EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201300124

Tuning the Electronic Properties of Porphyrin Dyes: Effects of *meso* Substitution on Their Optical and Electrochemical Behaviour

Maria-Eleni Ragoussi,[a] Gema de la Torre,*[a] and Tomás Torres*[a]

Dedicated to the memory of Professor Christian G. Claessens

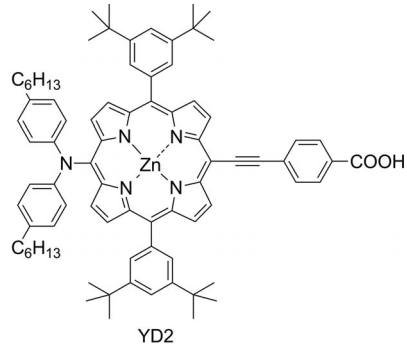
Keywords: Porphyrinoids / Dyes / Electronic structure / Redox chemistry / Structure–activity relationships

Two series of unsymetrically functionalized, carboxyethynylphenyl-containing porphyrins, bearing either 2,4,6-triisopropylphenyl or triphenylamino substituents at three of the four *meso* positions, have been prepared by Sonogashira coupling from the corresponding ethynyl- or iodo-functionalized porphyrin precursors. UV/Vis and electrochemical measurements have been performed to determine the electronic features of these new compounds and, hence, their potential as dyes for dye-sensitized solar cells.

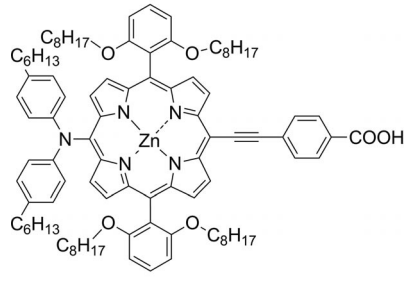
Introduction

In the last few years, porphyrins have proved to be realistic candidates for replacing the costly and environmentally unfriendly ruthenium-based sensitizers in dye-sensitized solar cells (DSSCs).[1] In addition to their well-known light-harvesting properties, porphyrins have redox properties appropriate for the sensitization of TiO_2 films; the LUMO level of the macrocycles lies above the TiO_2 conduction band, and the HOMO level is close to the redox potential of the electrolyte, which ensures efficient dye regeneration. Additionally, adjustment of the electronic levels of the macrocycle is possible by changing the porphyrin substitution at the *meso* and β positions, and also by changing the complexed metal, with Zn^{II} proving to be the best choice for obtaining efficient sensitizers.[2]

The best Zn^{II} porphyrin sensitizers, showing efficiency values of up to 12.3% (see Scheme 1),[3] have a "push–pull" substitution pattern, with an electron-donating arylamino group at one of the *meso* carbon atoms and an electron-withdrawing carboxyphenylethynyl anchoring group at the opposite *meso* position.[4] The beneficial effect of the substitution with electron-donating diarylamino groups has been rationalized in terms of broadening and redshifting of the absorption features of the porphyrins, together with more efficient electron-injection abilities.[5] The phenylethynyl unit is well-established and widely used as a bridging moiety between the porphyrin core and the acceptor/anchoring moiety (i.e., COOH) because it provides an optimal distance between the sensitizer and the semiconductor to retard undesired charge recombination.[6] Regarding the acceptor/anchoring moiety itself, some papers have been published in which the effect of double carboxylic acid substitution on porphyrins[7] and other chromophores[8] as a way to increase the stability and, therefore, the performance of the cell was explored.



YD2



YD2-*o*C8

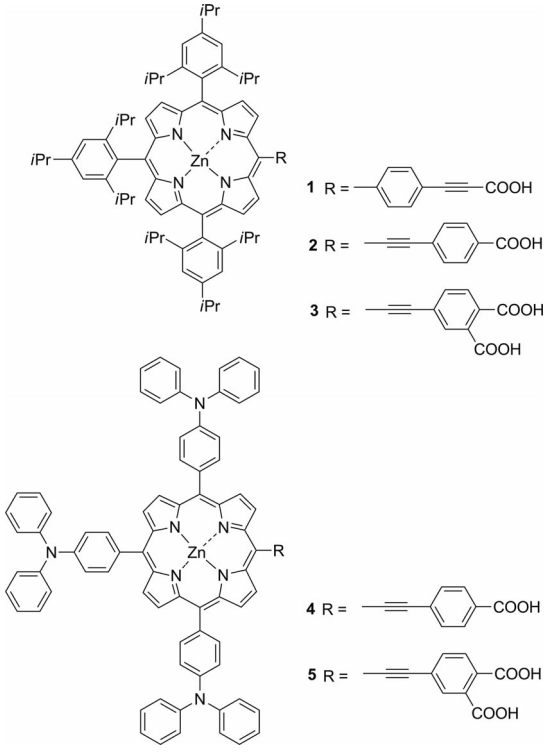
Scheme 1.

[a] Departamento de Química Orgánica, Universidad Autónoma de Madrid,
28049 Madrid, Spain
E-mail: tomas.torres@uam.es
Homepage: www.uam.es/phthalocyanines

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201300124

Another structural feature that has been shown to have a strong impact on the photovoltaic performance of Zn^{II} porphyrins is the substitution with linear alkoxy chains at the *ortho* position of the phenyl groups linked at the macrocyclic *meso* carbon atoms. The effect of these chains is twofold: to protect the porphyrin core and so impede charge recombination processes,[9] and also to effectively decrease the dye aggregation and so allow an efficient electron injection. Diau and co-workers have successfully used this approach.[2,10] In the meantime, *ortho*-alkoxy substitution raises both HOMO and LUMO levels, as can be seen, for example, on going from YD2[3] to YD2-*o*C8[2] (Scheme 1), and this would seem to be beneficial for maximizing electron injection and dye regeneration. Other authors have explored the *ortho*-substitution approach using methyl radicals, which turned out to be too short to effectively protect the porphyrins from dye aggregation.[11] Still, a "push–pull" derivative bearing *ortho*-methylphenyl rings has reached efficiencies as high as 7%.[12]

