Electric-Field-Induced Second Harmonic Generation Nonlinear Optic Response of A₄ β-Pyrrolic-Substituted Zn‖ Porphyrins: When Cubic Contributions Cannot Be Neglected

Gabriele Di Carlo, Maddalena Pizzotti, Stefania Righetto, Alessandra Forni,* and Francesca Tessore*

Cite This: Inorg. Chem. 2020, 59, 7561−7570

Abstract: In this work, we have prepared a series of A₄ Zn‖ porphyrins, carrying in the β-pyrrolic-position one or two π-delocalized ethynylphenyl moieties with a −NO₂ acceptor or a −NMe₂ donor pendant, and measured their second-order NLO response in CHCl₃ solution at 1907 nm via the electric-field-induced second harmonic generation (EFISH) technique. For some of these compounds, we have recorded an unexpected sign and/or absolute value of μβ₉₀⁰₇. Since their sterically hindered A₄ structure should ensure the lack of significant aggregation processes in solution, we explain such anomalous EFISH results by invoking a non-negligible contribution of the electronic cubic term γ(−2ω; ω, ω, 0) to γ nederland as supported by a qualitative evaluation of the third-order response through the measure of the cubic hyperpolarizability (γTHG) and by computational evidence.

Introduction

Coordination and organometallic compounds, due to the presence of a metal center, offer in comparison to organic chromophores some 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 are achieved (which is the figure of merit of the second-order NLO response). Moreover, the porphyrin ring is a flexible electronic system, where electron-rich (β-pyrrolic) and electron-poor (meso) carbon atoms can be identified.

Interestingly some of us reported for the first time an ambivalent donor/acceptor character of asymmetric monosubstituted porphyrin systems, when connected in the meso or β position of the ring to an organic π-delocalized acceptor or donor substituent, respectively. The second-order NLO response of molecular species can be measured in solution by different techniques, such as hyper-Rayleigh scattering (HRS), Stark effect, solvatochromism, and electric-field-induced second harmonic generation (EFISH). 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 eq 1:

\[ \gamma_{EFISH} = \mu_0 \beta_v (-2\omega; \omega, \omega) / kT + \gamma (2\omega; \omega, 0, 0) \] (1)

\[ \gamma_{EFISH} \] is the sum of a purely electronic cubic contribution \( \gamma (2\omega; \omega, 0, 0) \) (which is a third-order term at the frequency \( \omega \) of the incident light) and of a quadratic dipolar orientational contribution \( \mu_0 \beta_v (-2\omega; \omega, \omega) / kT \), where \( \mu_0 \) is the ground-state molecular dipole moment and \( \beta_v \) the projection along the dipole moment direction of the vectorial component \( \beta_v \) of the quadratic hyperpolarizability tensor, when working with the incident wavelength \( \lambda \). For the molecules usually investigated by the EFISH technique, the third-order contribution \( \gamma (2\omega; \omega, 0, 0) \) is considered to be smaller than the quadratic dipolar orientational term. However, for largely π-delocalized macrocyclic chromophores such as asymmetrically monosubstituted metal porphyrins, phtalocyanines, or porphyrazines which show significant third-order NLO properties (whose figure of merit is the cubic hyperpolarizability \( \gamma_{THG} \)), 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, with the cubic third-order contribution being comparable, at least on the order of magnitude, to the quadratic orientational one (eq 1).

For example, a $\gamma_{\text{EFISH}}$ value of $1.4 \times 10^{-33}$ esu and a $\gamma_{\text{THG}}$ value of $1.6 \times 10^{-33}$ esu were recorded for an A$_2$B-type Pt$^{II}$ porphyrin, with a para-OMe substituent on the phenyl groups in 5,10,15-meso-positions of the ring and a para-NO$_2$ group on the phenyl in the 20-position, and comparable $\gamma_{\text{EFISH}}$ ($-1.2 \times 10^{-33}$ esu) and $\gamma_{\text{THG}}$ ($-1.9 \times 10^{-33}$ esu) responses were also displayed by noncentrosymmetric metal-free phthalocyanines with tert-butyl and para-tolylsulfonyl substituents. Moreover, when the second-order NLO response obtained by the EFISH technique is characterized by an unexpected sign and/or absolute value of $\beta$, 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 interactions occurring in solution should be considered.

