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Electronic Characterisation and Significant Second-Order NLO Response of 10,20-Diphenylporphyrins and Their Zn^{II} Complexes Substituted in the *meso* Position with π-Delocalised Linkers Carrying Push or Pull Groups

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This work describes the synthesis and the electronic characterisation by electronic absorption spectroscopy, cyclic voltammetry and dipole moments of diphenyl porphyrins and their Zn^{II} complexes substituted at the *meso* position by a pseudo-linear π-delocalised substituent carrying an electron-donor or an electron-withdrawing group. The second-order NLO response was investigated by the EFISH technique working with a nonresonant incident wavelength of 1.907 µm. This work confirms the ambivalent role of the polarisable porphyrin ring, which, already in the ground state, acts as a donor or acceptor depending on the nature (acceptor or donor) of the substituent in the *meso* position, as was pointed out in our previous work on tetraphenyl porphyrins substituted at the β-pyrrolic position. The second-order NLO response has been discussed by comparing the nature of the substituent (electron donor or acceptor) and the kind of substitution (β pyrrolic or *meso*). This comparison evidenced a significant increase of the electron-donor properties of NBu_2 or NMe_2 when they are connected to the *meso* position or to the β-pyrrolic position, probably because of an auxiliary donor effect of the electron-rich porphyrin ring. When the substituent is the electron-withdrawing NO_2 group, the substituent position (*meso* or β pyrrolic) is influential, with the existance of a significant increase in the second order NLO response when substitution occurs at the *meso* position.

Introduction

Over the last two decades molecular materials for nonlinear optics (NLO) have been investigated for their promising applications in optoelectronics and photonics.[1] Although most studies deal with pseudo-linear 1D organic[2] or organometallic[3] push-pull chromophores with second-order nonlinear optical response, more recent investigations have been devoted to two-dimensional push-pull chromophores based on highly π-delocalised macrocycles such as porphyrins[4–6] and phthalocyanines.[7] Porphyrins and their metal complexes appear to be advantageous, given their acceptable solubility, good thermal and chemical stability, and potential processability as layers.[8]

In addition, the architectural flexibility of porphyrins is well exemplified by the large number of structures reported in the literature, as well as by a large variety of substituents that can be attached at the *meso* or β-pyrrolic positions[5,6] of the porphyrin ring or to the axial position of a metal complex.[9]

Starting from studies carried out by Suslick and coworkers at the beginning of the 90s[4a,4b] and later by Therien and coworkers,[5a,5b] and following the theoretical approach of Marks, Ratner et al.,[10] who suggested that the presence of a π spacer between an electron-donor or acceptor group and the porphyrin ring together with the right ring substitution (β pyrrolic or *meso*) could produce chromophores with a large second-order NLO response, we recently investigated the second-order NLO response of push-pull porphyrinic chromophores with electron-donor or withdrawing groups linked, through a π spacer, to the β-pyrrolic position of the 5,10,15,20-tetraphenylporphyrin or its Zn^{II} complex.[6]

Our experimental results, in agreement with the suggestion of Marks, Ratner et al.,[10] have shown that the second-order NLO response is enhanced when an electron-donor substituent is attached at the electron-rich β-pyrrolic position of the porphyrin ring. We also evidenced an ambivalent

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role of the porphyrin ring (in the ground state but also in charge transfer processes), behaving as an electron donor or as an electron-rich enhancer of the donor properties of an amino group, according to the nature of the substituent in the β-pyrrolic position.

Very few studies have been devoted to the experimental investigation of the second-order NLO response of push-pull porphyrinic chromophores according to the nature of the substituents and their position on the porphyrin ring. Thus, in an effort to produce additional evidence of the ambivalent role of the porphyrin ring, we extended our investigation to the electronic characterisation and second-order NLO response of a series of 10,20-diphenylporphyrins (H_2DPP) and their Zn^{II} complexes substituted, at the *meso* position, by electron-donor or electron-withdrawing groups connected through a π spacer.

In order to avoid resonance effects or interference resulting from fluorescent emissions, the second-order NLO response was measured by the EFISH technique working with a nonresonant 1.907 µm incident wavelength.[5a] Calculations based on density functional theory (DFT)[11] were also performed to evaluate the dipole moment of the optimised structures of the investigated porphyrinic macrocycles, using the BP86[12] functional and an all-electron valence triple-ξ basis set with polarisation functions on all atoms.[13]

Results and Discussion

Synthesis of Porphyrins and Their Zn^{II} Complexes

The asymmetrical 10,20-diphenylporphyrins and their Zn^{II} complexes investigated in this work are reported in Figure 1; the Zn^{II} complexes **2** and **4** have already been synthesised by Anderson et al.[14]

The porphyrin **1** was synthesised with a modification of the synthetic route described by Anderson et al.,[14] involving a Wittig condensation of 5-formyl-10,20-diphenylporphyrin with 4-nitrobenzyltriphenylphosphonium bromide in refluxing 1,2-dichloroethane, using solid NaOH 20–40 mesh beads as the base. This reaction afforded **1** in 49%

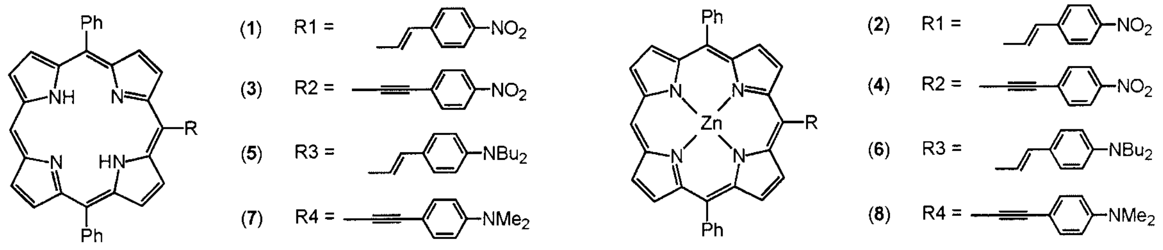
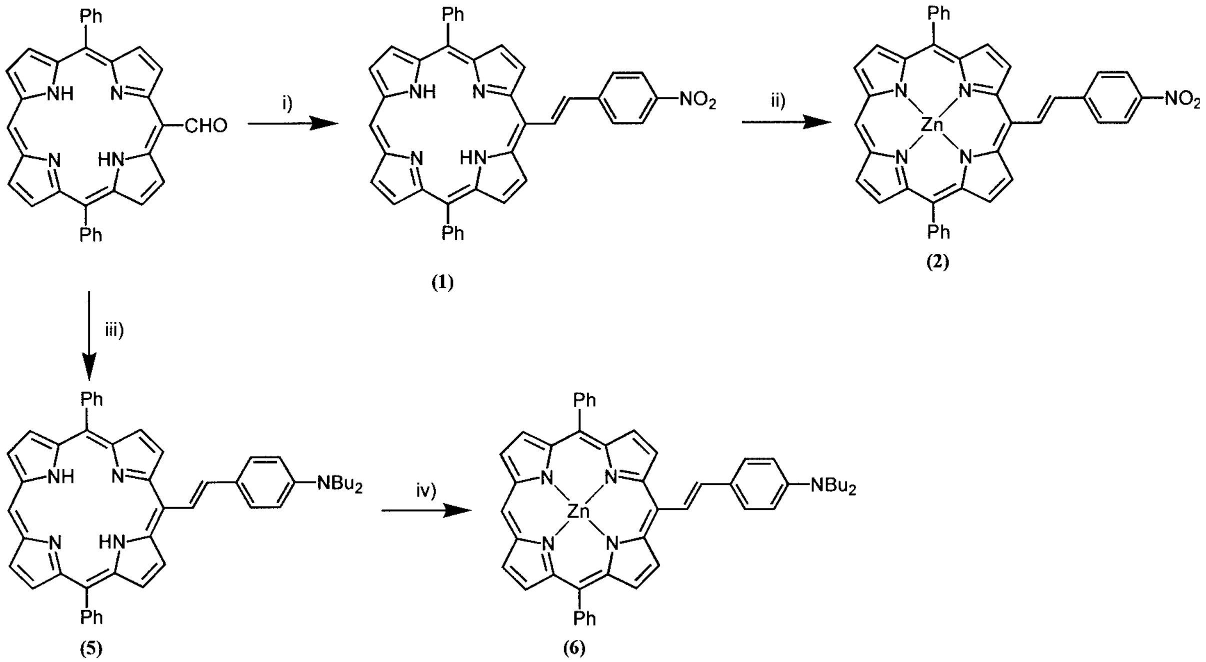
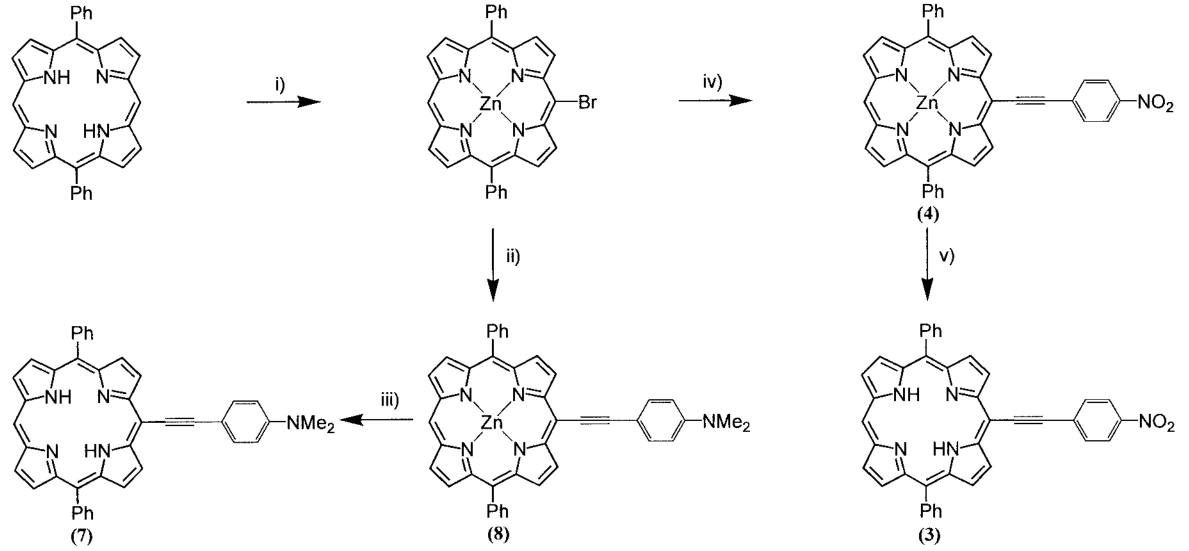


Figure 1. Asymmetrical 10,20-diphenylporphyrins and their Zn^{II} complexes substituted at the *meso* position with electron-withdrawing or electron-donor groups.



Scheme 1. i) 4-Nitrobenzyltriphenylphosphonium bromide, NaOH, CH_2Cl_2, reflux, 4 h; ii) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3$/MeOH, reflux, 1 h; iii) 4-(Dibutylamino)benzyltriphenylphosphonium chloride, NaOH, CH_2Cl_2, room temp., 4 h; iv) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3$/MeOH, reflux, 1 h.



Scheme 2. i) NBS, $CHCl_3$, room temp., 30 min.; $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH, reflux, 1 h; ii) catalyst (see Exp. Sect.), [4-(dimethylamino)phenyl]acetylene, pyridine, toluene, 80 °C, 1.5 h; iii) TFA, CH_2Cl_2, 18 h; iv) catalyst (see Exp. Sect.), (4-nitrophenyl)acetylene, pyridine, toluene, 80 °C, 1 h; v) TFA, CH_2Cl_2, 18 h.

yield after purification by column chromatography and crystallisation from CH_2Cl_2/MeOH.

Analogously, Wittig condensation of 5-formyl-10,20-diphenylporphyrin with 4-(dibutylamino)benzyltriphenylphosphonium chloride afforded **5** in 59% yield after purification by column chromatography.

