{ijkl} are the quadratic and cubic hyperpolarizabilities respectively. The terms $\beta_{ijk}E_jE_k$ and $\gamma_{ijkl}E_jE_kE_l$ correspond to the generation of light with double (2ω) or triple (3ω) frequency with respect to the incident one, through a nonlinear polarization process. Usually, higher order phenomena can be neglected, since their efficiency is very low for practical purposes.

In particular, over the last 15 years our research group has been deeply involved in the investigation of organic or organometallic molecular chromophores for frequency doubling (or Second Harmonic Generation, SHG) applications.

According to the “two-level” model of Oudar [1,2], the quadratic hyperpolarizability (β) of a molecule originates from the mobility of polarizable electrons and depends on electronic charge-transfer (CT) transitions. Under the assumption that the second order NLO response is

dominated by one major CT process, the component of the tensor β along the CT direction (β_{CT}) can be defined according to Equation (2):

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

where ν_{eg} is the frequency of the CT transition, r_{eg} the transition dipole moment, μ_{eg} the difference between the excited and the ground state dipole moments, and ν_L the frequency of the incident radiation.

Therefore, significant β values are expected for non-centrosymmetric push–pull molecules in which an electron-donor and an electron-acceptor group are linked through a π -conjugated polarizable spacer, with a CT transition at relatively low energy and large $\Delta\mu_{eg}$ and r_{eg} values.

In comparison to their organic counterparts, coordination and organometallic chromophores may offer additional electronic features, due to the presence of a metal center, such as intense CT transitions (ligand to metal, LMCT, or metal to ligand, MLCT), localized at relatively low energy and easily tunable by changing the oxidation state of the metal, its coordination sphere, and the stereochemistry [3–5].

Among the many examples reported in the literature [6,7], 2D architectures based on π -delocalized macrocycles such as porphyrins and metal porphyrins [8–13] have attracted great attention due to their thermal and chemical stability, their good solubility, and their potential processability as layers [14]. Moreover, through their polarizable π -conjugated ring, acting as a linker, they can induce a facile electronic exchange within a push–pull system, as required for large second order NLO response [15].

In addition, the architectural flexibility of porphyrins allows a large number of structures reported in the literature, as well as a large variety of substituents to be attached at the *meso* or β -pyrrolic positions of the porphyrin ring [10–13,16] or to the axial position of a metal porphyrin [17].

Heterocyclic rings can be electron-rich or electron-poor systems. In particular, pyrrole, due to its six π electrons and five π orbitals, belongs to the first category. Therefore, a porphyrin, having four pyrrolic rings, is an electron-rich system, where electron-rich (β -pyrrolic) or electron-poor (*meso*) carbon atoms can be recognized [18].

These interesting theoretical suggestions prompted us to investigate more deeply the second order NLO response of 10,20-diphenylporphyrins and 5,10,15,20-tetraphenylporphyrins, substituted in *meso* or in β -pyrrolic positions respectively, either as free bases or as M^{2+} complexes.

The correct determination of the quadratic hyperpolarizability of asymmetric porphyrins and metal porphyrins is of major importance. In fact, β can be measured by many different techniques, such as HRS (Hyper Rayleigh Scattering) [10], Stark effect [11], EFISH (Electric Field Second Harmonic Generation), and solvatochromic analysis [8,9,12,13,19]. Depending on the incident wavelength, these measurements can be affected by resonance [8,9] and in the case of the HRS technique, also by a fluorescent contribution to the second harmonic emission [10].

Moreover, the output of these measurements is quite different. Indeed, while HRS allows the estimation of different elements of the tensor β , Stark spectroscopy affords the value of the static hyperpolarizability β_0 , that is the extrapolation to zero frequency of β_{CT} (when $\nu_L = 0$ in Equation (2)). On the other hand, through EFISH only the tensor component β_{zzz} along the dipole moment direction is obtained (β_{EFISH}), while the solvatochromic method evaluates β_{CT} , which is the component of the tensor β along the charge-transfer direction. Therefore, when the direction of the dipole moment and that of the charge-transfer are not coincident, the difference between β_{EFISH} and β_{CT} is substantial, as occurs for many chromophores.

For this reason, in the particular case of electronically complex chromophores such as porphyrins, showing a strong absorption B band (Soret) at 400–500 nm and two or more Q bands between 600 nm and 700 nm, the discussion and the comparison of results obtained using a single technique or under different experimental conditions can be misleading, as was reported by some of us in 2004 [13]. In order to avoid these drawbacks, we have always measured the second order NLO response of our

porphyrin chromophores by the EFISH technique, working with a non-resonant incident wavelength of 1907 nm.

The EFISH technique [20,21] allows the evaluation of the quadratic hyperpolarizability from Equation (3):

$$\gamma_{\text{EFISH}} = \frac{\mu\beta_{\lambda}(-2\omega; \omega, \omega)}{5kT} + \gamma_0(-2\omega; \omega, \omega, 0) \quad (3)$$

where γ_{EFISH} is the sum of a cubic electronic contribution $\gamma_0(-2\omega; \omega, \omega, 0)$ and of a quadratic dipolar contribution $\mu\beta_{\lambda}(-2\omega; \omega, \omega)/5kT$, μ being the ground state dipole moment and β_{λ} the projection, along the dipole moment axis, of the vectorial component β_{vec} of the tensorial quadratic hyperpolarizability working with an incident wavelength λ .

The third order contribution to γ_{EFISH} [$\gamma_0(-2\omega; \omega, \omega, 0)$] has been reported to be much smaller than the dipolar orientational one for asymmetrically substituted phthalocyanines, structurally related to the porphyrinic chromophores, and therefore negligible [22]. In accordance, we neglected the third order contribution by Equation (3).

Inspired by the studies carried out by Suslik et al. at the beginning of the 90s [8,23] and later by Therien et al. [10,11] and following the theoretical approach of Marks et al. [18], suggesting that the presence of a π spacer between the electron donor or acceptor group and the porphyrin ring, together with the right ring substitution in the *meso* or β -pyrrolic position, could produce chromophores with large second order NLO response, we started to investigate the effect of the metal, of the nature and the position of the substituents, and the effect of the aggregation phenomena in solution on the quadratic hyperpolarizability of porphyrins.