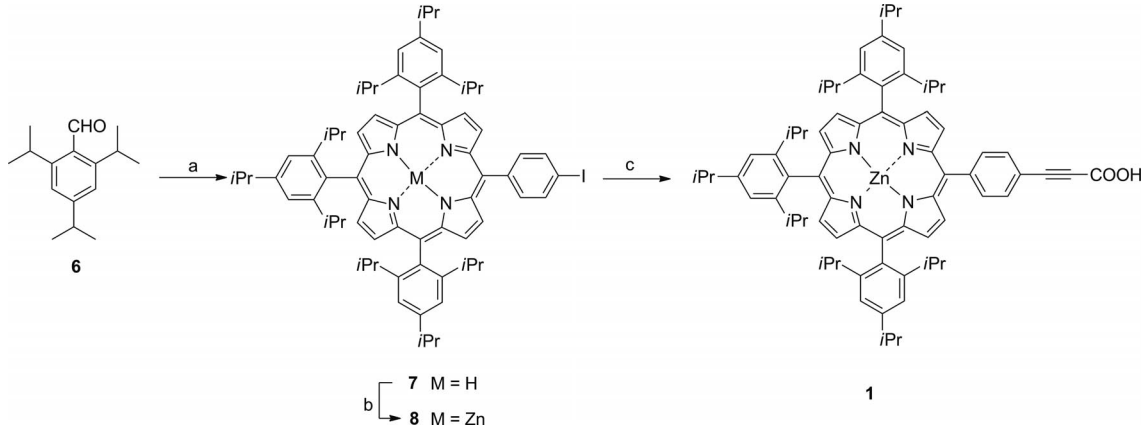
In a search for new hints to the rational molecular design and optimization routes, we are exploring *ortho* substitution of the phenyl rings of Zn^{II} tetraphenylporphyrins as a tool to adjust the electronic levels of the sensitizer to the conduction band of TiO_2 and to the redox potential of the electrolytes, and also to hinder aggregation of the macrocycles. In particular, we have prepared porphyrins functionalized at the *meso* positions with 2,4,6-triisopropylphenyl substituents. For the sake of comparison, we have also prepared porphyrins substituted with three arylamino moieties, which are well-established substituents for efficient DSSCs. Also, mono- and double carboxylic acid substitution is compared in the pursuit of compounds with better adsorption properties to the TiO_2 (Scheme 2).



Scheme 2.

Results and Discussion

Our investigation started with the porphyrins bearing 2,4,6-triisopropylphenyl units at the *meso*-positions (Scheme 3). For the sake of comparison, we prepared porphyrins having carboxyphenylethynyl anchoring moieties (i.e., compounds **2** and **3**), and also a porphyrin with a turnaround connectivity between the COOH and the porphyrin core (i.e., compound **1** bearing a *p*-carboxyethynylphenyl group). The preparation of **1** involved initially the synthesis of derivative **7** by reaction of 2,4,6-triisopropylbenzaldehyde,[13] 4-iodobenzaldehyde, and pyrrole, in the presence of $BF_3{\cdot}OEt_2$, under the standard conditions described in the literature[14] (see Exp. Sect. for details). Compound **7** was obtained in a rather low yield (7%), which, however, is not surprising considering the significant steric effect of the isopropyl groups. The isolation of this free-base derivative was followed by zinc(II) metalation with $Zn(OAc)_2$, and Sono-

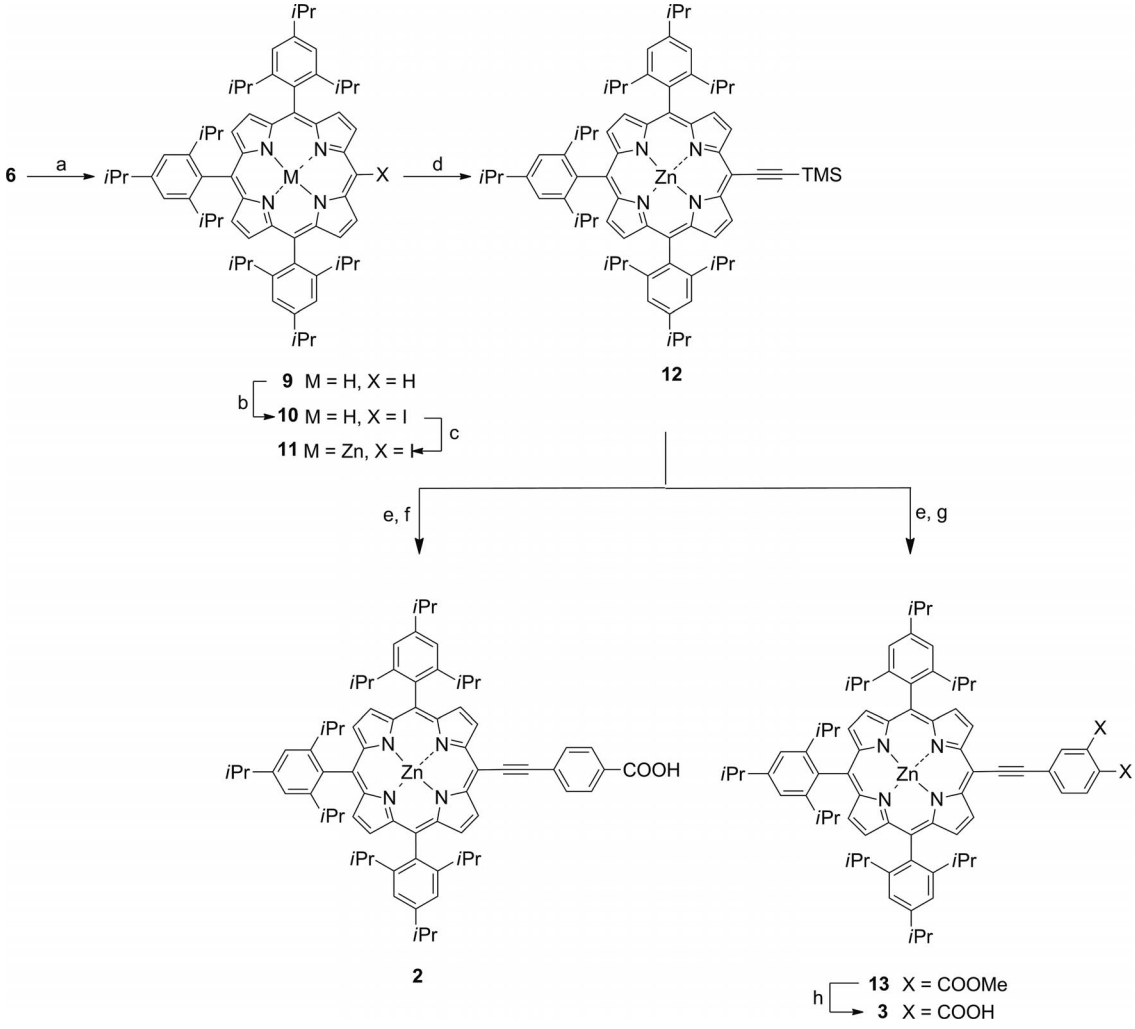


Scheme 3. (a) pyrrole, 4-iodobenzaldehyde, $BF_3{\cdot}OEt_2$, $CHCl_3$/EtOH, room temp., 1 h; followed by DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), room temp., 1.5 h, (b) $Zn(OAc)_2$, CH_2Cl_2/MeOH, room temp., 1 h, (c) propiolic acid, CuI, $PdCl_2(PPh_3)_2$, THF/Et_3N, room temp., 1 h.