The corresponding Zn^{II} complexes **2** and **6** were obtained in quantitative yield after refluxing **1** and **5** with Zn^{II} acetate in CH_2Cl_2/MeOH for 1 h[15] (Scheme 1).

5-Formyl-10,20-diphenylporphyrin was prepared in 80% yield by the Vilsmaier formylation of the Cu^{II} complex of 10,20-diphenylporphyrin, obtained in 83% yield by reaction of 10,20-diphenylporphyrin with Cu^{II} acetate in refluxing $CHCl_3$/MeOH, followed by quantitative demetallation of the Cu^{II} complex with a mixture of trifluoroacetic acid/concentrated sulfuric acid (9:1), as reported by Susumu et al.[15]

Zn^{II} complexes **4** and **8** (85% and 59% yields, respectively) were synthesised, as described by Anderson et al.,[14] by the coupling reaction of the Zn^{II} complex of 5-bromo-10,20-diphenylporphyrin with 4-nitrophenylacetylene and [4-(dimethylamino)phenyl]acetylene, respectively. The reaction was carried out in anhydrous toluene and pyridine at 80 °C in the presence of a Pd^0 catalyst, prepared in situ by the reaction, at 70 °C, of $[Pd_2(dba)_3]$ and PPh_3 in freshly distilled Et_3N in the presence of CuI.

The free base porphyrins **3** and **7** were obtained in quantitative yields by controlled demetallation, at room temperature, of the Zn^{II} complexes **4** and **8** with trifluoroacetic acid working in CH_2Cl_2 (Scheme 2).

Electronic Absorption and Emission Spectra

Anderson et al.[14] have already investigated the electronic absorption and emission spectra of the Zn^{II} complexes **2** and **4**, which evidence significant changes in comparison with those of the complex [Zn(DPP)]·THF of 10,20-diphenylporphyrin (H_2DPP). The significant red shift of both the Soret B band and the Q_α band at lower energy, with an increase in the intensity of this latter band suggests an electronic conjugation between the porphyrin ring and the π linker. The spectra, obtained in CH_2Cl_2 solution in the presence of 1% pyridine, refer to pentacoordinate species with a pyridine in the axial position.

Here we report (Table 1) and discuss the absorption and emission spectra of the Zn^{II} complexes **2** and **4** in $CHCl_3$ solution, with and without pyridine addition, together with those of the corresponding porphyrins **1** and **3**.

A comparison of the absorption spectra of the porphyrins **1** and **3** with those of **2** and **4** indicates a decrease in the number of Q bands, from four to two, with the complete disappearance of the Q_α band at low energy (around 655–660 nm) as expected for an increase of the microsymmetry upon coordination.[6] Compounds **2** and **4**, but also **1** and **3**, still show a significant red shift of the Soret B band and of the Q_α band at lower energy, which increases its intensity, in comparison with that of [Zn(DPP)]·THF and H_2DPP (Table 1). The red shift of the Soret B band is more significant for **4** than for **2**, in agreement with the suggested[14] better π conjugation of the triple bond with the π core of the porphyrin ring.

Differently from 5,10,15,20-tetraphenylporphyrin and its Zn^{II} complex substituted in the β-pyrrolic position by a similar series of π-delocalised substituents,[6] the Soret B band of porphyrins **1** and **3** and of their Zn^{II} complexes **2** and **4** is quite symmetric, but with an increase of the bandwidth of the Soret B bands, which is further evidence of electronic conjugation[6] (Table 1).

Both **2** and **4** show, in the presence of pyridine, an additional small red shift of the Soret B band, and a more significant red shift of the Q_α band at lower energy, which is expected for the axial coordination of pyridine[9] (Table 1). The Zn^{II} complex **4** is quite insoluble, suggesting

Table 1. Absorption (λ_{max}) and emission (λ_e) spectra in $CHCl_3$ (Soret B band in **bold**).

Compound	Soret B Half bandwidth $\Delta\nu_{1/2}$ [cm^{-1}][b]	λ_{max} [nm] (logε)	λ_e [nm][c]
H_2DPP[a]	874	**409** (5.49), 502 (4.27), 536 (3.74), 575 (3.78), 630 (3.18)	638, 695
[ZnDPP]·THF	718	**407** (5.65), 536 (4.19), 571 (2.84)	579, 627 594, 646[d][h]
(1*E*)-5-[2-(4′-Nitrophenyl)ethenyl]-10,20-H_2DPP (**1**)	2606	**422** (5.27), 518 (4.07), 564 (4.11), 594 (3.89), 655 (3.65)	673.5, 760 (sh)
(1*E*)-5-[2-(4′-Nitrophenyl)ethenyl]10,20 ZnDPP (**2**)	2629	**422** (5.23), 552 (4.19), 599 (4.04) **428** (5.05), 566 (3.72), 626 (3.89)[d]	647(sh), 692 671[d]
5-[2-(4′-Nitrophenyl)ethynyl]-10,20-H_2DPP (**3**)	1521	**436** (5.15), 529 (3.91), 573 (4.32), 602 (3.79), 661 (3.94)	665, 765 (sh)
5-[2-(4′-Nitrophenyl)ethynyl]-10,20-ZnDPP (**4**)	n.d.[e]	**439** (5.16), 560 (3.68), 608 (4.07) **449** (5.17), 575 (3.92), 634 (4.47)[d]	617, 667 (sh) 700[d]
(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-H_2DPP (**5**)	2550	**410** (5.06), 521 (4.00), 579 (4.15), 665 (3.76), 747 (3.52)	660 (sh), 702
(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-ZnDPP (**6**)	n.d.[f]	**408** (5.26), 554 (4.27), 606 (4.32) **428** (5.20), 563 (4.06), 613 (4.09)[d]	696 695[d]
5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-H_2DPP (**7**)	2514	**425** (5.02), **441** (sh), 523 (3.93), 587 (4.32), 673 (3.94)	697, 746 (sh)
5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-ZnDPP (**8**)	n.d.[g]	**428** (4.97), **448** (4.98), 565 (4.02), 615 (4.24) **451** (5.14), 579 (3.87), 632 (4.30)[d]	640, 688 654, 702[d]

[a] H_2DPP = 10,20-diphenylporphyrin. [b] Values were obtained according to equation $\Delta\nu_{1/2} = f/(4.33\times10^{-9}\times\varepsilon)$ (F. L. Pilar, *Elementary Quantum Chem.*, McGraw-Hill Book Comp., **1968**) where *f* is the oscillator strength and ε is the extinction coefficient of the maximum. [c] Values obtained by irradiation at the Soret wavelength. [d] With addition of pyridine. [e] Not soluble enough for a reliable determination. [f] Highly asymmetric band. [g] Two Soret bands of relative intensities depending on the concentration. [h] In CH_2Cl_2 solution from ref.[14]

strong association in the solid state.[16] In accordance it becomes soluble with the addition of pyridine.

When an *E*-ethylenic linker connects a basic dibutylamino electron-donor group with the porphyrin ring as in porphyrin **5** and its Zn^{II} complex **6** (Table 1), all the Q bands are notably red shifted, (notably for **5** the Q_α band at lower energy shifts from 630 to 747 nm), while the Soret B band is not red shifted when compared with H_2DPP and [ZnDPP]·THF. Both compounds **5** and **6** show a significantly asymmetric Soret B band, with the asymmetry centred at lower energy (Figure 2). Interestingly the compound with the same substituent bound to the β-pyrrolic position of the 5,10,15,20-tetraphenylporphyrin or its Zn^{II} complex, shows a symmetric Soret B band.[6]

The Zn^{II} complex **8** with a dimethylamino electron-donor group connected through a π-acetylenic linker to the porphyrin ring shows, in $CHCl_3$ solution even at concentrations about 10^{-6} M, two well-separated Soret B bands, with a relative intensity changing with the concentration (Table 1 and Figure 3, a), which is evidence of aggregation.[16]

The position of the two bands suggests that aggregation occurs via the interaction of the donor dimethylamino group of the π-delocalised substituent with the axial position of another molecule, since the Soret B band at 448 nm is typical of pentacoordination, while that at 428 nm may be because of some unassociated species. Intermolecular aggregation is also supported by the addition of traces of pyridine, which produces only one symmetric Soret B band at 451 nm (Figure 3, b) that does not shift on dilution as would be expected for an unaggregated pentacoordinate species.[9]

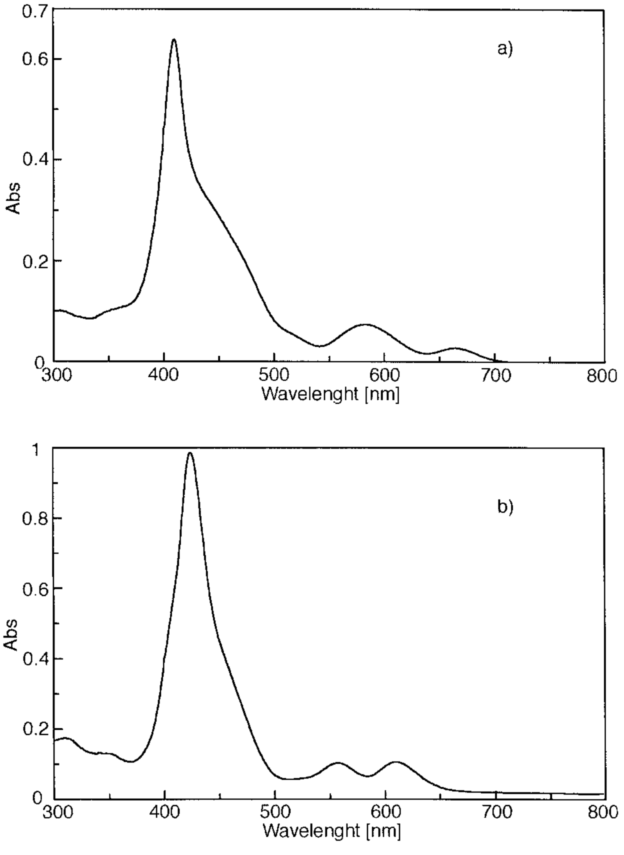


Figure 2. (a) Electronic absorption spectrum of **5** in $CHCl_3$, (b) Electronic absorption spectrum of **6** in $CHCl_3$.

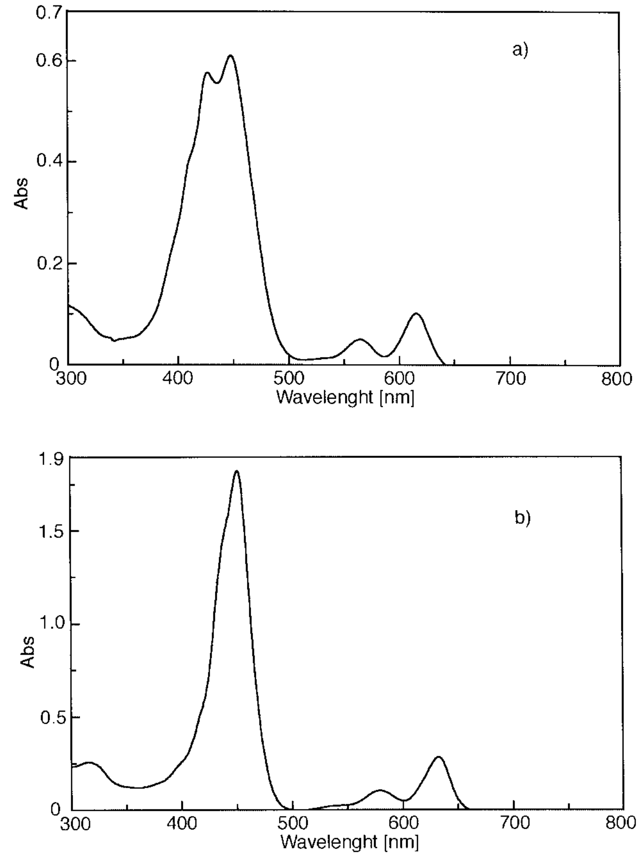


Figure 3. (a) Electronic absorption spectrum of **8** in $CHCl_3$, (b) Electronic absorption spectrum of **8** in $CHCl_3$ with the addition of pyridine.

