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Amplified Two-Photon Absorption in *Trans*-A₂B₂-Porphyrins Bearing Nitrophenylethynyl Substituents

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Abstract

We show that peripheral nitro groups enhance the maximum two-photon absorption cross-section of *trans*-A₂B₂-porphyrins bearing two phenylethynyl substituents by more than one order of magnitude. Maximum values as high as 1000 GM result from realization of suitable conditions for effective resonance enhancement along with a lowering of the energy and intensification of the two-photon allowed transitions in the Soret region.

Keywords

chromophores; nonlinear optics; porphyrinoids; two-photon absorption; π -expansion

1. Introduction

Porphyrin derivatives exhibit intriguing nonlinear optical properties that are useful for all-optical switching and other optoelectronic devices.^[1] There is great interest in developing porphyrins with increased efficiency of instantaneous (intrinsic) two-photon absorption (2PA) in the near-IR wavelength range, especially because such compounds may be used as sensitizers for deep-tissue photodynamic therapy.^[2]

Simple porphyrin monomers (both free-base and Zn metallated versions) have small peak 2PA cross-sections, typically not exceeding $\max(\sigma_2) \sim 10$ GM.^[3] Conjugated porphyrin dimers^[4] and oligomers^[5] are known to have large 2PA cross-sections, reaching high peak values, $\max(\sigma_2) \sim 10^3$ – 10^4 GM (1 GM = 10^{-50} cm⁴ s⁻¹ photon⁻¹). Large 2PA cross-sections

were also reported for some other porphyrinoids.^[6] However, the extensive π -conjugation in such systems may have drawbacks, such as limited photostability. The efficiency of 2PA in porphyrin monomers may be enhanced by decorating the core with strongly two-photon-absorbing chromophores,^[7] but in this case significant downsides include the complexity of the synthesis and the high molecular weight. The challenge thus is to find a simple way to increase the efficiency of 2PA in single-core porphyrin structures.

2. Results and Discussion

The high 2PA in conjugated porphyrin dimers and oligomers results from at least three different effects: Firstly, enhancement of the transition dipole moment from the ground state to an effective intermediate state, which may be directly observed as an increase of the extinction coefficient in the Q-band region.^[3–5] The second contributing factor is the increase of the excited-state transition dipole moment connecting the Q-band with the two-photon-allowed final state, which usually lies in the Soret region. A third contribution originates from the red-shift of the Q-band that brings the lowest one-photon-allowed transition closer to the laser frequency, thus increasing the resonance enhancement.^[8]

All these enhancement factors relate directly to the properties of the expanded π -conjugation system, and grow in proportion to the number of the encompassed porphyrin units. In the decorated single-core porphyrins, an additional 2PA enhancement effect arises from the lowering of the symmetry and related emergence of new two-photon allowed transitions below the Soret band.^[7] Enhanced 2PA in symmetrical porphyrin monomers was also reported in peripherally substituted tetraazaporphyrins, where the substituents with the strongest electron-accepting ability led to the largest increase of the 2PA.^[9]

Herein, we report the synthesis of a series of *meso*-arylethynylporphyrins and study how the incorporation of two symmetrical ethynyl moieties decorated with different electron-donating and electron-accepting end groups affects the 2PA in a broad spectral range encompassing both Q-band and Soret region. *Meso*-substituted arylethynyl porphyrins ever since the first seminal contributions by Therien^[10] and others^[11] continue to attract attention.^[12] The ethynyl moieties elongate the π -conjugation pathway, causing a characteristic bathochromatically shifted absorption.^[13, 14] Because simple tetraarylporphyrins lack any considerable 2PA enhancement,^[3] it would be of most interest to study the effect of various end groups. Quantum-chemical calculations on different *meso*-arylethynylporphyrins performed about a decade ago by Zhou et al.^[15] predict that the nitro end group, which is one of the strongest electron-withdrawing substituents, should lead to the largest 2PA enhancement. By the same token, electron-donating end groups are expected to have a smaller effect because the porphyrin core itself is relatively electron-rich. Specifically, Zhou et al. calculated that the peak 2PA of the nitro end-capped (NO_2 - π - NO_2) structure is about 3500 GM compared to 400 GM of the neutral (H- π -H) version. This prediction turns out to be in good qualitative agreement with the experimental finding presented here.