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, such as acid−base or dipolar interactions between adjacent chromophores or solvolysis induced by the solvent. The observed aggregation effects are closely related to the trans-A$_2$B$_2$C$_2$ architecture of the Zn$^{II}$ porphyrin. In fact, they are not observed at all when the push–pull system involves the 2,12-π-pyrrolic-positions of an A$_4$ Zn$^{II}$ porphyrin. 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 of 73.5–89.1°, thus lowering the overall flatness of the chromophore and inducing a remarkable steric hindrance to the system.

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 $\gamma_{\text{EFISH}}$ (that is, $\gamma_0(-2\omega; 0,0,0)$) may happen to be not negligible, even for some largely investigated Zn$^{II}$ porphyrinic architectures. In particular, we focused our attention on some derivatives of Zn$^{II}$ porphyrins, carrying in the 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 ensure the lack of significant aggregation processes in solution, 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 $\gamma_{\text{THG}}$ 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 $\gamma_{\text{EFISH}}$ and $\gamma_{\text{THG}}$. BAP1 was first synthesized by some of us as a dye for dye-synthesized solar cells and has a peculiar and nonclassical 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.

### EXPERIMENTAL SECTION

**Materials and Methods.** $^1$H NMR spectra were recorded on a Bruker Advance DRX-400 in pure CDCl$_3$. Due to the higher solubilities of A$_4$ β-substituted Zn$^{II}$ porphyrins in comparison to those of the trans-A$_2$B$_2$C$_2$ analogues, neither the addition of pyridine-δ$_2$ to CDCl$_3$ nor the use of expensive THF-d$_8$ was necessary to acquire well-resolved spectra in the 10$^{-3}$–10$^{-5}$ M concentration range. Mass spectra were obtained with a Bruker-Daltonics ICR-FTMS APX 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 PerkinElmer CHN 2400 instrument or on a VG Autospec M246 magnetic mass spectrometer with a LSIMS ionic source. Elemental analyses were carried out with a PerkinElmer CHN 2400 instrument or on a VG Autospec M246 magnetic mass spectrometer with a LSIMS ionic source. Elemental analyses were carried out with a PerkinElmer CHN 2400 instrument or on a VG Autospec M246 magnetic mass spectrometer with a LSIMS ionic source. Elemental analyses were carried out with a PerkinElmer CHN 2400 instrument or on a VG Autospec M246 magnetic mass spectrometer with a LSIMS ionic source.

**EFISH and THG Measurements.** The second-order NLO responses of chromophores BP1−5 and BAP1 were measured by the EFISH technique, 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 CHCl₃ at a concentration of 10⁻³ M. For BAP1, a measurement was also made at a concentration of 5 × 10⁻⁴ M. 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 CHCl₃ (λₑₓ₅ = 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 values reported in Table 3 are the mean values of 12 successive measurements performed on the same sample. All experimental EFISH values are defined according to the “phenomenological” convention.

THG experiments were carried out in 10⁻³ M CHCl₃ solution on the same apparatus used for EFISH experiments but without applying an electric field, providing the cubic hyperpolarizability γ₁₁₁(−ω; ω; ω; ω). Experimental γ₁₁₁ 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. 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. Geometry optimizations were performed with the 6-311G(d) basis set using the M06 functional, 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. Using the same basis set, SHG first hyperpolarizabilities, i.e., the β(−2ω; ω; ω; ω) 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 γ(−2ω; ω; ω; ω) tensors, were evaluated by finite field technique. The M06-2X functional, which has been recently recommended for hyperpolarizability calculations of midsize chromophores, was adopted for both β and γ calculation. The same functional was used for determining the dipole moments µ₀. 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 βi and γi were derived from the full tensors β and γ, respectively; βi corresponds to 3/5 times βj, the projection along the dipole moment direction of the vectorial component of the β tensor, that is, βi = (3/5) Σ(µβ)/µ, where βj = (1/5) Σ(µβ)/µ, βj and βj, respectively; γi corresponds to 3/5 times γj, the projection along the dipole moment direction of the vectorial component of the γ tensor, that is, γi = (3/5) Σ(µγ)/µ, where γj = (1/5) Σ(µγ)/µ, γj and γj, respectively.

### RESULTS AND DISCUSSION

Synthesis of A₈ β-Substituted Zn⁰ Porphyrins.

