Synthesis, Electronic Characterisation and Significant Second-Order Non-Linear Optical Responses of *meso*-Tetraphenylporphyrins and Their Zn^{II} Complexes Carrying a Push or Pull Group in the β Pyrrolic Position

Elisabetta Annoni,[a] Maddalena Pizzotti,*[a] Renato Ugo,[a] Silvio Quici,[b] Tamara Morotti,[b] Maurizio Bruschi,[c] and Patrizia Mussini[d]

Keywords: Cyclic voltammetry / Nonlinear optics / Porphyrins / UV/Vis spectroscopy / Zinc

This work describes the synthesis and characterisation by electronic absorption spectroscopy, cyclic voltammetry and by a solvatochromic investigation of *meso*-tetraphenylporphyrins and their Zn^{II} complexes substituted at the β pyrrolic position by a pseudo-linear, π-delocalised organic linker carrying either an electron-withdrawing (pull) or electron-donating (push) group. The second-order NLO response of these push-pull porphyrinic chromophores has been investigated by the EFISH technique working with a non-resonant incident wavelength of 1.907 μm. The porphyrin ring substituted at the β pyrrolic position by an electron-acceptor π-system behaves as a significant donor group, comparable to a ferrocenyl group or to a phthalocyanine. Unexpectedly, the porphyrin ring substituted at the β pyrrolic position with an electron-donor π-system shows a larger and significant second-order NLO response.

Introduction

A wide variety of push-pull organic π-conjugated chromophores have been extensively investigated, both theoretically and experimentally, for their significant second-order optical nonlinearities.[1–3] When compared to organic chromophores, pseudo-linear coordination and organometallic chromophores may offer additional electronic features, acting on the second-order non-linear optical (NLO) response, such as intense charge-transfer transitions (ligand to metal and vice versa) at relatively low energy that are easily tuneable by changing the oxidation state of the metal, its coordination sphere and stereochemistry.[4] Attempts have been made to design two-dimensional push-pull chromophores based on π-delocalised macrocycles such as porphyrins and metalloporphyrins,[5,6] metallophthalocyanines[7a] and subphthalocyanines,[7b,7c] and metallotriazolohemiporphyrazines.[8] Porphyrins and their metal complexes offer some additional advantages, such as good thermal and chemical stability, acceptable solubility for the determination of dipole moments and their second-order molecular NLO response and relatively easy synthetic pathways for the preparation of various architectures.[9] The highly polarisable π ring, with strong π→π* transitions,[10] of push-pull metal porphyrins asymmetrically substituted in the 5- and 15-positions, has been proposed as an excellent linker of the pseudo-linear push-pull chromophore.[11] This latter point was experimentally confirmed by Therien et al.,[6a,6b] Ng et al.[6c] and recently also by some of us.[6d] However, to the best of our knowledge, no-one, with the exception of two rather preliminary communications,[12] has experimentally investigated whether the π system of porphyrins or metalloporphyrins can act as a donor or acceptor group of a pseudo-linear push-pull chromophore. Depending on the number of π electrons, π orbitals, and on the heteroatom electronegativities, heterocyclic rings can act as electron-rich (donor) or electron-poor (acceptor) systems.[13] Pyrrole, with six π electrons and five π orbitals, is an electron-rich π system. Thus, a porphyrinic chromophore with four pyrrole rings may be considered, at first glance, as a π-electron-rich system in which electron-rich and electron-poor carbon atoms may be identified.[14] In order to experimentally prove some interesting theoretical suggestions,[14] we investigated the second-order NLO response of push-pull pseudo-linear chromophores based on a 5,10,15,20-tetraphenylporphyrin, either as free base or as Zn^{II} complex, carrying a push or a pull group linked to the β pyrrolic position through a π-delocalised spacer. One major prob-

---

[a] Dipartimento di Chimica Inorganica Metallorganica e Analitica dell'Università di Milano, Unità di Ricerca dell' INSTM, Centro di eccellenza CIMAINA dell'Università di Milano, e Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM),
Via G.Venezian 21, 20133 Milano, Italy
Fax: +39-02-50314405
E-mail: maddalena.pizzotti@unimi.it
[b] Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM),
Via Golgi 19, 20133 Milano, Italy
[c] Dipartimento di Biotecnologie e Bioscienze, Università di Milano Bicocca,
Piazza della Scienza 2, 20126 Milano, Italy
[d] Dipartimento di Chimica Fisica ed Elettrochimica dell'Università di Milano,
Via Golgi 19, 20133 Milano, Italy

DOI: 10.1002/ejic.200500292

lem with push-pull π-delocalised macrocycles is the correct determination of their molecular second-order NLO response. The quadratic hyperpolarizability of asymmetric porphyrins and their metal complexes has been measured by HRS (Hyper-Rayleigh Scattering),[6a] Stark effect[6b] and by EFISH (Electric Field Induced Second Harmonic) generation techniques.[5,6c,6d] Depending on the incident wavelength, these measurements can be affected by resonance enhancements[6a,6d] and in the case of the HRS technique also by a fluorescent contribution to the second harmonic.[6a]

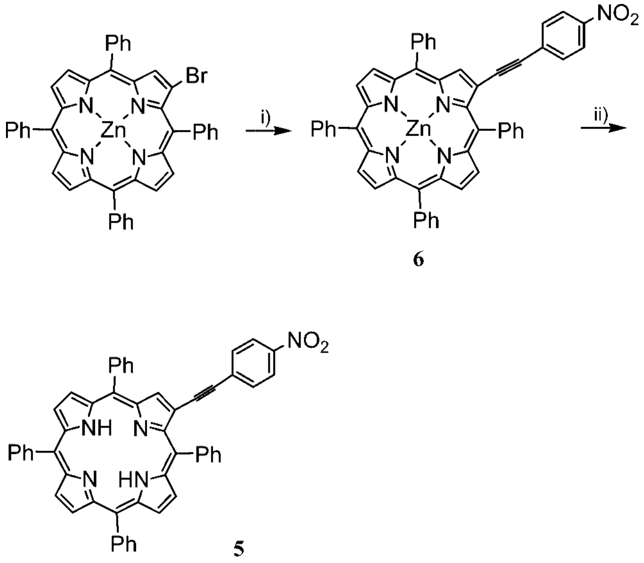
In order to avoid both these effects, the second order NLO responses of compounds investigated in this work were measured by the EFISH technique working at a nonresonant incident wavelength of 1.907 μm. In addition, density functional theory (DFT)[15] calculations were carried out in order to confirm experimental dipole moments and to define the best structural geometries using the BP86 functional[16] and an all-electron valence triple-ξ basis set with polarisation functions on all atoms.[17]

Results and Discussion

Synthesis of Porphyrins and Their Zn^{II} Complexes

The asymmetric 5,10,15,20-tetraphenylporphyrins and their Zn^{II} complexes investigated in this work are reported in Figure 1.

Porphyrin **1** was synthesised by reaction of 2-bromo-5,10,15,20-tetraphenylporphyrin, obtained by bromination of 5,10,15,20-tetraphenylporphyrin (TPP) with *N*-bromosuccinimide, first with Ni(acac), then with CuCN[18] to afford the Ni^{II} complex of **1**, and finally by controlled demetallation with concentrated sulfuric acid. Its Zn^{II} complex **2** was obtained by reaction of **1** with $Zn(OAc)_2$.[19] Porphyrin **3** was obtained by reaction of the Zn^{II} complex of TPP with I_2 and $AgNO_3$ to afford **4**,[20] followed by demetallation with concentrated HCl. Complex **6** was obtained by a Sonogashira coupling reaction of the Zn^{II} complex of 2-bromo-5,10,15,20-tetraphenylporphyrin with 4-nitrophenylacetylene in refluxing THF/Et_3N, using $[PdCl_2(PPh_3)_2]$ and CuI as catalysts, followed by demetallation with CF_3COOH in CH_2Cl_2 at room temperature to give porphyrin **5** (Scheme 1).



Scheme 1. i) 4-Nitrophenylacetylene, $[PdCl_2(PPh_3)_2]$ (cat), THF/NEt_3, reflux; ii) CF_3COOH, CH_2Cl_2, room temp., 20 h.

Porphyrins **7** and **11**, which are already known,[21] were synthesised by a new and easier method based on the Wittig condensation of 2-formyl-5,10,15,20-tetraphenylporphyrin (**13**) with (4-nitrobenzyl)triphenylphosphonium bromide and [4-(dibutylamino)benzyl]triphenylphosphonium chloride respectively (Scheme 2).

Reactions were carried out in CH_2Cl_2 at room temperature in the presence of solid NaOH as base to afford, after purification by column chromatography, a mixture of (*E*)-

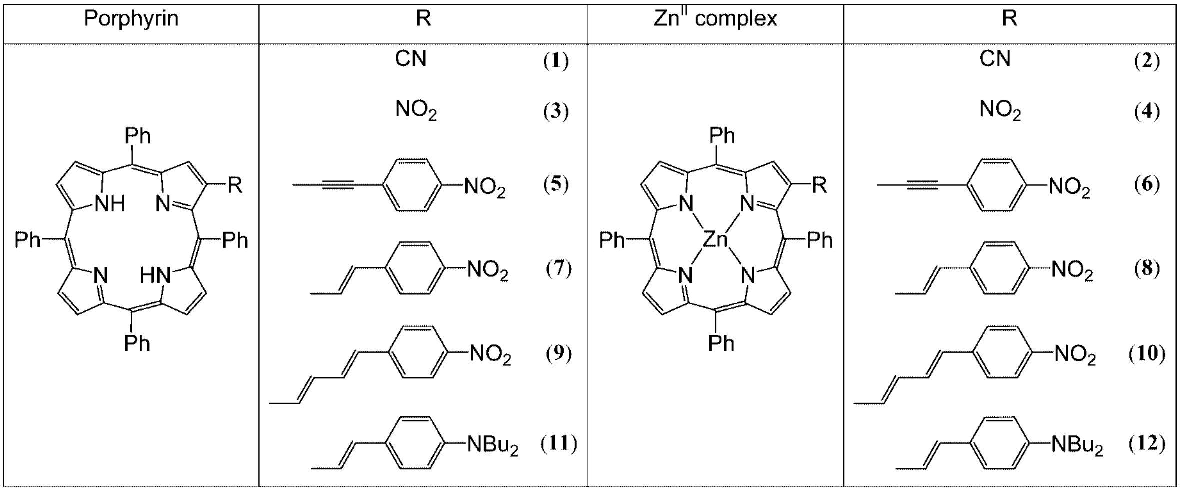
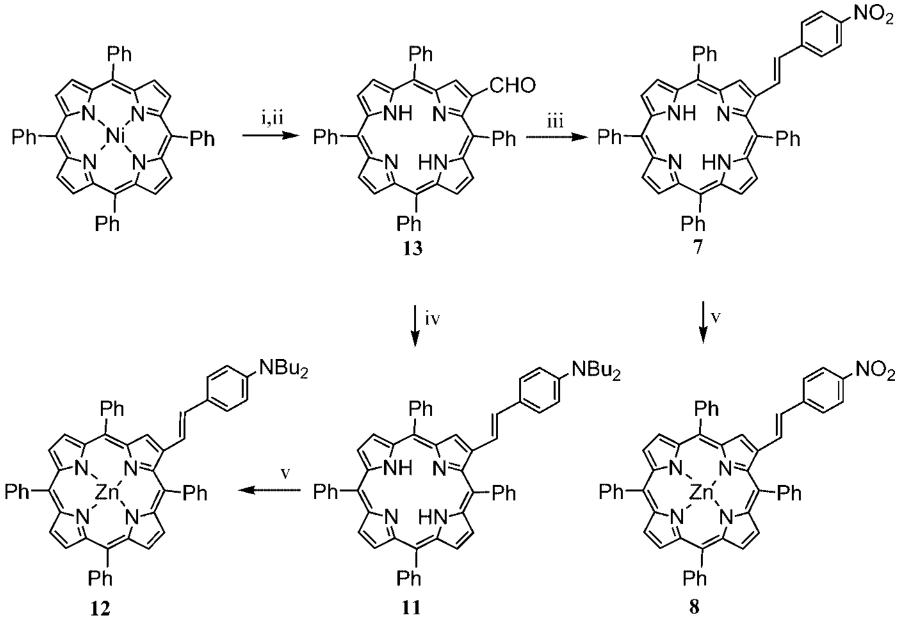
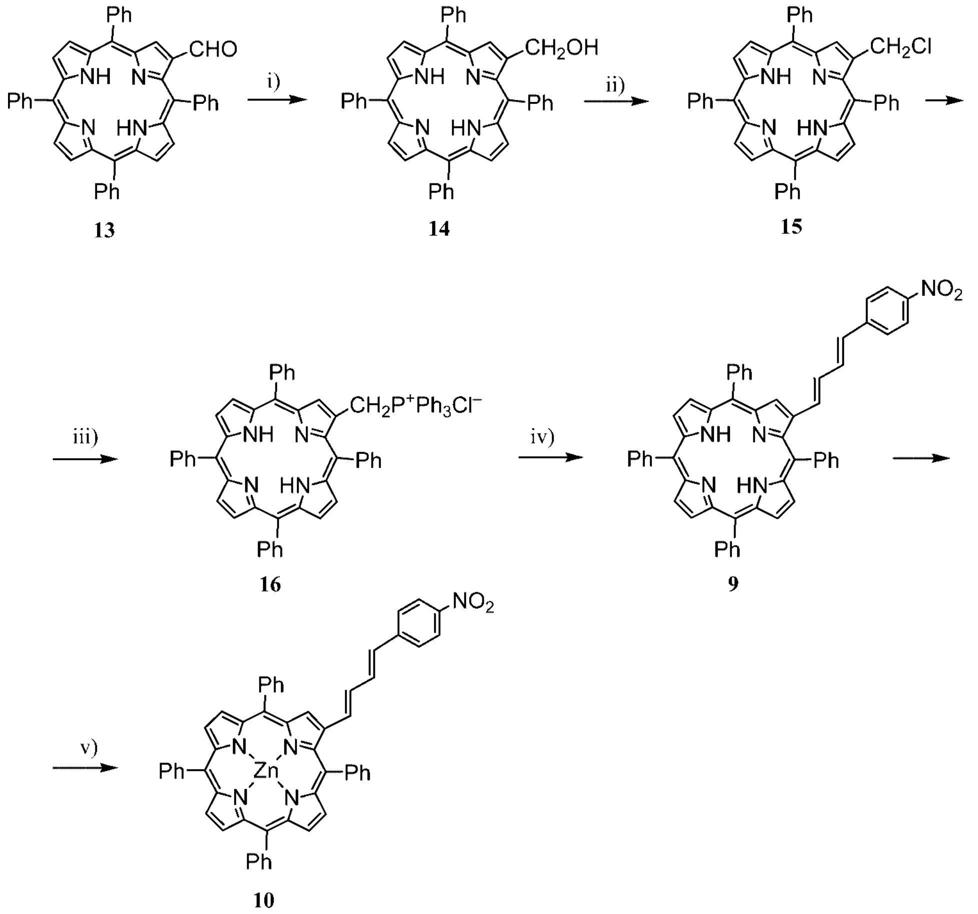


Figure 1. Asymmetrical *meso*-tetraphenylporphyrins and their Zn^{II} complexes with β pyrrolic substitution by electron-withdrawing or -donating groups.