From the synthetic perspective, *meso*-substituted porphyrins bearing two phenylethynyl substituents at the *meso*-positions are one of the conceptually easiest ways to modify the

porphyrin chromophore. The desire to achieve full comparison of linear and nonlinear data inclined us to design a broad library of *trans*-A₂B₂-porphyrins possessing two arylethynyl substituents in a 5,15-arrangement. One can envision that the two-photon absorption cross-section of such porphyrins will strongly depend on the electronic effect of the substituents. As the porphyrin core is an electron-rich heterocyclic scaffold, it should create an A-D-A system when combined with electron-withdrawing substituents. One may anticipate that σ_2 should be higher for this type of architecture than for an A- π -A system.^[1]

The aryl substituents directly connected to the other *meso* positions are expected to have little effect on the electronic structure because they are twisted at an angle of 60–90° with respect to the plane of the porphyrin. The main role of these substituents is to provide solubility and prevent aggregation. Here, we also compare the properties of free-base porphyrins with their zinc-metallated derivatives.

The *meso*-arylethynyl *trans*-A₂B₂-porphyrins **1–6** were prepared according to a known procedure (Figure 1).^[16] Porphyrin **2** was subjected to a typical zinc-insertion reaction to afford porphyrin **Zn-2** in 94% yield (see Scheme S1 of the Supporting Information). A different strategy was utilized for the synthesis of remaining porphyrins **9**, **Zn-9**, **Zn-13**, and **Zn-14**. Porphyrin **Zn-7** was prepared as reported by Osuka and coworkers.^[17] Free-base porphyrin **9** was synthesized from **Zn-7** via removal of zinc followed by deprotection of silyl units and Sonogashira coupling (Scheme 1). Deprotection of two silyl units followed by Sonogashira coupling with a range of aryl iodides **8**, **11–12** afforded final porphyrins **Zn-9**, **Zn-13** and **Zn-14** in good yields (Scheme 2).

Figure 2 shows the 2PA spectra of free-base *meso*-arylethynylporphyrins **1**, **2** and **3**. The spectra may be roughly divided into the Q-band region (1050–1500 nm) and the Soret region (<1000 nm). At the wavelengths shorter than 820–830 nm an increasing contribution from the linear Q-band absorption complicates accurate separation of the simultaneously occurring 1PA and 2PA processes.^[7] Comparison of the 2PA spectra shows that end-capping with the cyano-group (**1**) as well as the nitro-group (**2**) both amplify the 2PA with respect to the neutral (**3**) arylethynylporphyrin. The electron-withdrawing cyano group increases the cross section more or less uniformly in the entire range of the wavelengths 820–1500 nm by about a factor of 2. The nitro end groups increase the cross section relative to **3** by approximately an order of magnitude, in the Soret region of the spectrum. Both **1** and **3** show a pair of 2PA transitions at 840–960 nm, and the corresponding spectral shapes are very similar to both compounds.

The 2PA spectrum of the nitro-porphyrin **2** shows a significant shoulder at 900 nm, which dominates this part of the spectrum. The fact that none of these 2PA transitions could be attributed to features in the 1PA spectrum, including the peak of the Soret band, confirms that the corresponding two-photon allowed transitions are to states with *gerade* parity. The corresponding 2PA cross section values are collected in Table 1. In the Soret region all studied spectra show a steep increase due to the resonance enhancement effect,^[7] which contributes to ultimate maximum 2PA cross section value. As was mentioned above, this value depends not only on the two-photon allowed transitions in the Soret region, but also on the properties of 1PA transitions in Q-band.