Also the Zn^{II} complex **6** shows a Soret B band with some asymmetry (Figure 2, b), which disappears on addition of pyridine suggesting a similar kind of aggregation. A slow aggregation process of **6** is confirmed by an ^1H NMR spectroscopic investigation, but working at higher concentrations (about 10^{-3} M). In fact, the ^1H NMR spectrum of **6** in $CDCl_3$ is initially the one expected for a monomeric species, but after one hour significant changes take place.

A weaker intermolecular aggregation, probably by hydrogen bonding between the NH and NMe_2 groups of two molecules, seems to occur for porphyrin **7**, where two poorly resolved Soret B bands are seen (Figure 4, a). On dilution two isosbestic points were evidenced, as expected for the dissociation of a dimeric species, resulting in a monomeric species only at about 10^{-6} M concentration.

The addition of traces of trifluoroacetic acid to a 10^{-5} M solution of **7** in $CHCl_3$ produced only one Soret B band (Figure 4, b) as expected for the protonation of the dimethylamino group with disruption of the hydrogen bond and therefore of the intermolecular aggregation involving the dimethylamino group of the substituent.

Interestingly compounds **1**–**3**, with a π-delocalised substituent carrying an electron-withdrawing nitro group, did not show such spectroscopic evidence for significant aggregation, for instance by π stacking,[16] at concentrations of about 10^{-4}–10^{-6} M in $CHCl_3$.

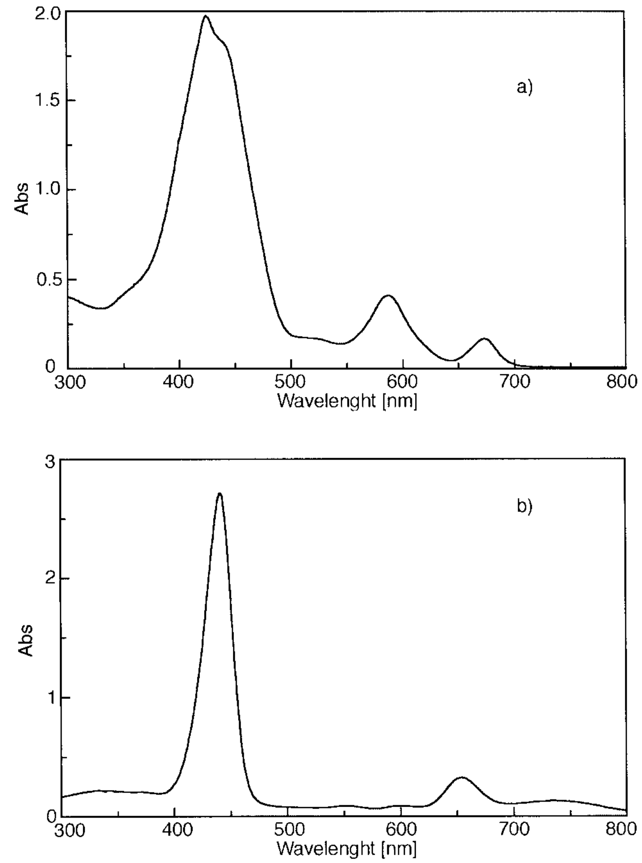


Figure 4. (a) Electronic absorption spectrum of **7** in $CHCl_3$, (b) Electronic absorption spectrum of **7** in $CHCl_3$ with the addition of trifluoroacetic acid.

Both H_2DPP and $[ZnDPP]{\cdot}THF$, when irradiated at the Soret B band wavelength in a $CHCl_3$ solution, show two well-separated emission bands, the one at lower energy being slightly more intense. On the contrary the porphyrins **1**, **3**, **5** and **7** show only one major emission with shoulders at lower (**1**, **3**, **7**) or at higher energies (**5**). Also the Zn^{II} complexes **2** and **4** in $CHCl_3$ solution show one major emission, with much weaker emission bands at lower (**4**) or higher energies (**2**). Only the Zn^{II} complexes **6** and **8** show one significant emission band and two well-separated emission bands of comparable intensity (Table 1). The shift at lower energy of the emission bands of **1**–**8** compared to those of H_2DPP and $[ZnDPP]{\cdot}THF$ (Table 1) is further evidence of conjugation of the π core of the porphyrin ring by the π-delocalised linker.

The Zn^{II} complexes **2** and **4** in $CHCl_3$ solution show, after the addition of traces of pyridine, only one emission band shifted at lower energy, while complex **6** shows the same unshifted emission band. Only the Zn^{II} complex **8** shows two well-separated emission bands as for $[ZnTPP]{\cdot}THF$, but at much lower energy (Table 1).

In summary, we have added further evidence to the proposal of Anderson et al.[14] for a conjugation of the π core of the porphyrin ring, particularly when the π-delocalised linker carries a nitro electron-withdrawing group. In addition, when the linker carries a donor dibutyl or dimethylamino group, we found evidence of significant aggregation by intermolecular processes involving donor amino groups or hydrogen bonds.

Voltammetric Investigation

The electronic properties of the porphyrins **1**, **3** and **5** and of their Zn^{II} complexes **2**, **4** and **6** were investigated by cyclic voltammetry in CH_2Cl_2 solution. The relevant oxidation and reduction peak potentials are reported in Table 2. The investigation was not extended to **7** and **8**, because of the previously discussed significant aggregation in $CHCl_3$ solution, in the concentration range used for the voltammetric investigation (10^{-3} to 10^{-4} м).

Oxidation Processes

The anodic oxidation of the porphyrins **1** and **3** and their Zn^{II} complexes **2** and **4** does not take place by two monoelectronic, chemically reversible steps as such oxidation does for compounds carrying the same π-delocalised substituents in the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrin or its Zn^{II} complex.[6] Porphyrins **1** and **3** show a partial return peak of the first oxidation step that can clearly be perceived only by reversing the potential scan immediately after the peak and increasing the potential scan rate. This behaviour, typical of the parent compound H_2DPP, suggests a short-lived radical cation formed in the first oxidation step. Continuing the potential scan beyond the first oxidation peak, porphyrins **1** and **3** give a complex, ill-defined anodic pattern, with multiple maxima without a neat second oxidation step, which on the contrary was easily detected not only for 5,10,15,20-tetraphenylporphyrins carrying the same substituents in the β-pyrrolic position,[6] but also, although to a lesser extent, for the parent compound H_2DPP (Table 2).

The Zn^{II} complex **2** shows the more usual pattern, with two subsequent neat oxidation peaks (but with the corresponding return peaks less distinguishable), while we have been unable to finely characterise the voltammetric behaviour of the Zn^{II} complex **4** because of its poor solubility.

The first oxidation peak potentials of the porphyrins **1** and **3** and of the Zn^{II} complex **2** are similar to those of the parent compounds H_2DPP and [ZnDPP]·THF or of the analogues carrying the same substituents in the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrin.[6] The oxidisability sequence is the same, since in both series the *E*-double bond of the π linker seems to negligibly transmit the electron attractor effect of the nitro group, resulting in slightly higher oxidisability when compared with the case of the triple bond. This observation is an additional support to the suggested easier π conjugation of the triple bond with the π core of the porphyrin ring.[14] The complexation of **1** and **3** to Zn^{II} results in the expected strong enhancement of oxidisability since the charge density on the porphyrin ring increases (negative shift of the first oxidation peak of 0.20 V for **2** compared with **1** and 0.17 V for **4** com-

Table 2. Oxidation and reduction peak potentials E_p/V(SCE) for porphyrins **1**, **3**, **5** and their Zn^{II} complexes **2**, **4**, **6**, and four reference compounds (CH_2Cl_2 + 0.1 м TBAP, glassy carbon electrode, potential scan rate: 0.2 V·s^{-1}).

Compound[a]	Reduction peaks[b]	Oxidation Peaks[b]
(1*E*)-5[2-(4'-Nitrophenyl)ethenyl-10,20-H_2DPP (**1**)	**–0.996** (*n* = 2; –0.961 V(SCE)^{i}; 0.043 V^{ii}; 0.071 V^{iii}), –1.65(*n* = 4)	1.02 (*n* = 1), *1.23, 1.37, 1.58*
(1*E*)-5-[2-(4'-Nitrophenyl)ethenyl]-10,20 ZnDPP (**2**)	–1.71, –1.56, –1.24, –1.06	**0.823** (*n* = 1; 0.789 V(SCE)^{i}; 0.059 V^{ii}; 0.068 V^{iii}), 1.09 (*n* = 1), *1.34, 1.55*
5-[2-(4'-Nitrophenyl)ethynyl]-10,20-H_2DPP (**3**)	–1.00 (*n* = 2), –1.65	1.09 (*n* = 1), *1.25, 1.58*
5-[2-(4'-Nitrophenyl)ethynyl]-10,20-ZnDPP (**4**)[c]	–1.59(*n* = 4), –0.96 (*n* = 2)	0.92 (*n* = 1)
(1*E*)-5-[2-(4'-Dibutylaminophenyl)ethenyl]-10,20-H_2DPP (**5**)	**–1.239** (*n* = 1; 1.202 V(SCE)^{i}; 0.060 V^{ii}; 0.075 V^{iii}), **–1.557** (*n* = 1; 1.519 V(SCE)^{i}; 0.059 V^{ii}; 0.077 V^{iii})	**0.657** (*n* = 1; 0.628 V(SCE)^{i}; 0.058 V^{ii}; 0.063 V^{iii}), **0.774** (*n* = 1; 0743 V(SCE)^{i}; 0.062 V^{iii}), 1.54
(1*E*)-5-[2-(4'-Dibutylaminophenyl)ethenyl]-10,20-ZnDPP (**6**)	**–1.369** (*n* = 1; 1.339 V(SCE)^{i}; 0.053 V^{ii}; 0.061 V^{iii}), **–1.721** (*n* = 1; 1.679 V(SCE)^{i}; 0.066 V^{ii}; 0.084 V^{iii})	**0.588** (*n* = 2; –0.557 V(SCE)^{i}; 0.047 V^{ii}; 0.062 V^{iii}), 1.41
H_2DPP	**–1.238** (*n* = 1; 1.207 V(SCE)^{i}; 0.056 V^{ii}; 0.062 V^{iii}), **–1.595** (*n* = 1; 1.565 V(SCE)^{i}; 0.055 V^{ii}; 0.060 V^{iii})	**1.084** (*n* = 1; 1.057 V(SCE)^{i}; 0.057 V^{ii}; 0.054 V^{iii}), **1.41** (*n* = 1)
[ZnDPP]·THF	**–1.404** (*n* = 1; 1.374 V(SCE)^{i}; 0.054 V^{ii}; 0.061 V^{iii}), **–1.807** (*n* = 1; 1.761 V(SCE)^{i}; 0.059 V^{ii}; 0.092 V^{iii})	**0.826** (*n* = 1; 0.798 V(SCE)^{i}; 0.053 V^{ii}; 0.056 V^{iii}), **1.159** (*n* = 1; 1.133 V(SCE)^{i}; 0.046 V^{ii}; 0.053 V^{iii})
4'-(*p*-Nitrophenyl)-2,2':6',2"-terpyridine	**–1.037** (*n* = 1; 1.006 V(SCE)^{i}; 0.057 V^{ii}; 0.063 V^{iii}), –1.42 (*n* = 3)	no peaks
Ferrocene		**0.513** (*n* =1; 0.484 V(SCE)^{i}; 0.056V^{ii}; 0.059 V^{iii})

[a] H_2DPP = 10,20-diphenylporphyrin. [b] Chemically reversible peaks (i.e. featuring a return peak) are underlined (in particular, a dotted line indicates partial return peaks, which are more evident at higher scan rates). The number of exchanged electrons, when assignable, is reported in parenthesis. Bold characters denote electrochemically reversible or quasi-reversible peaks; the corresponding half-wave potentials, $E_{1/2}$, half-peak widths, (E_p – $E_{p/2}$), and distances between anodic and cathodic peak ($E_{p,a}$ – $E_{p,c}$), are reported with ^{i}, ^{ii}, and ^{iii} superscripts, respectively. Italic characters denote shoulders or ill-defined peaks. [c] The voltammetric characterisation is poor because of the low solubility.

pared with **3**). This effect is only slightly lower than that found for the parent compounds H_2DPP and [ZnDPP]·THF and for the analogues carrying the same substituents in the β-pyrrolic position of the 5,10,15,20-tetraphenylporphyrin.[6] For porphyrins **1** and **3**, the poor chemical reversibility of the first step and the ill-defined anodic pattern beyond the first oxidation peak seems to suggest instability, introduced by the substitution at the *meso* position, of the radical cation produced by the first oxidation step. This instability after the first electron loss is not evident when porphyrin **1** is complexed to Zn^{II} with increased negative charge on the porphyrin ring, since complex **2** produces a more stable radical cation (possibly because it is generated at a far less positive potential), which can evolve to the dication upon loss of a second electron.