Scheme 2. i) $POCl_3$, DMF, 1,2-dichloroethane, reflux, 24 h; ii) 96% H_2SO_4, CH_3COONa 30% in H_2O; iii) (4-nitrobenzyl)triphenylphosphonium bromide, NaOH, CH_2Cl_2, room temp., 8 h; iv) [4-(dibutylamino)benzyl]triphenylphosphonium chloride, NaOH, CH_2Cl_2, room temp., 4 h; v) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH, reflux.



Scheme 3. i) $NaBH_4$, EtOH 96%, reflux, 4 h; ii) $SOCl_2$, pyridine, Et_2O; iii) PPh_3, $CHCl_3$, reflux; iv) 4-nitrocinnamaldehyde, DBU, room temp.; v) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH, reflux, 2 h.

and (*Z*)-isomers. From this mixture the pure (*E*)-isomers **7** and **11** were obtained, in 58% and 69% yields respectively, by repeated crystallisation from CH_2Cl_2/MeOH. Porphyrin **13** was prepared in 70% yield by Vilsmeier formylation of the commercially available Ni complex of TPP (Scheme 2) following a modification of the procedure reported in the literature.[22] (4-Nitrobenzyl)triphenylphosphonium bromide was easily obtained, in quantitative yield, by quaternisation of triphenylphosphane with 4-nitrobenzylbromide in refluxing toluene, while (4-dibutylamino)benzyltriphenylphosphonium chloride was prepared from (4-dibutylamino)benzyl alcohol, obtained by reduction of (4-dibutylamino)benzaldehyde with $NaBH_4$, by adapting a procedure reported in the literature.[23] The Zn^{II} complexes **8** and **12** were obtained in quantitative yield by treating porphyrins **7** and **11**, respectively, with $Zn(OAc)_2$ in $CHCl_3$/MeOH.[19] Porphyrin **9**, bearing a (1*E*,3*E*)-butadiene linker in the β position, was prepared by Wittig condensation of 4-nitrocinnamaldehyde with the phosphonium salt **16** in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base (Scheme 3).

The preparation of the phosphonium salt **16** was carried out, starting from the aldehyde **13**, according to the synthetic scheme reported in a preliminary communication by Bonfantini and Officer in 1993.[24] However the detailed experimental procedure was never published, hence a careful description of the synthesis and characterisation of intermediate porphyrins **14**, **15** and **16** is given in the Experimental Section.

Again, treatment of the free porphyrin **9** with $Zn(OAc)_2$ in $CHCl_3$/MeOH at reflux afforded the Zn^{II} complex **10** in quantitative yield. All porphyrins and their Zn^{II} complexes were characterised by elemental analysis, ^1H NMR spectroscopy and mass spectrometry

Electronic Absorption, Emission Spectra and Solvatochromic Behaviour

Metal complexation of tetraarylporphyrins increases the ring microsymmetry from D_{2h} to D_{4h}, with a parallel decrease of the number of Q absorption bands from four to two.[10,25,26] Although the introduction of a substituent in the β pyrrolic position should produce a lowering of the D_{4h} microsymmetry, the usual decrease of the number of Q bands from four to two was reported when comparing porphyrin **7** and its Ni^{II} complex.[21] For porphyrin **1** and its Cu^{II} complex, a decrease of the number of Q bands from four to three was originally published,[18] but later a decrease from four to two was reported when comparing porphyrins **1** and **3** with their Cu^{II} complexes.[25] When comparing porphyrins **1** and **3** with their Zn^{II} complexes **2** and **4**, we observed a decrease of the number of Q bands from four to three, with complete disappearance of the Q_α band above 600 nm but with a weak Q_β band at higher energy still detectable (Table 1 and Figure 2).[27]

A similar decrease of the number of Q bands was observed when comparing porphyrins **5** and **7** with their Zn^{II}

Table 1. Visibile and fluorescence spectra in $CHCl_3$.

Compound[a]	Soret B Half band width $\Delta\nu_{1/2}$ [cm^{-1}][c]	Soret B λ_a [nm] [logε]	Q bands λ_a [nm] [logε]	Fluorescent emission[b] λ_e [nm]
2-Cyano-H_2TPP[d] (**1**)	n.d.	420 [5.29][e]	517 [3.79], 552 [3.21] 593 [3.23], 648 [3.20]	659, 717 (659, 718)
2-Cyano-ZnTPP (**2**)	n.d.	427 [5.62][e]	518 [3.57], 555 [4.20] 593 [4.02]	607.5, 657 (606.5, 656.5)
2-Nitro-H_2TPP (**3**)	2974 (1574)	427 [5.24]	527 [4.14], 560 [3.56] 605 [3.53], 665 [3.88]	716 (706)
2-Nitro-ZnTPP (**4**)	1172 (1874)	425 [5.28]	522 [3.41], 555 [4.00] 598 [3.80]	661 (657)
2-(4-Nitrophenyl)ethynyl-H_2TPP (**5**)	2296 (1675)	430 [5.26]	525 [4.31], 562 [3.83] 601 [3.78], 657 [3.68]	677, 730 (671.5, 730.5)
2-(4-Nitrophenyl)ethynyl-ZnTPP (**6**)	1381 (1474)	431 [5.30]	521 [3.60], 557 [4.25] 594 [4.03]	621, 659.5 (614.5, 660)
(1*E*)-2-(4-Nitrophenyl)ethenyl-H_2TPP (**7**)	1800 (2497)	431 [5.31]	525 [4.34], 569 [4.13] 602 [3.94], 659 [3.47]	671, 732.5 (672, 734)
(1*E*)-2-(4-Nitrophenyl)ethenyl-ZnTPP (**8**)	3216 (2320)	432 [5.20]	526 [3.77], 558 [4.35] 597 [4.13]	617, 664 (616.5, 664.5)
(1*E*,3*E*)-2-(4-Nitrophenyl)buta-1,3-dienyl-H_2TPP (**9**)	3475 (2958)	425 [5.03]	523 [4.21], 572 [4.07] 601 [3.86], 665 [3.51]	668.5 (629, 678)
(1*E*,3*E*)-2-(4-Nitrophenyl)buta-1,3-dienyl-ZnTPP (**10**)	3341 (2741)	430 [4.94]	559 [4.11]; 599 [3.98]	616.5, 666 (616.5, 667)
(1*E*)-2-[4-(Dibutylamino)phenyl]ethenyl-H_2TPP (**11**)	1674 (1102)	422 [5.36]	521 [4.41], 579 [4.16] 603 [4.14], 656 [3.71]	660, 724(sh) (662, 728 sh)
(1*E*)-2-[4-(Dibutylamino)phenyl]ethenyl-ZnTPP (**12**)	1454 (1011)	422 [5.20]	556 [4.08], 601 [3.97]	650 (661)

[a] H_2TPP = 5,10,15,20-tetraphenylporphyrin. [b] Values obtained by irradiation at the Soret wavelength and at the lower energy Q_β band (in parentheses). [c] Values were obtained according to the equation $\Delta\nu_{1/2} = f/4.33\times10^{-9}\cdot\varepsilon$ (F. L. Pilar, *Elementary Quantum Chem.*, McGraw-Hill Book Comp., **1968**) where f is the oscillator strength and ε is the maximum extinction coefficient (values in parentheses are graphically measured[28]). [d] Slightly different values of λ_a are given in ref.[21] [e] An absorption band at 406 nm (logε = 4.65) was also detected for **2**, while **1** showed only a shoulder of the B band at higher energy.

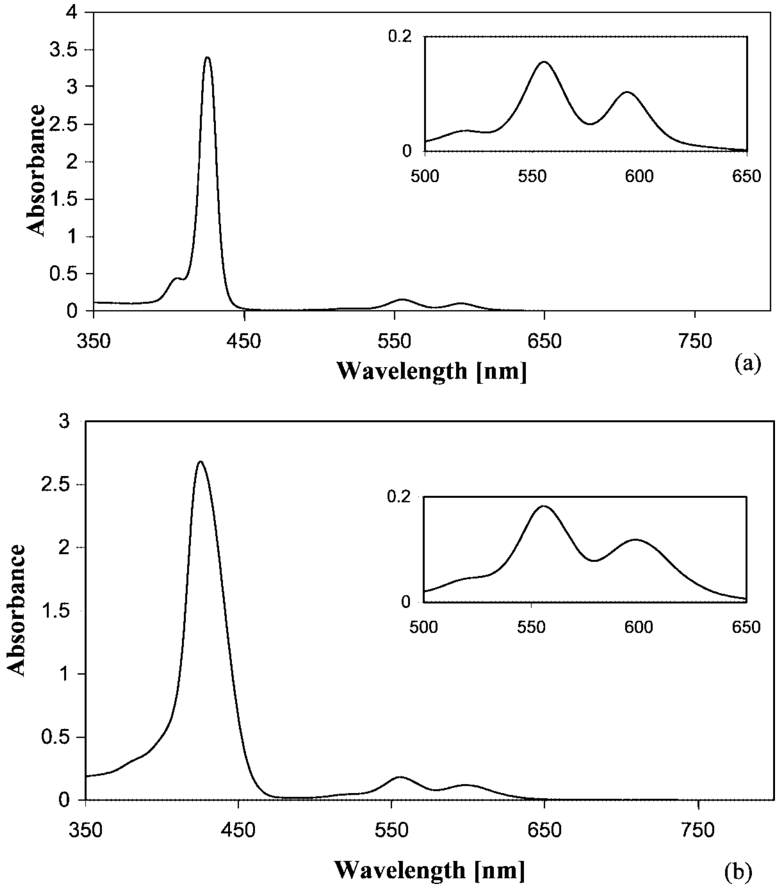


Figure 2. (a) Electronic absorption spectrum of 2-cyano-ZnTPP (**2**) in $CHCl_3$ (8.10×10^{-6} M). (b) Electronic absorption spectrum of 2-nitro-ZnTPP (**4**) in $CHCl_3$ (6.36×10^{-6} M).

complexes **6** and **8**.[27] However, when comparing porphyrin **9** with its Zn^{II} complex **10**, with the electron-withdrawing nitro group further away from the β pyrrolic carbon atom, the number of Q bands decreases from four to two (Table 1 and Figure 4). The above observations would suggest a significant electronic asymmetry of the porphyrin ring when the nitro group is linked to the β pyrrolic position directly or through an arylethenyl or an arylethynyl bridge. This suggestion is also supported by the asymmetry of the B Soret band, with evidence for a shoulder at lower energy (see Figure 3 and Figure 4) and by its bandwidth increase (Table 1).[26]

However, when an electron-donating dibutylamino group is linked to the β pyrrolic position through an arylethenyl linker, the Soret B band remains quite symmetric and its bandwidth does not increase significantly (Table 1). Interestingly, in the spectra of **1** and **2** we also observed an absorption band ($\log\varepsilon = 4.5$) close to the Soret B band but at higher energy (Figure 2 and Table 1) that has not been reported in previous investigations.[25]

The modulation of the π valence orbital levels of porphyrins and metalloporphyrins by substitution at the β pyrrolic position was investigated by a combination of cyclic voltammetry and electronic absorption spectroscopy.[25] A similar approach was later applied when comparing porphyrins **7** and **11** (the latter with a dimethylamino instead of a dibutylamino group) and their Ni^{II} complexes.[21] Electronic transitions from the a_{1u} and a_{2u} HOMO to the e_g LUMO orbitals in porphyrins and their metal complexes cause B and Q absorption bands whose wavelengths and oscillator strengths are defined by the interaction configuration between the a_{1u} and a_{2u} orbitals and therefore by their relative energies.[10] These latter are reported to be affected by substitution at the β pyrrolic position; the effect is more pronounced for the a_{1u} orbital, which has a non-vanishing electron density on both the α and β pyrrolic carbon atoms.[25] For porphyrin **7** and its Ni^{II} complex, with the nitro group not directly linked to the β pyrrolic position, the perturbation of the energy of the a_{1u} orbital has been suggested to be modest.[21] On the contrary, the decrease of Q bands from four to three upon complexation of **7** with Zn^{II}, together with the significant asymmetry of the B band and parallel increased bandwidth, would suggest a significant perturbation of the porphyrin π orbitals. Due to the π delocalised nature of the substituent at the β pyrrolic position, this effect could not be originated only by an inductive perturbation of the energy levels of the a_{1u} and a_{2u} frontier orbitals. As already suggested for porphyrin **7**,[21] this perturbation could be mainly due to the conjugation of the π orbitals of the linker with the π orbitals of the pyrrolic ring, which may induce some charge-transfer character to porphyrin $\pi\rightarrow\pi^*$ transitions that are no longer totally centred

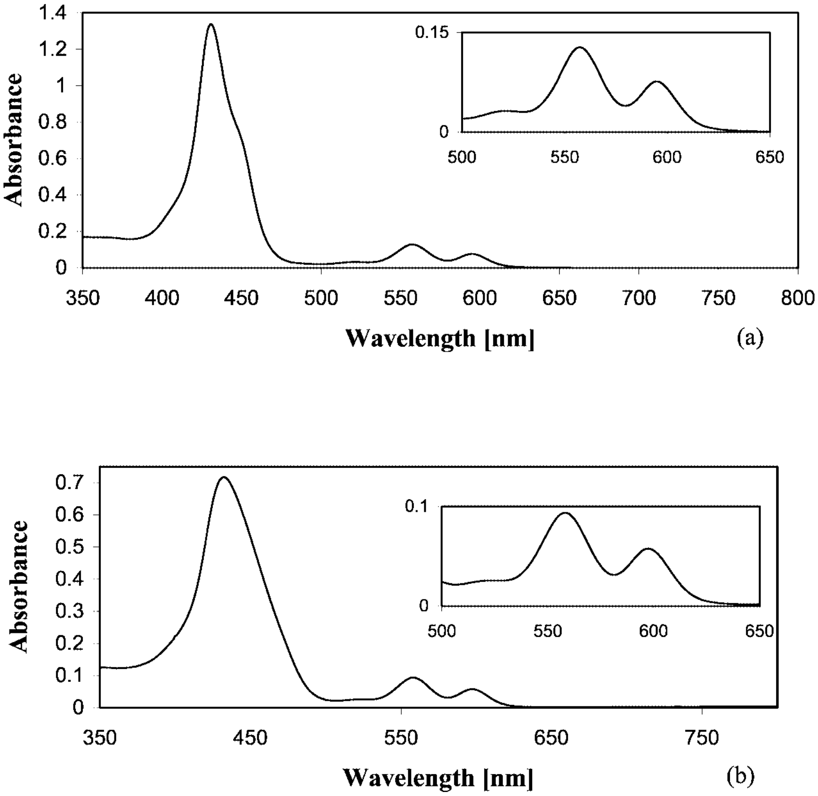


Figure 3. (a) Electronic absorption spectrum of 2-(4-nitrophenyl)ethynyl-ZnTPP (**6**) in $CHCl_3$ (6.25×10^{-6} M). (b) Electronic absorption spectrum of (1*E*)-2-(4-nitrophenyl)ethenyl-ZnTPP (**8**) in $CHCl_3$ (4.52×10^{-6} M).