While the peak extinction of the lowest Q-band is comparable for all compounds studied here, differences of the 1PA peak wavelengths and widths probably contribute to the cross-sections listed in Table 1. For example, the fact that at 840 and 900 nm **2** has an about three-times-larger 2PA cross-section than **Zn-2** may be due to a ~30 nm difference in the peak wavelengths of the corresponding Q-bands. In the case of **Zn-13** bearing electron-donating NBU₂ groups, the larger 2PA cross-section value in the Soret region may be attributed in part to the substituents, and in part to the resonance enhancement, which is increased because Zn-substitution causes the 1PA spectrum to shift to the red. The dependences observed here are similar to that reported for a series of electron-donating and electron-withdrawing end caps on fluorenyl-type chromophores.^[18] Otherwise, Zn-substitution appears to have minimal influence on the 2PA properties.

Therien and co-workers studied two-photon absorption of very similar π -extended porphyrins claiming that 2PA cross-sections are on the order of 10 GM, and that a significant portion of the detected fluorescence is the result of other, linear absorptive processes.^[19] However, direct comparison of these results is not justified in this case, because these authors used very different experimental conditions from ours. Their laser has high repetition rate (100 MHz) and low peak power (~1 nJ per laser pulse) whereas we used low-repetition-rate (1 kHz) / high-peak-power (>5 μ J) pulses. As a result, in quantitative terms, our peak intensity is about 1000–10 000 times higher, which explains why Therien and co-workers see much more linear absorption contribution.

It is interesting to compare our experimental 2PA values for **2** with the reported quantum-chemical calculations.^[15] The predicted 1PA peak wavelength in the region 370–400 nm (Soret peak) is very close to the observed values. At the same time, the calculations predicted the 2PA maxima at 640–650 nm, that is, above the 1PA Soret band, whereas the experimentally observed 2PA transition is at a considerably lower energy (900 nm). Nevertheless, the experimental data appear to confirm the main theoretical prediction that the maximum 2PA cross-section occurs in the Soret region and is amplified by electron-accepting nitro groups, rather than electron-donating groups. Also, our measured maximum 2PA values, 1000 and 110 GM, are in qualitative agreement with the theoretical predictions of 3500 and 450 GM for the nitro- and neutral end groups, correspondingly. In the Q-region, all three compounds have similar peaks that may be attributed to the peaks in the corresponding 1PA spectra.

3. Conclusions

In conclusion, we have demonstrated free-base and Zn-metallated porphyrin monomers with symmetrical peripheral nitro groups achieve large intrinsic 2PA in the near-IR range of wavelengths, with maximum values of $\sigma_2 > 1000$ GM. Due to their good photostability and simple design, these compounds may have practical applications in optoelectronics and photo-medicine.

Experimental Section

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2 , hexane) were distilled prior to use. All reported ^1H NMR and ^{13}C NMR spectra were collected using 500 or 400 MHz spectrometers. Chemical shifts (δ ppm) were determined with TMS as the internal reference; J values are given in Hz. The UV/Vis absorption spectra were recorded in CH_2Cl_2 , CH_2Cl_2 -pyridine or CCl_4 -THF. The absorption wavelengths are reported in nm with the extinction coefficient in $\text{M}^{-1} \text{cm}^{-1}$ in brackets. Chromatography was performed on silica (230–400 mesh). The mass spectra were obtained via field desorption MS (FD-MS), electrospray ionization (ESI-MS), and matrix-assisted laser desorption/ionization (MALDI). Porphyrins **1–6** and **Zn-7** were prepared according to the literature procedures.^{16, 17]}

