EFISH NLO response of A_4 β-pyrrolic substituted Zn^{II} porphyrins: when cubic contributions cannot be neglected

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Abstract

In this work we have prepared a series of A_4 Zn^{II} porphyrins, carrying in β-pyrrolic position one or two π-delocalized ethynylphenyl moieties with a $–NO_2$ acceptor or a $–NMe_2$ donor pendant, and measured their second order NLO response in $CHCl_3$ solution at 1907 nm by the EFISH technique. For some of these compounds we have recorded an unexpected sign and/or absolute value of $\mu\beta_{1907}$. Since their sterically hindered A_4 structure should assure the lack of significant aggregation processes in solution, we explain such anomalous EFISH results invoking a non-negligible contribution of the electronic cubic term $\gamma(-2\omega; \omega,\omega,0)$ to γ_{EFISH}, as supported by a qualitative evaluation of the third order response through the measure of the cubic hyperpolarizability (γ_{THG}), and by computational evidences.

Introduction

Coordination and organometallic compounds due to the presence of a metal center offer in comparison to organic chromophores interesting additional electronic features acting on their second order nonlinear optical (NLO) response, such as rather strong charge transfer (CT) transitions (ligand to metal and metal to ligand), which can be tuned by working on the oxidation state of the metal and on its coordination sphere. In particular, metal complexes of macrocyclic ligands with a large π electronic system such as porphyrins have been largely investigated, because, when their structures are characterized by a specific asymmetric push-pull arrangement, a significant directional charge transfer process involving π polarizable linkers is produced by connecting the donor-π-acceptor system, and significant values of the quadratic hyperpolarizability β (which is the figure of merit of the second order NLO response) are achieved.[1-3] Moreover, the porphyrin ring is a flexible electronic system, where electron rich (β pyrrolic) and electron poor (*meso*) carbon atoms can be identified.[2]

Interestingly some of us reported for the first time an ambivalent donor/acceptor character of asymmetric mono-substituted porphyrin systems, when connected in *meso* or β position of the ring to an organic π-delocalized acceptor or donor substituent, respectively.[4,5]

The second order NLO response of molecular species can be measured in solution by different techniques, such as Hyper Rayleigh Scattering (HRS),[6] Stark effect,[7] solvatochromism,[3,8] and Electric Field Induced Second Harmonic generation (EFISH). [9-11] The EFISH technique is used particularly for the determination of the quadratic hyperpolarizability β of asymmetric dipolar chromophores with an evident push-pull structure, through equation 1:

$$\gamma_{EFISH} = \mu_0\beta_\lambda(-2\omega;\ \omega,\ \omega)/5kT + \gamma(-2\omega;\ \omega,\omega,0) \qquad (1)$$

γ_{EFISH} is the sum of a purely electronic cubic contribution $\gamma(-2\omega;\omega,\omega,0)$ (which is a third order term at frequency ω of the incident light) and of a quadratic dipolar orientational contribution $\mu_0\beta_\lambda(-2\omega;\omega,\omega)/5kT$, where μ_0 is the ground-state molecular dipole moment and β_λ the projection along the dipole moment direction of the vectorial component β_{vec} of the quadratic hyperpolarizability tensor, when working with the incident wavelength λ.[9] For the molecules usually investigated by the EFISH technique, the third order contribution $\gamma(-2\omega;\ \omega,\omega,0)$, is considered to be smaller than the quadratic dipolar orientational term. However, for largely π-

delocalized macrocyclic chromophores such as asymmetrically mono-substituted metal porphyrins,[12] phtalocyanines,[13-15] or porphyrazines[16] which show significant third order NLO properties (whose figure of merit is the cubic hyperpolarizability γ_{THG}), such simplification must be carefully and critically applied, because the evaluation of the second order NLO response by the EFISH technique could be affected by a significant error, being the cubic third order contribution comparable, at least as order of magnitude, to the quadratic orientational one (eq. 1).

For example, a γ_{EFISH} value of 1.4×10^{-33} esu and a γ_{THG} value of 1.6×10^{-33} esu were recorded for an A_3B-type Pt^{II} porphyrin, with a *para* –OMe substituent on the phenyl groups in 5,10,15 *meso* position of the ring and a *para* $–NO_2$ group on the phenyl in 20 position,[12] and comparable γ_{EFISH} (-1.2×10^{-33} esu) and γ_{THG} (-1.9×10^{-33}esu) responses were also displayed by non-centrosymmetric metal free phthalocyanines with *tert*-butyl and *para*-tolylsulfonyl substituents.[15]

Moreover, when the second order NLO response obtained by the EFISH technique is characterized by an even unexpected sign and/or absolute value of β_λ, aggregation or other molecular interactions occurring in solution should be considered.

For instance, we evidenced a significant solvent effect on the second order NLO response in $CHCl_3$ solution for the well investigated 5,15 push-pull *meso* diaryl Zn^{II} porphyrin chromophore carrying a $-NO_2$ group as acceptor and a $-NMe_2$ group as donor, whose nature may control the intermolecular acid-base J aggregation between the basic $-NMe_2$ group of one chromophore and the Zn^{II} acid center of another one.[17]

Moreover, some of us recently reported that 5,15 push-pull *meso* diaryl Zn^{II} porphyrins with a π delocalized substituent carrying an acceptor -COOH group are affected by a complex variety of solvent-dependent aggregation processes in solution,[18] such as acid-base[17] or dipolar[19] interactions between adjacent chromophores or solvolysis induced by the solvent.[20] The observed aggregation effects are closely related to the *trans*-A_2BC architecture of the Zn^{II} porphyrin. In fact, they are not observed at all when the push-pull system involves the 2,12 β-pyrrolic positions of an A_4 Zn^{II}

porphyrin.[1,18] In this latter architecture the dihedral angles between the aryl rings and the mean plane of the porphyrin core were indeed reported to lie in the range 73.5°-89.1°, thus lowering the overall flatness of the chromophore and inducing a remarkable steric hindrance to the system.[21]

In this work we add evidence that, by safely excluding such secondary effects in solution due to aggregation, the third order contribution to the experimental value of γ_{EFISH} (that is $\gamma_0(-2\omega; \omega,\omega,0)$) may happen to be not negligible, even for some largely investigated Zn^{II} porphyrinic architectures.[12] In particular, we focused our attention on some derivatives of 5,10,15,20-tetra(3,5-di-*tert*-butylphenyl)Zn^{II} porphyrin, carrying in β-pyrrolic position one or two π-delocalized ethynylphenyl moieties with a $-NO_2$ acceptor or a $-NMe_2$ donor group (BP1-5, Figure 1). EFISH measurements in $CHCl_3$ solution provided an unexpectedly negative second order response for some of these compounds. Since their sterically hindered A_4 structure should assure the lack of significant aggregation processes in solution,[18,21] we explain such anomalous EFISH results by the involvement of third order contributions, also supported by a qualitative evaluation of the third order response through the measure of the cubic hyperpolarizability γ_{THG}, together with computational evidence.

In addition, to investigate the effect of an increase of the electron density and of the π-delocalization of the porphyrin core, we studied the NLO properties of the new chromophore BAP1 (Figure 1) by the determination of both γ_{EFISH} and γ_{THG}.

BAP1 was first synthesized by some of us[22] as a dye for Dye-Synthesized Solar Cells, and has a peculiar and non-classical 4D-π-1A push-pull electronic structure, due to the four π-delocalized strong donor substituents in the 5,10,15,20 *meso* positions of the ring.