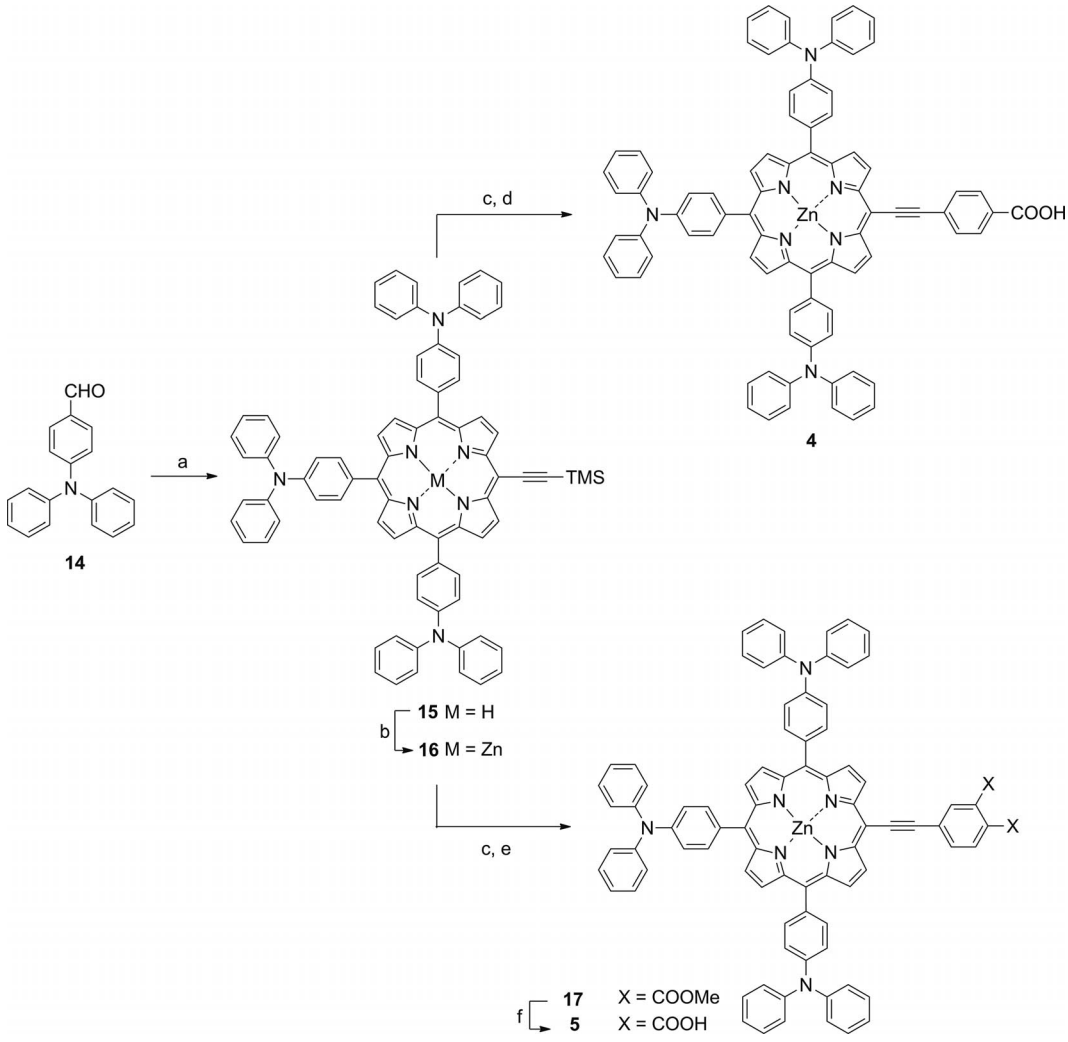
gashira coupling with propiolic acid to obtain the desired porphyrin. During this last step of the procedure, a fair amount of the starting material (compound **8**) remained unreacted after several hours of reaction. Efforts to improve the yield by varying the conditions and the catalyst of the coupling proved fruitless. Nonetheless, it is noteworthy that the yield based on the recovered starting material was moderate (55%).

The synthesis of porphyrins **2** and **3** was originally attempted following the same strategy, but replacing 4-iodobenzaldehyde by trimethylsilylpropynal as a way to install the alkyne moiety. However, this approach proved unsuccessful, since no trace of the desired porphyrin was detected. To overcome this problem, an alternative pathway was envisaged (Scheme 4). Condensation of 2,4,6-triisopropylbenzaldehyde and paraformaldehyde in the appropriate ratio (see Exp. Sect.), led to porphyrin **9**, which was singled out for having one of the four *meso* positions free. The yield of this step was equally low (7%). Compound **9** was subsequently subjected to iodination with $PhI(CF_3COO)_2$ and I_2, metallation with $Zn(OAc)_2$, and stepwise Sonogashira couplings to get to the final porphyrins bearing one (in **2**) or two (in **3**) carboxylic acid moieties. It is worth mentioning that even though the first Sonogashira coupling to install the trimethylsilylethynyl group was carried out using the most common catalytic system of $CuI/PdCl_2(PPh_3)_2$, the second coupling to attach the carboxyphenyl rings did not proceed under these conditions. Therefore, Lindsey's conditions[15] [i.e., $Pd_2(dba)_3$/$AsPh_3$] were used, and the reaction took place smoothly. Moderate to good yields were obtained in all of the steps following the formation of the porphyrin ring.

The synthesis of the arylamino analogues turned out to be more straightforward and higher-yielding (Scheme 5). Reaction of 4-(diphenylamino)benzaldehyde (**14**),[16] trimethylsilylpropynal, and pyrrole under the usual conditions



Scheme 4. (a) pyrrole, paraformaldehyde, $BF_3{\cdot}OEt_2$, $CHCl_3$/EtOH, room temp., 1 h followed by DDQ, room temp., 1.5 h, (b) $PhI(CF_3COO)_2$, I_2, $CHCl_3$, pyridine, 20 min, room temp., (c) $Zn(OAc)_2$, CH_2Cl_2/MeOH, room temp., 2 h, (d) ethynyltrimethylsilane, CuI, $PdCl_2(PPh_3)_2$, THF/Et_3N, room temp., 15 min, (e) TBAF (tetrabutylammonium fluoride), THF, 0 °C to room temp., 30 min, (f) 4-iodobenzoic acid, $AsPh_3$, $Pd_2(dba)_3$, THF/Et_3N, room temp., 30 min, (g) dimethyl 4-bromophthalate, $AsPh_3$, $Pd_2(dba)_3$, THF/Et_3N, 60 °C, 20 min, (h) NaOH, THF/MeOH, 60 °C, 30 min.