Two-photon absorption measurements were carried out using a wavelength-tunable femtosecond laser system that comprises a Ti:Sapphire femtosecond oscillator (Mira 900, Coherent Inc.) pumped by a CW frequency-doubled Nd:YAG laser (Verdi, Coherent Inc.) and a 1 kHz repetition rate Ti:sapphire femtosecond regenerative amplifier (Legend H, Coherent Inc.). The pulses from the Ti:sapphire amplifier were down-converted with an optical parametric amplifier, OPA (TOPAS-C, Quantronix), whose output signal (idler) was continuously tunable from 1100 to 1600 (1600 to 2200) nm. The second harmonic of idler was used for two-photon excitation in the $\lambda_{\text{ex}}=800\text{--}1100$ nm region and the fundamental of the signal in the 1100–1400 nm region. The OPA output signal pulse energy was 100–250 μJ (5–10 μJ after frequency doubling), and the pulse duration was 70–120 fs. A detailed description of the experimental procedure has been described earlier.^[20] Briefly, the linearly polarized excitation laser beam was slightly focused with an $f=25$ cm lens onto the sample solution contained in a $1 \times 1 \text{ cm}^2$ spectroscopic cell and placed 15 cm behind the lens. A small fraction of the beam was split off by a thin glass plate placed just before the sample and directed to the reference detector (Molelectron). The sample fluorescence was collected with a spherical mirror ($f=50$ cm, diameter $d=10$ cm) and focused with magnification ratio ~ 1 on the entrance slit of an imaging grating spectrometer (Jobin Yvon Triax 550). The 2PA spectrum (in relative units) was obtained by tuning the wavelength of OPA, and measuring the corresponding intensity of two-photon excited fluorescence. The wavelength tuning of OPA and data collection were computer-controlled with a LabView routine. At each wavelength, the fluorescence intensity was normalized to the square of the excitation photon flux, measured in the reference channel. The correction to the spectral variations of the OPA output (pulse duration and beam spatial profile) was done by using Rhodamine B in methanol as a standard, whose 2PA spectrum is well characterized.^[20] To exclude possible artifacts, for example, due to absorption at wavelengths close to the linear absorption, we checked that at each wavelength the fluorescence signal increased as a square of the excitation intensity. Absolute 2PA cross sections were measured using relative fluorescence technique as described^[20] with rhodamine B as a standard.^[20] To obtain absolute 2PA spectra in GM units, all relative 2PA spectra were calibrated to the known (at one wavelength in each spectral region) absolute cross section value. The 2PA properties were measured in CCl_4 solutions.

5,15-Bis[tris((*tert*-butoxycarbonyl)methyloxy)phenyl]-10,20-bis-(4-nitrophenylethynyl)porphyrinato]zinc(II) (Zn-2)

To the solution of porphyrin **2** (32 mg, 21 μ mol) in CHCl_3 (2 mL), MeOH (0.18 mL), and Et_3N (0.4 mL, 2.9 mmol) zinc(II) acetate dihydrate (24 mg, 0.11 mmol) was added and the reaction mixture was stirred in reflux for 19 h. Then, the reaction mixture was evaporated to dryness and the residue was chromatographed (silica, toluene: CHCl_3 :acetone 30:20:2 to 35:15:2). A solid was crystallized (CH_2Cl_2 /hexane) to afford **Zn-2** (31 mg, 94%) in form of green crystals: $R_f=0.38$ (CHCl_3 /toluene/acetone 6:4:1); UV/vis (CCl_4 /0.08% THF) λ_{max} (ϵ)=464 (294 000), 666 (53 700), 281 (25 600); ^1H NMR (500 MHz, $[\text{D}_8]\text{THF}$) $\delta=1.40$ (s, 36H, CH_3), 1.62 (s, 18 H, CH_3), 4.83 (s, 8H, OCH_2), 4.97 (s, 4H, OCH_2), 7.46 (s, 4H, ArH), 8.29 (AA'BB', $J=8.8$ Hz, 4H, ArH), 8.48 (AA'BB', $J=8.8$ Hz, 4H, ArH), 9.02 (d, $J=4.5$ Hz, 4H, βH), 9.74 ppm (d, $J=4.6$ Hz, 4H, βH); ^{13}C NMR (125 MHz, $[\text{D}_8]\text{THF}$) $\delta=28.3$, 28.5, 67.9, 71.1, 81.3, 81.9, 95.7, 99.2, 100.6, 117.1, 123.9, 124.8, 131.3, 131.7, 133.0, 133.8, 138.0, 139.2, 148.2, 150.8, 151.3, 152.9, 168.6, 168.9 ppm; HR MS (ESI) calcd for $\text{C}_{84}\text{H}_{86}\text{N}_6\text{O}_{22}\text{Zn}$ 1596.9886, found 1596.9897; isotope profiles match.