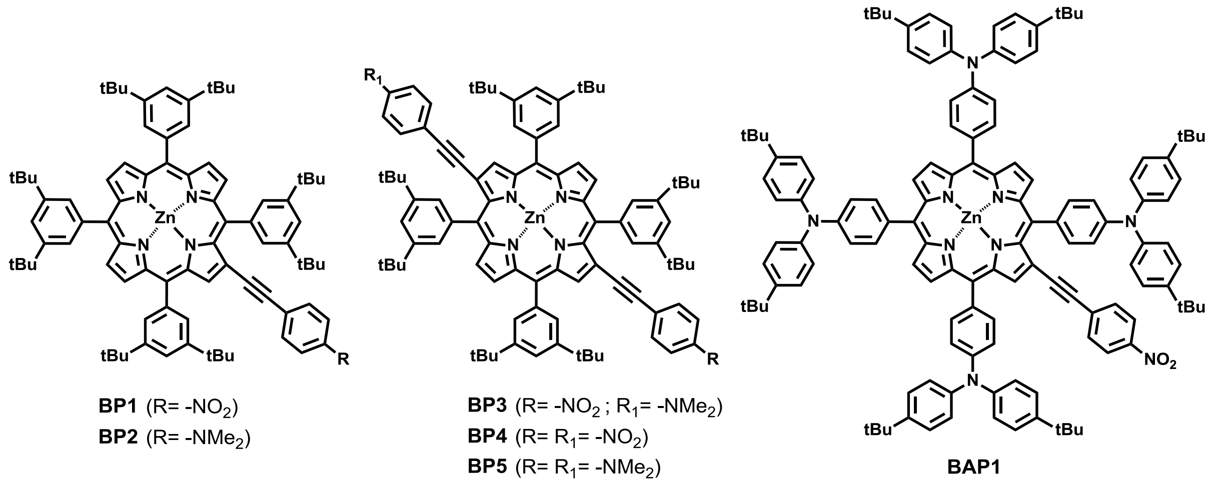


Figure 1. Zn^{II} porphyrins investigated in this work

Experimental

Materials and methods

^{1}H-NMR spectra were recorded on a Bruker Advance DRX-400 in pure $CDCl_3$. Due to the higher solubility of A_4 β-substituted Zn^{II} porphyrins in comparison to *trans*-A_2BC analogues, neither the addition of pyridine-d_5 to $CDCl_3$ nor the use of expensive THF-d_8 was necessary to acquire well-resolved spectra in the 10^{-2}-10^{-3} M concentration range. Mass spectra were obtained with a Bruker-Daltonics ICR-FTMS APEX II with an electrospray ionization source or on a VG Autospec M246 magnetic mass spectrometer with a LSIMS ionic source. Elemental analyses were carried out with a Perkin-Elmer CHN 2400 instrument in the Analytical Laboratories of the Department of Chemistry at the University of Milan. Electronic absorption spectra were recorded in CH_2Cl_2 solution (10^{-6}-10^{-5}M concentration range) at room temperature on a Shimadzu UV 3600 spectrophotometer. Details on the synthesis of BP1-BP5, BAP1 and of their precursors, including mass spectrometry data, elemental analyses, and ^{1}H-NMR data and spectra are reported in the Supporting Information (Figures S1-S6).

EFISH and THG Measurements

The second order NLO responses of chromophores BP1-BP5 and BAP1 were measured by the EFISH technique,[9-11] using a prototype apparatus made by SOPRA (France) and working with a 1907 nm incident wavelength. For each chromophore, measurements were performed on freshly prepared solutions in $CHCl_3$ at 10^{-3} M concentration. For BAP1 a measurement was made also at $5x10^{-4}$M concentration.

The 1907 nm laser incident wavelength was chosen because its second harmonic (at 953 nm) is far enough from the absorption bands of the chromophores in $CHCl_3$ (λ_{max} of the B band in the range 420−460 nm and of the Q bands in the range 560- 615 nm; see Table 1) to avoid possible enhancement of the second-order NLO response due to resonance effects. The incident beam was obtained by Raman shifting of the 1064 nm emission of a Q-switched Nd:YAG laser in a high-pressure hydrogen cell (60 bar). A liquid cell with thick windows in the wedge configuration was used to obtain the Maker fringe pattern originated by the harmonic intensity variation as a function of the liquid cell translation. In the EFISH experiments, this incident beam was synchronized with a direct current field applied to the solution, with 60 and 20 ns pulse duration respectively in order to break its centrosymmetry. The comparison of the harmonic signal of the chromophore solution with that of the pure solvent allowed the determination of its second-order NLO response (assumed to be real because the imaginary part was neglected).

The γ_{EFISH} values reported in Table 3 are the mean values of 12 successive measurements performed on the same sample. All experimental EFISH $\mu_0\beta_{1907}$ values are defined according to the "phenomenological" convention.[23]

THG experiments were carried out in 10^{-3} M $CHCl_3$ solution on the same apparatus used for EFISH experiments, but without applying an electric field,[24] providing the cubic hyperpolarizability $\gamma_{THG}(-3\omega;\omega,\omega,\omega)$. Experimental γ_{THG} values could be affected by resonant enhancement because the Q band absorptions are close to the third harmonic 3ω (635 nm), therefore these values should be taken in consideration mainly as an order of magnitude.[12]

EFISH and THG experiments were carried out in the Department of Chemistry of the University of Milano (Italy).

Computational calculations

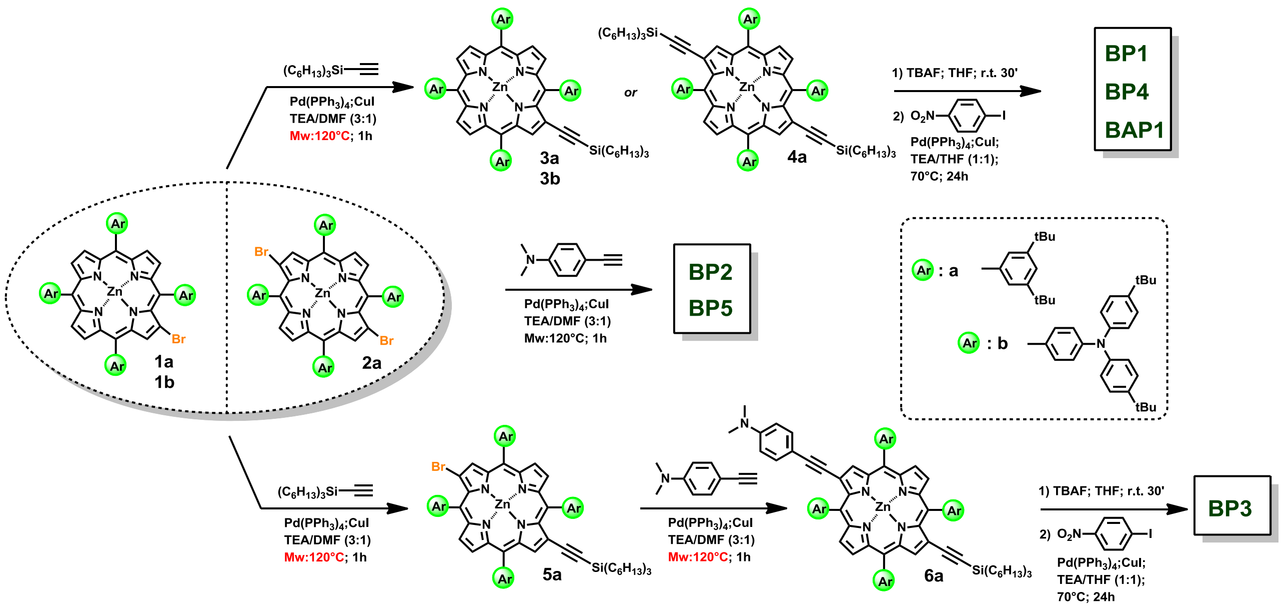
Density Functional Theory (DFT) calculations were performed on all compounds using the Gaussian16 suite of programs.[25]

Geometry optimizations were performed with the 6-311G(d) basis set using the M06 functional,[26] due to its specific parametrization on organometallic complexes. Excitation energies were computed at TD-B3LYP/6-311g(d) level in dichloromethane, on the basis of previously reported theoretical investigations of analogue porphyrin systems.[18] Using the same basis set, SHG first hyperpolarizabilities, i.e. the $\boldsymbol{\beta(-2\omega;\omega,\omega)}$ tensors, were computed within the Coupled Perturbed Kohn–Sham (CPKS) approach at the same frequency (1907 nm) used in the EFISH experiments. The SHG second hyperpolarizabilities, i.e. the $\boldsymbol{\gamma(-2\omega;\omega,\omega,0)}$ tensors, were evaluated by Finite Field technique. The M06-2X functional,[26] which has been recently recommended for hyperpolarizability calculations of mid-size chromophores,[27] was adopted for both $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ calculation. The same functional was used for determining the dipole moments μ_0. A pruned (99,590) grid was selected for computation and use of two-electron integrals and their derivatives. To get a meaningful comparison with the experimental data, the scalar quantities $\beta_{||}$ and $\gamma_{||}$ were derived from the full tensors $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$, respectively; $\beta_{||}$ corresponds to 3/5 times β_λ, the projection along the dipole moment direction of the vectorial component of the $\boldsymbol{\beta}$ tensor, that is $\beta_{||} = (3/5)\ \Sigma_i(\mu_i\beta_i)/\mu$, where $\beta_i = (1/5)\Sigma_j(\beta_{ijj} + \beta_{jij} + \beta_{jji})$.[28,29]