Therefore, this short review accounts for the main results that we have achieved to date.

2. The Role of the Metal

Therien et al. [10,11] and Ng et al. [12] first investigated the second order NLO response of 10,20-diphenylporphyrins and their Zn^{II} [10,11], Cu^{II} [10,11], and Ni^{II} [12] complexes, carrying in the *meso* 5- and 15-positions respectively an electron donor substituent (*p*- $\text{Me}_2\text{NC}_6\text{H}_4\text{-C}\equiv\text{C-}$) and a series of different electron acceptor substituents such as *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-}$ [5] or $-\text{CHO}$, $-\text{CH}=\text{C}(\text{CN})_2$, $-\text{CH}=\text{C}(\text{COOEt})_2$, *trans* $-\text{CH}=\text{CH-CHO}$ [12]. In these metal porphyrins, push and pull moieties are connected to the porphyrin macrocycle through a triple carbon-carbon bond, ensuring strong electronic coupling.

An exceptionally high quadratic hyperpolarizability β was reported by Therien et al. [10,11] for the Cu^{II} (**2**) ($\beta = 1501 \times 10^{-30}$ esu) and particularly for the Zn^{II} (**3**) ($\beta = 4933 \times 10^{-30}$ esu) complexes (Figure 1) measured by the HRS technique with a resonant incident wavelength of 1064 nm.

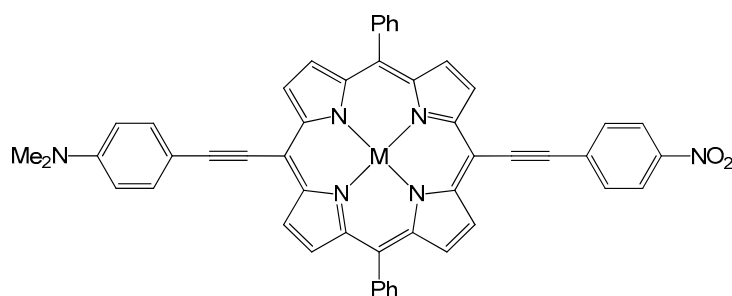


Figure 1. M = Ni (**1**), Cu (**2**), Zn (**3**).

Later the β value of **3**, deduced by absorption and electroabsorption data (Stark effect), was reported to be lower (1710×10^{-30} esu) [11] and lower values for the Ni^{II} porphyrin **1** (β about $80\text{--}100 \times 10^{-30}$ esu) were measured also by the EFISH technique working in CHCl_3 with a non-resonant incident wavelength of 1907 nm [13].

This disagreement of the experimental findings prompted us to evaluate the second order NLO response of the push–pull Ni^{II} porphyrin (**1**) (Figure 1) by different techniques, under similar and controlled conditions in order to define a consistent value of its quadratic hyperpolarizability.

Starting from the result obtained using the EFISH technique in non-resonant conditions [13], we evaluated the quadratic hyperpolarizability for Ni^{II} porphyrin **1** using also the solvatochromic method (β_{CT}) [19] as well as the static hyperpolarizability β_0 by a vibrational method [24,25], which are both totally not affected by fluorescence or resonance, as can occur with HRS or EFISH measurements. The results, confirming an order of magnitude of β_{1907} of about $80\text{--}100 \times 10^{-30}$ esu for **1**, lower than that reported for **2** and **3**, suggested that the quadratic hyperpolarizability of these chromophores could be affected by the nature of the metal.

In 2007 De Angelis et al. [26] reported the results of a theoretical investigation based on Density Functional Theory (DFT) and Hartree-Fock (HF) calculations on the linear and second order NLO response of Zn^{II}, Cu^{II}, and Ni^{II} complexes reported in Figure 1, showing that, different from what was experimentally reported [6,7,9], the second order NLO response of such systems is barely affected by the nature of the metal. This conclusion was confirmed in 2009, by a series of different experimental techniques and theoretical Time Dependent Density Functional Theory (TD-DFT) and coupled perturbed HF (CP-HF) calculations [27].

Moreover, the calculated quadratic hyperpolarizability values [26] seem to compare better with the experimental β_{1907} measured for **1** by the EFISH technique ($80\text{--}100 \times 10^{-30}$ esu) [13] rather than with the very high β values reported for **2** and **3** according to HRS measurements [10]. However, the large differences observed can be probably due to the different incident wavelengths used in the two experimental set-ups, as confirmed by the increased calculated value of β_{1064} if compared to that of β_{1907} .

Finally, the theoretical investigation by De Angelis et al. [26] showed that at the TD-DFT level, both the Q and B bands contribute to the second order NLO response.

3. The Effect of the Nature and the Position of the Substituents on the Porphyrin Core: The Ambivalent Donor or Acceptor Role of the Porphyrin Ring in a Push–Pull System

Albert, Marks and Ratner [18] in 1998 reported a pioneering paper on the second order NLO response of push–pull porphyrins, suggesting that a large NLO response may be obtained by: “(a) minimizing the dihedral twist of phenyl substituents with respect to the porphyrin plane and (b) functionalizing the electron excessive β -pyrrolic position with donor substituents and the electron deficient meso position with acceptor substituents”. Therefore, the second order NLO properties of the porphyrin ring in a push–pull system is also due to its intrinsic donor or acceptor properties [18].

Stimulated by this work we investigated the second order NLO response of a series of push–pull porphyrinic chromophores with electron donor or electron withdrawing groups linked, through a π spacer, to the β pyrrolic position of the 5,10,15,20-tetraphenylporphyrin [16] or to the meso position of the 10,20-diphenylporphyrin [28], either as a free base or as a Zn^{II} complex (Figure 2).

By DFT calculations a nearly planar geometry of the porphyrin ring with the ethylenic or acetylenic linkers was evidenced, producing an easy interaction between β or meso carbon atoms and the π linker [16,28].

Such an interaction was evidenced by the asymmetry of the Soret (or B) band when the nitro group is linked to the electron rich pyrrolic position as in **4**, **5** and **6**, **7** or when a donor dimethylamino group is linked to the electron deficient meso position as in **14**, **15**, and **16**, **17**. Such interaction, as shown by a solvatochromic investigation [16,28], suggests that both B and Q bands are not anymore centered on the porphyrin ring, so that the charge transfer also now involves the π orbitals of the linker.