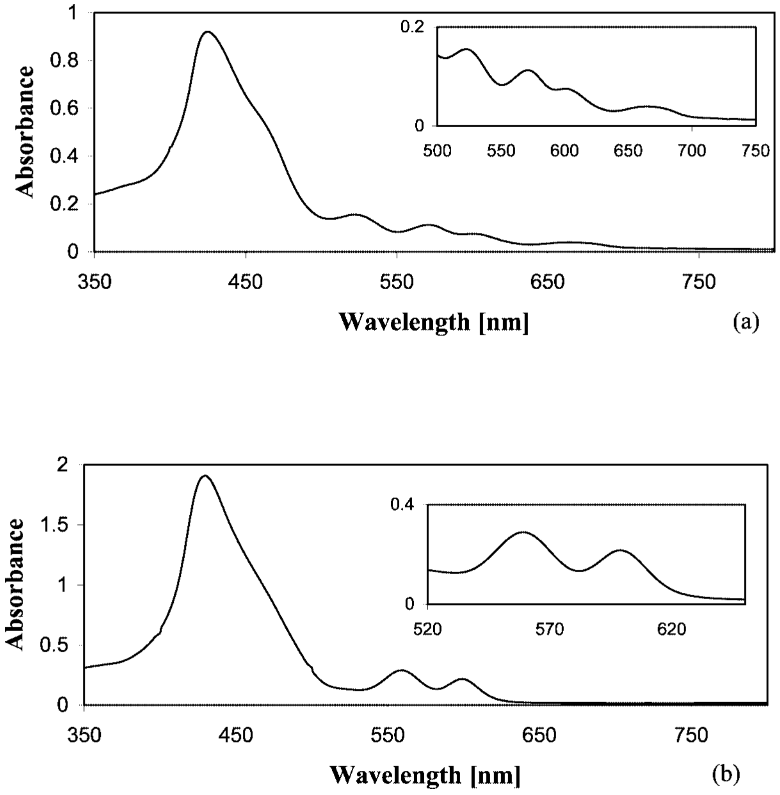


Figure 4. (a) Electronic absorption spectrum of (1*E*,3*E*)-2-(4-nitrophenyl)buta-1,3-dienyl-H_2TPP (**9**) in $CHCl_3$ (8.58×10^{-6} M). (b) Electronic absorption spectrum of (1*E*,3*E*)-2-(4-nitrophenyl)buta-1,3-dienyl-ZnTPP (**10**) in $CHCl_3$ (2.19×10^{-5} M).

on the porphyrin ring,[28] as supported by the increased bandwidth of the Soret B band.[26] In agreement with this hypothesis, the available structural data indicate, at least for the arylethenyl linker, that the porphyrin core and the styryl group are essentially coplanar,[21,29] a structural feature which should promote a facile interaction of the π orbitals of the linker with the porphyrin π orbitals. Such a nearly planar arrangement was confirmed as the best geometry, by an ab initio DFT method, for the Zn^{II} complexes **8** and **12** and the related porphyrins **7** and **11** (see below).

The effects of substituents upon the relative energies of the frontier orbitals a_{1u} and a_{2u} of metal porphyrin complexes may be evaluated, in a first instance, by the Shelnutt analysis,[28] which correlates the energies of the B and Q_α transitions with the ratio of the square of their transition dipole moments. Shelnutt suggests that the closer in energy the a_{1u} and a_{2u} orbitals are, the smaller the ratio of the square of the transition dipole moments of the Q_α and B transitions, respectively, and the difference in energy $E_B - E_{Q\alpha}$.

The substitution at the β pyrrolic position in the Zn^{II} porphyrin complexes investigated in this work produces a substantial increase of both $E_B - E_{Q\alpha}$ and the ratio of the square of the transition dipole moments of the Q_α and B transition, respectively, with respect to the parent complex ZnTPP (Table 2). Such an increase is more relevant when the π-delocalised substituent carries the strong donor dibutylamino group. This evidence adds further support to a significant perturbation of the energies of the a_{1u} and a_{2u} orbitals, which shift further apart. However, the so-called Shelnutt analysis[28] must be taken with some caution because different linkers may introduce different charge-transfer character to B or Q_α transitions, or to both of them.

In order to produce more evidence for a significant electronic perturbation, we also investigated the trends of a parameter of the electronic absorption spectra of Zn^{II} porphyrin complexes that is independent of the extent of the configurational interaction of the a_{1u} and a_{2u} orbitals. This is the centre of gravity of the B and Q_α bands, defined as $E = \frac{1}{2}(E_B + E_{Q\alpha})$, which is an indication of the relative perturbation of the energy levels of the a_{1u} and a_{2u} frontier orbitals.[25] A red shift of the centre of gravity with respect to CuTPP of about 350–700 cm^{-1} has been found for the substitution in the β pyrrolic position with a series of electron-withdrawing groups, while the red shift is much smaller (about 20–400 cm^{-1}) with electron-donating groups.[25] We have found a relevant blue shift of about 1500 cm^{-1} (Table 2) with respect to ZnTPP for complexes **4**, **6**, **8** and **10** carrying a nitro group directly or indirectly bound to the β pyrrolic carbon atom. The centre of gravity appears to be quite independent of the different nature and length of the π linker (Table 2). On the contrary, the centre of gravity of complex **12**, with a π linker carrying an electron-donating dibutylamino substituent, shows a completely different trend with a limited red shift of about 300 cm^{-1} (Table 2). The above observations suggest not only the presence of a perturbation, but also a completely opposite trend when passing from an electron-withdrawing to an electron-donating π delocalised substituent.[25] In conclusion, we have produced a significant and complementary body of evidence for a significant electronic perturbation of the π porphyrin system by β pyrrolic substitution with a π delocalised linker carrying a push or pull group. In order to confirm the role of π conjugation, which should introduce some charge-transfer character to both the B and Q absorption bands, we carried out a solvatochromic investigation using a set of solvents of increasing polarity, excluding those that show strong donor or hydrogen-bonding properties (see Experimental Section), so that mainly the orientational effect of the solvent polarity (and not hydrogen bonding or strong basic ligation) dependency was studied. With this limitation a poor solvatochromic behaviour of the B band of porphyrin complexes was usually reported.[30,31] However, the solvatochromic behaviour of the B band becomes significant for a series of Zn^{II} complexes of various isomers of H_2TPP bearing two NO_2 groups in different β pyrrolic positions.[32]

We have produced clear evidence for a significant solvatochromic behaviour of both B and Q_β (in porphyrins the Q band is at higher energy) bands for porphyrins and their Zn^{II} complexes investigated in this work when carrying a π delocalised linker (Table 3). With the exception of porphyrin **9**, the Soret B band is always shifted to higher energy (blue shift) with increasing polarity of the solvent when a nitro group is linked through a π spacer (Table 3).

The strength of the charge-transfer character, deduced from the absolute value of $\Delta\mu_{eg}$ (difference between excited and ground state dipole moments), which is negative for blue-shifted bands, is relatively small for porphyrins **5**, **7**

Table 2. Some characteristics of the electronic spectra of some 2-substituted Zn(TPP) complexes in $CHCl_3$.

Compound[a]	B band λ_{max} [nm] [r^2_{eg} 10^{-34}][c]	Q_α band λ_{max} [nm] [r^2_{eg} 10^{-36}][c]	Center of gravity[b] [cm^{-1}]	$E_B - E_{Q\alpha}$ [cm^{-1}]
ZnTPP	419 [1.22]	584 [1.16]	20494	5585.0
2-Cyano-ZnTPP (**2**)	427 [n.d.]	593 [n.d.]	21968	6555.8
2-Nitro-ZnTPP (**4**)	425 [0.873]	598 [5.73]	21956	6807.0
2-(4-Nitrophenyl)ethynyl-ZnTPP (**6**)	431 [1.09]	594 [3.67]	21975	6366.8
(1*E*)-2-(4-Nitrophenyl)ethenyl-ZnTPP (**8**)	432 [2.15]	597 [4.96]	21859	6397.7
(1*E*,3*E*)-2-(4-Nitrophenyl)buta-1,3-dienyl-ZnTPP (**10**)	430 [1.15]	599 [3.95]	21975	6561.3
(1*E*)-2-[4-(Dibutylamino)phenyl]ethenyl-ZnTPP (**12**)	422 [0.895]	601 [5.37]	20167	7057.8

[a] H_2TPP is 5,10,15,20-tetraphenylporphyrin. [b] The electronic centre of gravity is defined as $(E_B + E_{Q\alpha})/2$ according to ref.[25] [c] The transition dipole moment r_{eg} is related to the oscillator strength f by the following equation: $r^2_{eg} = 2.13 \times 10^{-30}\ f/\nu_{eg}$, where ν_{eg} is the absorption in cm^{-1} according to ref.[49b]

Table 3. Solvatochromic behaviour of the Soret B band and of the Q_β band at higher energy.

Compound[a]	Soret B		Q_β	
	$\Delta\mu_{eg}$ [D]	f	$\Delta\mu_{eg}$ [D]	f
ZnTPP		1.36		0.069
2-Cyano-ZnTPP (**2**)	[b]	[b]	–0.09	0.089
2-Nitro-H_2TPP (**3**)	0.7	2.19	1.5	0.068
2-Nitro-ZnTPP (**4**)	[b]	0.96	–0.6	0.061
2-(4-Nitrophenyl)ethynyl-H_2TPP (**5**)	–1.3	1.81	2.32	0.081
2-(4-Nitrophenyl)ethynyl-ZnTPP (**6**)	–5.7	1.19	–4.3	0.063
(1*E*)-2-(4-Nitrophenyl)ethenyl-H_2TPP (**7**)	–2.2	1.59	2.6	0.082
(1*E*)-2-(4-Nitrophenyl)ethenyl-ZnTPP (**8**)	–8.6	2.2	[b]	[b]
(1*E*,3*E*)-2-(4-Nitrophenyl)buta-1,3-dienyl-H_2TPP (**9**)	7.1	1.61	9.3	0.085
(1*E*,3*E*)-2-(4-Nitrophenyl)buta-1,3-dienyl-ZnTPP (**10**)	–19.6	1.26	–5.6	0.062
(1*E*)-2-[4-(Dibutylamino)phenyl]ethenyl-H_2TPP (**11**)	2.86	1.66	11.1	0.22
(1*E*)-2-[4-(Dibutylamino)phenyl]ethenyl-ZnTPP (**12**)	–16.8	0.99	–19.2	0.060

[a] H_2TPP is 5,10,15,20-tetraphenylporphyrin. [b] Not significantly solvatochromic.

and **9** but becomes more relevant for their Zn^{II} complexes **6** and **8**, with an abrupt increase for complex **10** (Table 3). The Q_β band of porphyrins **5**, **7** and **9**, which is only slightly shifted to lower energy (red shift) with increasing polarity of the solvent, becomes blue shifted in the Zn^{II} complexes **6** and **10** or remains unchanged in **8** (Table 3). As already reported,[32] the solvatochromic behaviour becomes insignificant when the nitro group is directly linked to the β pyrrolic position, suggesting that the solvatochromism must be ascribed to a charge-transfer process originated by a significant perturbation of the π frontier orbitals of the porphyrin ring through conjugation with π delocalised substituents (Table 3). Porphyrin **11**, with an arylethenyl linker carrying a dibutylamino group, and its Zn^{II} complex **12** show an unexpectedly significant solvatochromism, blue shifted for **12** and red shifted for **11**, of both B and Q_β bands. In this latter case it is difficult, however, to suggest that this solvatochromic behaviour may be due to a charge-transfer process involving conjugation of the π-delocalised linker and the porphyrin ring, since their B bands are symmetric with no increase of the bandwidth.[26] In this latter case the perturbation of the π system of the porphyrin, which influences the polarity of both the ground and excited states, probably involves the strongly donor dibutylamino group.

All porphyrins and their Zn^{II} complexes investigated in this work show a neat fluorescent emission band when irradiated either at the Soret B band or at the Q_β band. The intensity of the emission for both porphyrins and their Zn^{II} complexes is more relevant when the Soret B band is irradiated. Porphyrin **3** and its Zn^{II} complex **4**, with the nitro group directly bound to the β pyrrolic position, show, as already reported,[33] only one diffuse emission band (Table 1). The same behaviour is shown by the Zn^{II} complex **12**, with a dibutylamino group linked to the β pyrrolic position through an arylethenyl linker. The wavelength of the emission bands of both porphyrins and their Zn^{II} complexes is affected by the length of the π-delocalised linker, while it is not too affected by the substituents (Table 1). As with the absorption B and Q_β bands, the emission bands are also solvatochromic.

In conclusion, our detailed investigation of the electronic spectra and their solvatochromic behaviour has produced strong evidence for a significant perturbation of the π porphyrin ring by β pyrrolic substitution with a π-delocalised linker carrying a donor or acceptor group. This perturbation involves the conjugation of both the π orbital systems, as confirmed by the solvatochromic behaviour of both B and Q_β bands, but the significant excitation processes due to conjugation are different if the π-delocalised linker carries a push or a pull group.

Voltammetric Investigation

The anodic oxidation of porphyrins and their Zn^{II} complexes investigated in this work takes place by two reversible one-electron steps.[34,35] For porphyrin **11** and its Zn^{II} complex **12**, which carry a dibutylamino group, in addition to the two main peaks we noticed a small oxidation prewave located before the second (for **11**) and the first (for **12**) main oxidation peak (Table 4). Porphyrins **5**, **7** and **11**, with a different *para* substituent on the phenyl ring or a different π system connecting the phenyl group to the porphyrin ring, show the following oxidisability sequence for the first oxidation steps: **11** >> **7** > **5** (Table 4).