Porphyrin **5** and its Zn^{II} complex **6**, carrying a dibutylamino electron-donor group bound through an *E*-ethylene linker at the *meso* position, show a first chemically and electrochemically reversible oxidation peak at nearly the same potential as their analogues with the same substituent in the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrin.[6] In this last case, the first oxidation step was assumed to be centred out of the HOMO energies of the porphyrin π core, probably at the amino functionality.[6] This assumption was justified by several experimental observations, which still hold for **5** and **6**. For instance their $\Delta E_{(\text{ox-red})}$ parameters are 1.83 V and 1.89 V, respectively [considering half-wave potentials, defined as $(E_{\text{p,a}} + E_{\text{p,c}})/2$], which deviate significantly from the expected Kadish relationship [$\Delta E_{(\text{ox-red})} = 2.25 \pm 0.15$ V typical of the π porphyrin core].[17] In addition, complexation is not so effective since the first oxidation peak of the Zn^{II} complex **6** occurs at a potential that is only 0.070 V less positive than that of the parent porphyrin **5**.

If we assume for **5** and **6** that only the second oxidation peak is centred on the porphyrin π core, as suggested by the acceptable agreement of their potentials with the Kadish relationship (see later), and as proposed for the analogues with the same substitution in the β-pyrrolic position,[6] it seems more appropriate to discuss the oxidisability of their porphyrin core by comparing the first oxidation peak potentials of unsubstituted reference compounds H_2DPP (1.07 V) and [ZnDPP]·THF (0.84 V) with their second oxidation peak potentials, i.e. 0.77 V for **5** and 0.59 V for **6** (in which case the huge shift in the negative direction of the second peak results in a bielectronic peak accounting for both the first and the second oxidation steps). For the analogues substituted in the β-pyrrolic position, the second oxidation peak potentials are 1.01 V and 0.79 V, respectively.[6]

Since the second oxidation of **5** and **6** occurs at a significantly less positive potential (0.25–0.30 V) than the first oxidation of the unsubstituted reference compounds, and also those (0.20–0.24 V) of the analogues with the same substitution in the β-pyrrolic position, we can conclude that the increased oxidisability suggests a significant donor effect of the dibutylamino group together with a significant role of the position on the porphyrin ring (β pyrrolic or *meso*). Shifting the substituent from the β-pyrrolic to the *meso* position appears to enhance this donor effect.

In conclusion, if the oxidation peaks (the first for **1**, **2**, **3** and **4** and the second for **5** and **6**) can be taken as a first indication of the HOMO energy, we may conclude that its perturbation by substitution in the β-pyrrolic position or the *meso* is not so relevant when the π-delocalised substituent carries an electron-withdrawing nitro group; instead such perturbation will be quite significant, leading to destabilisation, if the substituent carries an electron-donor dibutylamino group, particularly when substitution occurs in the *meso* position.

Reduction Processes

Turning to the cathodic section of the voltammetric pattern (Table 2), the porphyrins **1** and **3** appear significantly more reducible than their analogues with the same kind of substitution in the β-pyrrolic position.[6] Complexes **2** and **4**, although characterised by a lower and broader pattern of the voltammetric cathodic portion, show a first reduction peak at nearly the same potential as the corresponding porphyrins **1** and **3** (Table 2) and appear to be slightly more reducible than their analogues with the same substituent in the β-pyrrolic position.[6]

It must be noted that we cannot reliably compare the potentials of the first reduction peak of **1**–**4** with those of the reference, unsubstituted compounds H_2DPP and [ZnDPP]·THF. In fact the cathodic portion of the voltammetric pattern of **1**–**4** is strongly influenced by the presence of the nitro group, which, when bound to a π-delocalised aromatic system, is more reducible than an unsubstituted porphyrin core {see Table 2 with potentials at –1.26 V and –1.03 V for reference compounds H_2DPP and [4′-(*p*-nitrophenyl)-2,2′:6′,2′′-terpyridine], respectively}. Therefore, when we have a nitro group interacting very closely with a reducible π-delocalised system, as in our case, it is particularly hard to discriminate whether the first electron enters at the nitro group or the porphyrin core. The effect of the nitro group on the reduction of the conjugated molecule is clearly perceived since the difference $\Delta E_{(\text{ox-red})}$ between the first oxidation and the first reduction process, which, for a strictly porphyrin ring-based redox process, should always be within 2.25 ± 0.15 V (Kadish relationship),[17] for porphyrins **1** and **3** is 1.96 V and 2.03 V, respectively. Interestingly, the above values of $\Delta E_{(\text{ox-red})}$ are significantly smaller than 2.18 V and 2.10 V, in quite good agreement with the Kadish relationship, found for the analogues with the same substituents in the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrin.[6] Therefore it appears that in compounds **1**–**4**, differently from their analogues with the same substituents in the β-pyrrolic position, the nitro group strongly influences the energy of the conjugated system so that we have a significant shift to less negative potentials of the first reduction peak with respect to Kadish's rule, an indication of a reduction process that does not involve just the π porphyrin core. The complexity of the first reduction step is, for instance, reflected by the observation that the first reduction peak of porphyrin **1** is bielectronic, unlike the classical monoelectronic first reduction peak of a nitro group bound to a π-delocalised aromatic system [see Table 2 for the properties of the first reduction peak of the reference aromatic compound 4′-(*p*-nitrophenyl)-2,2′:6′,2′′-terpyridine].

If the first reduction peak is an indication of the tendency of the whole molecule to be reduced, and therefore of the LUMO energy, we can suggest that while the shift from the β-pyrrolic to the *meso* position of π-delocalised substituents carrying a nitro group has little effect on the HOMO energy, it has a marked effect on the LUMO energy.

When the substituent carries an electron-donor dibutylamino group as in **5** and **6** or in their analogues substituted in the β-pyrrolic position,[6] the cathodic section of the voltammetric pattern is quite similar and closely resembles that of their unsubstituted reference compounds H_2DPP and [ZnDPP]·THF, with two neat monoelectronic reduction steps, chemically and electrochemically reversible. Considering the reduction potentials (Table 2 and ref.[6]) it appears that the displacement of the substituent carrying a dibutylamino group from the β-pyrrolic position to the *meso* one produces a less reducible system and thus has a marked effect on the LUMO energy, in agreement with the previously proposed enhancement of the electron donor effect of the dibutylamino group. The same conclusion can be applied to the reduction peaks of the Zn^{II} complex **6**, which are also characterised by the expected shift to the negative direction.

The increased role of the donor amino group on the π system of the conjugated molecule is reflected, in the case of substitution at the *meso* position, by the significant deviation from Kadish's rule; for instance let us consider the second oxidation peak discussed above: $\Delta E_{(ox-red)}$ is 1.90 V for **5** and 2.05 V for its analogue with the substituent in the β-pyrrolic position, compared with the regular value of 2.34 V for the reference unsubstituted compound H_2DPP. For the Zn^{II} complex **6** the value of $\Delta E_{(ox-red)}$ is 1.90 V, compared with 2.07 V for its analogue with the substituent in the β-pyrrolic position and 2.23 V for the unsubstituted ZnDPP.

Dipole Moments

Differently from 5,10,15,20-tetraphenylporphyrins and their Zn^{II} complexes substituted in the β-pyrrolic position,[6] the experimental determination by the Guggenheim method[18] of the dipole moment of 10,20-diphenyl porphyrins and their Zn^{II} complexes with the same substituents in the *meso* position, was not always reproducible because of insolubility or aggregation processes, the exceptions being the porphyrins **1** and **3** (Table 3). Therefore best geometries first, and then dipole moments, were theoretically calculated by an ab initio approach based on density functional theory (DFT),[11,12] using an extended basis set[13] (see Exp. Sect.).

As already suggested by the X-ray crystal structural determinations or by molecular mechanics modelling using the MM2 force field[14] our DFT calculations confirm that the aromatic ring of porphyrin Zn^{II} complexes with an *E*-ethylenic linker, such as **2** or **6**, is significantly twisted. (Table 4).

Our calculated angle of twisting for **2** (53.1°) is slightly higher than that obtained in the solid state by the X-ray crystal structure determination of the analogous compound, but without the nitro group in the *para* position (44.7°).[14] In general our calculations have produced an angle of twisting of 10,20-diphenylporphyrin Zn^{II} complexes with an *E*-ethylenic linker (about 52–54°) or an acetylenic linker (about 10–14.5°) (Table 4) that is higher than that calculated by the less sophisticated molecular mechanism modelling approach using the MM2 force field (about 38° for the *E*-ethylenic linker and about <0.1° for the acetylenic linker[14]).

The twisting of the porphyrin and aromatic rings calculated by our DFT approach is much less significant when the same *para*-substituted aromatic rings are bound, by the same linkers, to the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrin or its Zn^{II} complex, since the optimised geometries show a twisting angle of about 20–30° for an *E*-ethylenic linker (Table 4) or a much lower value for an acetylenic one.

In conclusion, we have produced additional structural evidence that the triple bond, because of the lower twisting

Table 3. Theoretical and experimental dipole moments (μ) in $CHCl_3$ and EFISH quadratic hyperpolarisability ($\beta_{1.907}$) measured in $CHCl_3$ working with an incident wavelength of 1.907 µm.

Compound[a]	μ_{theor}[b] (μ_{exp}) [D]	$\beta_{1.907}$ [10^{-30} esu][c]
(1*E*)-5[2-(4′-Nitrophenyl)ethenyl]-10,20-H_2DPP (**1**)	7.70[d] (6.45)	67
(1*E*)-5-[2-(4′-Nitrophenyl)ethenyl]10,20 ZnDPP (**2**)	7.73	–94
5-[2-(4′-Nitrophenyl)ethynyl]-10,20-H_2DPP (**3**)	8.54[d] (7.26)	64
5-[2-(4′-Nitrophenyl)ethynyl]-10,20-ZnDPP (**4**)	8.48	n.d.[e]
(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-H_2DPP (**5**)	6.07[d]	64
(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-ZnDPP (**6**)	5.89	87.5
5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-H_2DPP (**7**)	5.77[d]	99
5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-ZnDPP (**8**)	5.65	112

[a] H_2DPP = 10,20-diphenylporphyrin. [b] ab initio DFT calculations (see Experimental Section). [c] Mean values of measurements done at concencentrations 10^{-3} to 5×10^{-4} M. [d] Mean values of the two isomers with different locations of the NH bonds. [e] not soluble enough.

Table 4. Dihedral angle between the plane of the porphyrin ring and the plane of the aromatic ring (*meso* substituted porphyrinic molecules).