Porphyrins with one ethynyl substituent on β-pirrolic position...
are well-studied, and several synthetic procedures are reported in literature. The examples of porphyrins disubstituted at the pyrrolic sites to produce a push−pull systems are very rare, 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. 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-dibromo (2a) functionalized ZnII porphyrins, for the preparation of the monosubstituted porphyrins (BP1, BP2, and BAP1) and of the disubstituted ones (BP3, BP4, and BP5), 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 between proper ethynyl substituents and the brominated intermediates, 1a and 1b, was explored. While an effective insertion at the β-positions of 4-ethynyl-N,N-dimethylamine smoothly provided desired BP2 and BP5 (Scheme 1), in contrast, 1-ethynyl-4-nitrobenzene barely reacted in those conditions to get desired chromophores BP1, BP3, BP4, and BAP1. 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 first introduced into 2 and 12 positions (3a, 3b, 4a, 5a, and 6a in Scheme 1) by microwave-enhanced Sonogashira coupling reaction. The subsequent 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 successfully give desired products BP1, BP3, BP4, and BAP1. Thus, as depicted in Scheme 1 and detailed in the Supporting Information, the designed multistep approach allowed us to efficiently synthesize monosubstituted BP1, BP2 and BAP1, symmetric 2,12-disubstituted BP4 and BP5, and 2,12 asymmetric disubstituted BP3 porphyrinic chromophores.

**UV−Vis Absorption Spectroscopy.** The UV−vis absorption spectra of BP1−5 and BAP1 in CH2Cl2 solution at 1.0 × 10−5 M concentration are reported in Figure 2a,b, while the corresponding experimental data are given in Table 1. The UV−vis spectra of BP1 and BP2 (Figure 2a) show the typical pattern expected for A4 β-pyrrolic-monosubstituted ZnII porphyrins on the basis of the “four-orbital model” proposed by Gouterman, with a very strong (ε ∼ 105 M−1 cm−1) absorption B band at about 430 nm, due to the S0 → S2 transition (from the ground to the second excited state) and two weaker (ε ∼ 104 M−1 cm−1) Q bands in the range of 500−
2a). These spectroscopic features are in agreement with an \( \pi \) intensity, in addition to an increase of its bandwidth and a molecule, resulting in a lower HOMO with ethynyphenyl fragments carrying a donor and an acceptor.

Dichloromethane and BAP1 as Computed at the M06-2X/A

The asymmetric dissubstitution in 2,12-\( \beta \)-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 \( \pi \)- conjugation and the push–pull character of the molecule, resulting in a lower HOMO–LUMO gap (Table 2).

The electronic spectra of symmetric dissubstituted Zn\( \text{II} \) porphyrins BP4 and BP5 show an interesting doubling of the B band, which is more pronounced in the presence of electron-acceptor \( \text{NO}_2 \) groups (Figure 2b). Furthermore, we observed a significant redshift of the Q bands with respect to those of corresponding asymmetric monosubstituted Zn\( \text{II} \) porphyrins BP1 and BP2. Finally, in the spectra of dissubstituted complexes the intensity of the Q\(_b\) band is higher than that of the Q\(_a\) band, while the opposite behavior is noticed for monosubstituted complexes (Q\(_b\) > Q\(_a\)). All these features are in support of the perturbation of the electronic properties of the porphyrin core induced by \( \pi \)-delocalized ethynyphenyl moieties.

The replacement in the 5,10,15,20-meso-positions of the core of 3,5-di-\( \text{tert} \)-butylphenyl groups with bulky and strongly donor bis(4-\( \text{tert} \)-butylphenyl)anilines leads to dramatic changes of the UV–vis spectrum. If we compare the spectra of BP1 (Figure 2a) and BAP1 (Figure 2b), then 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 \( \text{NO}_2 \) acceptor substituent connected by an ethynyphenyl linker to the \( \beta \)-pyrrolic-position was swapped for a cyanoacrylic group, the spectrum showed only one single, although broad, B band. This suggests that the peculiar features of the B band of BAP1 are induced by the \( \text{NO}_2 \) group. The differences between BP1 and BAP1 cannot be ascribed to aggregation phenomena, since aggregation in solution is not relevant for sterically hindered \( \text{A}_2 \) \( \beta \)-pyrrolic-substituted Zn\( \text{II} \) porphyrins. Rather, they can be due to the peculiar electronic structure of the 4D-\( \pi \)-1A architecture of BAP1.