A significantly lower oxidation potential for the first oxidation step has already been reported for a porphyrin structurally related to **11** that carries a dimethylamino instead of a dibutylamino group.[21] For this latter porphyrin the second oxidation step was reported not to be reversible, while we found that for **11** it is reversible and not at significantly lower oxidation potential with respect to porphyrins **5** and **7** (Table 4). As a consequence, for porphyrin **11** it is better to take into account, when comparing its oxidisability with that of other porphyrins, the second oxidation step, which seems to be centred, as for other porphyrins, on the HOMO energies of the porphyrin π core. In fact, as already suggested,[21] the first step of oxidation of **11** could be centred off the HOMO energies of the porphyrin π core, probably at the dibutylamino functionality. The higher oxidisability of **11** and the slightly lower oxidisability of **5** with respect

Table 4. Oxidation and reduction peak potentials E_p (V vs. SCE) for three porphyrins and their Zn complexes (glassy carbon electrode, potential scan rate: 0.2 V s^{-1}).

	Cathodic peaks[a,b]		Anodic peaks[a,b]	
2-(4-Nitrophenyl)ethynyl-H$_2$TPP (**5**)	–1.53	–1.170 (–1.055)	*1.105*	*1.255*
(1*E*)-2-(4-Nitrophenyl)ethenyl-H$_2$TPP (**7**)		–1.180 (–0.955)	*1.075*	*1.225*
(1*E*)-2-[4-(Dibutylamino)phenyl]ethenyl-H$_2$TPP (**11**)	–1.55	–1.035	*0.655*	(0.935) *1.010*
2-(4-Nitrophenyl)ethynyl-ZnTPP (**6**)		*–1.015*	*0.862*	*1.155*
(1*E*)-2-(4-Nitrophenyl)ethenyl-ZnTPP (**8**)	–1.51	*–1.110*	*0.845*	*1.108*
(1*E*)-2-[4-(Dibutylamino)phenyl]ethenyl-ZnTPP (**12**)	–1.68	–1.28 (–1.0)	(0.390) *0.625*	*0.790*

[a] Reversibile monoelectronic peaks are italicised. [b] Prewaves are in parentheses.

to **7** (Table 4) can be interpreted as an increased stabilisation due to a significant perturbation, produced by the substituents carrying an electron-withdrawing nitro group, on the energy levels of the HOMO electrons, which stabilizes the π core of the porphyrin ring.

This effect is in agreement with a conjugation between the π system of the linker and the π orbitals of the porphyrin ring as proposed above. The slightly higher oxidisability of **7** with respect to **5** can be interpreted in terms of the higher efficiency of the triple bond of the linker in transmitting the perturbation of the electron-withdrawing nitro group to the porphyrin π core.

When a porphyrin ring is complexed to a metal like Zn^{II}, irrespective of the working medium and of the porphyrin structure, a fairly constant difference in the range from –0.31 to –0.16 V between the first oxidation potential of the Zn^{II} complex and that of its parent porphyrin has been reported.[35,36] This range of negative values is shown by two of the three couples investigated in this work: –0.24 V for **6** vs. **5** and –0.23 V for **8** vs. **7** (Table 4). When comparing **12** and **11**, the difference turns out to be –0.27 V only if taking into account the oxidation prewave of the Zn^{II} complex, while when comparing the first "regular" peak the difference (–0.03 V) appears to be anomalously low. However, when taking into account the second oxidation peak, as suggested above, the expected difference of –0.22 V is found. This is additional evidence that the first oxidation peak in porphyrin **11** does not involve the HOMO electrons of the π porphyrin core. The difference $\Delta E_{(\text{ox–red})}$ between the first oxidation and the first reduction process of porphyrins and their Zn^{II} complexes has been reported to be always within 2.25 ± 0.15 V (Kadish's relationship), as expected for a strictly ring-based process of oxidation and reduction.[35] For porphyrins **5** and **7**, the $\Delta E_{(\text{ox–red})}$ values obey Kadish's relationship (2.16 V and 2.26 V respectively), while again for porphyrin **11** this difference is only 1.69 V, if we consider the first "regular" reduction peak. It becomes 2.05 V, as expected, when the second reduction peak is taken into account. For Zn^{II} complexes **6**, **8** and **12** the values of $\Delta E_{(\text{ox–red})}$ deviate from Kadish's relationship (1.88 V for **6**, 1.96 V for **8** and 1.91 V for **12** when taking into account the first oxidation peak; the value becomes 2.07 V for **12** if we consider the second oxidation peak). It thus appears that the π levels of the Zn^{II} porphyrins investigated in this work are quite affected by the perturbation induced by the π system of the linker mainly when it carries a nitro group. Complexation of porphyrins to Zn^{II} results in a significant anticipation, with respect to the parent porphyrin, of both the first and second oxidation potentials, according to a relevant increase of the negative charge on the porphyrin ring (Table 4). However, complexation to Ni^{II} of porphyrin **7** results in only a slight difference of the oxidation potentials with respect to those of the parent porphyrin (e.g. +0.03 V for the first oxidation peak, 0.00 V for the second one),[21] in agreement with the suggestion of Kadish et al.[35] of a higher induction parameter of Ni^{II} (1.8) with respect to Zn^{II} (1.5), resulting in a negative charge on the porphyrin ring that is much less significant for the Ni^{II} complexes. Finally, although the detection of three or four one-electron reduction waves is usually reported for porphyrins and their metal complexes when working with an acceptably broad cathodic window,[37,38] in the present work, due to the less broad window when working in CH$_2$Cl$_2$ as solvent, we observed only the first two reduction peaks and only the first one for **6** and **7**. All the potentials but one (namely those of porphyrin **11**) fall within the expected range of 0.42 ± 0.03 V of difference between the first and the second reduction potential, namely 0.42 V for **5** (averaging between the first reduction peak and its shoulder), 0.40 V for **8**, 0.52 V for **11** and 0.40 V for **12**. The first reduction step appears to be clearly monoelectronic and reversible only for Zn^{II} complexes **6** and **8**.

As a conclusion, the voltammetric investigation has confirmed a perturbation of the HOMO levels of the porphyrin π core due to conjugation with the π orbitals of the linker bound to the β pyrrolic position. This perturbation is more significant if the π linker carries a nitro group and if the Zn^{II} ion is complexed to the porphyrin ring. When the π linker carries a donor dibutylamino group the perturbation of the π levels of the porphyrin ring is not only lower, but the HOMO levels are centred on the dibutylamino group.

Dipole Moments

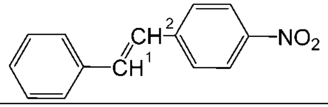
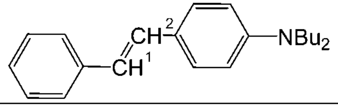
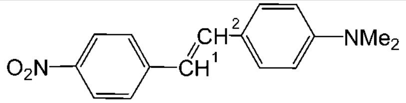
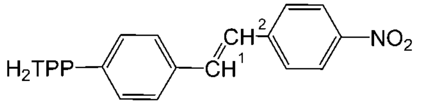
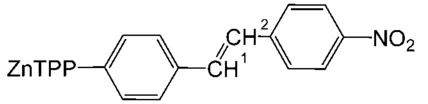
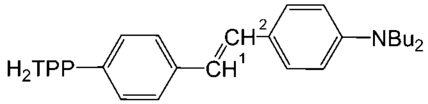
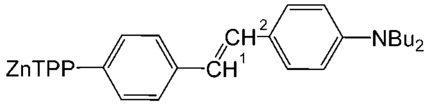
Although the experimental determination of the dipole moment by the Guggenheim method[39] was not reproducible for the push-pull porphyrins and their metal complexes investigated previously, such that it was always calculated by semi-empirical methods,[5,6] we obtained quite reproducible experimental measurements, with the exception of porphyrin **11** and its Zn^{II} complex **12** (see Exp. Sect.). Porphyrins **5**, **7** and **9**, which carry a linker with a nitro group, show a dipole moment comparable to that of their Zn^{II} complexes **6**, **8** and **10**. The nature of the linker, either phenylethynyl, phenylethenyl or even phenylbutan-1,3-dienyl, does not induce a significant effect on the order of magnitude of the experimental dipole moment (Table 5). The best geometries and dipole moments were calculated theoretically by an ab initio approach based on the density functional theory (DFT)[15,16] using an extended basis set[17] (see Experimental Section for details). The calculated optimised geometries always support a quite planar arrangement of the π porphyrin ring and the π system of the organic linker.

Table 5. Experimental and theoretical dipole moments, EFISH β_λ in $CHCl_3$ solution (1.907 µm incident wavelength) and β_0.

Compound[a]	μ_{exp} (μ_{theor}) [D]	$\beta_{1.907}$[b] [10^{-30} esu]	β_0[c] [10^{-30} esu]	$\mu\beta_0$ [10^{-48} esu]
2-Cyano-ZnTPP (**2**)	6.4 (5.43)	9.6[d]	7.30	46.7
2-Nitro-H_2TPP (**3**)	4.5 (5.40)[e]	6.8[d]	5.17	23.3
2-Nitro-ZnTPP (**4**)	6.4 (5.42)	13.4[d]	10.2	65.2
2-(4-Nitrophenyl)ethynyl-H_2TPP (**5**)	6.1 (8.55)[e]	30.1[f]	22.7	138.5
2-(4-Nitrophenyl)ethynyl-ZnTPP (**6**)	7.1 (8.82)	20.4[f]	11.3	80.2
(1*E*)-2-(4-Nitrophenyl)ethenyl-H_2TPP (**7**)	6.6 (8.31) [e]	39.3[f]	19.7	196.0
(1*E*)-2-(4-Nitrophenyl)ethenyl-ZnTPP (**8**)	7.0 (8.69)	29.7[f]	22.4	157
(1*E*,3*E*)-2-(4-Nitrophenyl)buta-1,3-dienyl-H_2TPP (**9**)	6.2 (9.30)[e]	42.8[f]	32.6	202
(1*E*,3*E*)-2-(4-Nitrophenyl)buta-1,3-dienyl-ZnTPP (**10**)	7.1 (9.46)	43.1[f]	32.6	231
(1*E*)-2-[4-(Dibutylamino)phenyl]ethenyl-H_2TPP (**11**)	(5.33)[e][h]	75.7[f][g]	57.9	308.6
(1*E*)-2-[4-(Dibutylamino)phenyl]ethenyl-ZnTPP (**12**)	(5.16)[h]	127.5 [f][g]	97.5	503.1

[a] H_2TPP is 5,10,15,20-tetraphenylporphyrin. [b] Obtained from Equation (2) (see text) omitting the cubic contribution γ(–2ω; ω, ω, 0). [c] Calculated from the two levels model assuming only the B band as the main charge-transfer process [Equation (2)]. [d] The error is ±20–30%. [e] The theoretical value is the semi-sum of the theoretical dipole moments of two isomeric structures. [f] The error is ±10–15%. [g] Using theoretical dipole moment. [h] Theoretical value calculated by an ab initio approach.

Table 6. A comparison of the dipole moments and ^{1}H NMR spectroscopic data of a series of (*E*)-arylethenyl structures.

Compound	µ(D)	H^1 [ppm])[a]	H^2 [ppm][a]	J_{H1-H2} [Hz][a]
	4.56[b]	7.13	7.25	16.2
	1.07[b]	6.92	7.03	–
	7.42[b]	6.93	7.21	16
[d] 	6.6[a] (8.31)[c]	7.11	7.29	16
[d] 	7.0[a] (8.69)[c]	7.18	7.24	16
[d] 	5.33[c]	6.72	7.28	16
[d] 	5.16[c]	6.82	7.22	16

[a] In $CHCl_3$ or $CDCl_3$ at 25 °C. [b] In benzene at 25 °C. [c] Calculated by an ab initio approach based on DFT Theory (see Exp. Sect. and Table 5). [d] The stilbene substituent is linked to the β pyrrolic position of the porphyrin ring.

The calculated dipole moments of the two isomeric structures of asymmetric porphyrins **3**, **5**, **7**, **9** and **11** are quite similar, thus the data reported in Table 5 are mean values. They are in good agreement with the experimental ones with the exception of the couple **9** and **10**. For porphyrin **11** and its Zn^{II} complex **12** the calculated dipole moments are, as expected, rather low and with inversion of polarity (Table 5). In this latter case, complexation to Zn^{II} induces a slight lowering of the dipole moment with respect to the free porphyrin, in agreement with an increased negative charge on the porphyrin ring acting as acceptor. As expected, the opposite effect is calculated and observed experimentally for the couples **5** and **6**, **7** and **8**, and **9** and **10** (Table 5). The order of magnitude of the dipole moments of porphyrins **5**, **7** and **9** and their Zn^{II} complexes **6**, **8** and **10**, with a linker carrying a nitro group, supports a significant electronic asymmetry.

In conclusion, according to theoretical calculations the substitution of the electron-withdrawing nitro group by the strongly electron-donating dibutylamino group introduces a lower electronic asymmetry with a completely opposite polarity. Therefore, we have further evidence that, already in the ground state, the conjugation of the π systems produces a completely opposite electronic effect: the porphyrin ring acts as an electron donor if the linker carries a nitro group, while it acts as an electron acceptor if the linker carries a dibutylamino group. This ambivalent picture of the ground-state electronic density of the porphyrins and their Zn^{II} complexes investigated in this work can be better measured when comparing their dipole moments and ^1H NMR chemical shifts with those of a series of (*E*)-stilbene structures (Table 6).

If compared to the benzene ring, the porphyrin ring, as such or as a Zn^{II} complex, behaves as a much better acceptor and a slightly better donor on the basis of both dipole moments and chemical shifts of the protons of the (*E*)-double bond when linked through the β pyrrolic position. It shows, however, lower donor properties than a benzene ring carrying a dimethylamino group in the *para* position. Therefore, already in the ground state, a porphyrin ring substituted in the β pyrrolic position with a push or pull aryl ethenyl system shows a relevant ambivalent role as donor or acceptor.

Determination of the Quadratic Hyperpolarizability by the EFISH Technique

The EFISH technique[40] allows the determination of the second-order NLO response, γ_{EFISH}, of a solute. In order to avoid resonance enhancement, we worked with an off-resonance incident wavelength of 1.907 µm (see Experimental Section).

In highly π conjugated two dimensional molecules, such as porphyrins and phthalocyanines, the electronic contribution to γ_{EFISH} in Equation (3) (see Experimental Section) cannot, at first instance, be ignored.[5c,41] However, for asymmetrically substituted phthalocyanines, structurally related to our porphyrinic chromophores, carrying an arylethenyl or an arylbutadienyl spacer with a nitro group in the *para* position, the electronic contribution to γ_{EFISH} was evaluated to be much smaller than the dipolar orientational one.[41] In accordance, we neglected the electronic contribution during the evaluation of EFISH $\beta_{1.907}$ from γ_{EFISH}.