Compound[a]	θ [°]
(1*E*)-5[2-(4′-Nitrophenyl)ethenyl]-10,20-H_2DPP (**1**)	54.8
(1*E*)-5-[2-(4′-Nitrophenyl)ethenyl]10,20 ZnDPP (**2**)	53.1
5-[2-(4′-Nitrophenyl)ethynyl]-10,20-H_2DPP (**3**)	10.1
5-[2-(4′-Nitrophenyl)ethynyl]-10,20-ZnDPP (**4**)	10.0
(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-H_2DPP (**5**)	52.7
(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-ZnDPP (**6**)	51.8
5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-H_2DPP (**7**)	14.3
5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-ZnDPP (**8**)	14.6

Dihedral angle between the plane of the porphyrin ring and the plane of the aromatic ring (porphyrinic molecules substituted in β-pyrrolic position)[6]

Compound[b]	θ [°]
(1*E*)-2-(4-Nitrophenyl)ethenyl-H_2TPP	29.2
(1*E*)-2-(4-Nitrophenyl)ethenyl-ZnTPP	17.6
(1*E*,3*E*)-2-(4-Nitrophenyl)buta-1,3-dienyl-H_2TPP	18.5
(1*E*,3*E*)-2-(4-Nitrophenyl)buta-1,3-dienyl-ZnTPP	19.3
(1*E*)-2-(4-Dibutylaminophenyl)ethenyl-H_2TPP	20.3
(1*E*)-2-(4-Dibutylaminophenyl)ethenyl-ZnTPP	27.9

[a] H_2DPP = 10,20-diphenylporphyrin. [b] H_2TPP = 5,10,15,20-tetraphenylporphyrin.

of the aromatic ring should, in all cases, favour a more facile electronic communication between the aromatic ring (and therefore the electron-withdrawing or electron-donor groups) and the porphyrin ring.

The porphyrins **1** and **3**, with a substituent carrying an electron-withdrawing nitro group, and their Zn^{II} complexes **2** and **4** show dipole moments that are higher, and completely opposite in polarity, than those of porphyrins **5** and **7** and their Zn^{II} complexes **6** and **8**, with a substituent carrying an amino electron-donor group (Table 3), as reported for porphyrins and their Zn^{II} complexes with the same series of substituents in the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrin or its Zn^{II} complex.[6]

When there is excellent π conjugation between the porphyrin ring and the π linker, as when the linker is acetylenic, the calculated dipole moments of the compounds with a substituent carrying a nitro group are quite independent (about 8.5–8.8 D) of the position of substitution on the porphyrin ring (*meso* or β pyrrolic).[6] However, when the nitro or the dibutylamino groups are connected to the porphyrin ring by an *E*-ethylenic linker, the calculated dipole moments are slightly higher when substitution occurs in the β-pyrrolic position (8.5–8.8 D compared with 7.70–7.73 D for a substituent carrying a nitro group and 6.07–5.89 D compared with 5.33–5.16 D for a substituent carrying a dibutylamino group). The validity of our DFT calculated dipole moments is supported by the fairly good agreement between calculated values of porphyrins **1** and **3** and those measured experimentally (Table 3).

In conclusion the DFT calculations also provide evidence that for compounds **1**–**8** the π core of the porphyrin ring, already in the ground state, acts as an electron donor if the π-delocalised substituent in the *meso* position carries a nitro group, while it acts as an electron acceptor if it carries a dimethylamino or dibutylamino group. Such a trend was already observed when the same substituents were bound to the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrin or its Zn^{II} complex.[6]

Determination of the Quadratic Hyperpolarisability by the EFISH Technique

The determination of the second-order NLO response was carried out by the EFISH technique[19], which allows the evaluation of the molecular quadratic hyperpolarisability, β_λ, from Equation (1) (see Exp. Sect.). In order to avoid resonance enhancement, we worked with an off resonance incident wavelength, λ, of 1.907 μm. When applying Equation (1) to highly π-conjugated two-dimensional molecules, such as porphyrins and phthalocyanines, the usual approach that ignores the third-order electronic contribution to γ_{EFISH}, could not be considered to be completely reliable.[4c,20] However, for asymmetrically substituted phthalocyanines, structurally related to the porphyrinic chromophores investigated in this work, and carrying an aryl ethenyl or an aryl butadienyl spacer connecting the phthalocyanine ring to a nitro group in the *para* position, the third-order electronic contribution to γ_{EFISH} was evaluated as being much smaller than the dipolar orientational one and therefore negligible.[20] In accordance we reliably neglected the third-order electronic contribution in the determination of the quadratic hyperpolarisability $\beta_{1.907}$ from γ_{EFISH} by Equation (1).

According to our DFT calculations, the push-pull porphyrinic chromophores investigated in this work are characterised by a dipole moment axis, parallel to the π linker axis, as in 1D pseudo-linear organometallic push-pull chromophores.[21] In this approximation β_{vec}, which is the vectorial part of the quadratic hyperpolarisability tensor, and EFISH $\beta_{1.907}$, which is the projection of β_{vec} along the dipole moment axis, should coincide.

Since our investigation of the electronic absorption spectra provided evidence, particularly for compounds carrying a donor amino group, of aggregation processes even at low concentrations in nondonor solvents of low polarity such as $CHCl_3$, we carried out a series of EFISH measurements in $CHCl_3$ solutions of different concentrations of compound **2**, which could aggregate at relatively high concentration only by π-π stacking[16] and of compounds **5**–**8**, which could aggregate by intermolecular hydrogen bonding, or by intermolecular interaction of the amino donor group of the π-delocalised substituent with Zn^{II} via the axial position of another molecule. For the Zn^{II} complexes **2**, **4**, **6** and **8** the EFISH measurements were also carried out in the presence of an excess of pyridine, while for porphyrins **5** and **7** in the presence of traces of trifluoroacetic acid in order to suppress any intermolecular aggregation (Table 5).

In the presence of pyridine or trifluoroacetic acid, the product $\mu\beta_{1.907}$, obtained from γ_{EFISH} using Equation (1), was shown not to be dependent on dilution (within the experimental error of EFISH measurements on diluted solutions) while, without these additions, a significant increase by dilution was observed as expected for an increased dissociation (Table 5). Such an effect is less relevant for the Zn^{II} complex **2** confirming, as already suggested by the investigation on electronic absorption spectra, that strong aggregation occurs mainly when the π-delocalised substituent carries a donor amino group. Measurements on the Zn^{II} complex **4** were done only in the presence of pyridine because of the low solubility of the complex. Interestingly the order of magnitude and the sign of the product $\mu\beta_{1.907}$ do not change upon addition of pyridine or trifluoroacetic acid (Table 5).

Since the $\mu\beta_{1.907}$ values of the porphyrins **5** and **7** and of the Zn^{II} complexes **2**, **6** and **8** are dependent on dilution, it is expected that monomeric species prevail at higher dilutions (concentrations lower than 10^{-4} M). However, at these dilutions EFISH measurements are affected by a larger experimental error. Therefore, the values of EFISH $\beta_{1.907}$ reported in Table 3 are the mean values of many measurements carried out at concentrations about 10^{-4} M, thus discussions mainly concern their order of magnitude, rather than their absolute value.

The EFISH $\beta_{1.907}$ values (Table 3) of the porphyrins **1** and **3** are positive and higher than those of porphyrins carrying the same substituents in the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrin[6] (about 65×10^{-30} esu for **1** and **3** against $30–40 \times 10^{-30}$ esu, respectively).

Unexpectedly, EFISH $\beta_{1.907}$ of the Zn^{II} complex **2** is negative and with a significant absolute value, while the value of EFISH $\beta_{1.907}$ of the analogous Zn^{II} complex with the same substituent in the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrin is positive and with a lower absolute value[6] (about -94×10^{-30} esu for **2** compared with 30×10^{-30} esu for the analogous Zn^{II} complex).

Both porphyrins **5** and **7** and their Zn^{II} complexes **6** and **8** show, at concentrations about 10^{-4} M, a positive and fairly high value of EFISH $\beta_{1.907}$ (Table 3). As suggested by the significant increase of $\mu\beta_{1.907}$ by dilution (Table 5), the value of EFISH $\beta_{1.907}$ of the monomeric species of **6**–**8** should be higher. For **5** and **6**, the value of EFISH $\beta_{1.907}$ is quite similar to that of the corresponding chromophores with the same π-delocalised substituent in the β-pyrrolic position (64×10^{-30} esu for **5** and 87.5×10^{-30} esu for **6** compared with 75.7×10^{-30} esu and 127.5×10^{-30} esu).

In summary, with the exception of the anomaly of the sign of EFISH $\beta_{1.907}$ of **2** and **4**, the major differences between the two classes of porphyrinic chromophores carrying the same π-delocalised substituents in the β-pyrrolic[6] or *meso* positions is given by the higher absolute values of EFISH $\beta_{1.907}$ when the substituent carrying a nitro electron-withdrawing group is bound to the *meso* position. This latter result is in accordance with the proposal of Ratner, Marks et al.,[10] who suggested that second-order NLO responses should increase when π-delocalised substituents

Table 5. $\mu\beta_{1.907}$ values at different concentrations in $CHCl_3$ and in $CHCl_3$ with addition of pyridine or trifluoroacetic acid.

Compound[a]	Concentration	$\mu\beta_{1.907}$ [10^{-48} esu][b]	$\mu\beta_{1.907}$ [10^{-48} esu]
(1*E*)-5-[2-(4′-Nitrophenyl)ethenyl]-10,20-ZnDPP (**2**)	10^{-3}	–630	–815[c]
	5×10^{-4}	–816	–1015[c]
	10^{-4}	–960	–1210[c]
5-[2-(4′-Nitrophenyl)ethynyl]-10,20-ZnDPP (**4**)	10^{-3}	n.d.[d]	–645[c]
	5×10^{-4}		–795[c]
(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-H_2DPP (**5**)	10^{-3}	350	525[e]
	5×10^{-4}	427	615[e]
	10^{-4}	690	660[e]
(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-ZnDPP (**6**)	10^{-3}	407	815[c]
	5×10^{-4}	611	930[c]
	10^{-4}	1450	950[c]
5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-H_2DPP (**7**)	10^{-3}	514	750[e]
	5×10^{-4}	629	860[e]
	10^{-4}	1260	940[e]
5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-ZnDPP (**8**)	10^{-3}	473	625[c]
	2×10^{-4}	789	755[c]
	10^{-4}	1630	830[c]

[a] H_2DPP = 10,20-diphenylporphyrin. [b] In $CHCl_3$. [c] In $CHCl_3$ with the addition of pyridine. [d] Too insoluble for acceptable measurements. [e] In $CHCl_3$ with traces of trifluoroacetic acid.

with electron-acceptor groups are appended to *meso* electron-deficient centres instead of β-pyrrolic electron-rich centres.

We previously suggested[6] that in porphyrinic chromophores with a π-delocalised substituent carrying a nitro group the second-order NLO response can originate mainly from a charge transfer from the occupied π orbitals of the porphyrin ring to the π*-antibonding orbitals of the π linker in accordance with a significant π conjugation between the π core of the porphyrin ring and the π linker. In this hypothesis the porphyrin ring acts as donor to the acceptor aromatic ring carrying the nitro group in the *para* position and the charge transfer takes place in the same direction as the dipole moment, in agreement with the positive value of the quadratic hyperpolarisability EFISH $\beta_{1.907}$.

For compounds **1**–**4**, our analysis of the absorption electronic spectra failed to produce clear direct evidence of such a charge transfer process. However, the voltammetric investigation not only has shown a significant effect on the LUMO energy of the porphyrin ring when conjugated with a π linker, but also revealed a more relevant effect when substitution occurs in the *meso* position, supporting a shift of the above proposed charge transfer process at lower energy, in agreement with the observed increased absolute value of EFISH $\beta_{1.907}$.

However, the anomalous negative sign of EFISH $\beta_{1.907}$ found for the Zn^{II} complexes **2** and **4** cannot be explained by such a charge transfer process, given that EFISH $\beta_{1.907}$ remains positive for analogous Zn^{II} complexes carrying the same π-delocalised substituents in the β-pyrrolic position.[6] At the moment only a detailed theoretical investigation, which is underway, may produce an explanation for the negative EFISH $\beta_{1.907}$ found for the Zn^{II} complexes **2** and **4**, since the involvement of aggregation by π-π stacking,[16] which occurs certainly more easily in derivatives of 10,20-diphenylporphyrin than in those of 5,10,15,20-tetraphenylporphyrin, can be discarded because the second-order NLO response of **2** and **4** remains negative also in the presence of pyridine (Table 5), which prevents this kind of aggregation.