However, to further exclude the presence of any aggregation phenomenon, UV–vis spectra in CH\(_2\)Cl\(_2\) at different concentrations in the range of \( 10^{-6} \)–\( 10^{-3} \) M were recorded (Figures S7–S12). As expected, neither deviation from the Lambert–Beer law, nor shift of the wavelength maximum or of the B or Q bands was detected by increasing concentration, different from that reported for trans-\( \text{A},\text{B} \) BC type Zn\( \text{II} \) porphyrins. The UV–vis evidence is supported also by the well-resolved signals in the \( ^1 \)H NMR spectra, acquired at a concentration 3 orders of magnitude higher (\( 10^{-2} \)–\( 10^{-3} \) M) (see the “Materials and Methods” section and Figures S1–S6).

DFT Calculations. In our previous investigation\(^3\) on \( \text{A}_2 \) \( \beta \)-pyrrolic-monosubstituted Zn\( \text{II} \) porphyrins, with a \( \pi \) substituent structurally similar to that of BP1 and BP2 but carrying a phenyl group in the 5,10,15,20-meso-positions 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 \( \beta \)-substituent in the \( \beta \)-position when this latter carries a strong \( \text{NO}_2 \) acceptor group or from the \( \pi \)-substituent to the porphyrin core, if the former carries a strong \( \text{NBu}_3 \) donor group. The ambivalent donor–acceptor character of this kind of \( \beta \)-substituted 5,10,15,20-tetraphenyl Zn\( \text{II} \) porphyrin was also supported by second-order NLO measurements based on the EFISH technique. Later, Anderson, Clays, and co-workers\(^6\) 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, neither investigation took into consideration the possible effects of aggregation in solution on the second-order NLO responses. 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 carried out a DFT investigation on BP1–5 and BAP1. The DFT HOMO–LUMO energy gaps of BP1–5 and BAP1 are reported in Table 2, and the HOMO and LUMO isodensity plots are given in Figure 3.

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 \( \text{C}_6\text{H}_4\)-\( \text{C}_6\text{H}_4\)-\( \text{C}_6\text{H}_4\)-\( \text{NO}_2 \) acceptor substituent linked to the \( \beta \)-pyrrolic-position. For BP2, an opposite electron transfer occurs from the \( \text{C}_6\text{H}_4\)-\( \text{C}_6\text{H}_4\)-\( \text{C}_6\text{H}_4\)-\( \text{NO}_2 \) donor substituent in the \( \beta \)-pyrrolic-position to the porphyrin core. Interestingly, DFT calculations suggest for BP1 a more significant electron transfer process than that for

Table 2. Correlation between Experimental \( \lambda_{\text{max}} \) of the Q\(_a\) Bands and the HOMO–LUMO Gap and Contribution of the HOMO–LUMO Transition to the Q\(_b\) Bands of BP1–5 and BAP1 as Computed at the M06-2X/6-311G(d) Level in Dichloromethane

| compound | experimental Q\(_b\) band \( \lambda_{\text{max}} \) nm | HOMO–LUMO gap, eV | contribution of the HOMO–LUMO transition to the Q\(_b\) band |
|----------|---------------------------------|-----------------|------------------------------------------------|
| BP1      | 605                             | 2.40            | 89%                                          |
| BP2      | 573                             | 2.60            | 78%                                          |
| BP3      | 643                             | 2.23            | 89%                                          |
| BP4      | 605                             | 2.34            | 90%                                          |
| BP5      | 605                             | 2.46            | 89%                                          |
| BAP1     | 694                             | 2.19            | 34%\(^a\)                                    |
|          | 639\(^b\)                       | 5.60\(^c\)      | 31%\(^b\)                                    |

\(^a\) Contribution of 61% HOMO–1 LUMO. \(^b\) Referred to as the Q\(_a\) band. \(^c\) Contribution of 31% HOMO–1 LUMO.
BP2 (Table 2), suggesting that the porphyrin core behaves better as a donor than as an acceptor.

The new push−pull ZnII 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 substituent, 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 −NMe2 groups (BP5), a substituent to the porphyrin core electronic transfer occurs, while in the presence of two −NO2 substituents (BP4), the electron transfer is from the porphyrin core to the ethynylphenyl fragment. Such DFT data are in agreement with the proposed “electronic softness” of the ZnII 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 the DFT-computed ground-state dipole moments (μ, Table 4). The value of 10.6 D for push−pull chromophore BP3 is quite close to that reported for the well-investigated push−pull ZnII porphyrin carrying in the 5,15-meso-positions the same acetylenic substituents (13.9 D).37 Dipole moments also confirm 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 −NMe2 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 the β-position by a donor acetylenic system.