$\gamma_{||}$ is related to the tensor components according to: $\gamma_{||} = (1/15)\ [3(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}) + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz} + \gamma_{yyxx} + \gamma_{zzxx} + \gamma_{zzyy}) + (\gamma_{xyyx} + \gamma_{xzzx} + \gamma_{yzzy} + \gamma_{yxxy} + \gamma_{zxxz} + \gamma_{zyyz})]$.[28]

Results and discussion

Synthesis of A_4 β-substituted Zn^{II} porphyrins



Scheme 1. Schematic synthetic procedure for BP1-5 and BAP1

Porphyrins with one ethynyl substituent on β-pirrolic position are well-studied and several synthetic procedures are reported in literature. As opposed, the examples of porphyrins di-substituted at the pyrrolic sites to produce a push-pull systems are very rare,[30] by antipodal insertion of an electron-donor at one end and electron-acceptor at the other end. To get porphyrins with such geometries, the crucial strategy lies in the regioselective bromination of the porphyrin core at the β-position as previously reported by some of us.[21] Thus the synthetic strategy (Scheme 1) to obtain the chromophores investigated in this contribution required to adopt building-blocks as 2-bromo (1a and 1b) and 2,12-di-bromo (2a) functionalized Zn^{II} porphyrins,[21,22,31] for the preparation of the mono-substituted porphyrins (BP1, BP2 and BAP1) and of the di-substituted ones (BP3, BP4 and B5), respectively. To further introduce the selected nitro and amino based pendants at the periphery of the porphyrin core, the Pd/catalyzed microwave-assisted Sonogashira coupling reaction[31] between proper ethynyl substituents and the brominated intermidiates, 1a and 1b, was explored. While an effective insertion at the β-positions of 4-ethynyl-*N*,*N*-dimethylaniline smoothly provided the desired BP2 and BP5 (Scheme 1), on the contrary 1-ethynyl-4-nitrobenzene barely reacted in those conditions to get the desired chromophores BP1, BP3, BP4 and BAP. As a result a multistep procedure was designed to push up the functionalization yield of pyrrolic carbons with the nitro terminal pendant. In order to overcome the reactivity barrier related to the direct functionalization of bromo porphyrins with nitro based acetylenic substituents, silyl-protected acetylenic terminal linkers were firstly introduced into 2 and 12 positions (3a, 3b, 4a, 5a and 6a in Scheme 1) by microwave enhanced Sonogashira coupling reaction. The following tetrabutylammonium fluoride (TBAF) treatment almost quantitatively yielded the unprotected acetylenic terminal intermediates which easily reacted, by a classic thermal Sonogashira coupling reaction, with 1-iodo-4-nitrobenzene to succesfully give the desired BP1, BP3, BP4 and BAP1 products. Thus, as depicted in Scheme 1 and detailed in the Supporting Information, the designed multistep approach allowed us to efficiently synthesize the mono-substituted BP1, BP2 and BAP1, the symmetric 2,12 di-substituted BP4 and BP5 and the 2,12 asymmetric di-substituted BP3 porphyrinic chromophores.

UV-Vis absorption spectroscopy

The UV-Vis absorption spectra of BP1-5 and BAP1 in CH_2Cl_2 solution at $1.0x10^{-5}$ M concentration are reported in Figures 2a and 2b, while the corresponding experimental data are in Table 1.

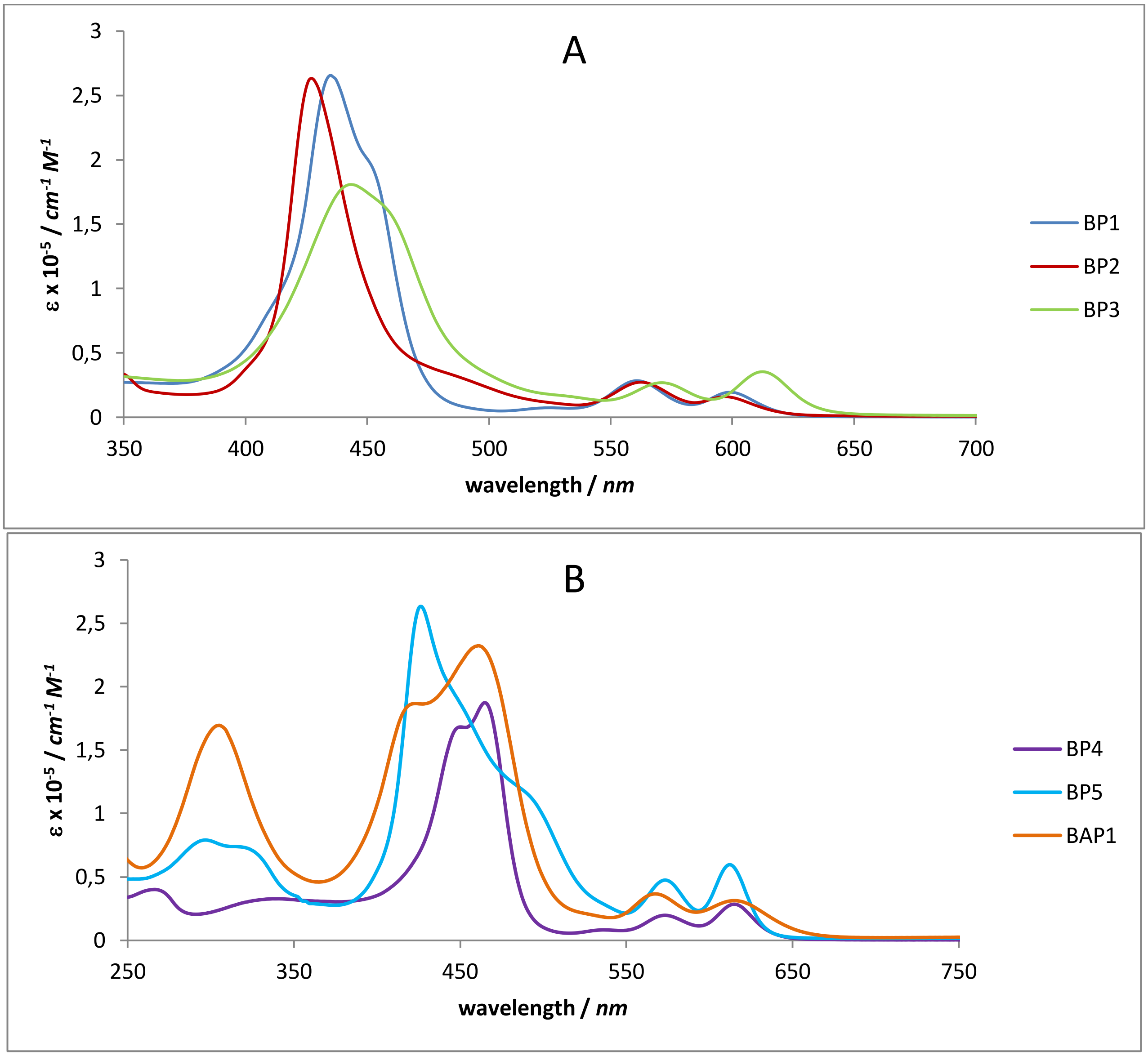


Figure 2. a) Electronic absorption spectra of BP1, BP2 and BP3 in CH_2Cl_2. b) Electronic absorption spectra of BP4, BP5 and BAP1 in CH_2Cl_2

Table 1. Electronic absorption data of BP1-5 and BAP1 in CH_2Cl_2 solution

Compound	B bands λ_{max}, nm (log ε)	Q_α and Q_β bands λ_{max}, nm (log ε)
BP1	435 (5.44) 458 (sh)	561 (4.45) 599 (4.30)
BP2	432 (5.25)	559 (4.26) 595 (4.04)
	443 (5.05)	571 (4.23)