The lack of a significant decrease of EFISH $\beta_{1.907}$ when the π-delocalised substituent, carrying a strong electron-donor group, is moved from the electron-rich β-pyrrolic position to the electron deficient *meso* position does not completely fit with the proposal of Ratner, Marks et al.[10].

As for the analogues of **5** and **6** with the same π-delocalised substituent in the β-pyrrolic position,[6] we can tentatively propose that the high and positive EFISH $\beta_{1.907}$ values of chromophores **5**–**8** originate from an enhancement of the donor properties of the dibutylamino or dimethylamino group, induced by the very electron-rich π system of the porphyrin, which produces a significant depletion of the electron density on the donor group and thereby a reduction of the ground state polarisation.[22] In this view there is no involvement of the π core of the porphyrin ring in the excitation process controlling the second-order NLO response.

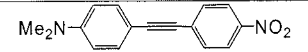
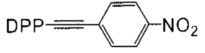
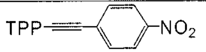
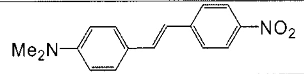
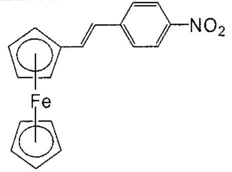
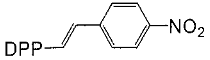
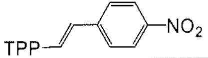
In agreement with this proposal, our voltammetric investigation has shown, in both classes of porphyrinic chromophores investigated by us up to now,[6] an enhanced donor effect of the dibutylamino or dimethylamino group.

Conclusions

This and our previous investigation[6] on push-pull chromophores with electron-withdrawing groups connected to the porphyrinic ring, either in the β-pyrrolic or *meso* position by an arylethenyl or arylethynyl linker, provide clear evidence for the significant π conjugation between the porphyrin π core and the π-delocalised substituent, as a possible origin of the second-order NLO responses by a charge transfer process. Such conjugation seems to be more facile, according to the voltammetric investigation, if the π-delocalised substituent is bound to the *meso* position instead of the β-pyrrolic one. Therefore if the substitution occurs in the *meso* position, the second-order NLO response is favoured due to a more facile charge transfer and to the increased push properties of the porphyrin ring if we assume a rather simplified description of these new push-pull chromophores as pseudo 1D push-pull systems.

Accordingly, the experimental values of EFISH $\beta_{1.907}$ of chromophores **1** and **3** are comparable with those of structurally related organic push pull chromophores having, as the push group, a *para*-dimethylamino phenyl moiety, and are more significant than that having, as the push group, a ferrocenyl or of a 5,10,15,20-tetraphenylporphyrin moiety substituted in the β-pyrrolic position (Table 6).

Table 6. Quadratic hyperpolarisability $\beta_{1.907}$ of some organic and organometallic push-pull systems measured in CHCl$_3$ by the EFISH technique at an incident wavelength of 1.907 μm.

Compound[a]	$\beta_{1.907}$ 10^{-30} (esu)
	46[b]
 **3**	64
	30.1[c]
	73[b]
	31[d]
 **1**	67
	39.3[c]

[a] DPP = 10,20-diphenylporphyrin substituted in the *meso* position; TPP = 5,10,15,20-tetraphenylporphyrin substituted in the β-pyrrolic position. [b] Ref.[23] [c] Ref.[6] [d] Ref.[24]

We also propose, when the substituent bound to the *meso* or β-pyrrolic position carries an electron-donor group, that the electron-rich and highly polarisable character of the porphyrin ring may be the origin of an electron screening of the ground-state polarisation, so that the electron-rich ring system weakly withdraws excessive electron density from the donor substituent through inductive effects, thereby increasing its donor properties.[22] Thus this process produces an enhancement of the second-order NLO response controlled by the $n \rightarrow \pi^*$ transition.

In accordance with this hypothesis the value of EFISH $\beta_{1.907}$ of chromophores **5**, **6** and **7**, **8** increases by complexation to Zn^{II} (e.g. **6** > **5** and **8** > **7** see Table 3), which produces a higher and more polarisable electron density on the porphyrin ring as supported by the voltammetric investigation.

Since the π-electron core of the porphyrin ring is not directly involved in the excitation process controlling the second-order NLO response, it becomes irrelevant if the π-delocalised substituent is appended to an electron-rich (β-pyrrolic) or electron-deficient (*meso*) position of the porphyrin ring, as experimentally observed.

Despite the above reported agreement with a series of experimental observations, our interpretation of the electronic origin of the second-order NLO response in the series of compounds investigated in this and in our previous work,[6] does not explain the negative sign of EFISH $\beta_{1.907}$ of the Zn^{II} complexes **2** and **4**.

Probably, the two-dimensional highly polarisable π system of the porphyrin core is far too complex for such a relatively simple approach based just on considerations typical of traditional 1D organic or organometallic push-pull chromophores. As already mentioned, ab initio time-dependent DFT investigations are underway in our laboratory in an effort to achieve a more profound understanding of the electronic origin of the significant second-order NLO response of these new push-pull chromophores based on the porphyrin ring.

In conclusion this and our previous work[6] have experimentally confirmed an interesting role of the porphyrin ring in push-pull chromophores, already theoretically suggested by Ratner, Marks et al.[10]

Experimental Section

All solvents and chemicals were of reagent-grade quality, purchased commercially and used without further purification unless otherwise stated. 10,20-diphenylporphyrin[25a] was prepared according to literature methods from dipyrrylmethane.[25b] 4-Nitrobenzyltriphenylphosphonium bromide and 4-(dibutylamino)benzyltriphenylphosphonium chloride were prepared following the new procedure described in our previous work.[6] 5-Bromo-10,20-diphenylporphyrin was synthesised using the method described by Yeung et al.[5c] 4-Nitrophenyl acetylene was prepared according to Takahashi el al.[26] ^{1}H NMR spectra were recorded with a Bruker AC-300 spectrometer in $CDCl_3$ as solvent; electronic absorption 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. 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, according to the Guggenheim method,[18] using a WTW-DM01 dipolemeter (dielectric constant) coupled with a Pulfrich Zeiss PR2 refractometer (refractive index).

Cyclic Voltammetry

The cyclovoltammetric (CV) investigation was carried out using an Autolab PGSTAT 12 potentiostat/galvanostat (EcoChemie, The Netherlands) run by a PC with GPES software, correcting the ohmic drop by the positive feedback technique,[27] with a glassy carbon GC (Amel, radius 1.5 mm) as the working electrode, a platinum counter-electrode, and an aqueous saturated calomel electrode (SCE) as the operating reference electrode (the half-wave potential of the ferrocinium|ferrocene redox couple, recommended by IUPAC for inter-solvent comparison of potential scales,[28] being 0.484 V when measured in CH_2Cl_2, added with 0.1 M TBAP against our aqueous SCE). The working solutions were made up in dichloromethane CH_2Cl_2 (Merck, HPLC grade), added with 0.1 M tetrabutylammonium perchlorate TBAP (FLUKA) as the supporting electrolyte, working in a cell thermostatted at 298 K. The solutions, carefully deaerated by nitrogen bubbling, had concentrations ranging from 5×10^{-4} to 7×10^{-4} M (with the exception of the less soluble porphyrin complex **4**, which reaches saturation at concentrations below 3×10^{-4} M). The optimised polishing procedure for the working GC electrode consisted of surface treatment with diamond powder (Aldrich diameter 1 µm) on a wet cloth (DP-Nap, Struers).

The electrochemical reversibility and electron number of each well-defined CV peak were checked by classical tests[29] including analysis of (a) the I_p vs. $v^{1/2}$ characteristics; (b) the E_p vs. $\log v$ characteristics; (c) the $(E_p - E_{p/2})$ vs. $\log v$ characteristics, and (d) the "stationary", step-like waves obtained by convolutive analysis of the original CV characteristics.

For comparison purposes, the CV characteristics of the reference compounds H_2DPP, [ZnDPP]·THF and 4′-(*p*-nitrophenyl)-2,2′:6′,2′′-terpyridine, recorded under the same experimental conditions, are reported in Table 2. The 4′-(*p*-nitrophenyl)-2,2′:6′,2′′-terpyridine has been included as a model for the nitro group reactivity.

EFISH Measurements

EFISH measurements were performed in $CHCl_3$ solutions, as a function of concentration, working at 1.907 µm incident wavelengths using a Q-switched Nd:YAG laser with 60 and 20 ns pulse durations, 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).[19] In the EFISH experiments the incident beam was synchronised with a DC field applied to the solution containing the molecular species 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 response

β_λ was determined (assumed to be real as the imaginary was neglected) from the experimental value γ_{EFISH}, using Equation (1).

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

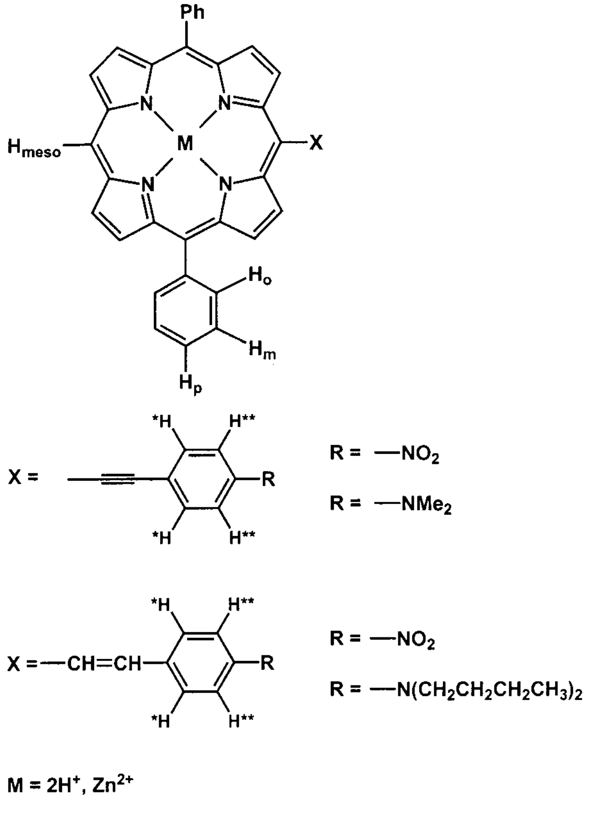
where γ_{EFISH} is the sum of a cubic electronic contribution $\gamma(-2\omega; \omega, \omega, 0)$ and of a quadratic orientational contribution $\mu\beta_\lambda(-2\omega; \omega, \omega)/5kT$; μ is the ground state dipole moment and β_λ is the projection along the dipole moment direction of the vectorial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

Computational Methods

Geometry optimisation and population analysis of the compounds **1**–**8** were carried out in the framework of the density functional theory (DFT) by using the BP86 functional[12] and an all-electron valence triple-ζ basis set with polarisation functions on all atoms (TZVP).[13] Values of the dipole moments moduli and components were computed using the Turbomole suite of programs[30] in connection with the resolution of identity (RI) approximation.[31]

Synthesis of Porphyrins

For the numering of atoms see below.



5-Formyl-10,20-diphenylporphyrin: This porphyrin was prepared by the following three steps:[15]

(a) 10,20-Diphenylporphyrinatocopper(II): A slightly warm solution of $Cu(OAc)_2 \cdot H_2O$ (125 mg, 0.627 mmol) in MeOH (15 mL) was slowly added to a refluxing solution of 10,20-diphenylporphyrin (264 mg, 0.570 mmol) in $CHCl_3$ (60 mL). After two hours the red reaction mixture was cooled and the solvents evaporated to dryness in vacuo. The red residue was collected with MeOH, filtered and washed with MeOH to afford 248 mg (83%) of a red powder. UV/Vis ($CHCl_3$): $\lambda_{\max}$ (logε) = 405 (5.63), 527 (4.23), 561 (3.65) nm. $C_{32}H_{20}CuN_4$ (523.5): calcd. C 73.35, H 3.82, N 10.70; found C 72.94, H 3.78, N 10.89.