5,15-Bis(3,5-dioctyloxyphenyl)-10,20-bis(trihexylsilylethynyl)porphyrin (7)

[5,15-Bis(3,5-dioctyloxyphenyl)-10,20-bis(trihexylsilylethynyl) porphyrinato]zinc(II) (**Zn-7**) (50 mg, 0.03 mmol) was dissolved in CHCl_3 (10 mL), TFA (1.32 mmol, 1.0 mL of 10% (v/v) solution in CHCl_3) was added and the mixture was stirred for 30 min. The reaction mixture was passed through a short silica gel column (CHCl_3 /1% pyridine) and the solvent was removed. Chromatography on silica gel (40–60 °C petroleum ether:EtOAc 100:1) gave a dark purple solid (39 mg, 78%): UV/vis (CH_2Cl_2) λ_{max} (ϵ)=436 (331 000), 584 (41 700), 679 (16 600), 544 nm (12 300); ^1H NMR (400 MHz, CDCl_3) $\delta=-2.20$ (br s, 2H, NH), 0.86–1.04 (m, 40H, CH_2 , CH_3), 1.26–1.58 (m, 78 H, CH_2), 1.72–1.92 (m, 20 H, CH_2), 4.14 (t, $J=6.4$ Hz, 8H, OCH_2), 6.90 (t, $J=2.2$ Hz, 2H, ArH^{para}), 7.34 (d, $J=2.2$ Hz, 4H, $\text{ArH}^{\text{ortho}}$), 8.94 (d, $J=4.8$ Hz, 4H, βH), 9.60 ppm (d, $J=4.8$ Hz, 4H, βH); MS LR (MALDI ToF MS+) calcd for $\text{C}_{104}\text{H}_{162}\text{N}_4\text{O}_4\text{Si}_2$ ($[M + \text{H}^+]$) 1588.6, found 1589.2.

5,15-Bis(3,5-dioctyloxyphenyl)-10,20-bis(4-nitrophenylethynyl)-porphyrin (9)

Tetra-*n*-butylammonium flouride (1.0 M solution in THF, 0.82 mL, 0.82 mmol) was added to a solution of 5,15-bis(3,5-dioctyloxyphenyl)-10,20-bis(trihexylsilylethynyl)porphyrin (**7**) (65 mg, 40.9 μ mol) in CH_2Cl_2 (10 mL) and stirred for 30 min. The reaction mixture was passed through a short silica gel column (CH_2Cl_2) and the solvent was removed. The residue was mixed with tris(dibenzylideneacetone)dipalladium(0) (35 mg, 38 μ mol), PPh_3 (40 mg, 0.152 mmol), and 1-iodo-4-nitrobenzene (**8**) (80 equiv, 1.26 g, 5.09 mmol) and dried under high vacuum before dry toluene (20 mL) and diisopropylamine (20 mL) were added. The mixture was degassed and the reaction stirred at 60 °C overnight. The volume was reduced and the mixture passed through a short silica gel column (CH_2Cl_2). Recrystallization by layer addition (CH_2Cl_2 /acetone) gave a dark green solid (34 mg, 66%): UV/vis (CH_2Cl_2) λ_{max} (ϵ)=455 (407 000), 609 (75 900), 694 nm (51 300); ^1H NMR (400 MHz, CDCl_3) $\delta=-2.03$ (br s, 2H, NH), 0.88 (t, $J=7.0$ Hz, 12H, CH_3), 1.26–1.43 (m, 32H, CH_2), 1.50–1.60 (m, 8H, CH_2), 1.87–1.94 (m, 8H, CH_2), 4.17 (t, $J=6.7$ Hz, 8H, OCH_2), 6.95 (t, $J=2.2$ Hz, 2H, ArH^{para}), 7.38 (d, $J=2.2$ Hz, 4H, $\text{ArH}^{\text{ortho}}$), 8.07 (d, $J=8.9$ Hz, 4H, ArH), 8.40 (d, $J=8.9$