Dipole moments, theoretically calculated by an ab initio approach based on DFT theory [29,30], using an extended basis set [31], of porphyrins and Zn^{II} porphyrins reported in Table 1 confirm this asymmetry, showing higher values when a substituent carrying an electron acceptor nitro group is

linked to the *meso* or β pyrrolic position, completely opposite in polarity than those of porphyrins with a substituent carrying and amino electron donor group (Table 1).

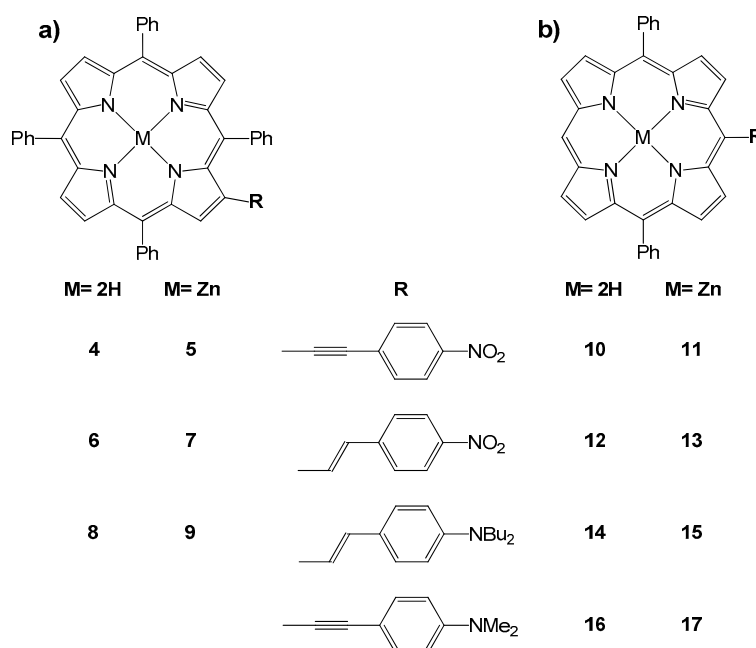


Figure 2. Asymmetrical tetraphenylporphyrins and Zn^{II} complexes with electron donor or electron acceptor substituents in β -pyrrolic position (a), and asymmetrical 10,20-diphenylporphyrins and Zn^{II} complexes with electron donor or electron acceptor substituents at the *meso* position (b). Adapted from *Eur. J. Inorg. Chem.* **2005**, 3857–3874 and from *Eur. J. Inorg. Chem.* **2006**, 1743–1757.

Table 1. Theoretical dipole moments, and Electric Field Second Harmonic Generation (EFISH) β_{1907} in $CHCl_3$ solution of chromophores 4–17.

Compound	$\mu_{(theor)}$ (D) ^a	β_{1907} (10^{-30} esu) ^b
4	8.55	30.1
5	8.82	20.4
6	8.31	39.3
7	8.69	29.7
8	5.33	75.7
9	5.16	127.5
10	8.54	64
11	8.48	n.d. ^c
12	7.70	67
13	7.73	−94
14	6.07	64
15	5.89	87.5
16	5.77	99
17	5.65	112

^a Ab initio Density Functional Theory (DFT) calculations; ^b obtained by Equation (1) omitting the cubic contribution; ^c not soluble enough.

Therefore, already in the ground state a porphyrin ring shows an ambivalent character acting as an electron donor if the substituent in the β pyrrolic or *meso* position carries a nitro group, while it acts as an electron acceptor if it carries a dimethylamino or dibutylamino donor group.

The dependence of the second order NLO response by the nature of the substituent and by the kind of substitution (pyrrolic or *meso*) was discussed, highlighting an increase of electron donor properties

of donor substituents when they are linked to the *meso* or particularly to the β pyrrolic position, while when the substituent is an electron acceptor one, a significant increase of the second order NLO response was observed when substitution occurs at the *meso* position. This latter result is in agreement with the proposal of Ratner, Marks et al. [18] who suggested that the second order NLO increases when the electron acceptor substituent is appended to the *meso* electron deficient position instead of the electron rich β pyrrolic position.

Interestingly the second order NLO response is positive when the substituent is an electron acceptor (4–7, 10–12) and also when it is electron donor (8, 9, 14–17) (Table 1), with the exception of the Zn^{II} complex 13, which is unexpectedly negative.

The origin of the quadratic hyperpolarizability of these chromophores with a $-NO_2$ acceptor group is due to a charge-transfer process between the porphyrin core and the π -orbitals of the linker, as it occurs in the case of push-pull organometallic complexes [32,33] and organic chromophores [34].

However, for porphyrins carrying an electron donor group as 8, 9, and 14–17, if this charge-transfer is the origin of the second order NLO response, the quadratic hyperpolarizability should be negative, in agreement with the opposite direction of the dipole moments. We suggest that the high and positive value of EFISH β_{1907} originates from an increase of the effective strength of the donor group due to the interaction with the very electron-rich π system of the porphyrin macrocycle, which produces a reduction of the ground state polarization with an increase of the second order NLO response [18].

With this view there is no involvement of the π core of the porphyrin ring in the excitation process controlling the second order NLO response.

4. The Effect of Coordination in the Axial Position

It has been reported [32,35,36] that, by coordination of *E*-stilbazoles to a metal center, a significant increase of their second order NLO response is produced, depending on the nature of the substituent in the *para* position of the aromatic ring, and by the metal ion acting as a Lewis acid [32,35]. Therefore, a donor group gives a positive and enhanced value of β_{λ} , while an electron acceptor produces a negative value if the metal center is quite soft.

Since metal ions coordinated to porphyrins show Lewis acid behavior, we were prompted to investigate if such metal complexes would induce the expected increase in the second order NLO response of axially coordinated stilbazoles.

In Figure 3 there are reported a series of Zn^{II} , Ru^{II} , and Os^{II} 5,10,15,20 tetraphenylporphyrin complexes substituted in the axial position with a push-pull *E*-stilbazole having an electron donor or electron acceptor substituent in the *para* position of the phenyl ring.