As far as disubstituted ZnII porphyrin BP3 is concerned, its HOMO−LUMO energy gap is lower than those of monosubstituted BP1 and BP2, suggesting an improved charge-transfer. However, if it is compared to the HOMO−LUMO gap of the corresponding 5,15-meso-disubstituted ZnII porphyrin, then it is higher (2.23 eV vs 2.03 eV), revealing a

Figure 3. Isodensity plots of HOMO and LUMO of BP1−5 (isosurface values: 0.02).

Figure 4. Isodensity plots of frontier orbitals of BAP1 (isosurface values: 0.02).
less efficient conjugation when the push–pull system involves 2,12-β-π-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 ZnII porphyrins with 3,5-di-tert-butylphenyl groups in the 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.7

In contrast, 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, different from BP1, with an electron transfer from one of the bulky and strongly donor bis(4-tert-butylphenyl)anilines in the meso-position to the adjacent π-conjugated ethynylphenyl moiety carrying the −NO$_2$ acceptor group in the β-π-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).

Moreover, it is also interesting that in BAP1 the HOMO energy level is not delocalized on the porphyrin ring, as occurs for BP1 and BP4, but rather is mainly distributed on the four bis(4-tert-butylphenyl)anilines substituents in the 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 the β-π-pyrrolic-position, as occurs for BP1 (Figure 3).

Experimental and Theoretical Investigation of the Second-Order NLO Properties. EFISH measurements of BP1–5 and BAP1 were carried out in CHCl$_3$ solution at a concentration of 10$^{-3}$ M with an incident wavelength of 1907 nm and are reported in Table 3. BAP1 was also tested at 5 × 10$^{-4}$ M, to exclude the presence of aggregation phenomena in solution.

| Table 3. Experimental $μβ_{1907}$ and $γ_{EFISH}$ Values of BP1–5 and BAP1 in CHCl$_3$ at 1907 nm |
|---|---|---|---|---|---|
| compound | $μβ_{1907}$ (× 10$^{-48}$), esu | $γ_{EFISH}$ (× 10$^{-33}$), esu |
| BP1* | 730 | 3.5 |
| BP2 | −320 | −2.23 |
| BP3 | 690 | 3.1 |
| BP4 | −157 | −0.87 |
| BP5 | −230 | −1.15 |
| BAP1* | −685$^*$ | −3.6 |

The $μβ_{1907}$ values were obtained by eq 1, assuming a negligible contribution to $γ_{EFISH}$ of the term $γ(−2ω; ω, ω, 0)$, and for this reason could be overestimated. However, $γ(−2ω; ω, ω, 0)$, cannot be always overlooked, as it was reported for some asymmetrically substituted metal phthalocyanines or metal porphyrins with $A_4$ 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 phthalocyanines and metal porphyrins have been often reported to be a fair way to assess the relevance of the third-order term contribution to $γ_{EFISH}$. In particular, $γ(−2ω; ω, ω, 0)$ 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 eq 1 to $γ_{EFISH}$.

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 $μβ_0/SKT$ to $γ_{EFISH}$. In agreement, the $μβ_{1907}$ values for BP1 and BP3 (Table 3) are positive and quite high, as for the ZnII porphyrin structurally analogous to BP1, but carrying in the 5,10,15,20-meso-positions simple phenyl groups instead of the bulker and slightly donor 3,5-ditert-butylphenyl groups.4

Moreover, CP-DFT calculations in vacuo provided, particularly for 2,12-β-disubstituted push–pull chromophore BP3, a high and positive value of $μβ_0$ $2.5$–$3$ times higher than those of monosubstituted BP1, BP2, and BAP1, characterized by a lower polarity.

However, the negative $μβ_{1907}$ 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 $γ(−2ω; ω, ω, 0)$ 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 the 5,10,15,20-meso-positions, but nevertheless display positive ($+1.5 × 10^{-33}$ esu) and negative ($−5.1 × 10^{-33}$ esu) $γ_{THG}$ values, respectively.

According to DFT calculations, providing negative $γ_1 = γ(−2ω; ω, ω, 0)$ values28 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 $μβ_0$ for symmetric BP4 and BP5 and particularly for slightly asymmetric BP2 chromophores, thus providing a negative $γ_{EFISH}$ value (Table 3).