Hz, 4H, ArH), 9.02 (d, $J=4.5$ Hz, 4H, βH), 9.61 ppm (d, $J=4.5$ Hz, 4H, βH); MS LR (MALDI ToF MS+) calcd for $C_{80}H_{92}N_6O_8$ ($[M + H]^+$) 1265.62, found 1266.44.

[5,15-Bis(3,5-dioctyloxyphenyl)-10,20-bis[4-(*N,N*-dibutylamino)-phenylethynyl]porphyrinato]zinc(II) (Zn-13)

[5,15-Bis(3,5-dioctyloxyphenyl)-10,20-bisethynylporphyrinato]zinc(II) (**Zn-10**) (40 mg, 37 μ mol), tris(dibenzylideneacetone)dipalladium(0) (4.4 mg, 4.7 μ mol), PPh_3 (9.2 mg, 35 μ mol) and CuI (3.3 mg, 18 μ mol) were dried under vacuum before dry NEt_3 (3 mL) was added and the mixture degassed. *N,N*-dibutyl-4-iodoaniline (4 equiv, 98 mg, 296 μ mol) was added and the mixture was stirred at 50 °C for 2 h when TLC (40–60 °C petroleum ether:EtOAc:pyridine 10:1:1, $R_f=0.80$) showed the reaction to be complete. The volume was reduced and the mixture passed through a short silica gel column (CH_2Cl_2). Column chromatography (40–60 °C petroleum ether:EtOAc:pyridine 100:1:1 to 100:8:1) followed by recrystallization by layer addition (CH_2Cl_2 /MeOH) gave a dark green solid (34 mg, 62%): UV/vis (CH_2Cl_2 /1% pyridine) λ_{max} (ϵ)=476 (25 7000), 692 (79 400), 297 (39 800), 329 nm (34 700); 1H NMR (400 MHz, $CDCl_3$ /5% $[D_5]$ pyridine) δ =0.88–1.63 (m, 80H, CH_2CH_3), 1.91 (m, 8H, CH_2), 3.16 (s, 8H, NCH_2), 4.16 (t, $J=6.4$ Hz, 8H, OCH_2), 6.42 (d, $J=7.8$ Hz, 4H, ArH), 6.90 (s, 2H, ArH^{para}), 7.42 (s, 4H, ArH^{ortho}), 7.46 (d, $J=7.8$ Hz, 4H, ArH), 9.00 (d, $J=4.4$ Hz, 4H, βH), 9.62 ppm (d, 4H, $J=4.4$ Hz, βH); ^{13}C NMR (100 MHz, $CDCl_3$ /5% $[D_5]$ pyridine) δ =14.04, 14.12, 20.35, 22.68, 26.15, 29.29, 29.35, 29.46, 31.84, 50.60, 68.43, 90.64, 98.41, 101.04, 103.20, 109.18, 110.96, 114.19, 122.18, 130.74, 132.23, 132.51, 144.26, 147.63, 149.30, 152.04, 158.26 ppm; LR MS (MALDI ToF MS+) calcd for $C_{96}H_{127}N_6O_4Zn$ ($[M+H]^+$) 1491.92, found 1492.79.