Scheme 5. (a) pyrrole, trimethylsilylpropynal, $BF_3{\cdot}OEt_2$, $CHCl_3$/EtOH, room temp., 1 h, followed by DDQ, room temp., 1.5 h, (b) $Zn(OAc)_2$, CH_2Cl_2/MeOH, room temp., 1 h, (c) TBAF, THF, 0 °C to room temp., 1 h, (d) 4-iodobenzoic acid, $AsPh_3$, $Pd_2(dba)_3$, THF/Et_3N, room temp., 1 h, (e) dimethyl 4-bromophthalate, $AsPh_3$, $Pd_2(dba)_3$, THF/Et_3N, 60 °C, 18 h (f) NaOH, THF/MeOH, 60 °C, 30 min.

gave porphyrin derivative **15** in 13% yield. The conversion to **4** and **5** was accomplished by metallation followed by Sonogashira couplings, following the same procedure as described above, with good yields in all steps.

Spectroscopic and Electrochemical Studies

Figure 1 shows the UV/Vis absorption spectra of compounds **1**–**5** in $CHCl_3$. The monocarboxylic acid derivatives, namely **1**, **2**, and **4**, showed significantly higher extinction coefficients than their dicarboxyl analogues, with **4** having the highest. In addition, porphyrin **1**, the only derivative bearing a phenyl ring instead of an alkyne directly connected to the porphyrin ring, was blueshifted in comparison to the other porphyrins. The peak positions and molar absorption coefficients of Soret and Q-bands are listed in Table 1. It is also noteworthy that **3** and **5**, which bear two anchoring groups, present very broad Soret and Q-bands, and their extinction coefficients are more than one order of magnitude lower than their monocarboxylic analogues, probably due to the aggregation of these dyes in solution.

The steady-state fluorescence spectra of compounds **1**–**5** were measured in $CHCl_3$ by exciting at the maxima of the corresponding Soret bands (Figure 2 and Figure S1 in the Supporting Information). The wavelengths for the emission maxima are listed in Table 1. The zero–zero excitation energy (E_{0-0}) values were estimated from the intersection of the normalized absorption and emission spectra, and are also shown in Table 1.

The HOMO and LUMO energy levels of compounds **1**–**5** were determined by cyclic voltammetry measurements and square-wave voltammetry, as shown in Figure 3 and Figure S2 in the Supporting Information. The electrochemical and optical data, together with the HOMO/LUMO values, are summarized in Table 1. The first oxidation reactions of compounds **1**–**5** are observed in the range of 0.31–0.40 V vs. Fc/Fc^+, and are consistent with the formation of the porphyrin radical cation. The second oxidative wave of

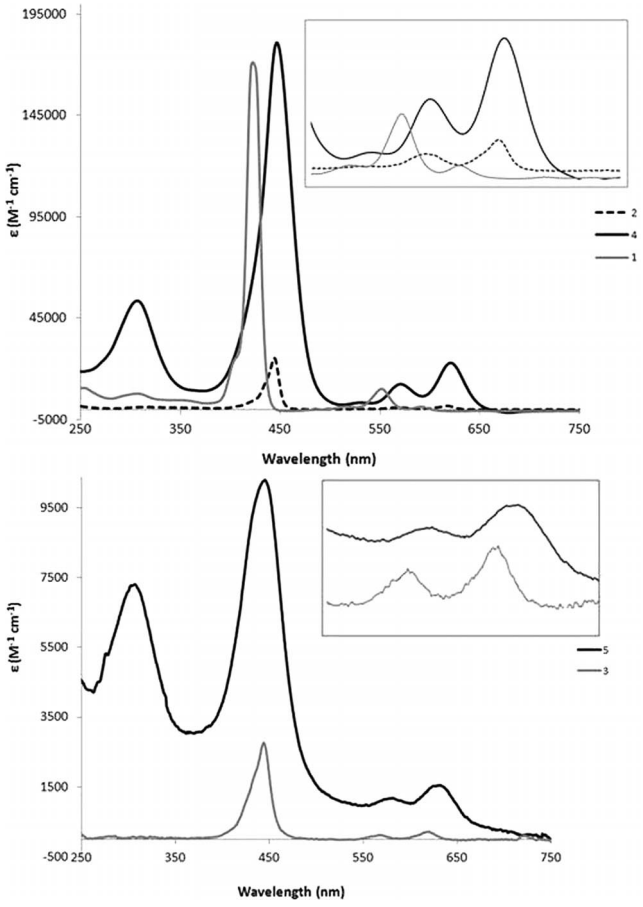


Figure 1. UV/Vis spectra in $CHCl_3$ of (a) monocarboxylic acid derivatives (**1**, **2**, and **4**), and (b) dicarboxylic acid derivatives (**3** and **5**). An enlargement of the Q-band region is shown in the inset.

compounds **4** and **5** matches that of the reference triphenylamine (TPA) (Figure 3 and Figure S2 in the Supporting Information) and, consequently, it can be assigned as a redox event taking place at the triphenylamino substituents, as previously established for other arylamino-substituted derivatives.[18]

Remarkably, the first oxidation waves of the porphyrins bearing 2,4,6-triisopropylphenyl substituents (i.e., compounds **1**–**3**) are cathodically shifted by 90–160 mV compared to the first oxidation waves of the compounds functionalized with arylamino moieties (i.e., compounds **4** and **5**). Binding energies of 0.90 and 1.06 eV, respectively, vs. normal hydrogen electrode (NHE) were determined for

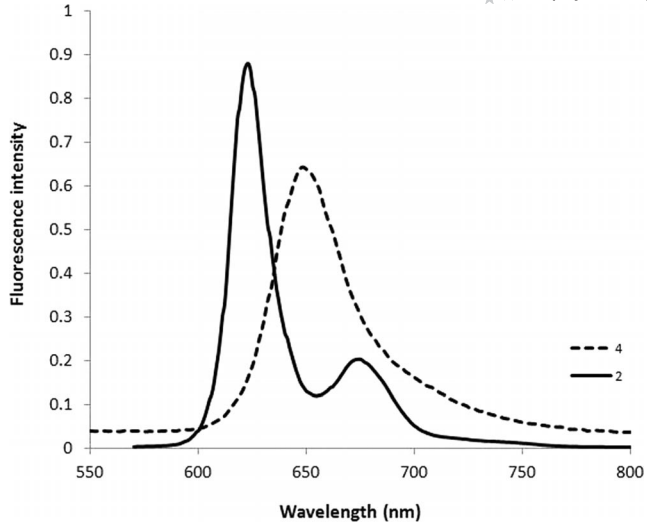


Figure 2. Fluorescence spectra of porphyrins **2** and **4** in $CHCl_3$. Excitation wavelength for compound **2**, 444 nm; compound **4**, 446 nm.