Our push-pull porphyrinic chromophores are characterised by a dipole moment axis directed quite parallel to the π linker axis, as confirmed by our DFT calculations on the dipole moments and best geometries. It follows that a charge-transfer process involving the π linker, which may control the second-order NLO response, is probably located quite parallel to this axis, as in traditional two-dimensional, pseudo-linear, organometallic push-pull chromophores.[42] If so, the component of β_{vec} along the dipole moment axis, that is EFISH $\beta_{1.907}$ (see Experimental Section), should be quite coincident with β_{vec}, which is the vectorial part of the quadratic hyperpolarizability tensor. EFISH $\beta_{1.907}$ turns out to be small for porphyrin **3** and for the Zn^{II} complexes **2** and **4**, with the electron-withdrawing group linked directly to the β pyrrolic position (Table 5). The order of magnitude of the quadratic hyperpolarizabilities of **3** and **4** is in agreement with that of a structurally related porphyrin and its Zn^{II} complex but carrying completely fluorinated aromatic rings in *meso* positions, although in this latter case the quadratic hyperpolarizability was measured with the HRS technique (Hyper Raleigh Scattering) working with a resonant incident wavelength of 1.064 µm.[12b] In this latter case, on the basis of solvatochromic evidence the major contribution to the second-order NLO response was attributed to a charge-transfer process from the porphyrin ring (as donor) to the nitro group linked to the β pyrrolic carbon atom (as acceptor) along the dipole moment axis, as assumed above.[43] The very low second-order NLO response of chromophores **2**–**4** is in accordance with the assumption that acceptor groups appended to an electron-rich centre, like the β position of the porphyrin ring, should not produce large NLO responses.[13,14] The values of EFISH $\beta_{1.907}$ increase upon introduction of a π-delocalised linker between the β pyrrolic position of the porphyrin ring and the electron-withdrawing nitro group (Table 5). As in structurally related pseudo-linear, organometallic, push-pull chromophores[42] and in structurally related push-pull phthalocyanines,[41] EFISH $\beta_{1.907}$ increases slightly upon increasing the length of the linker or by substitution of a triple bond with an (*E*)-double bond. We have also shown that EFISH $\beta_{1.907}$ always decreases slightly on going from the free porphyrin to its Zn^{II} complex, with the exception of the couple **9** and **10**, which show comparable values (Table 5).

This limited effect of coordination to Zn^{II} is in agreement with the assumption that the second-order NLO response is controlled by a charge-transfer process, favoured by conjugation, from the occupied π levels of the pyrrolic ring, acting as a push system, to the π* antibonding orbitals of the linker. In fact, this latter process should be scarcely affected by coordination of the porphyrin to Zn^{II}, which mainly influences the energy of the a_{2u} porphyrin orbital, with nodes at the metal centre and little electron density on the *exo* pyrrole positions.[10,25]

The positive value of the second-order NLO response of porphyrins with a nitro group linked to the β pyrrolic position by a π linker (**5**, **7**, **9** and **6**, **8**, **10**) also supports the role of such a charge-transfer process, which is characterised by the same polarity of the dipole moment.[42]

Interestingly, the values of EFISH $\beta_{1.907}$ of our porphyrinic chromophores **5**–**10** are comparable to that of structurally related chromophores based on the phthalocyanine ring.[41]

A larger and still positive second-order NLO response, confirmed by a series of experimental determinations in two different laboratories (see Experimental Section), was found by substitution of the nitro group with the strongly electron donating dibutylamino group as in porphyrin **11** and its Zn^{II} complex **12**. The second-order NLO response increases by complexation to Zn^{II} (Table 5). This response of both **11** and **12** cannot be due to a charge-transfer process, as above, from the occupied π orbitals of the pyrrolic ring to the π* antibonding orbitals of the π linker, since this process should produce a negative second-order NLO response as its polarity is opposite to that of the calculated dipole moment.[42] It is known that in push-pull NLO molecules the nature of the π conjugation can alter the electron donating ability of push substituents.[13] Thus, we can tentatively propose that the high EFISH $\beta_{1.907}$ values of both **11** and **12** are due to a relevant increase of the electronic effects of the donor properties of the dibutylamino group induced by an extended π system involving the porphyrin ring, possessing π segments that are either electron rich or electron poor.[14] The conjugation process of the overall π system of the linker with the extended π system of the porphyrin ring should stabilize the π* antibonding levels, thus producing a shift of the n→π* transition, which is the main origin of the second order NLO response, to much lower energy. In accordance with this hypothesis, this latter transition, which is usually located around 370–390 nm in *para*-dimethylaminostilbazoles,[42] is absent in the electronic spectra of both **11** and **12**, thus supporting a relevant red shift, probably under the large B band or even under the Q bands at much lower energy. In any case, our experimental observations are in agreement with the suggestion, based on a theoretical approach, of Marks, Ratner et al.[14] that the linkage to the electron-rich β pyrrolic position of a π system carrying a strong electron donating dibutylamino group may be the origin of some depletion of electron density on the donor and thereby of the reduction of the ground-state polarisation with an increase of the effective strength of the donor substituent and thereby of the second-order NLO response.[14] The significant increase of EFISH $\beta_{1.907}$ by coordination of **11** to Zn^{II} is in agreement with this hypothesis because complexation introduces a significant increase of the electron density on the porphyrinic ring, as confirmed by our voltammetric investigation. The significant second-order NLO response cannot be attributed to a aggregation process, which was discarded by a careful spectroscopic investigation carried out over a large range of concentrations.

Finally, the static quadratic hyperpolarizability EFISH, β_0, was calculated with the two-levels model,[44] according to Equation (1), assuming that the major charge-transfer process affecting the second-order NLO response is under the Soret B band.

$$\beta_0 = \beta_{1907}\left[1-\left(\frac{2\lambda_{\max}}{1907}\right)^2\right]\left[1-\left(\frac{\lambda_{\max}}{1907}\right)^2\right] \quad (1)$$

The dominant role of the Soret B band is supported by its significant charge-transfer character in all our porphyrinic chromophores, as evidenced by the solvatochromic investigation (Table 3) and by its high intensity. Any contribution due to the Q bands, in particular the Q_β band, which is not only slightly solvatochromic, but also of much lower intensity, should be much less relevant.

Obviously, the application of the two-levels model to an extended two-dimensional π system, although already applied to porphyrins[6a,6b] and phthalocyanines,[41] is quite debatable. Therefore, the β_0 values calculated by this approach should be considered only for their order of magnitude.

Conclusions

In this work we have produced, for the first time, clear evidence for a significant perturbation of the energy of the π electron core of the porphyrin ring due to conjugation between the porphyrinic π system, when substituted at the β pyrrolic position with a π delocalised linker carrying a nitro group, and the π system of the linker itself. The asymmetric shape and increased bandwidth of the B band, the Shelnutt analysis,[28] the trend of the centre of gravity of the B and Q_α bands and the sensitivity of the first two voltammetric oxidation steps, which involve the HOMO orbitals, with respect to the nature of the π linker, all support this perturbation, where the porphyrin ring, because of the electron-richness of the β position,[14] acts as an electron donor. This effect seems to be less relevant when the π linker carries a dibutylamino group. In this latter case the HOMO orbitals are centred on this group. Therefore, we have produced clear evidence that, already in the ground state, the porphyrin ring shows an ambivalent character, acting also as an acceptor, as supported, for instance, by the value and polarity of the dipole moments of porphyrin **11** and its Zn^{II} complex **12**, both of which have a linker carrying the strongly electron-donating dibutylamino group.

In the electron excitation process, the significant conjugation of the π levels of both the porphyrin ring and linker facilitates a charge transfer from the occupied π levels of the porphyrin π core, acting as a push group, to the antibonding π* orbitals of the linker carrying the pull nitro group, thus producing positive values of EFISH $\beta_{1.907}$ of the chromophores either as porphyrins (**5**, **7** and **9**) or as their Zn^{II} complexes (**6**, **8** and **10**) (Table 5). Evidence for a charge-transfer process from the porphyrin ring is also provided by the significant solvatochromic behaviour of both B and Q_β bands and by the asymmetric shape and increased bandwidth of the B band of chromophores **5**–**10**.

In order to evaluate the unknown push properties of the β position of the porphyrin ring we can compare, for instance, the quadratic hyperpolarizability EFISH $\beta_{1.907}$ of the push-pull chromophore **8** with that of structurally related push-pull chromophores having an organic aryl moiety or an organometallic system like ferrocene as push groups (Figure 5). The EFISH $\beta_{1.907}$ of **8** is comparable to that of the chromophore carrying a ferrocenyl push group[45] but much smaller than the organic chromophore with *para*-dimethylamino as the push group.[46] A similar trend is observed for the porphyrinic chromophore having a butadienyl linker like the Zn^{II} complex **10**, which shows a value of EFISH $\beta_{1.907}$ comparable to that of the structurally related chromophore carrying a push ferrocenyl group,[45] but much smaller than that of the organic chromophore with the *para*-dimethylamino push group.[46] Not very different is the trend with respect to the structurally related organic chromophore when the linker is acetylenic (Figure 5).

Therefore, *meso*-tetraphenylporphyrins and their Zn^{II} complexes, carrying in the β pyrrolic position a π-delocalised linker with an electron-withdrawing nitro group, behave, in a push-pull chromophore, as a push group similar to the ferrocenyl group.

The ambivalent character of the porphyrin ring in the porphyrins and their Zn^{II} complexes investigated in this work is confirmed also by properties involving excited states, like the second-order NLO response. The lack of bandwidth increase of the B band, its symmetry and the lower perturbation of the centre of gravity of the B and Q_α bands for both **11** and **12** do not produce evidence for an excitation process involving a significant charge-transfer from the π porphyrin core to the π linker, as occurs in the series of chromophores **5**–**10**. On the contrary, the significant positive EFISH $\beta_{1.907}$ values of **11** and **12** would suggest an effective screening of the ground-state polarisation induced by the electron-rich β pyrrolic position of the porphyrin ring, which behaves as a kind of acceptor and increases, in the excitation process, the donor properties of the dimethylamino push group.[14]

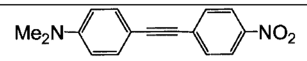
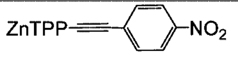
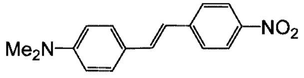
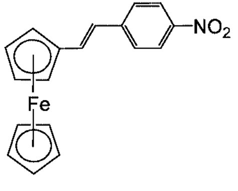
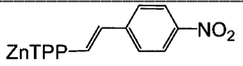
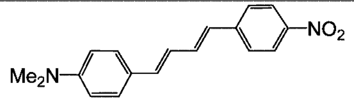
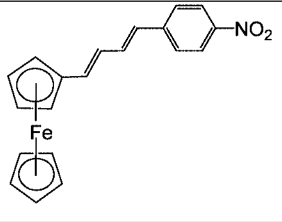
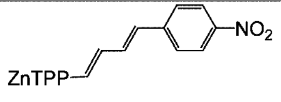
Compound	$\beta_{1.907}$ 10^{-30} [esu]
	46[a]
 **(6)**	20.4[b]
	73[a]
	31[c]
 **(8)**	29.7[b]
	107[a]
	47[c]
 **(10)**	43.1[b]
[a] Ref. [46]; [b] This work; [c] Ref. [45]	

Figure 5. Quadratic hyperpolarizability ($\beta_{1.907}$) of some organic and organometallic push-pull systems measured in $CHCl_3$ by the EFISH technique at an incident wavelength of 1.907 µm.

Experimental Section

All the commercially available solvents and chemicals were of reagent-grade quality and, unless otherwise stated, were used without further purification. Porphyrin **3**,[20] its Zn^{II} complex **4**[20] and 4-nitrophenylacetylene[47] were prepared according to literature methods. ^1H NMR spectra were recorded on a Bruker AC-300 Spectrometer in $CDCl_3$ as solvent. Electronic spectra were obtained in $CHCl_3$ with a Jasco V-530 Spectrometer. Emission spectra were obtained in $CHCl_3$ with a Jasco FP-777 spectrofluorimeter. FAB-MS measurements were performed with an analytical VG 7070 EQ instrument. Elemental analyses were carried out in the Analytical Laboratories of the Department of Inorganic, Metallorganic and Analytical Chemistry of Milan University. Dipole moments were determined in $CHCl_3$ solution with a WTW-DM01 dipolmeter (dielectric constant) coupled with a Pulfrich Zeiss PR2 refractometer (refractive index) according to the Guggenheim method.[39]

Cyclic Voltammetry: Cyclovoltammetric investigations (CV) were carried out on carefully deaerated solutions with a station including an AMEL 2049 potentiostat/galvanostat, an AMEL 568 function generator and a Lynseis LY16100-II *x*/*y* recorder. The working solutions were made up with HPLC-grade CH_2Cl_2 and tetrabutylammonium perchlorate (TBAP; >99% Fluka) at concentrations ranging from 3×10^{-4} M to 7×10^{-4} M. Data were obtained at different potential scan rates (ranging from 0.02 to 0.5 V s^{-1}) working with two different electrodes: (a) an AMEL glassy carbon disk electrode (GC, 2 mm diameter), and (b) a platinum wire electrode (Pt, 1 cm length, 0.05 cm diameter), using a platinum counter-electrode and a saturated calomel electrode (SCE) as reference. The nearly identical voltammograms indicate that the electrode materials have no catalytic effect on the oxidation process.

The electrochemical reversibility and electron number of each well-defined peak were checked by classical tests,[48] including analysis of the I_p vs. $v^{1/2}$ characteristics, the E_p vs. log$v$ characteristics, the (E_p – $E_{p/2}$) vs. log$v$ characteristics and the "stationary", step-like waves obtained by convolutive analysis of the original CV characteristics.