5,15-Bis-(3,5-dioctyloxyphenyl)-10,20-bis(4-butylphenylethynyl)-porphyrinato]zinc(II) (Zn-14)

[5,15-Bis(3,5-dioctyloxyphenyl)-10,20-bisethynylporphyrinato]zinc(II) (**Zn-10**) (30 mg, 28 μ mol), tris(dibenzylideneacetone) dipalladium(0) (3.3 mg, 3.5 μ mol), PPh_3 (6.9 mg, 26 μ mol) and CuI (2.5 mg, 13 μ mol) were dried under vacuum before dry NEt_3 (6 mL) was added and the mixture degassed. 1-Butyl-4-iodobenzene (4 equiv, 57 mg, 222 μ mol) was added and the reaction was stirred at 50 °C for 0.5 h when TLC (40–60 °C petroleum ether:EtOAc:pyridine 10:1:1, $R_f=0.80$) showed the reaction to be complete. The volume was reduced and the mixture passed through a short silica gel column (CH_2Cl_2). Column chromatography (40–60 °C petroleum ether:EtOAc:pyridine 100:1:1 to 100:3:1) followed by recrystallization by layer addition (CH_2Cl_2 /MeOH) gave a dark green solid (35 mg, 93%): UV/vis (CH_2Cl_2 /1% pyridine) λ_{max} (ϵ)=453 (245 000), 661 (75 900), 310 (38 000), 606 nm (17 000); 1H NMR (400 MHz, $CDCl_3$ /5% $[D_5]$ pyridine) δ =0.88 (t, $J=6.7$ Hz, 12H, CH_3), 1.01 (t, $J=7.4$ Hz, 6H, CH_3), 1.25–1.57 (m, 40 H, CH_2), 1.69–1.76 (m, 8H, CH_2), 1.84–1.93 (m, 8H, CH_2), 2.76 (t, $J=7.7$ Hz, 8H, Ar CH_2), 4.16 (t, $J=6.6$ Hz, 8H, OCH_2), 6.91 (t, $J=2.1$ Hz, 2H, ArH^{para}), 7.36 (d, $J=2.1$ Hz, 4H, ArH^{ortho}), 7.38 (d, $J=8.0$ Hz, 4H, ArH), 7.94 (d, $J=8.0$ Hz, 4H, ArH), 8.98 (d, $J=4.6$ Hz, 4H, βH), 9.70 ppm (d, $J=4.6$ Hz, 4H, βH); ^{13}C NMR (100 MHz, $CDCl_3$ /5% $[D_5]$ pyridine) δ =14.01, 14.10, 22.66, 26.14, 28.26, 29.42, 31.81, 68.35, 101.57, 114.49, 121.54, 122.29, 128.80, 130.55, 131.46, 132.40, 143.46, 144.58, 149.69, 151.98, 158.14 ppm; LR MS (MALDI ToF MS+) calcd for $C_{88}H_{108}N_4O_4Zn$ (M^+) 1348.76, found 1349.59.

5,15-Bis(3,5-dioctyloxyphenyl)-10,20-bis(4-nitrophenylethynyl)-porphyrinato]zinc(II) (Zn-9)