BP3		612 (4.35)
BP4	450 (5.02) 464 (5.09)	572 (4.11) 614 (4.28)
BP5	426 (5.27) 485 (sh)	572 (4.52) 611 (4.63)
BAP1	423 (5.02) 461 (5.13)	567 (4.33) 615 (4.26)

The UV-Vis spectra of BP1-2 (Figure 2a) show the typical pattern expected for A_4 β-pyrrolic mono-substituted Zn^{II} porphyrins on the basis of the "four orbital model" proposed by Gouterman,[32] with a very strong ($\varepsilon \sim 10^5$ $M^{-1}cm^{-1}$) absorption B band at about 430 nm, due to the $S_0 \rightarrow S_2$ transition (from the ground to the second excited state), and two weaker ($\varepsilon \sim 10^4$ $M^{-1}cm^{-1}$) Q bands in the range 500-600 nm, due to the $S_0 \rightarrow S_1$ transition (from the ground to the first excited state). Q_α is the band at higher energy and Q_β that at lower energy.[33]

In the case of BP1 a weaker band appears as a shoulder at lower energy of the B band, as a result of the electron-withdrawing properties of the $-NO_2$ group. As reported for the corresponding Zn^{II} porphyrin with a cyanoacrylic moiety, strong electron acceptors induce a remarkable perturbation to the "four orbital model", breaking the degeneracy of the LUMO and LUMO+1 orbitals and stabilizing the LUMO energy level. Moreover, the LUMO+2 and LUMO+1 orbitals become nearly degenerate, with a decrease of the HOMO-LUMO energy gap and the formation in the electronic absorption spectrum of a red-shifted shoulder of the B band.[31,34,35]

On the other hand, when the ethynylphenyl moiety in β-position carries a $-NMe_2$ donor group as in BP2, the B band is symmetrical, as reported to occur when the aryls in 5,10,15,20 *meso* positions are simple phenyl group.[4] In addition, both the B and the Q bands show a slight hypsochromic shift in comparison to BP1.

The asymmetric di-substitution in 2,12 β-pyrrolic positions with ethynyphenyl fragments carrying a donor and an acceptor group (as in BP3) leads to a slight lowering of the B band intensity, in addition to an increase of its bandwidth and a sizable bathochromic shift, particularly for the Q bands (Figure 2a). These spectroscopic features are in agreement with an increased π-conjugation and push-pull character of the molecule, resulting in a lower HOMO-LUMO gap (Table 2).

The electronic spectra of symmetric di-substituted Zn^{II} porphyrins BP4 and BP5 show an interesting doubling of the B band, which is more pronounced in the presence of electron acceptor $–NO_2$ groups (Figure 2b). Furthermore, a significant red shift of the Q bands with respect to those of the corresponding asymmetric mono-substituted Zn^{II} porphyrins BP1 and BP2 is observed.

Finally, in the spectra of di-substituted complexes the intensity of the Q_β band is higher than that of the Q_α band, while the opposite behavior is noticed for mono-substituted complexes ($Q_\alpha > Q_\beta$).

All these features are in support of the perturbation of the electronic properties of the porphyrin core induced by π-delocalized ethynylphenyl moieties.[4]

The replacement in the 5,10,15,20 *meso* positions of the core of 3,5-di-*tert*-butylphenyl groups with bulky and strongly donor bis(4-*tert*-butylphenyl)anilines leads to dramatic changes of the UV-Vis spectrum. If we compare the spectra of BP1 (Figure 2a) and BAP1 (Figure 2b), a doubling of the B band appears for the latter, with a remarkable increase of bandwidth and a sizable red-shift of the Q bands. Interestingly, when the $–NO_2$ acceptor substituent connected by an ethynylphenyl linker to the β-pyrrolic position was swapped for a cyanoacylic group, the spectrum showed only one single, although broad, B band.[22] This suggests that the peculiar features of the B band of BAP1 are induced by the $–NO_2$ group.

The differences between BP1 and BAP1 cannot be ascribed to aggregation phenomena, since aggregation in solution is not relevant for sterically hindered A_4 β-pyrrolic substituted Zn^{II} porphyrins.[18,21] Rather, they can be due to the peculiar electronic structure of the 4D-π-1A architecture of BAP1.

However, to further exclude the presence of any aggregation phenomenon, UV-Vis spectra in CH_2Cl_2 at different concentrations in the range 10^{-6}-10^{-5}M were recorded (Figures S7-S12). As expected, no deviation from the Lambert-Beer law and no shift of the wavelength maximum neither of the B band nor of the Q bands was detected by increasing concentration, differently from what reported for *trans*-A_2BC type Zn^{II} porphyrins.[17] The UV-Vis evidence is supported also by the well-resolved signals in the ^{1}H-NMR spectra, acquired at a three order of magnitude higher concentration (10^{-2}-10^{-3} M) (see *Materials and methods* and Figures S1-S6).

DFT Calculations

In our previous investigation[4] on A_4 β-pyrrolic mono-substituted Zn^{II} porphyrins, with a π substituent structurally similar to that of BP1 and BP2, but carrying a phenyl group in 5,10,15,20 *meso* position of the ring, we evidenced for the first time (by UV-Vis electronic absorption spectroscopy, solvatochromism and voltammetry) a charge transfer process from the porphyrin core to the π substituent in β position when this latter carries a strong -NO_2 acceptor group, or from the π substituent in β position to the porphyrin core, if the former carries a strong –NBu_2 donor group. The ambivalent donor-acceptor character of this kind of β-substituted 5,10,15,20-tetraphenyl Zn^{II} porphyrins were also supported by second order NLO measurements based on the EFISH technique. Later on, Anderson, Clays and coworkers[36] have confirmed that the porphyrin core can behave as an acceptor by Hyper Rayleigh Scattering measurements on a system carrying an electron donor attached to one *meso* position of the ring. However, in neither investigation the possible effects of aggregation in solution on the second order NLO responses were taken into consideration. Moreover, no theoretical evidence to support the proposed charge transfer process from or to the porphyrin core was given. Therefore in the present work we have carrier out a DFT investigation on BP1-5 and BAP1.

The DFT HOMO-LUMO energy gaps of BP1-BP5 and BAP1 are reported in Table 2, and the HOMO and LUMO isodensity plots are in Figure 3.

Table 2. Correlation between the experimental λ_{max} of the Q_β bands and the HOMO-LUMO gap, and contribution of the HOMO-LUMO transition to the Q_β bands of BP1-BP5 and BAP1, as computed at M06-2X/6-311G(d) level in dichloromethane

Compound	**Experimental Q_β band λ_{max}, nm**	**HOMO-LUMO gap, eV**	**Contribution of the HOMO-LUMO transition to the Q_β band**
BP1	605	2.40	89%
BP2	573	2.60	78%
BP3	643	2.23	89%
BP4	624	2.34	90%
BP5	605	2.46	89%
BAP1	694 639[b]	2.19	34%[a] 56%[b,c]

[a] 61% HOMO-1 – LUMO; [b] referred to Q_α band; [c] 31% HOMO-1 - LUMO

The plots clearly confirm our previous qualitative suggestions. For BP1, the HOMO→LUMO transition is characterized by a significant charge transfer from the porphyrin core to the –C≡C-C_6H_4-NO_2 acceptor substituent linked to the β–pyrrolic position. For BP2 an opposite electron transfer occurs from the C≡C-C_6H_4-NMe_2 donor substituent in β–pyrrolic position to the porphyrin core. Interestingly, DFT calculations suggest for BP1 a more significant electron transfer process than for BP2 (Table 2), suggesting that the porphyrin core behaves better as a donor than as an acceptor.

The new push-pull Zn^{II} porphyrin BP3, involving the 2,12 β-pyrrolic positions of the porphyrinic ring,[21] is characterized by a significant electron transfer from the donor acetylenic substituent to the acceptor one, as confirmed by its isodensity plot (Figure 3), with a limited involvement of the electron density of the porphyrin core, which seems to play the role of a simple bridge of the push-pull electronic system.

For symmetric chromophores BP4 and BP5 the HOMO→LUMO transition is characterized by an electron transfer which involves the porphyrin core. When the ethynylphenyl moieties in 2,12 carry

$-NMe_2$ groups (BP5), a substituent to porphyrin core electronic transfer occurs, whilst in the presence of two $–NO_2$ substituents (BP4) the electron transfer is from the porphyrin core to the ethynylphenyl fragment.