Solvatochromic Investigation: The solvatochromic behaviour of the Soret B and Q_β bands was investigated by using a set of polar, nonprotic and only weakly donor solvents (CH_3CN, acetone, dichloroethane, CH_2Cl_2, THF, ethyl acetate, $CHCl_3$, toluene, CCl_4, cyclohexane, *n*-hexane). The values of $\Delta\mu_{eg}$, the difference between the dipole moments of the excited and of the ground state, were obtained from the Mc Rae equation (2)[49] evaluating the radius of the cavity, *a*, occupied by the solute in the solvent empirically from the molecular weight:

$$\nu_a = \nu_a^{\,g} + A\frac{2(n^2-1)}{a^3(2n^2-1)} + B\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right); \quad B = \frac{-2\mu\Delta\mu_{eg}}{hca^3} \qquad (2)$$

where ν_a and $\nu_a^{\,g}$ are the frequencies of the absorption maximum in a given solvent and in the gas phase, respectively, μ is the dipole moment, *a* is the radius of the cavity (cm), and ε and *n* are the solvent dielectric constant and refractive index, respectively. Since in the determination of $\Delta\mu_{eg}$ of both B and Q_β bands we were not interested in their absolute value, but only in their order of magnitude and sign, the use of the molecular weight for a rather approximate assignment of the value of *a* (cavity radius) to rather flat molecules, such those studied in this work, may be considered acceptable.

EFISH Measurements: EFISH measurements were performed in our department in $CHCl_3$ solutions, as a function of concentration, working at an incident wavelength of 1.907 µm using a Q-switched Nd:YAG laser with a 60- and 20-ns pulse duration, manufactured by Atalaser. The 1.907 µm fundamental wavelength was obtained by Raman shifting of the 1.064 µm emission of the 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 (harmonic intensity variation as a function of liquid cell translation).[40] In the EFISH experiments the incident beam was synchronised with a DC field applied in order to break the centrosymmetry of the solution. The apparatus for the EFISH measurements was a prototype made by SOPRA (France).

From the concentration dependence (10^{-3}–10^{-4} M) of the harmonic signal with respect to that of the pure solvent, the NLO responses EFISH β_λ, were determined from the calculated γ_{EFISH}, according to Equation (3):

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

where γ_{EFISH} is the sum of a cubic electronic contribution $\gamma(-2\omega;\omega,\omega,0)$ and of a quadratic orientational contribution $\mu\beta_\lambda(-2\omega;\omega,\omega)/5kT$, where μ is the dipole moment and EFISH β_λ is the projection along the dipole moment direction of the vectorial component β_{vec} of the tensorial quadratic hyperpolarizability, β, at the incident wavelength λ.

Computational Methods: The optimised geometry of porphyrins as two geometric isomers and of their Zn^{II} complexes was determined at an ab initio level using the DFT (Density Functional Theory) approach[15] adopting the BP86 functional[16] and an all-electron valence triple-ξ basis set with polarisation functions on all atoms (TZVP).[17] The ab initio DFT approach was undertaken because previous experiences[6d] have shown that semi-empirical Hamiltonians like MNDO or AM1 do not produce optimised geometries for the extended π conjugation when the linker is based on a styryl or phenylbutadienyl structure. A loss of planarity of the π linker and therefore a decrease of the π conjugation is usually the final result.

The final geometry of all the porphyrinic systems investigated, either as the free-base porphyrin or its Zn^{II} complex, shows a good planarity of the π linker with the π system of the porphyrinic moiety. The values of the dipole moments moduli and components were finally computed using the Turbomole suite of programs[50] in connection with the resolution of the identity (RI) approximation.[51]

Synthesis of Porphyrins and Their Zn^{II} Complexes

2-Bromo-5,10,15,20-tetraphenylporphyrinatonickel(II): 2-Bromo-5,10,15,20-tetraphenylporphyrin (205 mg, 0.296 mmol) was dissolved in slightly warmed 1,2-dichloroethane (30 mL) whilst stirring, then $Ni(acac)_2$ (84 mg, 0.326 mmol) was added. After 45 minutes the complete disappearance of the starting porphyrin was evidenced by TLC (*n*-hexane/toluene, 7:3) and by the change of the colour of the reaction mixture from brown to red and finally to orange. After removal of the solvent in vacuo, the crude product was crystallised with CH_2Cl_2/pentane and washed with pentane to afford the complex in quantitative yield.

2-Cyano-5,10,15,20-tetraphenylporphyrin (1): This porphyrin was prepared by demetallation of its Ni^{II} complex, synthesised according to a literature procedure.[18] 2-Cyano-5,10,15,20-tetraphenylporphyrinatonickel(II) (50 mg) was dissolved in 95% H_2SO_4 (2 mL) with magnetic stirring. The green solution was slowly added to a saturated solution of $(NH_4)_2CO_3$ and the dark brown suspension was filtered. The mother liquor was extracted with CH_2Cl_2 (2×60 mL), and the organic phase was washed with H_2O, dried with Na_2SO_4 and the solvents evaporated to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane, 1:1) to afford 43 mg (94%) of pure **1** as a dark brown powder. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.80 (br. s, 2 H, NH), 7.71–7.81 (m, 12 H, $H_{m,pPh}$), 8.16–8.19 (m, 8 H, H_{oPh}), 8.74 (s, 2 H, $H_{pyrrolic}$), 8.90–8.98 (m, 4 H, $H_{pyrrolic}$), 9.36 (s, 1 H, $H_{pyrrolic}$) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 420 (5.29), 517 (3.79), 552 (3.21), 605 (3.53), 593 (3.23), 648 (3.20) nm. $C_{45}H_{29}N_5$ (639): calcd. C 84.48, H 4.57, N 10.95; found C 84.40, H 4.73, N 10.94. MS-FAB(+): *m*/*z* = 640 $[M + 1]^+$.

2-Nitro-5,10,15,20-tetraphenylporphyrin (3): A solution of the Zn^{II} complex **4** (68.3 mg, 0.094 mmol) in 50 mL of CH_2Cl_2 was stirred at room temperature with 1.5 mL of concentrated HCl for 5 min, then the pH was raised to 7–8 by addition of NEt_3. The brown solution was transferred into a separating funnel and washed with H_2O, the organic phase was separated, dried with Na_2SO_4, evaporated and the residue purified by column chromatography (silica gel, toluene) to afford pure **3** (quantitative yield) as a violet powder. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.58 (br. s, 2 H, NH), 7.71–7.83 (m, 12 H, $H_{m,pPh}$), 8.20–8.29 (m, 8 H, H_{oPh}), 8.91–9.05 (m, 6 H, $H_{pyrrolic}$), 9.07 (s, 1 H, $H_{pyrrolic}$) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 427 (5.24), 527 (4.14), 560 (3.56), 605 (3.53), 665 (3.88) nm. $C_{44}H_{29}N_5O_2$ (659): calcd. C 80.10, H 4.43, N 10.62; found C 80.40, H 4.42, N 10.60. MS-FAB(+): *m*/*z* = 660 $[M + 1]^+$.

2-[2-(4-Nitrophenyl)ethyn-1-yl]-5,10,15,20-tetraphenylporphyrin (5): A solution of Zn^{II} complex **6** (60 mg, 0.073 mmol) and trifluoroacetic acid (1 mL) in CH_2Cl_2 (25 mL) was stirred at room temperature for 12 h. The volatiles were removed in vacuo to afford a dark-green residue which was dissolved in CH_2Cl_2 (100 mL) and carefully washed with a 5% aqueous solution of $NaHCO_3$ (2×50 mL) and with H_2O (2×50 mL), dried with Na_2SO_4 and the solvents evaporated to dryness. The residue was crystallised from CH_2Cl_2/*n*-hexane to afford 52 mg (94%) of **5** as a red-brown powder. ^1H

NMR (300 MHz, $\mathrm{CDCl_3}$): δ = –2.65 (br. s, 2 H, NH), 7.49 (AA′BB′, 2 H, $\mathrm{H_{Ar}}$), 7.60–7.83 (m, 12 H, $\mathrm{H}_{m,p\mathrm{Ph}}$), 8.15–8.22 (m, 10 H, 8$\mathrm{H}_{o\mathrm{Ph}}$, 2$\mathrm{H_{Ar}}$), 8.78–8.91 (m, 6 H, $\mathrm{H_{pyrrolic}}$), 9.13 (s, 1 H, $\mathrm{H_{pyrrolic}}$) ppm. UV/Vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$ (logε) = 430 (5.26), 525 (4.31), 562 (3.83), 601 (3.78), 657 (3.68) nm. $\mathrm{C_{52}H_{33}N_5O_2}$ (759): calcd. C 82.19, H 4.38, N 9.22; found C 81.75, H 4.40, N 8.96. MS-FAB(+): *m*/*z* = 760 $[\mathrm{M} + 1]^+$.

2-[(1*E*)-2-(4-Nitrophenyl)ethen-1-yl]-5,10,15,20-tetraphenylporphyrin (7): Solid NaOH (400 mg, 10 mmol) was added to a solution of (4-nitrobenzyl)triphenylphosphonium bromide (596 mg, 1.25 mmol) and 2-formyl-5,10,15,20-tetraphenylporphyrin (**13**; 160 mg, 0.25 mmol) in 30 mL of 1,2-dichloroethane and the resulting suspension was heated at reflux and stirred for 8 h. Then, the reaction mixture was diluted with 150 mL of $\mathrm{CH_2Cl_2}$, washed with 100 mL of $\mathrm{H_2O}$ and the organic phase was separated, dried with $\mathrm{Na_2SO_4}$ and the solvents evaporated. The residue was purified by column chromatography (silica gel, $\mathrm{CH_2Cl_2}$) to afford 160 mg of product as a mixture 80:20 of (*E*)- and (*Z*)-isomers. This mixture was purified by crystallisation from $\mathrm{CH_2Cl_2/CH_3OH}$ to afford 110 mg (58%) of pure (*E*)-isomer **7**. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = –2.60 (br. s, 2 H, NH), 7.11 (d, *J* = 16.0 Hz, 1 H, $\mathrm{H_{ethenyl}}$), 7.29 (d, *J* = 16.0 Hz, 1 H, $\mathrm{H_{ethenyl}}$), 7.30 (d, *J* = 8.6 Hz, 2 H, $\mathrm{H_{Ar}}$), 7.74–7.86 (m, 12 H, $\mathrm{H}_{m,p}$), 8.14–8.24 (m, 10 H, 8$\mathrm{H}_{o\mathrm{Ph}}$, 2$\mathrm{H_{Ar}}$), 8.70–8.82 (m, 6 H, $\mathrm{H_{pyrrolic}}$), 9.01 (br. s, 1 H, $\mathrm{H_{pyrrolic}}$) ppm. UV/Vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$ (logε) = 431 (5.31), 525 (4.34), 569 (4.13), 602 (3.94), 659 (3.47) nm. $\mathrm{C_{52}H_{35}N_5O_2}$ (761): calcd. C 81.9, H 4.64, N 9.20; found C 81.6, H 4.62, N 9.16. MS-FAB(+): *m*/*z* = 762 $[\mathrm{M} + 1]^+$.

2-{(1*E*)-2-[4-(Dibutylamino)phenyl]ethen-1-yl}-5,10,15,20-tetraphenylporphyrin (11): Solid NaOH (480 mg, 12 mmol) was added to a solution of [4-(dibutylamino)benzyl]triphenylphosphonium bromide (258 mg, 0.5 mmol) and 2-formyl-5,10,15,20-tetraphenylporphyrin (**13**; 193 mg, 0,3 mmol) in 25 mL of $\mathrm{CH_2Cl_2}$, and the resulting suspension was stirred at room temperature for 4 h. Then, the reaction mixture was purified by column chromatography (silica gel, $\mathrm{CH_2Cl_2}$) to afford 205 mg of product as a 9:1 mixture of (*E*)- and (*Z*)-isomers. This product was crystallised from $\mathrm{CH_2Cl_2}$/*n*-pentane to give 175 mg (69%) of pure (*E*)-isomer **11**. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = –2.60 (br. s, 2 H, NH), 1.01 (t, *J* = 7.20 Hz, 6 H, $\mathrm{CH_{3\ butyl}}$), 1.20–1.70 (m, 4 H, 2$\mathrm{CH_{2\ butyl}}$), 3.34 (t, *J* = 7.60 Hz, 4 H, $\mathrm{NCH_2}$), 6.60 (d, *J* = 8.80 Hz, 2 H, $\mathrm{H_{Ar}}$), 6.72 (d, *J* = 16.0 Hz, 1 H, $\mathrm{H_{ethenyl}}$), 7.12 (d, *J* = 8.80 Hz, 2 H, $\mathrm{H_{Ar}}$), 7.28 (d, *J* = 16.0 Hz, 1 H, $\mathrm{H_{ethenyl}}$), 7.65–7.88 (m, 12 H, $\mathrm{H}_{m,p\mathrm{Ph}}$), 8.15–8.30 (m, 8 H, $\mathrm{H}_{o\mathrm{Ph}}$), 8.65–8.85 (m, 6 H, $\mathrm{H_{pyrrolic}}$), 8.96 (s, 1 H, $\mathrm{H_{pyrrolic}}$) ppm. UV/Vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$ (logε) = 422 (5.36), 521 (4.41), 579 (4.16), 603 (4.14), 660 (3.71) nm. $\mathrm{C_{60}H_{53}N_5}$ (843): calcd. C 85.37, H 6.33, N 8.30; found C 85.0, H 6.35, N 8.26. MS-FAB(+): *m*/*z* = 844 $[\mathrm{M} + 1]^+$.

2-[(1*E*,3*E*)4-(4-Nitrophenyl)-1,3-butadienyl]-5,10,15,20-tetraphenylporphyrin (9): 1,8-Diazabicyclo[5.4.0]-undec-7-ene (DBU; 509 mg, 3.34 mmol) was added to a solution of the phosphonium salt of the tetraphenylporphyrin **16** (52 mg, 0.0562 mmol) and 4-nitrocinnamaldehyde (12 mg, 0.0674 mmol) in $\mathrm{CH_2Cl_2}$ (5 mL), and the mixture was maintained under magnetic stirring and at room temperature for one hour. The product was isolated by column chromatography (silica gel; toluene/cyclohexane, 9:1) and further purified by crystallisation from $\mathrm{CH_2Cl_2}$/*n*-hexane to afford 38 mg (86%) of pure **9** as a purple solid. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = –2.56 (s, 2 H, NH), 6.40 (d, 1 H, $\mathrm{H_{butyl}}$), 6.74 (d, 2 H, $\mathrm{H_{butyl}}$), 7.17 (m, 1 H, $\mathrm{H_{butyl}}$), 7.54 (d, 2 H, $\mathrm{H_{Ar}}$), 7.78 (m, 12 H, $\mathrm{H}_{o,p\mathrm{Ph}}$), 7.79 (m, 6 H, $\mathrm{H_{pyrrolic}}$), 8.15 (d, *J* = 6.98 Hz, 2 H, $\mathrm{H_{Ar}}$), 8.23 (m, 8 H, $\mathrm{H}_{m\mathrm{Ph}}$), 8.95 (s, 1 H, $\mathrm{H_{pyrrolic}}$) ppm. UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ (logε) = 425 (5.03), 523 (4.21), 572 (4.07), 601 (3.86), 665 (3.51) nm. $\mathrm{C_{54}H_{37}N_5O_2}$ (787): calcd. C 82.32, H 4.73, N 8.89; found C 82.0, H 4.60, N 8.70. MS-FAB(+): *m*/*z* = 788 $[\mathrm{M} + 1]^+$.