(b) 5-Formyl-10,20-diphenylporphyrinatocopper(II): A solution of dimethylformamide (1.1 mL, 14.2 mmol) and phosphoryl chloride (1.1 mL, 12.0 mmol) was left at room temperature and under magnetic stirring for 30 min. After this time, a solution of 10,20-diphenylporphyrinatocopper(II) (114 mg, 0.218 mmol) in 1,2-dichloroethane (50 mL) was added and the reaction mixture was stirred at 60 °C for 2 h. The dark green solution was then diluted with a saturated aqueous solution of CH_3COONa (150 mL) and maintained at 60 °C whilst stirring for a further 2 h. The organic phase was separated, washed with H_2O (2 × 100 mL), dried with Na_2SO_4 and evaporated in vacuo. Purification of the residue by column chromatography (silica gel, CH_2Cl_2/*n*-hexane, 7:3) afforded 96 mg (80%) of pure product. UV/Vis ($CHCl_3$): $\lambda_{\max}$ (logε) = 417 (5.42), 547 (3.97), 591 (4.15) nm. $C_{33}H_{20}CuN_4O$ (551.5): calcd. C 71.80, H 3.63, N 10.15; found C 72.30, H 3.76, N 10.30.

(c) 5-Formyl-10,20-diphenylporphyrin: A solution of 5-formyl-10,20-diphenylporphyrinatocopper(II) (251 mg, 0.455 mmol) in a mixture of H_2SO_4/TFA (1:10 v/v, 15 mL) was stirred for 10 min at room temperature, and then quenched by adding an excess of ice. The product was extracted with CH_2Cl_2 (2 × 50 mL), the organic phase was washed with aqueous NaOH (20%, 50 mL) and with H_2O (2 × 50 mL), the solvent was evaporated to dryness and the residue was washed with pentane to afford 220 mg (quantitative yield) of a violet powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 12.62 (s, 1 H, CHO), 10.28 (s, 1 H, H_{meso}), 10.10 (d, J = 4.98 Hz, 2 H, H_{pyrrolic}), 9.30 (d, J = 4.44 Hz, 2 H, H_{pyrrolic}), 9.08 (d, J = 4.98 Hz, 2 H, H_{pyrrolic}), 8.91 (d, J = 4.44 Hz, 2 H, H_{pyrrolic}), 8.22 (m, 4 H, H_o), 7.85 (m, 6 H, $H_{m,p}$), –2.41 (s, 2 H, NH) ppm. UV/Vis ($CHCl_3$): $\lambda_{\max}$ (logε) = 420 (5.35), 520 (4.01), 559 (3.95), 593 (3.77), 648 (3.81) nm. $C_{33}H_{22}N_4O$ (490): calcd. C 80.82, H 4.49, N 11.43; found C 80.65, H 4.36, N 11.60.

(1*E*)-5-[2-(4′-Nitrophenyl)ethenyl]-10,20-diphenylporphyrin (1): A suspension of 5-formyl-10,20-diphenylporphyrin (238 mg, 0.484 mmol), 4-nitrobenzyltriphenylphosphonium bromide (670 mg, 1.407 mmol) and solid NaOH 20–40 mesh beads (400 mg, 10 mmol) in anhydrous 1,2-dichloroethane (25 mL) was refluxed, with magnetic stirring and under a nitrogen atmosphere for 4 h. After this time the solvent was evaporated to dryness, the residue was purified by column chromatography (silica gel CH_2Cl_2/*n*-hexane, 7:3). The product obtained from the column chromatography was first washed with MeOH and then crystallised from CH_2Cl_2/MeOH to give 145 mg (49%) of pure **1**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.17 (s, 1 H, H_{meso}), 9.89 (d, J = 15.87 Hz, 1 H, =CH), 9.50 (d, J = 4.83 Hz, 2 H, H_{pyrrolic}), 9.30 (d, J = 4.65 Hz, 2 H, H_{pyrrolic}), 8.97 (d, J = 4.77 Hz, 4 H, H_{pyrrolic}), 8.43 (d, J = 8.76 Hz, 2 H, H**), 8.24 (m, 4 H, H_o), 8.05 (d, J = 8.76 Hz, 2 H, H*), 7.80 (m, 6 H, $H_{m,p}$), 7.42 (d, J = 15.93 Hz, 1 H, CH=), –2.78 (s, 2 H, NH) ppm. UV/Vis ($CHCl_3$): $\lambda_{\max}$ (logε) = 422 (5.27), 518 (4.07), 564 (4.11), 594 (3.89), 655 (3.65) nm. $C_{40}H_{27}N_5O_2$ (609): calcd. C 78.82, H 4.43, N 11.49; found C 78.65, H 4.30, N 11.48.

5-[2-(4′-Nitrophenyl)ethynyl]-10,20-diphenylporphyrin (3): Trifluoroacetic acid (2 mL) was added in four portions to a suspension of 5-[2-(4′-nitrophenyl)ethynyl]-10,20-diphenylporphyrinatozinc(II) (**4**) (100 mg, 0.149 mmol) in CH_2Cl_2 (50 mL) and the reaction mixture was stirred at room temperature for 18 h. After this time, water (30 mL) was added and the mixture was carefully neutralised with a saturated aqueous solution of $NaHCO_3$. The organic phase was separated, dried with $MgSO_4$ and the solvent evaporated in vacuo to afford 90 mg (quantitative yield) of porphyrin **3**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.21(s, 1 H, H_{meso}), 9.76 (d, J = 4.83 Hz, 2 H, $H_{pyrrolic}$), 9.30 (d, J = 4.62 Hz, 2 H, $H_{pyrrolic}$), 9.01 (d, J = 4.80 Hz, 2 H, $H_{pyrrolic}$), 8.95 (d, J = 4.62 Hz, 2 H, $H_{pyrrolic}$), 8.41(d, J = 8.76 Hz, 2 H, H**), 8.23 (m, 4 H, H_o), 8.13 (d, J = 8.73 Hz, 2 H, H*), 7.81 (m, 6 H, $H_{m,p}$), –2.54 (s, 2 H, NH) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 436 (5.15), 529 (3.91), 573 (4.32), 602 (3.79), 661 (3.94) nm. $C_{40}H_{25}N_5O_2$ (607): calcd. C 79.08, H 4,12, N 11.53; found C 78.96, H 4.16, N 11.53.

(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-diphenylporphyrin (5): A suspension of 5-formyl-10,20-diphenylporphyrin (103 mg, 0.211 mmol), 4-(dibutylamino)benzyltriphenylphosphonium chloride (185 mg, 0.358 mmol) and solid NaOH 20–40 mesh beads (337 mg, 8.436 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred at room temperature, under a nitrogen atmosphere, for 4 h. After this time the solvent was evaporated and the residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane, 7:3) to afford 87 mg (59%) of **5** as a violet powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.08 (s, 1 H, H_{meso}), 9.56 (m, 3 H, CH, $H_{pyrrolic}$), 9.27 (d, J = 4.53 Hz, 2 H, $H_{pyrrolic}$), 8.96 (d, J = 4.53 Hz, 2 H, $H_{pyrrolic}$), 8.91 (d, J = 4.68 Hz, 2 H, $H_{pyrrolic}$), 8.26(m, 4 H, H_o), 7.82, (m, 8 H, H*, $H_{m,p}$), 7.27 (d, J = 16.0 Hz, 1 H, =CH), 6.86 (d, J = 8.58 Hz, 2 H, H**), 3.43 (t, J = 7.45 Hz, 2 H, CH_{2Butyl}), 1.72 (m, 2 H, CH_{2Butyl}), 1.46 (m, 2 H, CH_{2Butyl}), 1.05 (t, J = 7.23 Hz, 3 H, CH_{3Butyl}), –2.62 (s, 2 H, NH) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 353 (4.34), 410 (5.06), 521 (4.00), 579 (4.15), 665 (3.76), 747 (3.52) nm. $C_{48}H_{45}N_5$ (691): calcd. C 83.36, H 6.51, N 10.13; found C 82.95, H 6.57, N 9.97.

5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-diphenylporphyrin (7): Trifluoroacetic acid (2 mL) was added in four portions to a suspension of 5-[2-(4′-dimethylaminophenyl)ethynyl]-10,20-diphenylporphyrinatozinc(II) (**8**) (100 mg, 0.150 mmol) in CH_2Cl_2 (50 mL) and the reaction mixture was stirred at room temperature for 18 h. After this time, water (30 mL) was added and the mixture was carefully neutralised with a saturated aqueous solution of $NaHCO_3$. The organic phase was separated, dried with $MgSO_4$ and the solvent evaporated in vacuo to afford 90 mg (quantitative yield) of porphyrin **7**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.09 (s, 1 H, H_{meso}), 9.81 (d, J = 4.74 Hz, 2 H, $H_{pyrrolic}$), 9.24 (d, J = 4.65 Hz, 2 H, $H_{pyrrolic}$), 8.93 (d, J = 4.35 Hz, 2 H, $H_{pyrrolic}$), 8.92 (d, J = 4.20 Hz, 2 H, $H_{pyrrolic}$), 8.23 (m, 4 H, H_o), 7.91 (d, J = 8.76 Hz, 2 H, H*), 7.79 (m, 6 H, $H_{m,p}$), 6.87 (d, J = 8.82 Hz, 2 H, H**), 3.11 (s, 6 H, NCH_3), –2.47 (s, 2 H, NH) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 425 (5.02), 441, 523 (3.93), 587 (4.32), 673 (3.94) nm. $C_{42}H_{31}N_5$ (605): calcd. C 83.31, H 5.12, N 11.57; found C 82.98, H 5.17, N 11.46.

Synthesis of Zn^{II} Complexes

Zn^{II} complexes **2** and **6** were synthesised following the general procedure described in the literature.[32] In a typical preparation the free porphyrin (100 mg) was dissolved in slightly warmed $CHCl_3$ (20 mL) and a solution of $Zn(OAc)_2 \cdot 2H_2O$ (free porphyrin/metal salt = 1:1.1) in MeOH (10 mL) was then added. The mixture was refluxed for 1 h, was then evaporated to dryness and the residue was collected with MeOH, filtered and washed with MeOH.

(1*E*)-5-[2-(4′-Nitrophenyl)ethenyl]-10,20-diphenylporphyrinatozinc(II) (2): This compound was obtained in quantitative yield as a violet powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.10 (s, 1 H, H_{meso}), 9.89 (d, J = 16.32 Hz, 1 H, =CH), 9.56 (d, J = 4.41 Hz, 2 H, $H_{pyrrolic}$), 9.35 (d, J = 4.29 Hz, 2 H, $H_{pyrrolic}$), 9.04 (d, J = 3.99 Hz, 4 H, $H_{pyrrolic}$), 8.43 (d, J = 7.59 Hz, 2 H, H**), 8.22 (m, 4 H, H_o), 8.05 (d, J = 7.74 Hz, 2 H, H*), 7.79 (m, 6 H, $H_{m,p}$), 7.41 (d, J = 16.24 Hz, 1 H, CH=) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) 422 (5.23), 552 (4.19), 599 (4.04) nm; ($CHCl_3$ with addition of pyridine): λ_{max} (logε) = 428 (5.05), 566 (3.72), 626 (3.89) nm. $C_{40}H_{25}N_5O_2Zn$ (672.4): calcd. C 71.39, H 3.72, N 10.41; found C 71.50, H 3.61, N 10.30.