The axial coordination of *E*-stilbazoles L1 and L2, with NMe_2 electron donor groups does not produce, with the exception or $Ru(TPP)(CO)L1$, the expected increase of the quadratic hyperpolarizability β_{1907} which usually occurs when they are coordinated to a metallic center (Table 2). This can be due to, with the exception of L3, a significant metal to ligand π -backdonation from the d orbitals of the metal to the π^* antibonding orbitals of the stilbazole ligand, which balances the positive effect of the ligand to metal σ -donation, producing a negative effect on the second order NLO response.

When the axial ligand is L3, the axial back donation becomes very relevant and already prevails in the ground state resulting in a significant increase of the dipole moment, with respect to free L3, and a significant and positive EFISH second order NLO response.

The solvatochromic investigation shows, for Ru^{II} and Os^{II} complexes, a good agreement of EFISH β_{1907} and β_{CT} values (Table 2), opposite to the Zn^{II} complexes which show positive EFISH β_{1907} and negative β_{CT} . This disagreement can be explained assuming that the charge-transfer process controlling $\Delta\mu_{eg}$ in the two cases is different.

In the Zn^{II} complexes a back donation from the metal to the porphyrin ring by an equatorial back donation $d_{\pi,metal} \rightarrow e_g(\pi)$ orbitals of the porphyrin ring, perpendicular to the dipole moment axis, prevails, while in Ru^{II} and Os^{II} complexes the $d_{\pi} \rightarrow \pi$ charge transfer along the stilbazole axis is

more relevant. Therefore in the case of Zn^{II} complexes EFISH β_{1907} and β_{CT} values are not comparable because the dipole moment axis is not coincident with the charge transfer direction.

Table 2. Dipole moments (μ), solvatochromic data (β_{CT}) and EFISH quadratic hyperpolarizability (β_{1907}) in $CHCl_3$ working with an incident wavelength of 1907 nm.

Compound	μ (D)	$\Delta\mu_{eg}$ (D)	β_{CT} (10^{-30} esu)	β_{1907} (10^{-30} esu)
L1	3.9 ^a	n.d. ^c	n.d.	35
L2	4.5 ^a	n.d.	n.d.	69
L3	2.0 ^b	n.d.	n.d.	36
[Zn(TPP)L1] 18	4.8	-3.31 -3.55	-78.2 -11 -89.2	40
[Zn(TPP)L2] 19	4.8	-2.31 -3.08	-56.9 -9.9 -66.8	82
[Zn(TPP)L3] 20	3.9	-3.78 -4.57	-76.1 -14.4 -90.5	35
[Ru(TPP)(CO)L1] 21	4.2	2.94 2.30	94.6 6.3 101	100
[Ru(TPP)(CO)L2] 22	5.7	2.77 0.17	64.8 4.0 68.8	75
[Ru(TPP)(CO)L3] 23	7.2	1.46 0.16	34.2 3.8 38.0	46
[Os(TPP)(CO)L1] 24	7.4	1.15 2.26	21.4 8.4 29.8	28
[Os(TPP)(CO)L2] 25	5.1	4.74 1.74	75.3 5.3 80.6	73
[Os(TPP)(CO)L3] 26	4.7	1.17 -1.52	13.4 -4 9.4	95

^a from ref. [32]; ^b theoretical value from ref. [36]; ^c n.d. = not determined.

The lack of increase of the second order NLO response in these compounds seems to be due to the axial back donation $d \rightarrow \pi^*$ of the *E*-stilbazole, opposite in direction to the σ donation, which offsets the increase in EFISH β due to the σ donation [32,35].

The positive value of the EFISH quadratic hyperpolarizability suggests that the polarity of the dipole moment does not change because of the back donation, even when the ligand is L3.

In summary the various metal centers behave as Lewis acids due not only to the axial but also to the equatorial π -backbonding processes which act as a buffer of σ electron donation to the metal.

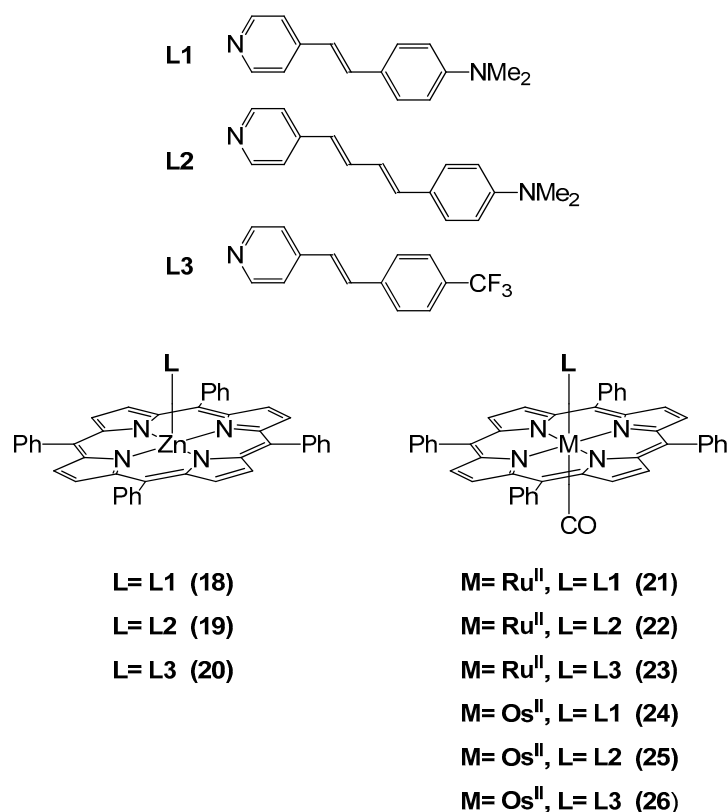


Figure 3. Metal porphyrins axially substituted with donor or acceptor *E*-stilbazoles. Adapted from *Inorg. Chim. Acta* **2006**, *359*, 3029–3041.