Such DFT evidences are in agreement with the proposed "electronic softness" of the Zn^{II} porphyrin core with respect to the perturbation introduced by β-pyrrolic substitution with a push or a pull acetylenic system.[4]

The introduction of a significant electronic asymmetry in the porphyrin architecture was confirmed by DFT computed ground state dipole moments (μ, Table 4). The value of 10.6 D for the push-pull chromophore BP3 is quite close to that reported for the well-investigated push-pull Zn^{II} porphyrin carrying in 5,15 *meso* positions the same acetylenic substituents (13.9 D).[37] Dipole moments confirm also a higher charge asymmetry for BP1 (μ = 7.8 D) than for BP2 (μ = 2.7 D), in agreement with the proposed lower perturbation of the ground state of the porphyrin core induced by an ethynylphenyl moiety with a $-NMe_2$ donor group.[4] Such lower perturbation is also supported by the HOMO-LUMO energy gap (Table 2). Indeed, it is higher for BP2 (2.60 eV) than for BP1 (2.40 eV), as expected for a less easy electron transfer when the porphyrin core is substituted in β position by a donor acetylenic system.

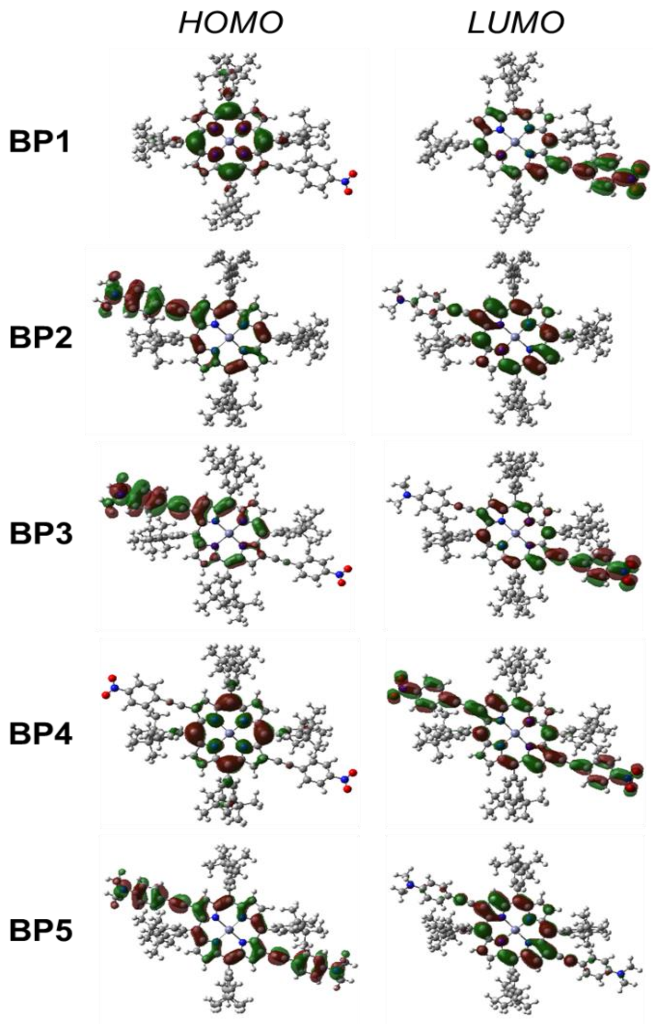


Figure 3. Isodensity plots of HOMO and LUMO of BP1-BP5 (isosurface values: 0.02).

As far as di-substituted Zn^{II} porphyrin BP3 is concerned, its HOMO-LUMO energy gap is lower than those of mono-substituted BP1 and BP2, suggesting an improved charge-transfer. However, if it is compared to the HOMO-LUMO gap of the corresponding 5,15 *meso* di-substituted Zn^{II} porphyrin, it is higher (2.23 eV *vs* 2.03 eV), revealing a less efficient conjugation when the push-pull system involves 2,12 β-pyrrolic positions.

Finally, the contribution of the HOMO-LUMO transition to the Q_β band is about 90% for both BP1 and BP2, while for BP2 it is only 78%, in agreement with the limited acceptor properties of the porphyrin core (Table 2).

To sum up, our DFT investigation evidenced that in A_4 B-pyrrolic Zn^{II} porphyrins with 3,5-di-*tert*-butylphenyl groups in 5,10,15,20 *meso* positions the porphyrin core behaves as a good donor but as a weaker and less efficient acceptor, as expected from the electron rich nature of the pyrrolic position, first highlighted by Marks and Ratner.[2]

On the other hand, BAP1 shows quite different and interesting electronic properties. Indeed, the Q_β band of this compound is due for only 34% to the HOMO-LUMO transition, while the (HOMO-1) - LUMO transition becomes relevant with a 61% contribution (Table 2). Looking at the isodensity plots (Figure 4), this transition is mainly associated, differently from BP1, to an electron transfer from one of the bulky and strongly donor bis(4-*tert*-butylphenyl)anilines in *meso* position to the adjacent π-conjugated ethynylphenyl moiety carrying the -NO_2 acceptor group in β-pyrrolic position. The electron density of the porphyrin core is involved only in the less important HOMO-LUMO transition, which has a minor role in the Q_β band composition (Figure 4).

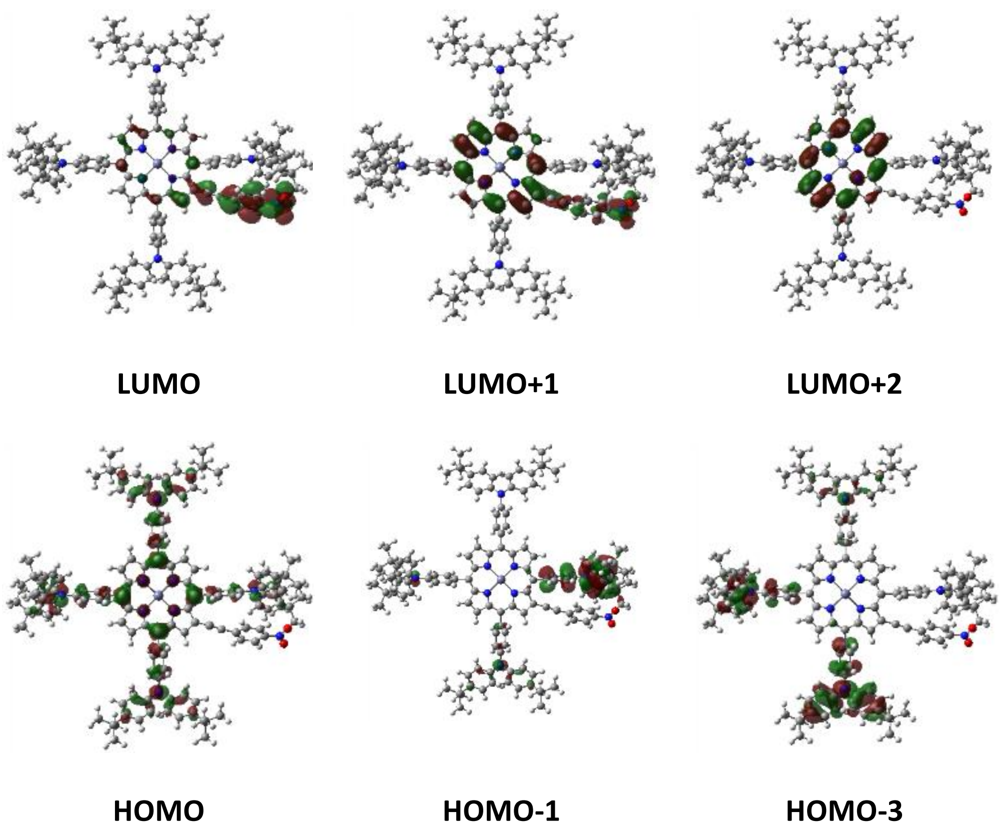


Figure 4. Isodensity plots of frontier orbitals of BAP1 (isosurface values: 0.02).

Moreover, it is interesting to emphasize also that in BAP1 the HOMO energy level is not delocalized on the porphyrin ring, as it occurs for BP1 and BP4, but it is mainly distributed on the four bis(4-*tert*-butylphenyl)anilines substituents in *meso* position (Figure 4).

Therefore, in BAP1 the porphyrin core cannot be considered a classical donor system in the electron transfer process to the $–NO_2$-substituted acetylenic moiety in β-pyrrolic position, as it occurs for BP1 (Figure 3).