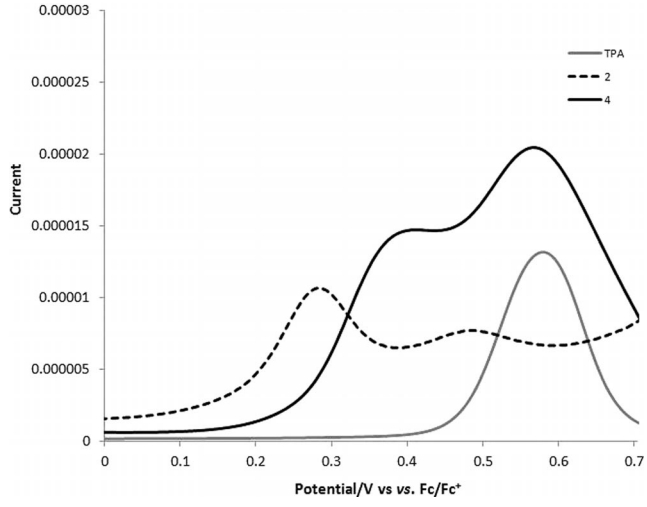


Figure 3. Square-wave voltammetry of porphyrins **2** and **4** and triphenylamine in CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte. Working electrode: Pt; reference electrode: $Ag/AgNO_3$; calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an external reference. Counter electrode: Pt.

these derivatives (Table 1). Although one would expect an increase in the energy of the HOMO level upon substitution of the porphyrin with strongly electron-donating amino

Table 1. Optical, electrochemical data and HOMO/LUMO levels for porphyrins **1**–**5**.

Dye	λ_{abs}[a] [nm] (ε [10^3 M^{-1} cm^{-1}])	λ_{em}[b] [nm]	$E_{ox}^{1/2}$ [V] (vs. Fc/Fc^+)	HOMO [eV] (vs. NHE)	E_{0-0}[c] [eV]	LUMO[d] [eV] (vs. NHE)	ΔG_{inj} [eV]	ΔG_{reg} [eV]
1	403 (5.23), 551 (4.1), 591 (3.40)	608, 652	0.31	0.95	2.06	–1.11	–0.61	–0.42
2	444 (4.4), 568 (3.05), 617 (3.29)	623	0.28	0.92	1.93	–1.01	–0.51	–0.39
3	444 (3.85), 568 (2.99), 616 (3.0)	628	0.26	0.90	1.92	–1.02	–0.52	–0.37
4	446 (5.26), 571 (4.11), 622 (4.36)	656	0.42	1.06	1.88	–0.82	–0.32	–0.53
5	445 (4.04), 577 (3.28), 629 (3.36)	662	0.40	1.04	1.86	–0.82	–0.32	–0.51

[a] Wavelengths for Soret and Q-band maxima in $CHCl_3$. [b] Wavelengths for emission maxima in $CHCl_3$ by exciting at 440 nm. [c] E_{0-0} was estimated from the interception of the corresponding absorption and emission spectra. [d] LUMO was calculated using the equation $E_{LUMO} = E_{HOMO} - E_{0-0}$.

groups, it was recently reported that the HOMO levels of a series of related Zn^{II} porphyrins with an increasing number of triphenylamino substituents (i.e., where the triphenylamine is bound to the *meso* position of the porphyrin core through the *para* position of one of the phenyl rings) are virtually identical.[18] This result indicates that functionalization with triphenylamine moieties causes an insignificant variation of the HOMO energy, probably as a consequence of the orthogonal disposition of the phenyl rings, and the resulting low level of conjugation between the electrons of the N atom and the aromatic cloud of the porphyrin. In contrast, it was recently published that the presence of alkyl and alkoxy chains at the *ortho* positions of phenyl rings linked to the porphyrin core has a strong impact on the HOMO levels and, therefore, *ortho*-substituted compounds show higher HOMO energy levels than related *meta*- or *para*-functionalized derivatives.[10a] On the other hand, substitution of the porphyrin core with two carboxylic acids does not affect the HOMO energy compared to the monosubstituted counterparts.

As the reduction processes of compounds **1**–**5** could not be recorded by cyclic voltammetry or by square-wave experiments, the LUMO binding energies were estimated by subtracting the E_{0-0} values from the electrochemically determined HOMO binding energies. This yielded LUMO binding energies ranging from –1.11 to –0.82 eV (vs. NHE). In general, porphyrins bearing 2,4,6-triisopropylphenyl substituents (i.e., compounds **1**–**3**) showed more negative LUMO values than those functionalized with triphenylamine groups. Remarkably, compound **1**, with tris-(isopropyl)phenyl moieties and a carboxyethynylphenyl anchoring group (i.e., with a connectivity that is opposite to that commonly used in reported porphyrin sensitizers) showed the most negative LUMO value of the series, and this would, in principle, contribute to a better electron injection from this dye to TiO_2 in a DSSC cell. As for the HOMO values, substitution of the porphyrin core with two carboxylic acid moieties does not have an influence on the LUMO energies compared to the monosubstituted counterparts.

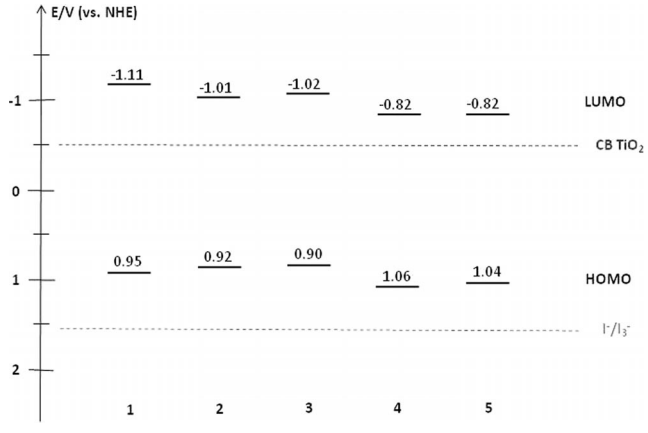


Figure 4. Schematic energy level diagram (HOMO–LUMO) for dyes **1**–**5**.

Figure 4 shows an energy-level diagram for the porphyrin dyes, comparing their HOMO–LUMO levels with the standard potential for the conducting band (CB) of TiO_2 vs. NHE: E_{CB} = –0.5 V, and for the iodide/triiodide (I^-/I_3^-) redox couple vs. NHE: E = 0.53 V.[5,17] The driving forces for electron injection from the porphyrin excited singlet state to the CB of TiO_2 (ΔG_{inj}) and for the regeneration of the porphyrin radical cation by the I^-/I_3^- redox couple (ΔG_{reg}) in a conventional DSSC have been determined (Table 1). Both processes are thermodynamically feasible, and the driving forces values (< -0.3 V) would allow efficient electron transfer in a solar cell.