5. The Effect of Aggregation

Although it has been demonstrated in the porphyrin complexes reported in Figure 1 that the NLO response is not influenced by the nature of the metal [26], in solvents allowing aggregation processes however, involving the tendency of the metals to coordinate in the axial position, the NLO response can be dependent on the solvent and the metal plays a role in tuning it.

For compounds 1 and 3 (Figure 1), the formation in CHCl_3 solution of different types of aggregates has been experimentally and theoretically evidenced, due to a different tendency of the metal (Ni^{II} and Zn^{II}) to stabilize J aggregation by axial interaction of the metal center with the NMe_2 group [27].

In fact, while the Zn^{II} chromophore 3 shows a significant tendency to coordinate in the axial position with donor molecules such as pyridine, such coordination does not take place in the case of Ni^{II} chromophore 1. Since a dimeric J aggregate is stabilized by a donor–acceptor interaction of NMe_2 of one chromophore with the M^{II} center of the other chromophore, such stabilization is possible for Zn^{II} chromophore 3 but not for 1 (Figure 4).

This tendency has been confirmed by PGSE (^1H pulsed-gradient spin echo) NMR investigation, which has shown that in CHCl_3 a more stable J aggregate is possible for 3, while a less stable dimeric H aggregate is more possible for 1. This hypothesis is confirmed by the doubling of the EFISH β_{1907} values, measured for 3 in CHCl_3 , and due to the stabilization of a J aggregate, with respect to those obtained in CHCl_3 after addition of pyridine or in DMF solution (Table 3).

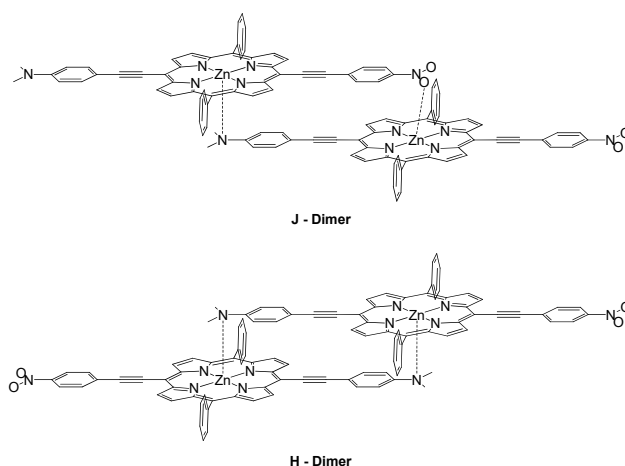


Figure 4. Suggested J and H aggregates of chromophore 3. Adapted from *J. Phys. Chem. C* **2009**, *113*, 11131–11141.

Table 3. EFISH $\mu\beta_{1907}$ values as a function of the concentration and of the solvent for chromophore 3. Adapted from *J. Phys. Chem. C* **2009**, *113*, 11131–11141.

Concentration (mol L ⁻¹)	$M\beta_{1907}$ ($\times 10^{-48}$ esu)	β_{1907} ($\times 10^{-30}$ esu)
5×10^{-5}	6093 ^a	438 ^d
10^{-5}	5438 ^a	391 ^d
5×10^{-6}	6412 ^a	461 ^d
5×10^{-5}	2921 ^b	208 ^e
5×10^{-5}	2600 ^c	188 ^e

^a In CHCl₃; ^b in CHCl₃ with addition of pyridine; ^c in DMF; ^d $\mu = 13.9$ D calculated by DFT [26]; ^e $\mu = 14.0$ D calculated by DFT for the adduct with pyridine in the axial position.

At the same time the decrease of β_{1907} for **1** with increasing concentration, is due to a small amount of a H aggregate stabilized in an antiparallel arrangement of the two chromophores (Table 4).

From these results it is evident that the nature of the solvent must be carefully taken into consideration in evaluating the second order NLO response of chromophores which can aggregate in a non-donor solvent of low polarity such as CHCl₃.

More recently our group synthesized a series of push–pull 5,15-diarylzinc(II) porphyrins structurally analogous to those reported in Figure 1, but carrying, instead of an acceptor –NO₂ group, one or two –COOH groups, as sensitizers for porphyrin-sensitized solar cells (Figure 5) [37]. The carboxylic group is necessary to ensure the anchoring of the porphyrinic sensitizer to the TiO₂ semiconductor surface [38,39].

Table 4. EFISH $\mu\beta_{1907}$ values as a function of the concentration and of the solvent for chromophore 1. Adapted from *J. Phys. Chem. C* **2009**, *113*, 11131–11141.

Concentration (mol L ⁻¹)	$\mu\beta_{1907}$ ($\times 10^{-48}$ esu)	β_{1907}^d ($\times 10^{-30}$ esu)
7.5×10^{-4}	676 ^a	50
2×10^{-4}	1200 ^a	90
5×10^{-5}	3076 ^a	230
5×10^{-5}	2627 ^b	196
5×10^{-5}	2864 ^c	214

^a In CHCl₃; ^b in CHCl₃ with addition of pyridine; ^c in DMF; ^d $\mu = 13.4$ D calculated by DFT [26].

In this case the second order NLO response of chromophores **27–32** (Figure 5), measured by EFISH technique working at non resonant 1907 nm incident wavelength, could be strongly influenced by the presence of one or two $-\text{COOH}$ or $-\text{COOCH}_3$ groups, which could introduce additional aggregation with a basic solvent as DMF. For comparative purposes the push-pull zinc(II) porphyrin **33** was also reported.

In fact, DMF is able to interact by hydrogen bonding with the $-\text{COOH}$ group [40], while carboxylic acids may dimerize by hydrogen bonding to form a cyclic 1:1 dimeric species, particularly in low polarity solvents like CHCl_3 [41].