Experimental and theoretical investigation of the second order NLO properties

EFISH measurements of BP1-BP5 and BAP1 were carried out in $CHCl_3$ solution at 10^{-3}M concentration, with an incident wavelength of 1907 nm, and are reported in Table 3. BAP 1 was also tested at $5x10^{-4}$M concentration, to exclude the presence of aggregation phenomena in solution. The $\mu_0\beta_{1907}$ values were obtained by equation 1, assuming a negligible contribution to γ_{EFISH} of the term $\gamma(-2\omega; \omega,\omega,0)$, and for this reason could be overestimated. However, $\gamma(-2\omega; \omega,\omega,0)$ cannot be always overlooked, as it was reported for some asymmetrically substituted metal phtalocyanines,[15,38,39] or metal porphyrins with an A_4 or A_3B architecture.[12] In particular, this occurs when the order of magnitude of the cubic hyperpolarizability (γ_{THG}), which expresses the third order NLO properties of the molecule, is comparable to that of γ_{EFISH}. For this reason for largely π-delocalized molecules it is sometimes useful to combine EFISH and THG measurements.[40]

Indeed, γ_{THG} values of largely π-delocalized molecular architectures such as metal phtalocyanines[39] and metal porphyrins[12] have been often reported to be a fair way to assess the relevance of the third order term contribution to γ_{EFISH}. In particular, $\gamma(-2\omega; \omega,\omega,0)$ was considered not negligible when γ_{EFISH} and γ_{THG} differ by less than 5–20%.[40] Therefore, significant values of γ_{THG} compared with γ_{EFISH} may support a not trivial contribution of the electronic cubic term in equation 1 to γ_{EFISH}.

Table 3. Experimental $\mu_0\beta_{1907}$ and γ_{EFISH} values of BP1-BP5 and BAP1 in $CHCl_3$ at 1907 nm

compound	$\mu_0\beta_{1907}$ ($x10^{-48}$), esu	γ_{EFISH} ($x10^{-33}$), esu
BP1[a]	730	3.5
BP2	-320	-2.23
BP3	690	3.1
BP4	-157	-0.87
BP5	-230	-1.15
BAP1[b,c]	-685	-3.6

[a] $\gamma_{THG} = 1.5x10^{-33}$ esu; [b] $\gamma_{THG} = -5.1x10^{-33}$ esu; [c] $-740x10^{-48}$ at $5x10^{-4}$M

Table 4. Theoretical μ_0, $\beta_{||}$, $\mu\beta_{||}/5kT$ and $\gamma_{||}$ values of BP1-BP5 and BAP1

compound	μ_0, D	$\beta_{||}$ ($x10^{-30}$), esu	$\mu\beta_{||}$ /5kT($x10^{-36}$), esu	$\gamma_{||}$ ($x10^{-36}$), esu
BP1	7.8	72	2720	–773
BP2	2.7	60	790	-888
BP3	10.6	189	9800	-2139
BP4	0.6	3	8	-1514
BP5	0.6	4	12	-1971
BAP1	6.2	64	1950	-2042

The quite high DFT values of the ground state dipole moments (μ_0) of BP1 and particularly of BP3 (Table 4) would suggest for these chromophores a predominant contribution of the dipolar orientational term $\mu_0\beta/5kT$ to γ_{EFISH}. In agreement, the $\mu_0\beta_{1907}$ values for BP1 and BP3 (Table 3) are positive and quite high, as for the Zn^{II} porphyrin structurally analogous to BP1, but carrying in 5,10,15,20 *meso* positions simple phenyl groups instead of the bulkier and slightly donor 3,5-di-*tert*-butylphenyl groups.[4]

Moreover, CP-DFT calculations in *vacuo* (Table 4) provided, particularly for the 2,12 β-di-substituted push-pull chromophore BP3, a high and positive value of $\beta_{||}$, from 2.5 to 3 times higher than that of mono-substituted BP1, BP2 and BAP1, characterized by a lower polarity.

On the other hand, the negative $\mu_0\beta_{1907}$ and γ_{EFISH} values recorded for BP2 and BAP1 (Table 3) are totally unexpected. Since they cannot be ascribed to molecular aggregations, due to the significant steric hindrance of the molecular architectures,[18,21] we tentatively attribute them to a negative contribution of the electronic cubic term $\gamma(-2\omega;\ \omega,\omega,0)$ to γ_{EFISH}. In order to support this hypothesis, we have experimentally measured the γ_{THG} values of BP1 and BAP1, as the more emblematic cases in our series of compounds, since they differ only for the aryl groups in 5,10,15,20 *meso* positions, but nevertheless display a positive ($+1.5\times10^{-33}$ esu) and negative (-5.1×10^{-33} esu) γ_{THG} value, respectively.

According to DFT calculations, providing negative $\gamma_{||} = \gamma(-2\omega;\ \omega,\omega,0)$ values[28] for all the porphyrin chromophores here investigated (Table 4), we suggest that the electronic third order term may overwhelm the positive value of the dipolar orientational term $\mu\beta_{||}$ for symmetric BP4, BP5 and particularly for slightly asymmetric BP2 chromophore, thus providing a negative γ_{EFISH} value (Table 3).

Such suggestion is further supported by comparing the negative value of $\gamma_{||}$ calculated for BAP1 (Table 4) with the relevant negative value of its measured γ_{THG}. The increased π-delocalization of the molecular structure of BAP1 due to the presence of the four bis(4-*tert*-butylphenyl)anilines enhances the third order NLO properties, as expected,[l4,41] leading to a twofold γ_{THG} with respect to that reported for an A_3B-type Zn^{II} porphyrin (2.2×10^{-33} esu).[12]

Furthermore, the $\mu\beta_{1907}$ recorded at lower concentration (-740×10^{-48} esu) remains constant within the experimental error of the EFISH technique (±15%),[17] thus confirming the absence of aggregation in solution, in agreement with the UV-Vis and ^{1}H-NMR spectroscopy evidences.

In conclusion there is some indirect evidence suggesting a negative electronic third order contribution to γ_{EFISH} as the origin of the negative value of the experimental γ_{EFISH} of BP2, BP4, BP5 and BAP1.

In the case of BP2, BP4 and BP5 the negative experimental value of γ_{EFISH} (Table 3) is a direct consequence of the rather low orientational dipolar contribution $\mu_0\beta_\lambda/5kT$, in accordance with the low ground state dipole moments (Table 4), so that the negative electronic cubic term $\gamma(-2\omega;\ \omega,\omega,0)$ prevails and produces a negative γ_{EFISH}.

Only when the dipole moment is high enough, as for BP1 and particularly BP3, the positive contribution of the orientational dipolar term predominates on $\gamma(-2\omega; \omega,\omega,0)$, thus leading to positive γ_{EFISH} values.

Our interpretation is also confirmed by the negative experimental values of γ_{EFISH} for the symmetric Zn^{II} porphyrins BP4 and BP5. Indeed, they are characterized by dipole moments close to zero (Table 4), in agreement with their symmetrical structure, so that the negative value of γ_{EFISH} is completely representing that of the $\gamma(-2\omega; \omega,\omega,0)$ third order term.

It is worth stressing the relevant role of the steric hindrance characterizing the chromophores investigated in this work. For instance, in the case of asymmetric mono-substituted BP2 carrying an ethynylphenyl linker with a donor pendant, we have a negative value of γ_{EFISH}, which suggests a rather low second order NLO response. However, this evidence is totally opposite to what reported in our previous investigation for a structurally related mono-substituted Zn^{II} porphyrin with simple phenyl groups in 5,10,15,20 *meso* position, thus lacking the steric effects and electronic effects induced by more hindered and slightly donor 3,5-di-*tert*-butylphenyl groups.[4]

Therefore, the high EFISH second order NLO response reported in that investigation[4] could be tentatively explained by a J aggregation process in solution, due to the interaction between the donor $-NR_2$ group of the substituent and the acid Zn^{II} center of another adjacent chromophore. In fact, J intermolecular aggregation is well-known to produce an increase of the second order NLO response.[17]

Conclusion

In this work we have reported the synthesis of a series of A_4 β-pyrrolic substituted Zn^{II} porphyrins, carrying one or two ethynylphenyl moieties with an electron acceptor or an electron donor terminal group, and bulky aryl substituents in 5,10,15,20 *meso* positions. Due to their sterically hindered architectures, these porphyrins are reasonably deemed to not show significant aggregation processes in solution.