Conclusions

Two series of unsymetrically functionalized, carboxyethynylphenyl-containing porphyrins (**1**–**5**) have been prepared in the search for new structural parameters that can bring about higher efficiencies in DSSCs based on porphyrin dyes. A comparison of the optical and electrochemical features and, therefore, of the HOMO–LUMO levels between triisopropylphenyl- (**1**–**3**) and triphenylamino-substituted (**4** and **5**) derivatives indicates that the former have higher HOMO and LUMO levels, close to those of the best porphyrin dyes reported in the literature with maximal electron-injection and dye-regeneration abilities. In addition, the presence of bulky isopropyl groups hinders the aggregation of the macrocycles, which is also beneficial. In this way, functionalization with triisopropylphenyl moieties at the *meso* positions of carboxyporphyrins arises as a plausible substitution pattern for obtaining efficient dyes for DSSCs. The construction and measurements of DSSCs based on these derivatives is currently underway.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, at 25 °C with a BRUKER AC-300 instrument. Chemical shifts are given in parts per million, coupling constants are given in Hertz. UV/Vis spectra were recorded with a JASCO V-660 spectrophotometer. Fluorescence spectra were recorded with a JASCO J-810 spectropolarimeter equipped with a JASCO PTC-4235 temperature controller, using Hellma® precision cells made of Quartz Suprasil® (0.2 mm, 106-QS). IR spectra were recorded with a Bruker Vector 22 spectrophotometer. HRMS spectra were recorded with a VG AutoSpec instrument. MALDI-TOF mass spectra were recorded with a Bruker Reflex III spectrometer. Electrochemical measurements were performed at room temperature in a potentiostate/galvanostate Autolab PGSTAT30 using a home-built one-compartment cell with a three-electrode configuration, containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å), and TLC was carried out on aluminum sheets pre-coated with silica gel 60 F254 (E. Merck). Chemicals were purchased from commercial suppliers and used without further purification.

5-(4-Iodophenyl)-10,15,20-tris[(2,4,6-triisopropyl)phenyl]porphyrin (7): Pyrrole (0.445 mL, 6.54 mmol), 4-iodobenzaldehyde (0.378 g, 1.63 mmol), and EtOH (4.9 mL) were added to a solution of **6**

(1.14 g, 4.91 mmol) in $CHCl_3$ (654 mL). The mixture was deoxygenated by bubbling argon through it for 15 min, after which $BF_3{\cdot}OEt_2$ (0.290 mL, 2.30 mmol) was added, and the resulting mixture was stirred at room temperature in the dark for 1 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 1.11 g, 4.91 mmol) was subsequently added, and the mixture was stirred for a further 1.5 h. Finally, addition of Et_3N (1.5 mL) and filtration through silica gave a crude mixture, which was purified by column chromatography (CH_2Cl_2/hexane, 1:2) and washing with MeOH, to give porphyrin **7** (0.13 g, 7%) as a dark reddish powder. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.47 (s, 2 H, N*H*), 0.80–0.90 (m, 54 H, CH_3), 2.21–2.25 (m, 6 H, C*H*), 3.19–3.28 (m, 3 H, C*H*), 7.35 (d, J = 6.0 Hz, 6 H, Ar*H*), 7.96 (d, J = 6.0 Hz, 2 H, Ar*H*), 8.08 (d, J = 6.0 Hz, 2 H, Ar*H*), 8.59 (d, J = 6.0 Hz, 4 H, Ar*H*), 8.73 (s, 4 H, Ar*H*) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 298 (3.77), 371 (3.84), 404 (4.37), 418 (4.74), 517 (3.77), 552 (3.44), 591 (3.26), 647 (3.14) nm. MS (MALDI-TOF, dithranol): m/z = 1118.6 $[M]^+$.

5-(4-Carboxyethynylphenyl)-10,15,20-tris[(2,4,6-triisopropyl)phenyl]porphyrinatozinc(II) (1): $Zn(OAc)_2$ (200 mg, 1.09 mmol) was added to a solution of porphyrin **7** (110 mg, 0.098 mmol) in CH_2Cl_2 (45 mL) and MeOH (15 mL). The mixture was stirred at room temperature for 1 h, after which the solvents were evaporated in vacuo. The crude was extracted with CH_2Cl_2 and, after evaporation of the solvent, the solid residue was washed with MeOH. It was then redissolved in THF (3 mL) and Et_3N (1 mL), and CuI (4 mg, 0.02 mmol) and $PdCl_2(PPh_3)_2$ (6 mg, 0.0085 mmol) were added. The mixture was deoxygenated, by bubbling argon through it for 15 min, and then propiolic acid (6 μL, 0.098 mmol) was added. After stirring at room temperature for 1 h, the solvents were evaporated in vacuo, and the residue was extracted with CH_2Cl_2. Purification by column chromatography and subsequent washing with MeOH/H_2O (4:1) gave porphyrin **1** (27 mg, 25%; yield based on recovered starting material, 55%) as a dark pink solid. ^1H NMR (300 MHz, [D$_8$]THF): δ = 0.79–0.89 (m, 34 H, CH_3), 1.50 (t, J = 6.0 Hz, 20 H, CH_3), 2.29–2.33 (m, 6 H, C*H*), 3.16–3.23 (m, 3 H, C*H*), 7.39 (s, 6 H, Ar*H*), 7.98 (d, J = 9.0 Hz, 2 H, Ar*H*), 8.23 (d, J = 6.0 Hz, 2 H, Ar*H*), 8.50 (d, J = 4.5 Hz, 2 H, Ar*H*), 8.54 (d, J = 4.5 Hz, 2 H, Ar*H*), 8.70 (d, J = 6.0 Hz, 2 H, Ar*H*), 8.78 (d, J = 6.0 Hz, 2 H, Ar*H*), 10.84 (s, 1 H, COO*H*) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 306 (4.0), 403 (4.41), 422 (4.61), 517 (3.37), 551 (4.10), 591 (3.40) nm. HRMS (MALDI-TOF, dithranol): calcd. for $C_{74}H_{82}N_4O_2Zn$ 1122.5729; found 1122.5724.