[5,15-Bis(3,5-dioctyloxyphenyl)-10,20-bisethynylporphyrinato]zinc(II) (**Zn-10**) (40 mg, 37 μmol), tris(dibenzylideneacetone) dipalladium(0) (4.4 mg, 4.7 μmol), PPh_3 (9.2 mg, 35 μmol) and CuI (3.3 mg, 18 μmol) were dried under vacuum before dry NEt_3 (3 mL) was added and the mixture degassed. 1-Iodo-4-nitrobenzene (**8**) (4 equiv, 74 mg, 296 μmol) was added and the reaction stirred at 50 °C for 2 h when TLC (40–60 °C petroleum ether:EtOAc:pyridine 10:1:1, $R_f=0.60$) showed the reaction to be complete. The volume was reduced and the mixture passed through a short silica gel column (CH_2Cl_2). Column chromatography (40–60 °C petroleum ether:EtOAc:pyridine 100:5:5 to 100:10:5) followed by recrystallization by layer addition ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) gave a dark green solid (37 mg, 75%): UV/vis ($\text{CH}_2\text{Cl}_2/1\%$ pyridine) λ_{max} (ϵ)=466 (302 000), 678 (83 200), 343 (25 700), 598 nm (8 500); ^1H NMR (400 MHz, $\text{CDCl}_3/5\%$ $[\text{D}_5]\text{pyridine}$) δ =0.88 (t, J =6.7 Hz, 12H, CH_3), 1.44–1.26 (m, 32 H, CH_2), 1.60–1.51 (m, 8H, CH_2), 1.95–1.88 (m, 8H, CH_2), 4.19 (t, J =6.6 Hz, 8H, OCH_2), 6.92 (s, 2H, ArH^{para}), 7.39 (d, J =1.8 Hz, 4H, $\text{ArH}^{\text{ortho}}$), 7.88 (d, J =8.4 Hz, 4H, ArH), 8.22 (d, J =8.4 Hz, 4H, ArH), 9.09 (d, J =4.4 Hz, 4H, βH), 9.57 ppm (d, J =4.4 Hz, 4H, βH); ^{13}C NMR (100 MHz, $\text{CDCl}_3/5\%$ $[\text{D}_5]\text{pyridine}$) δ =14.09, 22.65, 29.15, 29.25, 29.43, 31.81, 68.42, 94.58, 99.17, 99.60, 100.58, 114.61, 123.76, 130.44, 130.94, 131.60, 132.95, 144.12, 146.48, 150.15, 151.97, 158.29 ppm; MS LR (MALDI ToF MS+) calcd for $\text{C}_{80}\text{H}_{91}\text{N}_6\text{O}_8\text{Zn}$ ($[\text{M}+\text{H}]^{++}$) 1327.62, found 1328.56).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Structures of porphyrins **1–6**.

Figure 2.

Dependence of the 2PA cross-section spectrum on the end group in the free-base *meso*-arylethynylporphyrins in CCl_4 solution in **3**, **1** and **2** (symbols). The thin solid line shows the extinction (right vertical scale) as a function of the 1PA transition wavelength (upper horizontal scale). The shaded interval indicates a gap in the wavelength tuning of the OPA; vertical arrows indicate the distinct bands in the Soret region.

Scheme 1.
Preparation of porphyrin **9**.

Scheme 2.
 Synthesis of porphyrins **Zn-9**, **Zn-13** and **Zn-14**.

Table 1

Linear and nonlinear optical properties of porphyrins **1–6, 9, Zn-9, Zn-13** and **Zn-14** in CCl₄.

Compd.	EWG/EDG	λ_{1PA}^{max} [nm]	λ_{2PA} [nm] [σ_2 [GM]]
1	CN	446, 691 ^[a]	870 [150], 960 [10], 1260 [20]
2	NO ₂	453, 694 ^[a]	870 [1600], 900 [1000], 1260 [40]
Zn-2	NO ₂	464, 666 ^[b]	870 [540], 900 [360], 1210 [23]
3	H	443, 689 ^[a]	840 [200], 1250 [10]
4	CN	445, 692 ^[a]	840 [100]
5	OMe	450, 700 ^[a]	840 [30]
6	CN	457, 671 ^[c]	840 [10]
9	NO ₂	456, 697 ^[d]	870 [750], 1240 [70]
Zn-9	NO ₂	466, 679 ^[d]	870 [650], 1250 [40]
Zn-13	NBu ₂	475, 685 ^[d]	850 [650]
Zn-14	Bu	455, 663 ^[d]	850 [30]
H₂TPP	H	421, 654 ^[b]	800 [7], 1180 [4] ¹³

^[a] in CH₂Cl₂.

^[b] in CCl₄/0.08 % THF.

^[c] in TFA.

^[d] in CCl₄/1 % pyridine.