By a combined DFT and EFISH investigation we produced clear evidence of the presence of charge transfer processes from the porphyrin core to the acetylenic fragment in β-pyrrolic position or vice versa, thus confirming the ambivalent donor or acceptor properties of the Zn^{II} porphyrin core suggested by some of us some years ago.[4]

Moreover, DFT calculations and the large differences of the EFISH second order NLO response of BP1 and BP2, in the absence of significant aggregation processes, have shown that the A_4 β-pyrrolic Zn^{II} porphyrins considered in this work behave as better donors than acceptors, in agreement also with the enhanced electron richness of the porphyrin core induced by the presence of 3,5-di-*tert*-butylphenyl groups in 5,10,15,20 *meso* position.

The UV-Vis electronic absorption spectra and the trend of the calculated dipole moments have confirmed that the introduction in β-pyrrolic position of π-delocalized ethynylphenyl spacers equipped with either an acceptor or a donor group changes significantly the electronic properties of the porphyrin core.

Furthermore, the two new Zn^{II} porphyrins BP3 and BAP1 have allowed us to highlight some relevant points, such as: i) the less facile electron transfer within the push-pull system involving the 2,12 β–pyrrolic positions in comparison to the well-investigated push-pull system involving the 5,15 *meso* positions, and ii) the noticeable effect of the introduction in the 5,10,15,20 *meso* positions of the porphyrin core of four bulky donor bis(4-*tert*-butylphenyl)anilines, as in BAP1, which leads to a substantially diminished involvement of the porphyrin core in the electron transfer process to the π-conjugated acceptor substituent in β position.

Finally, we have produced both theoretical and experimental evidence that in this kind of Zn^{II} porphyrins the electronic cubic contribution to γ_{EFISH}, $\gamma(-2\omega; \omega,\omega,0)$, cannot be neglected, if the polarity of the Zn^{II} porphyrin is so low that the dipolar orientational term to γ_{EFISH} becomes too small and if γ_{EFISH} and γ_{THG} are characterized by comparable values. In these particular cases, the determination of the second order NLO properties by the EFISH technique may lead to overestimated or even negative values, if the purely electronic cubic contribution is neglected.

As a general conclusion, our investigation proves that the determination of γ_{EFISH} for largely π–delocalized structures of low polarity must be carried out very carefully.

ASSOCIATED CONTENT

Supporting Information. The SI report the synthetic procedures to obtain BP1-5 and BAP1, their characterization, the ^{1}H-NMR spectra and the UV-Vis spectra at different concentrations. The following files are available free of charge.

ESI_final.pdf

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References

1) Tessore, F.; Orbelli Biroli, A.; Di Carlo, G.; Pizzotti, M. Porphyrins for Second Order Nonlinear Optics (NLO): An Intriguing History. *Inorganics* **2018**, *6*, 81-98.

2) Albert I.D.L.; Marks, T.J.; Ratner, M.A. Large Molecular Hyperpolarizabilities in "Push-Pull" Porphyrins. Molecular Planarity and Auxiliary Donor-Acceptor Effects. *Chem. Mater.* **1998**, *10*, 753-762.

3) Pizzotti, M.; Annoni, E.; Ugo, R.; Bruni, S.; Quici, S.; Fantucci, P.; Bruschi, M.; Zerbi, G.; Del Zoppo, M. A multitechnique investigation of the second order NLO response of 10, 20-diphenylporphyrinato nickel(II) complex carrying a phenylethynyl based push-pull system in the 5 and 15-positions. *J. Porph. Phtalo.* **2004**, *8*, 1311-1324.

4) Annoni, E.; Pizzotti, M.; Ugo, R.; Quici, S.; Morotti, T.; Bruschi, M.; Mussini, P. Synthesis, Electronic Characterisation and Significant Second Order Non-Linear Optical Response of *meso*-Tetraphenylporphyrins and Their Zn^{II} complexes Carrying a Push or Pull Group in the β Pyrrolic Position. *Eur. J. Inorg. Chem*. **2005**, 3857-3874.

5) Morotti, T. Pizzotti, M.; Ugo, R.; Quici, S.; Bruschi, M.; Mussini, P.; Righetto, S. Electronic Characterisation and Significant Second Order NLO Response of 10,20-diphenylporphyrins and their Zn(II) Complexes Substituted in the *meso* Position with π Delocalised Linkers Carrying Push or Pull Groups. *Eur. J. Inorg. Chem*. **2006**, 1743-1757.

6) Le Cours, S.M.; Guan, H.W.; Di Magno, S.G.; Wang, C.H.; Therien, M.J. Push–pull Arylethynyl Porphyrins: New Chromophores That Exhibit Large Molecular First-Order Hyperpolarizabilities. *J. Am. Chem. Soc*. **1996**, *118*, 1497–1503.

7) Karki, L.; Vance, F.W.; Hupp, J.T.; LeCours, S.M.; Therien, M.J. Electronic Stark Effect Studies of a Porphyrin-Based Push–pull Chromophore Displaying a Large First yperpolarizability: State-Specific Contributions to β. *J. Am. Chem. Soc*. **1998**, *120,* 2606–2611.

8) Bruni, S.; Cariati, F.; Cariati, E.; Porta, F.A.; Quici, S.; Roberto, D. Determination of the quadratic hyperpolarizability of trans-4-[4-(dimethylamino)styryl]pyridine and 5-dimethylamino-1,10-phenanthroline from solvatochromism of absorption and fluorescence spectra: A comparison with the electric-field-induced second-harmonic generation technique. *Spectrochim. Acta Part. A* **2001**, *57,* 1417–1426.

9) Levine, B.F.; Bethea, C.G. Molecular hyperpolarizabilities determined from conjugated and nonconjugated organic liquids. *Appl. Phys. Lett.* **1974**, 24, 445-447.

10) Singer, K.D.; Garito, A.F. Measurements of molecular second order optical susceptibilities using dc induced second harmonic generation. *J. Chem. Phys.* **1981**, *75*, 3572-3580.

11) Ledoux, I.; Zyss, J. Influence of the molecular environment in solution measurements of the Second-order optical susceptibility for urea and derivatives. *J. Chem. Phys*. **1982**, *73,* 203–213.

12) Pizzotti, M.; Ugo, R.; Annoni, E.; Quici, S.; Ledoux-Rak, I.; Zerbi, G.; Del Zoppo, M.; Fantucci, P.; Invernizzi, I. A critical evaluation of EFISH and THG non-linear optical responses of asymmetrically substituted *meso*-tetraphenyl porphyrins and their metal complexes. *Inorg. Chim. Acta,* **2002**, *340,* 70-80.

13) Rojo, G.; De la Torre, G.; Garcia-Ruiz, J.; Ledoux, I.; Torres, T.; Zyss, G.; Agullo-Lopez, F. Novel unsymmetrically substituted push–pull phthalocyanines for second-order nonlinear optics. *Chem. Phys*. **1999***, 245,* 27–34.

14) De La Torre, G.; Vasquez, P.; Agullo-Lopez, F.; Torres, T. Role of structural factors in the Nonlinear Optical properties of Phtalocyanines and Related Compounds. *Chem. Rev.* **2004**, *104*, 3723-3750.

15) De la Torre, G; Vasquez, P.; Agullo`-Lopez, F.; Torres, T. Phthalocyanines and related compounds: organic targets for nonlinear optical applications. *J. Mater. Chem.* **1998**, *8*, 1671-1683.

16) Belviso, S.; Santoro, E.; Penconi, M.; Righetto, S.; Tessore, F. Thioethylporphyrazines: attractive chromophores for second order nonlinear optics and DSSCs. *J. Phys. Chem. C* **2019**, *123*, 13074-13082.

17) Pizzotti, M.; Tessore, F.; Orbelli Biroli, A.; Ugo, R.; De Angelis, F.; Fantacci, S.; Sgamellotti, A.; Zuccaccia, D.; Macchioni, A. An EFISH, theoretical, and PGSE NMR investigation on the relevant role of aggregation on the second order NLO response in $CHCl_3$ of the push-pull chromophores [5-[[4′-(Dimethylamino)phenyl]ethynyl]-15-[(4″-nitrophenyl)ethynyl]-10,20-diphenylporphyrinate] M(II) (M= Zn, Ni). *J. Phys. Chem. C* **2009**, *113*, 11131−11141.