5,10,15-Tris[(2,4,6-triisopropyl)phenyl]porphyrin (9): Pyrrole (0.367 mL, 5.39 mmol), paraformaldehyde (40 mg, 1.33 mmol), and EtOH (4.0 mL) were added to a solution of **6** (940 mg, 4.05 mmol) in $CHCl_3$ (540 mL). The mixture was deoxygenated by bubbling argon through it for 15 min, after which $BF_3{\cdot}OEt_2$ (0.226 mL, 1.80 mmol) was added, and the resulting mixture was stirred at room temperature in the dark for 1 h. DDQ (920 mg, 4.05 mmol) was subsequently added, and the mixture was stirred for a further 1.5 h. Finally, addition of Et_3N (1.5 mL) and filtration through silica gave a crude mixture, which was purified by column chromatography (CH_2Cl_2/hexane, 1:4) to give porphyrin **9** (0.103 g, 7%) as a dark reddish powder. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.69 (s, 2 H, N*H*), 0.81–0.91 (m, 54 H, CH_3), 2.18–2.28 (m, 6 H, C*H*), 3.17–3.29 (m, 3 H, C*H*), 7.36 (d, J = 12.0 Hz, 6 H, Ar*H*), 8.61–8.65 (m, 4 H, Ar*H*), 8.86 (d, J = 6.0 Hz, 2 H, Ar*H*), 9.23 (d, J = 6.0 Hz, 2 H, Ar*H*), 10.09 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.87 (isopropyl), 31.50 (isopropyl), 34.04 (isopropyl), 34.72 (isopropyl), 104.13 (*meso*-*C*H), 117.55 (Ar*C*), 120.30 (Ar*C*), 122.21 (Ar*C*), 130.43 (Ar*C*), 130.87 (Ar*C*), 135.60 (Ar*C*), 139.52 (Ar*C*), 147.59 (Ar*C*), 149.48 (Ar*C*), 150.05 (Ar*C*) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 300 (3.27), 365.5 (3.60), 416 (4.95), 510.5 (3.57), 543 (2.83), 583 (2.93), 638.5 (2.25) nm. MS (MALDI-TOF, dithranol): m/z = 916.6 $[M]^+$.

5-Iodo-10,15,20-tris[(2,4,6-triisopropyl)phenyl]porphyrin (10): A solution of $PhI(CF_3COO)_2$ (15 mg, 0.035 mmol) in $CHCl_3$ was added to a solution of porphyrin **9** (50 mg, 0.055 mmol) and I_2 (8 mg, 0.031 mmol) in $CHCl_3$ (6 mL), and then pyridine (1 drop) was added to the mixture. The mixture was stirred at room temperature for 1 h, after which it was quenched with $Na_2S_2O_3$ and extracted with CH_2Cl_2. Purification by column chromatography (hexane/CH_2Cl_2, 2:1) gave compound **10** (56 mg, quant.) as a dark pink solid. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.34 (s, 2 H, N*H*), 0.83–0.95 (m, 54 H, CH_3), 2.19–2.28 (m, 6 H, C*H*), 3.20–3.30 (m, 3 H, C*H*), 7.37 (d, J = 12.0 Hz, 6 H, Ar*H*), 8.55–8.61 (m, 4 H, Ar*H*), 8.78 (d, J = 6.0 Hz, 2 H, Ar*H*), 9.60 (d, J = 6.0 Hz, 2 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.81 (isopropyl), 31.50 (isopropyl), 34.40 (isopropyl), 34.71 (isopropyl), 114.22 (Ar*C*), 119.02 (Ar*C*), 120.39 (Ar*C*), 122.17 (Ar*C*), 130.35 (Ar*C*), 131.24 (Ar*C*), 135.57 (Ar*C*), 137.59 (Ar*C*), 139.43 (Ar*C*), 147.67 (Ar*C*), 148.80 (Ar*C*), 149.63 (Ar*C*), 149.89 (Ar*C*), 150.00 (Ar*C*) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 310.5 (2.97), 434 (4.48), 519.5 (2.24), 564.5 (3.03), 605.5 (2.89), 618 (2.74) nm. MS (MALDI-TOF, dithranol): m/z = 1042.5 $[M]^+$.

5,10,15-Tris[(2,4,6-triisopropyl)phenyl]-20-(trimethylsilylethynyl)porphyrinatozinc(II) (12): Porphyrin **10** (56 mg, 0.055 mmol) was dissolved in CH_2Cl_2 (33 mL) and MeOH (11 mL), and $Zn(OAc)_2$ (96 mg, 0.52 mmol) was added. The mixture was stirred at room temperature for 30 min, after which the solvents were evaporated in vacuo, and the residue was extracted with CH_2Cl_2. It was then redissolved in THF (1 mL) and Et_3N (1 mL), and CuI (0.8 mg, 0.004 mmol) and $PdCl_2(PPh_3)_2$ (2 mg, 0.003 mmol) were added. The mixture was deoxygenated by bubbling argon through it for 15 min, and then trimethylsilylacetylene (15 μL, 0.11 mmol) was added. After stirring at room temperature for 20 min, the solvents were evaporated in vacuo, and the residue was extracted with CH_2Cl_2. Purification by column chromatography (hexane/THF, 4:1) gave porphyrin **12** (46 mg, 80%) as a dark pink solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.61 (s, 9 H, 3 CH_3Si), 0.90–0.94 (m, 54 H, CH_3), 2.82–2.94 (m, 6 H, C*H*), 3.50–3.66 (m, 3 H, C*H*), 7.35 (d, J = 12.0 Hz, 6 H, Ar*H*), 8.54 (dd, J = 3.0, 15.0 Hz, 4 H, Ar*H*), 8.79 (d, J = 6.0 Hz, 2 H, Ar*H*), 9.62 (d, J = 6.0 Hz, 2 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.67 (SiC), 28.82 (isopropyl), 31.53 (isopropyl), 34.45 (isopropyl), 34.73 (isopropyl), 86.05 (alkyne), 88.24 (alkyne), 120.07 (Ar*C*), 122.21 (Ar*C*), 125.70 (Ar*C*), 130.53 (Ar*C*), 135.97 (Ar*C*), 139.41 (Ar*C*), 147.25 (Ar*C*), 147.67 (Ar*C*), 148.81 (Ar*C*), 149.07 (Ar*C*), 149.62 (Ar*C*), 150.27 (Ar*C*), 151.17 (Ar*C*), 151.69 (Ar*C*), 152.57 (Ar*C*) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 313 (2.96), 434 (4.46), 521 (2.24), 564 (3.01), 604 (2.85), 617.5 (2.73) nm. MS (MALDI-TOF, dithranol): m/z = 1074.6 $[M]^+$.