Synthesis of $\mathrm{Zn^{II}}$ Complexes: $\mathrm{Zn^{II}}$ complexes **2**, **8**, **10** and **12** were synthesised following the general procedure described in the literature.[19] In a typical preparation, the free porphyrin (100 mg) was dissolved in slightly warmed $\mathrm{CHCl_3}$ (50 mL) and a solution of $\mathrm{Zn(OAc)_2 \cdot 2H_2O}$ (free porphyrin/metal salt = 1:3) in MeOH (5 mL) was then added. The mixture was heated at reflux for 2 h and the progress of the reaction was monitored by TLC. After removal of the solvent in vacuo, the crude product was purified by crystallisation or by washing with methanol.

2-Cyano-5,10,15,20-tetraphenylporphyrinatozinc(II) (2): The violet powder was crystallised from $\mathrm{CH_2Cl_2}$/*n*-pentane. Yield: 98%. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = 7.60–7.80 (m, 12 H, $\mathrm{H}_{m,p\mathrm{Ph}}$), 8.12–8.20 (m, 8 H, $\mathrm{H}_{o\mathrm{Ph}}$), 8.87–8.93 (m, 6 H, $\mathrm{H_{pyrrolic}}$), 9.46 (br. s, 1 H, $\mathrm{H_{pyrrolic}}$) ppm. UV/Vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$ (logε) = 427 (5.62), 518 (3.57), 555 (4.20), 593 (4.02) nm. $\mathrm{C_{45}H_{27}N_5Zn}$ (702): calcd. C 76.87, H 3.87, N 9.96; found C 76.52, H 3.88, N 9.92. MS-FAB(+): *m*/*z* = 703 $[\mathrm{M} + 1]^+$.

2-[(1*E*)-2-(4-Nitrophenyl)ethen-1-yl]-5,10,15,20-tetraphenylporphyrinatozinc(II) (8): The blue-violet powder was washed with *n*-hexane and a small amount of MeOH in order to eliminate the excess of $\mathrm{Zn(OAc)_2}$. Yield: 90%. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = 7.18 (d, *J* = 16.0 Hz, 1 H, $\mathrm{H_{ethenyl}}$), 7.24 (d, *J* = 16.0 Hz, 1 H, $\mathrm{H_{ethenyl}}$), 7.37 (d, *J* = 8.6 Hz, 2 H, $\mathrm{H_{Ar}}$), 7.76- 7.85 (m, 12 H, $\mathrm{H}_{m,p\mathrm{Ph}}$), 8.19–8.28 (m, 10 H, 8$\mathrm{H}_{o\mathrm{Ph}}$, 2$\mathrm{H_{Ar}}$), 8.82–8.96 (m, 6 H, $\mathrm{H_{pyrrolic}}$), 9.16 (br. s, 1 H, $\mathrm{H_{pyrrolic}}$) ppm. UV/Vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$ (logε) = 432 (5.20), 526 (3.77), 558 (4.35), 597 (4.13) nm. $\mathrm{C_{52}H_{33}N_5O_2Zn}$ (824): calcd. C 75.70, H 4.04, N 8.49; found C 75.4, H 4.03, N 8.45. MS-FAB(+): *m*/*z* = 825 $[\mathrm{M} + 1]^+$.

2-[(1*E*,3*E*)4-(4-Nitrophenyl)1,3-butadienyl]-5,10,15,20-tetraphenylporphyrinatozinc(II) (10): The dark green powder was washed with *n*-hexane and a small amount of MeOH in order to eliminate the excess of $\mathrm{Zn(OAc)_2}$. Yield 90%. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = 6.40 (d, 1 H, $\mathrm{H_{butyl}}$), 6.75 (d, 2 H, $\mathrm{H_{butyl}}$), 7.14 (dd, 1 H, $\mathrm{H_{butyl}}$), 7.55 (d, 2 H, $\mathrm{H_{Ar}}$), 7.78 (m, 12 H, $\mathrm{H}_{m,p\mathrm{Ph}}$), 8.15 (d, 2 H, $\mathrm{H_{Ar}}$), 8.24 (m, 8 H, $\mathrm{H}_{o\mathrm{Ph}}$), 8.88 (m, 6 H, $\mathrm{H_{pyrrolic}}$), 9.07 (br. s, 1 H, $\mathrm{H_{pyrrolic}}$) ppm. UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ (logε) = 430 (4.94), 559 (4.11), 599 (3.98) nm. $\mathrm{C_{54}H_{35}N_5O_2Zn}$ (850): calcd. C 76.20, H 4.14, N 8.23; found C 76.20, H 4.05, N 8.01. MS-FAB(+): *m*/*z* = 851 $[\mathrm{M} + 1]^+$.

2-{(*1E*)-2-[4-(Dibutylamino)phenyl]ethen-1-yl}-5,10,15,20-tetraphenylporphyrinatozinc(II) (12): The dark powder was washed with *n*-hexane and a small amount of MeOH in order to eliminate the excess of $\mathrm{Zn(OAc)_2}$. Yield: 85%. ^{1}H NMR [300 MHz, $\mathrm{(CD_3)_2CO}$]: δ = 1.02 (t, *J* = 7.2 Hz, 6 H, $\mathrm{CH_3}$), 1.45–1.51 (m, 4 H, $\mathrm{CH_2}$), 1.60–1.73 (m, 4 H, $\mathrm{CH_2}$), 3.41 (t, *J* = 7.2 Hz, 4 H, $\mathrm{CH_2N}$), 6.69 (d, *J* = 8.8 Hz, 2 H, $\mathrm{H_{Ar}}$), 6.82 (d, *J* = 16.0 Hz, 1 H, $\mathrm{H_{ethenyl}}$), 7.14 (d, *J* = 8.8 Hz, 2 H, $\mathrm{H_{Ar}}$), 7.22 (d, *J* = 16.0 Hz, 1 H, $\mathrm{H_{ethenyl}}$), 7.72- 7.88 (m, 12 H, $\mathrm{H}_{m,p\mathrm{Ph}}$), 8.15–8.30 (m, 8 H, $\mathrm{H}_{o\mathrm{Ph}}$), 8.70–8.90 (m, 6 H, $\mathrm{H_{pyrrolic}}$), 9.01 (s, 1 H, $\mathrm{H_{pyrrolic}}$) ppm. UV/Vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$ (logε) = 422 (5.20), 556 (4.08), 601 (3.97) nm. $\mathrm{C_{60}H_{51}N_5Zn}$ (906): calcd. C 79.47, H 5.63, N 7.73; found C 79.60, H 5.61, N 7.70. MS-FAB(+): *m*/*z* = 907 $[\mathrm{M} + 1]^+$.

2-Nitro-5,10,15,20-tetraphenylporphyrinatozinc(II) (4): A solution of $\mathrm{AgNO_3}$ (97.8 mg, 0.576 mmol) in 20 mL of $\mathrm{CH_3CN}$ and a solution of $\mathrm{I_2}$ (75 mg, 0.295 mmol) in 20 mL of $\mathrm{CH_2Cl_2}$ were rapidly added to a solution of 5,10,15,20-tetraphenylporphyrinatozinc(II) (301 mg, 0.434 mmol) in 80 mL of $\mathrm{CH_2Cl_2/CH_3CN}$ (1:1, v/v); the resulting mixture was stirred at room temperature, under nitrogen, in the dark, for two hours. The reaction mixture was filtered, the solvent was evaporated in vacuo and the residue was purified by column chromatography (silica gel, CH_2Cl_2) to afford 71.7 mg (22%) of a violet powder. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.95 (m, 12 H, $H_{m,pPh}$), 8.19–8.22 (m, 8 H, H_{oPh}), 8.98–9.00 (m, 6 H, $H_{pyrrolic}$), 9.22 (s, 1 H, $H_{pyrrolic}$) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 425 (5.28), 522 (3.41), 555 (4.00), 598 (3.80) nm. $C_{44}H_{27}N_5O_2Zn$ (722): calcd. C 73.08, H 3.76, N 9.69; found C 73.20, H 3.89, N 9.80. MS-FAB(+): *m*/*z* = 723 [M + 1]$^+$.

2-[2-(4-Nitrophenyl)ethyn-1-yl]-5,10,15,20-tetraphenylporphyrinatozinc(II) (6): A mixture of 2-bromo-5,10,15,20-tetraphenylporphyrinatozinc(II) (150 mg, 0.182 mmol), $[PdCl_2(PPh_3)_2]$ (19 mg, 0.027 mmol), CuI (15.4 mg, 0.0081 mmol), 4-nitrophenylacetylene (61.5 mg, 0.42 mmol) and triethylamine (3 mL) in 40 mL of THF was heated at reflux under nitrogen, in the dark, for 5 h. The solvent was evaporated in vacuo and the residue was purified by column chromatography (silica-gel, toluene/cyclohexane, 1:1) to afford 63 mg (42%) of pure **6** as a dark-violet powder. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.79 Hz, 2 H, H_{Ar}), 7.61–7.83 (m, 12 H, $H_{m,pPh}$), 8.17–8.22 (m, 10 H, $8H_{oPh}$, $2H_{Ar}$), 8.65–8.93 (m, 6 H, $H_{pyrrolic}$), 9.27 (br. s, 1 H, $H_{pyrrolic}$) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 431 (5.30), 521 (3.60), 557 (4.25), 594 (4.03) nm. $C_{52}H_{31}N_5O_2Zn$ (822): calcd. C 75.87, H 3.80, N 8.51; found C 76.2, H 3.89, N 8.35. MS-FAB(+): *m*/*z* = 823 [M + 1]$^+$.

2-Formyl-5,10,15,20-tetraphenylporphyrin (13): A solution of dimethylformamide (2 mL) and phosphoryl chloride (2 ml) in 10 mL of 1,2-dichloroethane was left at room temperature and stirred magnetically for 30 min. After this time, a solution of tetrakis-5,10,15,20-tetraphenylporphyrinatonickel(II) (300 mg, 0.449 mmol) in 100 mL of 1,2-dichloroethane was added and the reaction mixture was refluxed for 24 h. The dark-green solution was then evaporated to dryness and the residue was treated, while cooling with an ice bath, with 10 mL of 96% H_2SO_4 to afford a green viscous solution, which was diluted with a saturated aqueous solution of CH_3COONa until the pH was basic. The product was extracted with CH_2Cl_2 (3 × 150 mL), the organic phase was washed with aqueous 5% NaOH (100 mL) and then with H_2O (150 mL) and the solvents evaporated in vacuo to afford 320 mg of crude product. Purification by column chromatography (silica gel, CH_2Cl_2) afforded 220 mg (70%) of pure **13** as a purple solid. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.60 (br. s, 2 H, NH), 7.64–7.84 (m, 12 H, $H_{m,pPh}$), 7.95–8.05 (m, 2 H, H_{oPh}), 8.12–8.28 (m, 6 H, H_{oPh}), 8.65–8.81 (m, 2 H, $H_{pyrrolic}$), 8.85–8.87 (m, 4 H, $H_{pyrrolic}$), 9.23 (br. s, 1 H, $H_{pyrrolic}$), 9.42 (s, 1 H, CHO) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 432 (5.47), 526 (4.21), 568 (3.80), 605 (3.70), 664 (3.83) nm. $C_{45}H_{30}N_4O$ (642): calcd. C 84.09, H 4.70, N 8.72; found C 84.35, H 4.83, N 8.79. MS-FAB(+): *m*/*z* = 643 [M + 1]$^+$.

2-Hydroxymethyl-5,10,15,20-tetraphenylporphyrin (14): A sample of 2-formyl-5,10,15,20-tetraphenylporphyrin (**13**; 375 mg, 0,583 mmol) was dissolved in 50 mL of refluxing dry tetrahydrofuran, then $NaBH_4$ (609 mg, 16.1 mmol) was added and the suspension was stirred for 15 min. The reaction mixture was cooled to room temperature, 100 mL of H_2O was added in order to eliminate the excess of $NaBH_4$, then the reaction mixture was transferred into a separating funnel and extracted with 100 mL of $CHCl_3$. The organic phase was separated, dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by crystallisation with CH_2Cl_2/*n*-hexane to afford 335 mg (89%) of pure **14** as a purple solid. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.75 (br. s, 2 H, NH), 1.95 (t, 1 H, exchange with D_2O), 4.88 (d, *J* = 5.06 Hz, 2 H, CH_2O), 7.64–7.80 (m, 12 H, $H_{m,pPh}$), 8.08–8.11 (m, 2 H, H_{oPh}), 8.17–8.22 (m, 6 H, H_{oPh}), 8.50–8.61 (m, 2 H, $H_{pyrrolic}$), 8.75 and 8.87 (m, 4 H, $H_{pyrrolic}$), 8.94 (s, 1 H, $H_{pyrrolic}$) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 419 (5.71), 515 (4.27), 549 (3.77), 589 (3.74), 645 (3.50) nm. $C_{45}H_{32}N_4O$ (644): calcd. C 83.83, H 5.00, N 8.69; found C 83.9, H 5.02, N 8.72. MS-FAB(+): *m*/*z* = 645 [M + 1]$^+$.

2-(Chloromethyl)-5,10,15,20-tetraphenylporphyrin (15): A solution of thionyl chloride (0.13 g, 1.36 mmol) in 5 mL of Et_2O was slowly added, keeping the temperature in the range 0–5 °C, to a stirred solution of porphyrin **14** (87.5 mg, 0.136 mmol) and pyridine (0.13 g, 1.63 mmol) in 30 mL of Et_2O. Once the addition was complete, the temperature was raised to room temperature and the reaction mixture was stirred for 30 min. The mixture was then transferred into a separating funnel, diluted with 100 mL of CH_2Cl_2 and washed with water (70 mL) and aqueous 5% $NaHCO_3$ (60 mL). The organic phase was dried with Na_2SO_4 and the solvents evaporated in vacuo to afford 95 mg of residue, which was purified by crystallisation from CH_2Cl_2/*n*-pentane to give 85 mg (95%) of a purple solid. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.79 (br. s, 2 H, NH), 4.79 (s, 2 H, CH_2Cl), 7.64- 7.75 (m, 12 H, $H_{m,pPh}$), 8.10–8.25 (m, 8 H, H_{oPh}), 8.65 (d, *J* = 4.87 Hz, 2 H, $H_{pyrrolic}$), 8.78–8.87 (m, 4 H, $H_{pyrrolic}$), 8.96 (s, 1 H, $H_{pyrrolic}$) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 420 (5.54), 516 (4.26), 550 (3.84), 592 (3.73), 650 (3.81) nm. $C_{45}H_{31}ClN_4$ (662): calcd. C 81.50, H 4.71, N 8.45; found C 81.15, H 4.78, N 8.49. MS-FAB(+): *m*/*z* = 663 [M + 1]$^+$, 628 [M – Cl]$^+$.