Such a suggestion is further supported by comparing the negative value of $γ_1$ 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 as expected enhances the third-order NLO properties, leading to a 2-fold $\gamma_{THG}$ with respect to that reported for an A3B-type Zn$^{II}$ porphyrin (2.2 $\times$ $10^{-33}$ esu). Furthermore, the $\mu\beta_{007}$ recorded at a lower concentration ($-740$ $\times$ $10^{-46}$ esu) remains constant within the experimental error of the EFISH technique ($\pm$15%), thus confirming the absence of aggregation in solution, in agreement with the UV–vis and $^1$H NMR spectroscopy evidence.

In conclusion, there is some indirect evidence suggesting a negative electronic third-order contribution to $\gamma_{EFISH}$ as the origin of the negative value of the experimental $\gamma_{EFISH}$ of BP2, BP4, BP5, and BAP1. In the case of BP2, BP4, and BP5 the negative experimental value of $\gamma_{EFISH}$ (Table 3) is a direct consequence of the rather low orientational dipolar contribution $\mu\beta_{007}/SKT$, in accordance with the low ground-state dipole moments (Table 4), so the negative electronic cubic term $\gamma(-2\omega; \omega, \omega, 0)$ prevails and produces a negative $\gamma_{EFISH}$. Only when the dipole moment is high enough, as for BP1 and particularly BP3, does the positive contribution of the orientational dipolar term predominate on $\gamma(-2\omega; \omega, \omega, 0)$, thus leading to positive $\gamma_{EFISH}$ values.

Our interpretation is also confirmed by the negative experimental values of $\gamma_{EFISH}$ for 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 the negative value of $\gamma_{EFISH}$ is completely representative of 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 monosubstituted BP2 carrying an ethynylphenyl linker with a donor pendant, we have a negative value of $\gamma_{EFISH}$ 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 monosubstituted Zn$^{II}$ porphyrin with simple phenyl groups in the 10,15,20-meso-positions, thus lacking the steric effects and electronic effects induced by more hindered and slightly donor 3,5-di-tert-butylphenyl groups.

Therefore, the high EFISH second-order NLO response reported in that investigation could be tentatively explained by a J aggregation process in solution, due to the interaction between the donor and 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.

Moreover, DFT calculations and the large differences of the EFISH second-order NLO responses of BP1 and BP2, in the absence of significant aggregation processes, have shown that the A$_4$ $\beta$-pyrrolic Zn$^{II}$ porphyrins considered in this work behave better as 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 the 5,10,15,20-meso-positions.

The UV–vis electronic absorption spectra and the trend of the calculated dipole moments have confirmed that the introduction in $\beta$-pyrrolic-position of $\pi$-delocalized ethynyl-phenyl 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-$\beta$-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, leading to a substantially diminished involvement of the porphyrin core in the electron transfer process to the $\pi$-conjugated acceptor substituent in $\beta$ position.

Finally, we have produced both theoretical and experimental evidence that in this kind of A$_4$ $\beta$-pyrrolic substituted Zn$^{II}$ porphyrins the electronic cubic contribution to $\gamma_{EFISH}$ $\gamma(-2\omega; \omega, \omega, 0)$, cannot be neglected, if the polarity of the Zn$^{II}$ porphyrin is so low that the dipolar orientational term to $\gamma_{EFISH}$ becomes too small and if $\gamma_{EFISH}$ and $\gamma_{THG}$ 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 $\gamma_{EFISH}$ for largely $\pi$-delocalized structures of low polarity must be carried out very carefully.

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00451. Synthetic procedures to obtain BP1–5 and BAP1, their characterization, the $^1$H NMR spectra and the UV–vis spectra at different concentrations (PDF)
Stefania Righetto – Department of Chemistry, University of Milan, 20133 Milano, Italy; orcid.org/0000-0002-2537-3220

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c00451

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

SmartMatLab Centre project (Fondazione Cariplo Grant 2013–1766 Piano Sostengo alla Ricerca 2018 LINEA 2 Azione A - Giovanni Ricercatori).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Regione Lombardia and Fondazione Cariplo are gratefully acknowledged for the use of instrumentation purchased through the SmartMatLab Centre project (Fondazione Cariplo Grant 2013-1766). G.D.C. greatly thanks the Universita degli Studi di Milano (Piano Sostengo alla Ricerca 2018 LINEA 2 Azione A - Giovanni Ricercatori) for financial support.