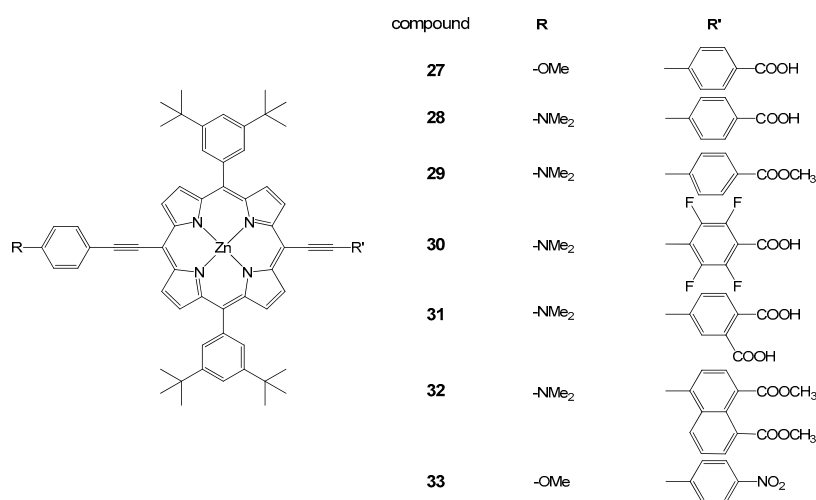


Figure 5. *meso* 5,15-Diarylzinc(II) porphyrins investigated. Adapted from *Inorg. Chem.* **2017**, *56*, 6438–6450.

EFISH measurements were supported by theoretical density functional theory (DFT) and coupled perturbed DFT (CP-DFT) calculations [37].

PGSE (¹H pulsed-gradient spin echo) NMR investigation was also carried out on structurally different chromophores **28** and **32**, to evaluate the role of the $-\text{COOH}$ group through the entity of the intermolecular aggregation [37]. The $\mu\beta_{1907}$ values of chromophores **27–33** are reported in Table 5.

Table 5. EFISH $\mu\beta_{1907}$ values of **27–33** in DMF and in CHCl_3 at different concentrations.

Chromophores	$\mu\beta_{1907}$ ($\times 10^{-48}$ esu) DMF	$\mu\beta_{1907}$ ($\times 10^{-48}$ esu) CHCl_3
27	−1600 ^a −3055 ^b −3320 ^c	−215 ^b
28	−1720 ^a −2520 ^b −3010 ^c	−670 ^b −970 ^c
29	−1080 ^a −1096 ^b	−357 ^b
30	−4180 ^a −7470 ^b −7940 ^c	−830 ^b
31	−490 ^a	−457 ^b
32	−1240 ^a −1490 ^b	+586 ^b
33	+1030 ^a	+2978 ^d

^a 10^{-3} M solution; ^b 5×10^{-4} M solution; ^c 10^{-4} M solution; ^d 5×10^{-5} M.

Despite the CP-DFT calculations in vacuo providing positive values of β for all 27–32 chromophores, supported also by the solvatochromism of the Q band which is characterized by a red shift on increasing the polarity of the solvent, suggesting a positive second order NLO response, chromophores 27–32 show negative $\mu\beta_{1907}$ values both in DMF and CHCl_3 , with the exception of 32 in CHCl_3 , taking into consideration that, under similar experimental conditions, the $\mu\beta_{1907}$ value of 33 is always positive.

Endowing the chromophore with a $-\text{COOR}$ group ($\text{R} = \text{H}$ or $-\text{CH}_3$) provides an inversion of the sign of the second order NLO response in both DMF and CHCl_3 , independently of the nature of the donor group, due to the presence of aggregation phenomena in solution (Figure 6). Therefore, the $-\text{COOR}$ groups appear to play a critical role, as confirmed by the dependence of the $\mu\beta_{1907}$ values on the solvent. Indeed they are significantly lower in CHCl_3 than in DMF for chromophores 27–32, with an opposite trend to that of 33, which shows a positive $\mu\beta_{1907}$ value in both solvents.