18) Orbelli Biroli, A.; Tessore, F.; Righetto, S.; Forni, A.; Macchioni, A.; Rocchigiani, L.; Pizzotti, M.; Di Carlo, G. Intriguing Influence of –COOH-Driven Intermolecular Aggregation and Acid-Base Interactions with N,N-Dimethylformamide on the Second Order Nonlinear Optical Response of 5,15 Push-Pull Diarylzinc(II) Porphyrinates. *Inorg. Chem.* **2017**, *56*, 6438-6450.

19) Kang, H.; Facchetti, A.; Jiang, H.; Cariati, E.; Righetto, S.; Ugo, R.; Zuccaccia, C.; Macchioni, A.; Stern, C.; Liu, Z.; Ho, S. − T.; Brown, E. C.; Ratner, M. A.; Marks, T. J. Ultralarge hyperpolarizability twisted π-electronsystem electro-optic chromophores: synthesis, solid state and solution-phase structural characteristics, electronic structures, linear and nonlinear optical properties, and computational studies. *J. Am. Chem. Soc.* **2007**, *129*, 3267−3286.

20) Tessore, F.; Locatelli, D.; Righetto, S.; Roberto, D.; Ugo, R.; Mussini, P. An investigation on the role of the nature of sulfonated ancillary ligands on the strength and concentration dependence of the second-order NLO responses in $CHCl_3$ of Zn(II) complexes with 4,4′-trans-

$C_5H_4CH{\equiv}CHC_6H_4NMe_2$ and 4,4′-trans,trans- $NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$. *Inorg. Chem.* **2005**, *44*, 2437−2442.

21) Di Carlo, G.; Orbelli Biroli, A.; Tessore, F.; Rizzato, S.; Forni, A.; Magnano, G.; Pizzotti, M. Light-induced regiospecific bromination of *meso*- tetra(3,5-di-*tert*-butylphenyl)porphyrin on 2,12 β-pyrrolic positions. *J. Org. Chem.* **2015**, *80*, 4973-4980.

22) Covezzi, A.; Orbelli Biroli, A.; Tessore, F.; Forni, A.; Marinotto, D.; Biagini, P.; Di Carlo, G.; Pizzotti, M. 4D–π–1A type β-substituted Zn^{II}-porphyrins: ideal green sensitizers for building-integrated photovoltaics. *Chem. Commun*. **2016**, *52*, 12642-12645.

23) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. Problems in the comparison of theoretical and experimental hyperpolarizabilities. *J. Chem. Phys*. **1992**, 97, 7590−7599.

24) Diaz-Garcia, M.A.; Ledoux, I.; Fernandez-Lazaro, F.; Sastre, A.; Torres, T.; Agullo-Lopez, F.; Zyss, J. Third-order nonlinear optical properties of soluble metallotriazolylhemiporphyrazines. *J. Phys. Chem.* **1994**, *98*, 4495-4497.

25) Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.

26) Zhao, Y.; Truhlar, D.G. The Mo6 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four Mo6-class functionals and 12 other functionals. *Theor. Chem. Acc*. **2008**, *120*, 215–241.

27) Johnson, L.E.; Dalton, L.R.; Robinson, B.H. Optimizing calculations of electronic excitations and relative hyperpolarizabilities of electrooptic chromophores. *Acc. Chem. Res.*, **2014**, *47*, 3258–3265.

28) Kurtz, H.A.; Dudis, D. Quantum mechanical methods for predicting nonlinear optical properties. *Rev. Comput. Chem.* **1998**, *12*, 241-279.

29) Pielak, K.; Tonnelé, C.; Sanguinet, L.; Cariati, E.; Righetto, S.; Muccioli, L.; Castet, F.; Champagne, B. Dynamical Behaviour and Second Harmonic Generation Responses in Acido-Triggered Molecular Switches. *J. Phys. Chem.* C **2018**, *122,* 26160-26168.

30) Di Carlo, G.; Orbelli Biroli, A.; Tessore, F.; Caramori, S.; Pizzotti, M. β-substituted Zn^{II} porphyrins as dyes for DSSC: a possible approach to photovoltaic windows. *Coord. Chem. Rev.* **2018**, *358*, 153-177.

31) Di Carlo, G.; Orbelli Biroli, A.; Pizzotti, M.; Tessore, F.; Trifiletti, V.; Ruffo, R.; Abbotto, A.; Amat, A.; De Angelis, F.; Mussini, P. R. Tetraaryl Zn^{II} porphyrinates substituted at β-pyrrolic positions as sensitizers in dye-sensitized solar cells: a comparison with *meso*-di-substituted push-pull Zn^{II} porphyrinates. *Chem. Eur. J.* **2013**, *19*, 10723-10740.

32) Gouterman, M. Spectra of porphyrins. *J. Mol. Spectr.* **1961**, *6*, 138-163.

33) Giovannetti, R. The use of spectrometry UV-Vis for the study of porphyrins. Macro to Nanospectroscopy Jamal Uddin, IntechOpen. Available online at: https://www.intechopen.com/books/macro-to-nano-spectroscopy/the-use-of-spectrophotometry-uv-vis-for-the-study-of-porphyrins (accessed June 29, 2012).

34) Di Carlo, G.; Orbelli Biroli, A.; Pizzotti, M.; Tessore, F. Efficient sunlight harvesting by A_4 β-pyrrolic substituted Zn^{II} porphyrins: a mini-review. *Front. Chem.* **2019**, *7*, 177.

35) Orbelli Biroli, A.; Tessore, F.; Vece, V.; Di Carlo, G.; Mussini, P.R.; Trifiletti, V.; De Marco, L.; Giannuzzi, R.; Manca, M.; Pizzotti, M. Highly improved performance of Zn^{II} tetraarylporphyrinates in DSSCs by the presence of octyloxy chains in the aryl rings. *J. Mater. Chem. A* **2015**, *3*, 2954-2959.

36) Lopez-Duarte, I.; Reeve, J. E.; Perez-Moreno, J.; Boczarow, I.; Depotter, G.; Fleischhauer, J.; Clays, K.; Anderson, H.L. "Push-no-pull" porphyrins for second harmonic generation imaging. *Chem. Sci.* **2013**, *4*, 2024-2027.

37) De Angelis, F.; Fantacci, S.; Sgamellotti, A.; Pizzotti, M.; Tessore, F.; Orbelli Biroli, A. Time-dependent and coupled-perturbed DFT and HF investigations on the absorption spectrum and non-linear optical properties of push–pull M(II)–porphyrin complexes (M = Zn, Cu, Ni). *Chem. Phys. Lett.* **2007**, *447*, 10-15.

38) De la Torre, G.; Torres, T.; Agullo-Lopez, F. The phthalocyanine approach to second harmonic generation. *Adv. Mater.* **1997**, *9*, 265-269.

39) Diaz-Garcia, M.A.; Ledoux, I.; Fernandez-Lazaro, F.; Sastre, A.; Torres, T.; Agullo-Loperz, F.; Zyss, J. Third order nonlinear optical properties of soluble metallotriazolylhemiporphyrazines. *J. Phys. Chem.* **1994**, *98*, 4495-4497.

40) Colombo, A.; Locatelli, D.; Roberto, D.; Tessore, F.; Ugo, R.; Cavazzini. M.; Quici, S.; De Angelis, F.; Fantacci, S.; Ledoux-Rak, I.; Tancrez, N.; Zyss, J. New [(D-terpyridine)-Ru-(D or A-terpyridine)][4-EtPhCO2]2 complexes (D = electron donor group; A = electron acceptor group) as active second-order non linear optical chromophores. *Dalton Trans.* **2012**, *41*, 6707-6714.

41) Senge, M.O.; Fazekas, M.; Notaras, E.G.A.; Blau, W.J; Zawadzka, M.; Locos, O.B.; Ni Mhuircheartaigh, E.N. Nonlinear Optical Properties of Porphyrins. *Adv. Mater*. **2007**, 19, 2737-2774.

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If the polarity of β-substituted Zn^{II} porphyrins is low, the contribution of the third order term $\gamma_0(-2\omega;\omega,\omega,0)$ to γ_{EFISH} cannot be neglected.