REFERENCES

(1) Tessore, F.; Orbelli Biroli, A.; Di Carlo, G.; Pizzotti, M. Porphyrins for Second Order Nonlinear Optics (NLO): An Intriguing History. Inorg. Chem. 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.; Fantacci, 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 S and 15-positions. J. Porphyrins Phthalocyanines 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 Pyrrolic Position. Eur. J. Inorg. Chem. 2005, 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 Delocalised Linkers Carrying Push or Pull Groups. Eur. J. Inorg. Chem. 2006, 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 hyperpolarizability: State-Specific Contributions to C. 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-(dimethylamino)styrylpyridine 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.; Bethia, 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. 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. Chem. 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.; Vazquez, P.; Agullo-Lopez, F.; Torres, T. Role of structural factors in the Nonlinear Optical properties of Phthalocyanines and Related Compounds. Chem. Rev. 2004, 104, 3722–3750.

(15) De la Torre, G.; Vazquez, P.; Agullò-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. Thioethylyporphyrinines: 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.; Gammelotti, 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 CHCl3 of the push-pull chromophores \([15\{(4^4-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-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.; Stem, C.; Liu, Z.; Ho, S.-T.; Brown, E. C.; Ratner, M. A.; Marks, T. J. Ulralarge hyperpolarizability twisted π-electron-system 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 CHCl3 of Zn(II) complexes with 4,4′-trans-C3H7CH=CH=CH=NMe2 and 4,4′-trans,trans-NC3H4(CH=CH)2C6H4NMe2. 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-pyriclic 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-&-1A type 1-substituted Zn(II)-porphyrins: ideal green sensitizers for building-integrated photovoltaics. Chem. Commun. 2016, 52, 12642–12650.

(23) Willett, 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 metallotriazolylhemiporphyrin derivatives. J. Phys. Chem. 1994, 98, 4495–4497.

(25) 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.; Ao, 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.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; 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 16, revision A.03; Gaussian, Inc.: Wallingford CT, 2016.

(26) Zhao, Y.; Truhlár, D. G. The Mo6 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent 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. 2007, 12, 241–279.

(29) Pielak, K.; Tonnellé, C.; Sanguinet, L.; Cariati, E.; Righetto, S.; Muccioli, L.; Castet, F.; Champagne, B. Dynamical Behaviour and Second Harmonic Generation Responses in Acido-Triggrered 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 ZnII 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.; Trifilitti, V.; Ruffo, R.; Abbuto, A.; Amat, A.; De Angelis, F.; Mussini, P. R. Tetraaryl ZnII porphyrinines substituted at -pyrrolic positions as sensitizers in dye-sensitized solar cells: a comparison with meso-disubstituted push-pull ZnII porphyrinines. Chem. - Eur. J. 2013, 19, 10723–10740.

(32) Gouterman, M. Spectra of porphyrins. J. Mol. Spectrosc. 1961, 6, 138–160.

(33) Giovannetti, R. The use of spectrometry UV-Vis for the study of porphyrins. Macro to Nanospectroscopy 2012, 38797.

(34) Di Carlo, G.; Orbelli Biroli, A.; Pizzotti, M.; Tessore, F. Efficient sunlight harvesting by A4 -pyrrolic substituted ZnII porphyrins: a mini-review. Front. Chem. 2019, 7, 177.

(35) Orbelli Biroli, A.; Tessore, F.; Vece, V.; Di Carlo, G.; Mussini, P. R.; Trifilitti, V.; De Marco, L.; Giannuzzi, R.; Manca, M.; Pizzotti, M. Highly improved performance of ZnII tetraarylporphyrinines 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.; Depoetter, 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 nonlinear optical properties of push-pull MII-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-Lazarro, F.; Sastre, A.; Torres, T.; Agullo-Lopez, F.; Zyss, J. Third order nonlinear optical properties of soluble metallotriazolylhemiporphyrin derivatives. 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.; Tancrèze, N.; Zyss, J. New [(D-terpyridine)-Ru-(D or A-terpyridine)]-4-EtPhCO2 complexes (D = electron donor group; A = electron acceptor group) as active second-order nonlinear optical chromophores. Dalton Trans. 2012, 41, 6707–6714.

(41) Senge, M. O.; Fazezak, 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, 2737–2747.