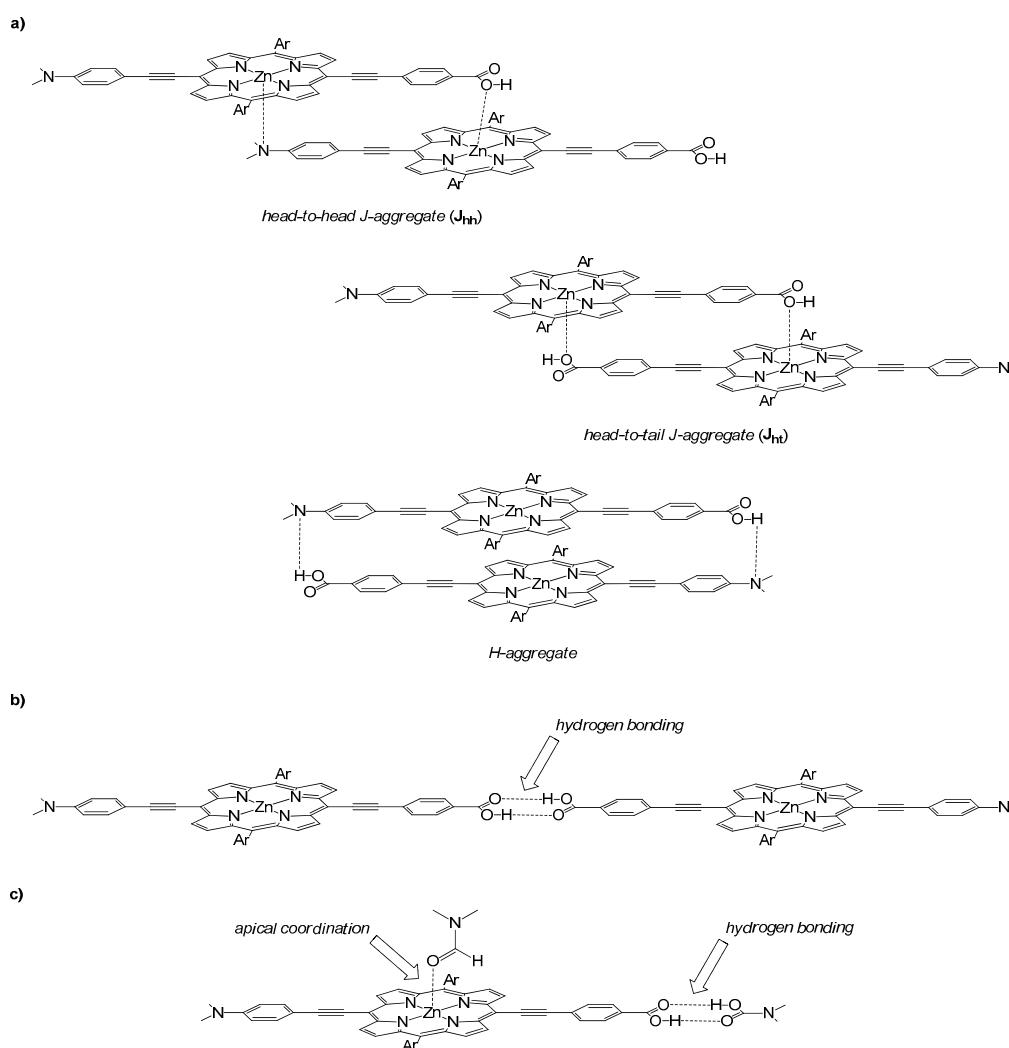


Figure 6. Schematic representation of possible aggregation in CHCl_3 and DMF solution. (a) J_{hh} , J_{ht} , and H aggregates; (b) hydrogen bonding; (c) axial coordination of the solvent DMF and hydrogen bond.

The relative energetic stabilization of the various possible aggregations of compounds 27–32 in CHCl_3 and DMF, evaluated by DFT calculations performed in vacuo, has shown that the J_{hh} (head to head) aggregation, strongly stabilized by the $-\text{COOH}$ group, is the most relevant (Figure 6a), but also the formation of the less stable 1:1 symmetrical hydrogen bonded dimer involving $-\text{COOH}$, is present (Figure 6b).

Moreover, an additional stabilization of monomeric or dimeric J_{hh} aggregates can be achieved by the formation of hydrogen bonds between the free $-\text{COOH}$ groups and DMF.

A significant solvent effect had already been reported by some of us [27] for Zn^{II} porphyrins similar to **33**, carrying a $-\text{NO}_2$ group instead of $-\text{COOH}$ group, for which only a J_{hh} aggregation was evidenced, involving acid–base interaction between the basic $-\text{NMe}_2$ group and the Zn^{II} acid center of another adjacent chromophore (Figure 4).

It appears that such significant effects of aggregation are closely related to the pseudolinear structure of porphyrinic chromophores, in fact when a sterically hindered β pyrrolic porphyrin is considered, such as **34** (Figure 7), no effect of the presence of the $-\text{COOH}$ group is evidenced, $\mu\beta_{1907}$ being positive and equivalent in all solvents ($\mu\beta_{1970} = +520 \times 10^{-30}$ esu in DMF and $+550 \times 10^{-30}$ esu in CHCl_3) [37].

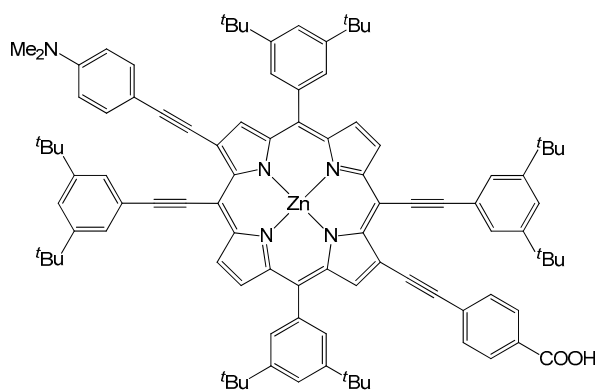


Figure 7. 2,12 β -pyrrolic tetra-arylzinc(II) porphyrin **34**.

Therefore, it is evident that specific molecular substitutions can favor interesting solvent effects originated, for instance, by acid–base [20] or dipolar interactions [42] between adjacent chromophores or by solvolysis of coordination compounds [43], which can strongly affect NLO measurements.