[2-(5,10,15,20-Tetraphenylporphyrin-2-yl)methylene]triphenylphosphonium Chloride (16): A solution of porphyrin **15** (75.1 mg, 0.113 mmol) and triphenylphosphane (240 mg, 0.9 mmol) in 50 mL of $CHCl_3$ was refluxed under magnetic stirring for 16 h. The solvent was then evaporated in vacuo, the residue was washed with *n*-hexane in order to remove the excess of PPh_3, and the purple solid residue was dried to afford 84 mg (80%) of pure **16**. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.78 (br. s, 2 H, NH), 5.31 (d, *J* = 15 Hz, 2 H, CH_2P), 7.10- 7.20 (m, 6 H, 3 $H_{m,pPh}$ + 3 $H_{pAr–P}$), 7.22–7.35 (m, 5 H, 3 $H_{o\ Ar–P}$ + 2 H_{oPh}), 7.41 (d, *J* = 7.2 Hz, 2 H, 2 H_{oPh}), 7.50–7.95 (m, 18 H, 3 $H_{oAr–P}$ + 6 $H_{mAr–P}$ + 9 $H_{m,pPh}$), 8.10–8.20 (m, 4 H, $4H_{oPh}$), 8.34 (d, *J* = 3.6 Hz, 1 $H_{pyrrolic}$), 8.45 (d, *J* = 4.9 Hz, 1 $H_{pyrrolic}$), 8.70–8.90 (m, 5 $H_{pyrrolic.}$) ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 423 (5.60), 519 (4.26), 556 (3.72), 595 (3.69), 652 (3.70) nm. $C_{63}H_{46}ClN_4P$ (924): calcd. C 81.76, H 5.01, N 6.05; found C 81.50, H 5.03, N 6.10. MS-FAB(+): *m*/*z* = 889 [M – Cl]$^+$, 627 [M – Cl – PPh_3]$^+$.

4-(Dibutylamino)benzyl Alcohol: A sample of 4-(dibutylamino)-benzaldehyde (2.33 g, 10 mmol) was dissolved in 100 mL of 96% EtOH. Then, $NaBH_4$ (760 mg, 20 mmol) was added and the suspension was stirred at reflux for 2 h. The reaction mixture was evaporated in vacuo, the residue was taken up into a separating funnel with 60 mL of H_2O and 100 mL of Et_2O and the organic phase was separated. The aqueous phase was extracted with Et_2O (2 × 50 mL). The organic phase was dried with $MgSO_4$ and the solvents evaporated to dryness to afford 2.28 g (97%) of pure product as a thick, colourless oil. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.2 Hz, 6 H, CH_3), 1.25–1.45 (m, 5 H, CH_2 + OH), 1.45–1.65 (m, 4 H, CH_2), 3.26 (t, *J* = 7.2 Hz, 4 H, CH_2N), 4.54 (d, *J* = 5.7 Hz, 2 H, CH_2O), 6.62 (d, *J* = 8.8 Hz, 2 H, AA′BB′), 7.20 (d, *J* = 8.8 Hz, 2 H, AA′BB′) ppm.

[4-(Dibutylamino)benzyl]triphenylphosphonium Chloride: A suspension of 4-(dibutylamino)benzyl alcohol (1.18 g, 5 mmol) in 20 mL of CH_3CN, cooled to 0 °C, was saturated with gaseous HCl until a light yellow solution had formed. This solution was heated at reflux and stirred for 40 h. The reaction mixture was evaporated in vacuo, the residue was taken up in a separating funnel with 120 mL of CH_2Cl_2, washed with aqueous 10% Na_2CO_3 (2 × 30 mL) and 50 mL of brine. The organic phase was dried with $MgSO_4$ and the solvents evaporated to dryness to give a white solid residue which was ground with Et_2O and filtered to give 2.41 g (93%) of a white solid. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.2 Hz, 6 H, CH_3), 1.18–1.35 (m, 4 H, CH_2), 1.35–1.55 (m, 4 H, CH_2), 3.16 (t, J = 7.2 Hz, 4 H, CH_2N), 5.14 (d, J = 13 Hz, 2 H, CH_2P^+), 6.36 (d, J = 8.8 Hz, 2 H, AA′BB′), 6.82 (dd, J = 8.8, J = 2.5 Hz, 2 H, AA′BB′), 7.55–7.80 (m, 15 H, H_{phenyl}) ppm.

Acknowledgments

This work was supported by the Ministero dell'Istruzione, dell'Università e della Ricerca (Programma di Ricerca FIRB 2001; Research Title: Nano-organisation of hybrid organic-inorganic molecules with magnetic and non linear optical properties) and by the Consiglio Nazionale delle Ricerche. We thank Dr. Stefania Righetto for help with EFISH measurements and Mr. Pasquale Illiano for NMR measurements.

---

[1] a) J. Zyss, *Molecular Non-linear Optics: Materials, Physics and Devices*, Academic Press, Boston **1993**; b) I. Ledoux, J. Zyss, *Novel Optical Materials and Application* (Eds.: I. C. Khoo, F. Simoni, C. Venatri), John Wiley and Sons, New York, **1997**.

[2] M. Blanchard-Desce, S. R. Marder, M. Barzoukas, in *Comprehensive Supramolecular Chemistry*, Vol. 10 (Ed.: D. N. Reinhoudt), Pergamon Press, **1996**, p. 833 and references cited therein.

[3] a) D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195; b) P. M. Burland, R. D. Miller, C. A. Walash, *Chem. Rev.* **1994**, *94*, 31; c) T. J. Marks, M. A. Ratner, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155.

[4] a) I. R. Whittal, A. M. McDonagh, M. G. Humphrey, *Adv. Organomet. Chem.* **1998**, *42*, 291; b) S. Di Bella, *Chem. Soc. Rev.* **2001**, *30*, 355; c) N. J. Long, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21.

[5] a) K. S. Suslick, C. T. Chen, G. R. Meredith, L. T. Cheng, *J. Am. Chem. Soc.* **1992**, *114*, 6928; b) H. Chou, K. S. Suslick, *J. Phys. Chem.* **1994**, *98*, 383; c) M. Pizzotti, R. Ugo, E. Annoni, S. Quici, I. Ledoux-Rak, G. Zerbi, M. Del Zoppo, P. Fantucci, I. Invernizzi, *Inorg. Chim. Acta* **2002**, *340*, 70–80.

[6] a) S. M. Le Cours, H. W. Guan, S. G. Di Magno, C. H. Wang, M. J. Therien, *J. Am. Chem. Soc.* **1996**, *118*, 1497; b) L. Karki, F. W. Vance, J. H. Hupp, S. M. Le Cours, M. J. Therien, *J. Am. Chem. Soc.* **1998**, *120*, 2606; c) M. Yeung, A. C. H. Ng, M. G. B. Drew, E. Vorpagel, E. M. Breitung, R. J. McMahon, D. K. P. Ng, *J. Org. Chem.* **1998**, *63*, 7143; d) M. Pizzotti, E. Annoni, R. Ugo, S. Bruni, S. Quici, P. Fantucci, M. Bruschi, G. Zerbi, M. Del Zoppo, *J. Porphyrins Phthalocyanines* **2004**, *8*, 1311–1324.

[7] a) G. de La Torre, P. Vázquez, F. Agulló-López, T. Torres, *Chem. Rev.* **2004**, *104*, 3723 and references cited therein; b) C. G. Claessens, D. González-Rodríguez, T. Torres, *Chem. Rev.* **2002**, *102*, 835–853; c) C. G. Claessens, D. González-Rodríguez, T. Torres, G. Martin, F. Agulló-López, I. Ledoux, J. Zyss, V. R. Ferro, J. M. García de la Vega, *J. Phys. Chem. B* **2005**, *109*, 3800–3806.

[8] a) M. A. Diaz-García, I. Ledoux, F. Agulló-López, J. Zyss, *J. Phys. Chem.* **1994**, *98*, 4495; b) F. Fernandez-Lázaro, T. Torres, B. Hanschel, M. Hanack, *Chem. Rev.* **1998**, *98*, 563 and references cited therein.

[9] J. S. Lindsey, in *Metalloporphyrin-Catalysed Oxidations* (Eds.: F. Montanari, L.Casella), Kluwer Academic Publishers, **1994**, p. 49 and references cited therein.

[10] M. Gouterman, in *The Porphyrins*, Vol. III (Ed.: D. Dolphin) Academic Press, New York, **1978**.

[11] S. Priyadarshy, M. J. Therien, D. N. Beratan, *J. Am. Chem. Soc.* **1996**, *118*, 1504.

[12] a) D. N. Quin, T. Wada, H. Sasabe, *Mol. Cryst. Liq. Cryst.* **1992**, *217*, 47; b) A. Sen, P. C. Ray, P. K. Das, V. Krishnan, *J. Phys. Chem.* **1996**, *100*, 19611.

[13] P. R. Varanasi, A. K.-Y. Jen, J. Chandrasekhar, I. N. N. Namboothiri, A. Rathna, *J. Am. Chem. Soc.* **1996**, *118*, 12443.

[14] I. D. L. Albert, T. J. Marks, M. A. Ratner, *Chem. Mater.* **1998**, *10*, 753 and references cited therein.

[15] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev.* **1998**, *37*, 785.

[16] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[17] A. Schafer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.

[18] H. J. Callot, *Bull. Soc. Chim. Fr.* **1974**, 1492.

[19] a) A. D. Adler, F. R. Longo, F. Kampas, J. Kim, *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443; b) A. R. Menotti, P. Rothemund, *J. Am. Chem. Soc.* **1948**, *70*, 1808.

[20] J. A. Baldwin, M. J. Crossley, J. DeBernardis, *Tetrahedron* **1982**, *38*, 685.

[21] E. E. Bonfantini, A. K. Burrell, D. L. Officer, D. C. W. Reid, M. R. McDonald, P. A. Cocks, K. C. Gordon, *Inorg. Chem.* **1997**, *36*, 6270 and references cited therein.

[22] H. H. Callot, *Tetrahedron* **1973**, *296*, 899.

[23] A. Mylona, J. Nokavouras, I. M. Tekakis, *J. Org. Chem.* **1988**, *53*, 3838.

[24] E. E. Bonfantini, D. L. Officer, *Tetrahedron Lett.* **1993**, *34*, 8531.

[25] R. A. Binstead, M. J. Crossley, N. S. Hush, *Inorg. Chem.* **1991**, *30*, 1259.

[26] J. H. Fuhrhop, *Struc. Bond.* **1974**, *18*, 1.

[27] This latter band cannot be attributed to some impurity of porphyrins **1** or **3** because, taking into consideration the intensity of their Q_β bands at higher energy (Table 1), their concentration should be high enough to be detected by ^1H NMR spectroscopy (signal due to the NH protons). This comment applies also to porphyrins **5** and **7** and their Zn^{II} complexes **6** and **8**.

[28] a) J. A. Shelnutt, *J. Phys. Chem.* **1984**, *88*, 4988; b) J. A. Shelnutt, V. Ortiz, *J. Phys. Chem.* **1985**, *89*, 4733.

[29] A. K. Burrel, D. L. Officer, D. C. Reid, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 900.

[30] O. W. Kolling, *J. Phys. Chem.* **1989**, *93*, 3436 and references cited therein.

[31] M. Karlson, K. Pihlaja, T. Tamm, A. Uri, M. C. Zerner, *J. Photochem. Photobiol.* **1995**, *85*, 119.

[32] S. Dahal, V. Krishnan, *J. Photochem. Photobiol.* **1995**, *89*, 105.

[33] K. Takahashi, S. Hase, T. Komura, H. Imanaga, O. Ohno, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1475.

[34] A. Wolberg, J. Manassen, *J. Am. Chem. Soc.* **1970**, *92*, 2982.

[35] J. H. Fuhrhop, K. M. Kadish, D. G. Davis, *J. Am. Chem. Soc.* **1973**, *95*, 5140.

[36] A. Stanienda, G. Biebl, *Z. Phys. Chem.* **1967**, *52*, 254.

[37] D. W. Clack, N. S. Hush, *J. Am. Chem. Soc.* **1965**, *87*, 4238.

[38] R. H. Felton, H. Linschitz, *J. Am. Chem. Soc.* **1966**, *88*, 1113.

[39] E. A. Guggenheim, *Trans. Faraday Soc.* **1949**, *45*, 203.

[40] a) I. Ledoux, J. Zyss, *Chem. Phys.* **1982**, *73*, 202; b) D. J. Williams, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 690 and references cited therein.

[41] G. Rojo, G. de la Torre, J. García-Ruiz, I. Ledoux, T. Torres, J. Zyss, F. Agulló-López, *Chem. Phys.* **1999**, *245*, 27 and references cited therein.

[42] a) D. Roberto, R. Ugo, S. Bruni, E. Cariati, F. Cariati, P. Fantucci, S. Quici, I. Ledoux, J. Zyss, *Organometallics* **2000**, *19*, 1775; b) E. Lucenti, E. Cariati, C. Dragonetti, L. Manassero, F. Tessore, *Organometallics* **2004**, *23*, 687.

[43] P. J. Spellane, M. Gouterman, A. Antipas, S. Kim, Y. C. Liu, *Inorg. Chem.* **1980**, *19*, 386.

[44] a) J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664; b) J. L. Oudar, *J. Chem. Phys.* **1977**, *67*, 446.

[45] D. R. Kanis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 10338 and references cited therein.

[46] L. T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, *J. Phys. Chem.* **1991**, *95*, 10631.

[47] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627.
[48] A. J.Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, **2002**.
[49] a) E. G. Mc Rae, *J. Phys. Chem.* **1957**, *61*, 562; b) S. Bruni, F. Cariati, E. Cariati, F. A. Porta, S. Quici, D. Roberto, *Spectrochim. Acta, Part A* **2001**, *57*, 1417.
[50] R. Ahlrichs, M. Bar, M. Haser, C. Horn, C. Kolmel, *Chem. Phys. Lett.* **1989**, *162*, 165.
[51] a) K. Eichkorn, O. Treutler, H. Öhm, M. Haser, R. Ahlirchs, *Chem. Phys. Lett.* **1995**, *240*, 283; b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlirchs, *Theor. Chem. Acc.* **1997**, *97*, 119.

Received: April 6, 2005