(1*E*)-5-[2-(4′-Dibutylaminophenyl)ethenyl]-10,20-diphenylporphyrinatozinc(II) (6): This compound was obtained in quantitative yield as a violet powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.06 (s, 1 H, H_{meso}), 9.61 (d, J = 4.65 Hz, 2 H, $H_{pyrrolic}$), 9.48 (d, J = 15.75 Hz, 1 H, CH=), 9.28 (d, J = 4.53 Hz, 2 H, $H_{pyrrolic}$), 8.99 (d, J = 4.53 Hz, 4 H, $H_{pyrrolic}$), 8.96 (d, J = 4.65 Hz, 2 H, $H_{pyrrolic}$), 8.21 (m, 4 H, H_o), 7.77 (m, 8 H, H*, $H_{m,p}$), 7.25 (d, J = 15.75 Hz, 1 H, =CH), 6.82 (d, J = 8.55 Hz, 2 H, H**), 3.40 (t, J = 7.52 Hz, 2 H, CH_{2Butyl}), 1.67 (m, 2 H, CH_{2Butyl}), 1.43 (m, 2 H, CH_{2Butyl}), 1.02 (t, J = 7.28 Hz, 3 H, CH_{3Butyl}) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 349 (4.35), 408 (5.26), 554 (4.27), 606 (4.32) nm; ($CHCl_3$ with addition of pyridine): λ_{max} (logε) = 428 (5.20), 563 (4.06), 613 (4.09) nm. $C_{48}H_{43}N_5Zn$ (754.4): calcd. C 76.35, H 5.70, N 9.28; found C 75.99, H 5.68, N 9.41.

5-[2-(4′-Nitrophenyl)ethynyl]-10,20-diphenylporphyrinatozinc(II) (4): The catalytic solution was prepared by heating $Pd_2(dba)_3$ (9.5 mg, $9.9 \cdot 10^{-3}$ mmol), PPh_3 (21.8 mg, $8.3 \cdot 10^{-2}$ mmol) and CuI (7.8 mg, 4.1×10^{-2} mmol) in freshly distilled Et_3N (25 mL) at 70 °C for 30 min under a nitrogen atmosphere. This solution was transferred into a solution of 5-bromo-10,20-diphenylporphyrinatozinc(II) (100 mg, 0.165 mmol) and (4-nitrophenyl)acetylene (74 mg, 0.50 mmol) in anhydrous toluene (25 mL) and pyridine (0.6 mL) under a nitrogen atmosphere, and the mixture was heated at 80 °C and stirred for 1 h. After this time the solution was cooled and filtered through silica eluting with toluene and the solvent was evaporated to dryness. The residue was washed several times with small amounts of MeOH and $CHCl_3$ alternately to afford 93 mg (85%) of pure **4**. ^{1}H NMR (300 MHz, $CDCl_3$ + Pyridine d_5): δ = 10.12 (s, 1 H, H_{meso}), 9.74 (d, J = 4.59 Hz, 2 H, $H_{pyrrolic}$), 9.26 (d, J = 4.47 Hz, 2 H, $H_{pyrrolic}$), 8.99 (d, J = 4.59 Hz, 2 H, $H_{pyrrolic}$), 8.92 (d, J = 4.44 Hz, 2 H, $H_{pyrrolic}$), 8.36 (d, J = 7.47 Hz, 2 H, H**), 8.20 (m, 4 H, H_o), 8.08 (d, J = 7.47 Hz, 2 H, H*), 7.75 (m, 6 H, $H_{m,p}$) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 439 (5.16), 560 (3.68), 608 (4.07) nm; ($CHCl_3$ with addition of pyridine): λ_{max} (logε) = 449 (5.17), 575 (3.92), 634 (4.47) nm. $C_{40}H_{23}N_5O_2Zn$ (670.4): calcd. C 71.60, H 3.43, N 10.44; found C 71.51, H 3.48, N 10.32.

5-[2-(4′-Dimethylaminophenyl)ethynyl]-10,20-diphenylporphyrinatozinc(II) (8): The catalytic solution was prepared by heating a solution of $Pd_2(dba)_3$ (9.5 mg, $9.9 \cdot 10^{-3}$ mmol), PPh_3 (21.8 mg, $8.3 \cdot 10^{-2}$ mmol) and CuI (7.8 mg, $4.1 \cdot 10^{-2}$ mmol) in freshly distilled Et_3N (25 mL) at 70 °C for 30 min under a nitrogen atmosphere. This solution was transferred into a solution of 5-bromo-10,20-diphenylporphyrinatozinc(II) (100 mg, 0.165 mmol) and [4-(dimethylamino)phenyl]acetylene (73 mg, 0.50 mmol) in anhydrous toluene (25 mL) and pyridine (0.6 mL) under a nitrogen atmosphere, and the mixture was heated at 80 °C and stirred for 1.5 h. After this time the solution was cooled, filtered through silica gel, eluted with toluene, and the solvent was evaporated to dryness. The residue was washed several times with small amounts of MeOH and $CHCl_3$ alternately to afford 65 mg (59%) of pure **8**. ^{1}H NMR (300 MHz, $CDCl_3$ with addition of Pyridine d_5): δ = 10.05 (s, 1 H, H_{meso}), 9.83 (d, J = 4.56 Hz, 2 H, $H_{pyrrolic}$), 9.25 (d, J = 4.47 Hz, 2 H, $H_{pyrrolic}$), 8.95 (d, J = 4.92 Hz, 2 H, $H_{pyrrolic}$), 8.94 (d, J = 4.98 Hz, 2 H, $H_{pyrrolic}$), 8.23 (m, 4 H, H_o), 7.92 (d, J = 8.82 Hz, 2 H, H*), 7.77 (m, 6 H, $H_{m,p}$), 6.89 (d, J = 8.88 Hz, 2 H, H**), 3.11 (s, 6 H, NCH_3) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 428 (4.97), 448 (4.98), 565 (4.02), 615 (4.24) nm; ($CHCl_3$ with addition of pyridine):

λ_{max} (logε) = 451 (5.14), 579 (3.87), 632 (4.30) nm. $C_{42}H_{29}N_5Zn$ (668.4): calcd. C 75.40, H 4.34, N 10.47; found C 75.47, H 4.30, N 10.33.

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[1] a) J. Zyss, *Molecular Non Linear Optics: Materials, Physics and Devices*, Ed Academic Press, Boston **1993**; b) B. E. A. Saleh, M. C. Telch, *Fundamentals of Photonics*, Wiley: New York **1991**.

[2] a) D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195–242; b) P. M. Burland, R. D. Miller, C. A. Walash, *Chem. Rev.* **1994**, *94*, 31–75; c) T. J. Marks, M. A. Ratner, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155–173.

[3] a) I. R. Whittal, A. M. McDonagh, M. G. Humphrey, *Adv. Organomet. Chem.* **1998**, *42*, 291–362; b) S. Di Bella, *Chem. Soc. Rev.* **2001**, *30*, 355–366; c) N. J. Long, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21–38; d) B. J. Coe, *Comprehensive Coordination Chemistry II* (Eds.: J. A. Meyer, T. J. McCleverty); Elsevier Pergamon: Oxford, U. K., **2004**; vol. 9, pp. 621–687.

[4] a) K. S. Suslick, C. T. Chen, G. R. Meredith, L. T. Cheng, *J. Am. Chem. Soc.* **1992**, *114*, 6928–6930; b) H. Chou, C.-T. Chen, K. F. Stork, P. W. Bohn, K. S. Suslick, *J. Phys. Chem.* **1994**, *98*, 383–385; 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.

[5] a) S. M. Le Cours, H. W. Guan, S. G. Di Magno, C. H. Wang, M. J. Therien, *J. Am. Chem. Soc.* **1996**, *118*, 1497–1503; b) L. Karki, F. W. Vance, J. H. Hupp, S. M. Le Cours, M. J. Therien, *J. Am. Chem. Soc.* **1998**, *120*, 2606–2611; c) M. Yeung, A. C. H. Ng, M. G. D. Drew, E. Vorpagel, E. M. Breitung, R. J. McMahon, D. K. P. Ng, *J. Org. Chem.* **1998**, *63*, 7143–7150; 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.

[6] E. Annoni, M. Pizzotti, R. Ugo, S. Quici, T. Morotti, M. Bruschi, P. Mussini, *Eur. J. Inorg. Chem.* **2005**, 3857–3874.

[7] a) G. de La Torre, P. Vàsquez, F. Agullò-Lòpez, T. Torres, *J. Mater. Chem.* **1998**, *8*, 1671–1683 and references cited therein; b) G. de La Torre, T. Torres, F. Agullò-Lòpez, *Adv. Mater.* **1997**, *9*, 265–269 and references cited therein; c) G. de la Torre, P. Vazquez, F. Agullò-Lòpez, T. Torres, *Chem. Rev.* **2004**, *104*, 3723–3750.

[8] D. A. Offord, S. B. Sachs, M. S. Ennis, T. A. Eberspacher, J. H. Griffin, C. E. D. Chidsey, J. P. Collman, *J. Am. Chem. Soc.* **1998**, *120*, 4478–4487.

[9] a) M. Nappa, J. S. Valentine, *J. Am. Chem. Soc.* **1978**, *100*, 5075–5080; b) A. Antipas, J. W. Buchler, M. Gouterman, P. D. Smith, *J. Am. Chem. Soc.* **1978**, *100*, 3015–3024.

[10] I. D. L. Albert, T. J. Marks, M. A. Ratner, *Chem. Mater.* **1998**, *10*, 753–762.

[11] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[12] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

[13] A. Schafer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.

[14] T. E. O. Screen, I. M. Blake, L. H. Rees, W. Clegg, S. J. Borwick, H. L. Anderson, *J. Chem. Soc., Perkin Trans. 1* **2002**, 320–329.

[15] K. Susumu, T. Shimidzu, K. Tanaka, H. Segawa, *Tetrahedron Lett.* **1996**, *37*, 8399–8402.

[16] W. I. White, *The Porphyrins*, vol. V, pp. 303–335 (Ed.: D. Dolphin), Acad. Press, New York, **1978**.

[17] J. H. Furhop, K. M. Kadish, D. G. Davis, *J. Am. Chem. Soc.* **1973**, *95*, 5140–5147.

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

[19] a) I. Ledoux, J. Zyss, *Chem. Phys.* **1982**, *73*, 203–213; b) D. J. Williams, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 690–703 and references cited therein.

[20] G. Rojo, G. de la Torre, J. Garcia-Ruiz, I. Ledoux, T. Torres, J. Zyss, F. Agullo-Lopez, *Chem. Phys.* **1999**, *245*, 27–34 and references cited therein.

[21] a) D. Roberto, R. Ugo, S. Bruni, E. Cariati, F. Cariati, P. Fantucci, S. Quici, I. Ledoux, J. Zyss, *Organometallics* **2000**, *19*, 1775–1788; b) E. Lucenti, E. Cariati, C. Dragonetti, L. Manassero, F. Tessore, *Organometallics* **2004**, *23*, 687–692.

[22] I. D. L. Albert, T. J. Marks, M. A. Ratner, *J. Am. Chem. Soc.* **1997**, *119*, 6575–6582.

[23] L. T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, *J. Phys. Chem.* **1991**, *95*, 10631–10643.

[24] D. R. Kanis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 10338–10357.

[25] a) S. G. Di Magno, V. S. Y. Lin, M. J. Therien, *J. Org. Chem.* **1993**, *58*, 5983–5993; b) M. J. Plater, S. Aiken, G. Bourhill, *Tetrahedron* **2002**, *58*, 2405–2413.

[26] S. Takahashi, Y. Kuroyama, K. Sorogashira, N. Hagihara, *Synthesis* **1980**, 627–629.

[27] D. Britz, *Electroanal. Chem.* **1978**, *88*, 309–352.

[28] G. Gritzner, J. Kuta, *Pure Appl. Chem.* **1984**, *56*, 461–466.

[29] A. J. Bard, L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, Wiley, New York, **2002**.

[30] R. Ahlrichs, M. Bar, M. Haser, C. Horn, C. Kolmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169.

[31] a) K. Eichkorn, O. Treutler, H. Öhm, M. Haser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283–289; b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124.

[32] A. D. Adler, F. R. Longo, F. Kampas, J. Kim, *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.

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