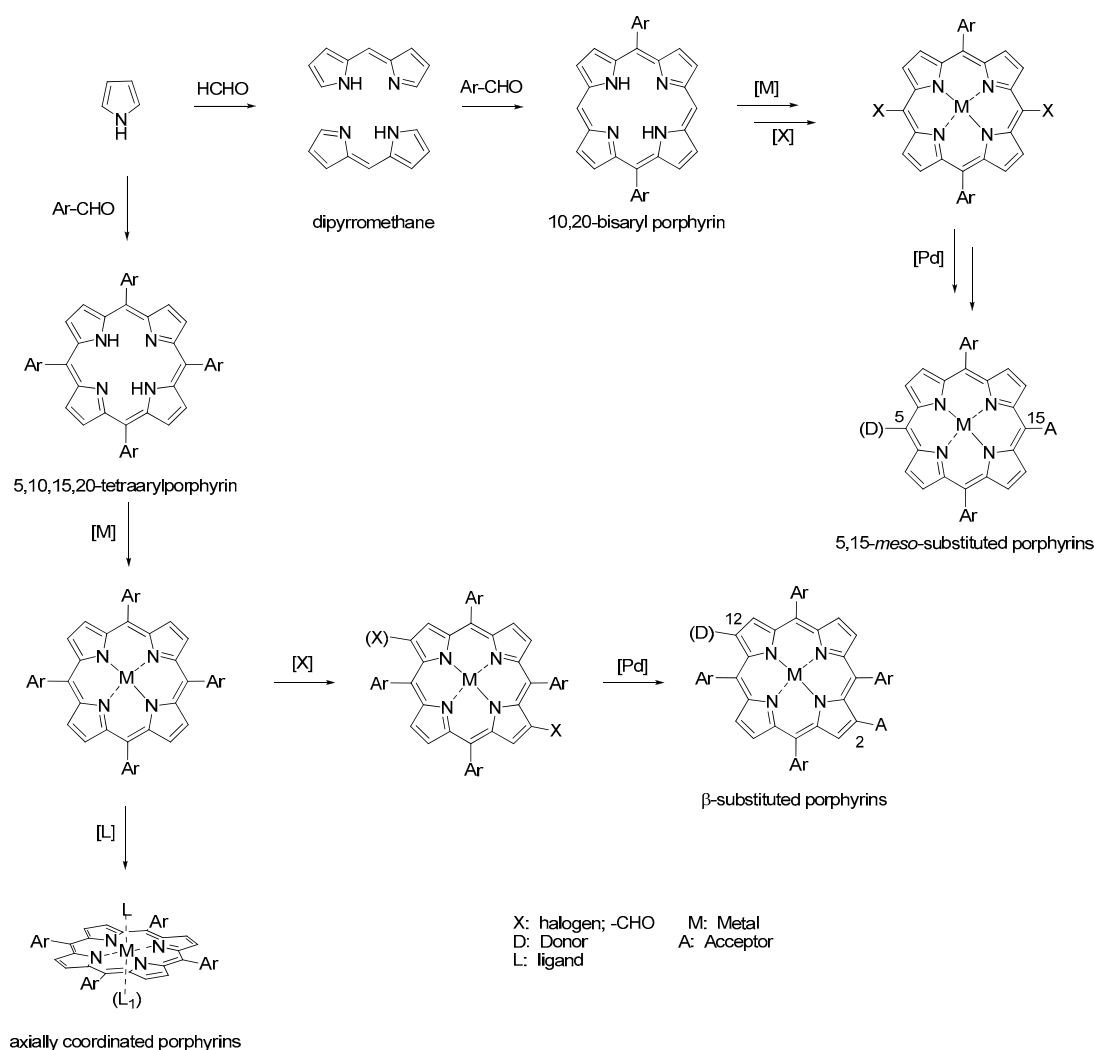
6. About the Synthesis

The high versatility of porphyrins is mainly ascribed to their unique tunable characteristics by a rational tailoring of the molecular structure. In fact, the tetrapyrrolic ring can rely on four *meso*, eight β -pyrrolic positions, and up to two metal–ligand axial bonds opening several opportunities for a fine modulation of their spectroscopic, electrochemical, optical, and catalytic properties.

Very recently we addressed the synthetic issues of porphyrin based chromophores for dye-sensitized solar cells (DSSC) discussing in depth the procedures to get *meso* and β -substituted porphyrins [44].

NLO and DSSC research fields share the same structural engineering design of porphyrin based chromophores, and, in particular when the acceptor units bear carboxylic terminal groups, even the final chromophores are the same. Hence in this panorama we can discuss the synthetic strategies used to obtain porphyrin sensitizers for DSSC application as for NLO. However, the synthetic procedures have been widely discussed elsewhere, thus, herein, we only want to give a short overview of the most accredited strategies to obtain porphyrin based NLO-phores.

As reported in Scheme 1, the synthesis of 5,15-*meso*-substituted porphyrins [38,45] involves a cyclization of the tetrapyrrolic core by two sequential condensation steps between formaldehyde and pyrrole giving dipyrromethane which, in turn, reacts with an appropriate arylaldehyde to produce the basic starting 10,20-bisaryl A_2 -type porphyrin core.



Scheme 1. Schematic synthetic approaches to *meso*-, β - and axially-substituted porphyrins.

The subsequent functionalization of the methenyl bridges at the two 5,15-*meso* positions provides a valuable halogenated substrate for the synthesis of push-pull donor-acceptor systems. If the substituents reactivity is very different, a sequential introduction of donor and acceptor units is required, although in certain cases 5,15-diiodo-porphyrins can undergo a one-pot Sonogashira coupling reaction with both donor and acceptor showing acetylenic terminal moiety [38]. The *meso*-patterned porphyrins, thanks to the strong charge-transfer character through the push-pull system on the 5,15 position [46], show a more significant NLO response when compared with the β -arranged analogues. Nevertheless mass scale production is limited by their synthetic approach being very far from trivial.

On the contrary the β -substituted 5,10,15,20-tetraarylporphyrins, featured by a more modest charge-separation character [47,48], can rely on less demanding and effective synthetic procedures [39]. Indeed, the more symmetric porphyrin core can be easily obtained by one-pot cyclization of pyrrole with suitable aldehydes, afterwards the functionalization of the β -pyrrolic positions [49] and the insertion of π -conjugated substituents provide a viable synthetic route for a multi-gram scale production of β -substituted porphyrins [50–53].

The axially coordinated porphyrins are even easier to obtain, indeed the unsubstituted tetrapyrrolic cores can be effectively achieved as in the case of the β -substituted ones. Subsequently, one or two linkers, depending on the metal center, can be smoothly connected orthogonally by simple coordination involving a few minutes step reaction [17]. Nevertheless, up to date, very few examples

have been reported for NLO application and we believe that there is plenty of room for further investigation on axially decorated porphyrin based NLO-phores.

7. Conclusions

This series of investigations has pointed out the ambivalent role of the polarizable porphyrin ring which, already in the ground state, behaves as a donor or acceptor depending on the nature of the substituent either in the β -pyrrolic or *meso* position, showing a charge-transfer process between the porphyrin core and the substituent as the origin of the second order NLO response.

When the substituent is an electron donor a significant increase of the electron donor properties is observed when the substituent is in the β -pyrrolic or *meso* position, probably due to an auxiliary donor effect of the electron rich porphyrin ring. However, when the substituent is an electron acceptor, an increase of the second order NLO response is observed particularly when the substituent is in the *meso* position.

It has also been experimentally demonstrated, as theoretically suggested, that in porphyrin complexes, the second order NLO response is not influenced by the nature of the metal, but its ability to coordinate in the free axial position leading to aggregated species. Therefore, the metal plays an indirect role tuning the NLO response, only in solvents allowing aggregation processes.

For this reason, the nature of the solvent must also be carefully taken into consideration when discussing the second order NLO response of chromophores such as porphyrins which can aggregate in non-donor solvents of low polarity such as CHCl_3 .

The presence of a $-\text{COOH}$ group or $-\text{COOCH}_3$ group in the substituent of the porphyrin investigated is responsible for the formation of J or H aggregates of different nature and, in the case of $-\text{COOH}$ groups, also of additional acid–base interactions with a basic solvent as DMF. In these processes the role of the $-\text{COOH}$ group appears to be critical.

Finally, this review highlights an interesting role of the porphyrin ring as push–pull chromophore for second order NLO response but also a warning that, for electronically complex chromophores such as porphyrins, it is not appropriate to discuss the results by using a single technique, or to compare results obtained by different techniques under different conditions. Moreover, the solvent effect, the kind of coordination (axial or peripheral), and the possible aggregation cannot be neglected.

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