5,10,15-Tris[(2,4,6-triisopropyl)phenyl]-20-(4-carboxyphenylethynyl)porphyrinatozinc(II) (2): TBAF (1 M in THF; 0.15 mL, 0.15 mmol) was added to a solution of compound **12** (50 mg, 0.05 mmol) in dry THF (4 mL) at 0 °C, and the mixture was stirred at room temperature for 15 min. The reaction was quenched with H_2O, and the mixture was extracted with CH_2Cl_2. Without any further purification, the deprotected derivative was redissolved in dry THF (4 mL), and Et_3N (1.5 mL), and 4-iodobenzoic acid (24 mg, 0.1 mmol) was added. The mixture was deoxygenated by bubbling argon through it for 15 min, after which $AsPh_3$ (30 mg, 0.1 mmol) and $Pd_2(dba)_3$ (10 mg, 0.01 mmol) were added, and the reaction mixture was stirred at reflux for 30 min. The solvents were then evaporated, and the residue was extracted with CH_2Cl_2. After

purification by column chromatography (CH_2Cl_2 followed by CH_2Cl_2/MeOH, 10:1) and washing with MeOH, porphyrin **2** was obtained (47 mg, 85%) as a bright green solid. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 0.91–0.99 (m, 54 H, *CH*$_3$), 2.30–2.41 (m, 6 H, C*H*), 3.34–3.48 (m, 3 H, C*H*), 7.76 (d, *J* = 3.0 Hz, 6 H, Ar*H*), 8.08 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 8.24 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 8.49 (dd, *J* = 3.0, 15.0 Hz, 4 H, Ar*H*), 8.76 (d, *J* = 6.0 Hz, 2 H, Ar*H*), 9.70 (d, *J* = 6.0 Hz, 2 H, Ar*H*) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 313 (3.12), 444 (4.4), 568 (3.05), 617 (3.29) nm. HRMS (MALDI-TOF, dithranol): calcd. for $C_{74}H_{82}N_4O_2Zn$ 1122.5729; found 1122.5724.

5-(3,4-Dimethoxycarbonylphenylethynyl)-10,15,20-tris[(2,4,6-triisopropyl)phenyl]porphyrinatozinc(II) (13): TBAF (1 M in THF; 0.12 mL, 0.12 mmol) was added to a solution of compound **12** (30 mg, 0.03 mmol) in dry THF (2 mL) at 0 °C, and the mixture was stirred at room temperature for 15 min. The reaction was quenched with H_2O, and the mixture was extracted with CH_2Cl_2. Without any further purification, the deprotected derivative was redissolved in dry THF (2 mL) and Et_3N (1 mL), and 4-bromophthalate (24 mg, 0.09 mmol) was added. The mixture was deoxygenated by bubbling argon through it for 15 min, after which $AsPh_3$ (18 mg, 0.06 mmol) and $Pd_2(dba)_3$ (7 mg, 0.007 mmol) were added, and the reaction mixture was stirred at reflux for 1 h. The solvents were then evaporated and the residue was extracted with CH_2Cl_2. After purification by column chromatography (hexane/CH_2Cl_2, 2:1), compound **13** was obtained as a dark green solid (30 mg, 85%). ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 0.85–0.97 (m, 54 H, *CH*$_3$), 2.27–2.39 (m, 6 H, C*H*), 3.19–3.30 (m, 3 H, C*H*), 7.38 (d, *J* = 3.0 Hz, 6 H, Ar*H*), 7.97 (d, *J* = 9.0 Hz, 1 H, Ar*H*), 8.22 (dd, *J* = 3.0, 9.0 Hz, 1 H, Ar*H*), 8.33 (s, 1 H, Ar*H*), 8.50 (dd, *J* = 3.0, 15.0 Hz, 4 H, Ar*H*), 8.77 (d, *J* = 6.0 Hz, 2 H, Ar*H*), 9.69 (d, *J* = 6.0 Hz, 2 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 32.14 (isopropyl), 35.45 (isopropyl), 52.49 (COO*C*H$_3$), 52.61 (COO*C*H$_3$), 97.79 (alkyne), 120.12 (Ar*C*), 120.61 (Ar*C*), 125.85 (Ar*C*), 126.37 (Ar*C*), 128.89 (Ar*C*), 129.43 (Ar*C*), 131.52 (Ar*C*), 132.28 (Ar*C*), 132.54 (Ar*C*), 134.55 (Ar*C*), 135.22 (Ar*C*), 136.14 (Ar*C*), 137.60 (Ar*C*), 142.86 (Ar*C*), 149.88 (Ar*C*), 150.07 (Ar*C*), 150.19 (Ar*C*), 150.73 (Ar*C*), 150.83 (Ar*C*), 151.79 (Ar*C*), 152.98 (Ar*C*), 187.94 (C=O) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 328.5 (3.84), 443 (4.63), 567.5 (3.26), 617.5 (3.50) nm. MS (MALDI-TOF, dithranol): *m*/*z* = 1194.6 [M]$^+$.

5-(3,4-Dicarboxyphenylethynyl)-10,15,20-tris[(2,4,6-triisopropyl)-phenyl]porphyrinatozinc(II) (3): A mixture of compound **13** (30 mg, 0.025 mmol) and NaOH (0.5 M; 1.2 mL, 0.6 mmol) in THF (3 mL) and MeOH (1.2 mL) was heated at reflux for 20 min. It was then cooled to room temperature, extracted with CH_2Cl_2, and purified by reverse-phase column chromatography (H_2O/THF, 1:1) to give porphyrin **3** (18 mg, 60%) as a dark green solid. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 0.9–1.0 (br. m, 54 H, *CH*$_3$), 2.2–2.4 (br. m, 6 H, C*H*), 3.1–3.4 (br. m, 3 H, C*H*), 7.1–7.5 (br. m, 6 H, Ar*H*), 8.2–8.9 (br. m, 9 H, Ar*H*), 9.5–9.9 (br. m, 2 H, Ar*H*) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 444 (3.85), 568 (2.99), 616 (3.0), 630 (2.95) nm. HRMS (MALDI-TOF, dithranol): calcd. for $C_{75}H_{82}N_4O_4Zn$ 1166.5628; found 1166.5622.

5,10,15-Tris[(4-diphenylamino)phenyl]-20-(trimethylsilylyethynyl)porphyrin (15): Pyrrole (0.611 mL, 8.98 mmol), trimethylsilylpropynal (0.333 mL, 2.24 mmol), and EtOH (6.5 mL) were added to a solution of **14** (1.84 g, 6.73 mmol) in $CHCl_3$ (898 mL). The mixture was deoxygenated by bubbling argon through it for 15 min, after which $BF_3{\cdot}OEt_2$ (0.284 mL, 2.25 mmol) was added, and the resulting mixture was stirred at room temperature in the dark for 1 h. DDQ (1.53 g, 6.73 mmol) was subsequently added, and the mixture was stirred for a further 1.5 h. Finally, addition of Et_3N (1.5 mL) and filtration through silica gave a crude mixture, which was purified by column chromatography (CH_2Cl_2/hexane, 1:1) and washing with MeOH to give porphyrin **15** (0.33 g, 13%) as a dark brown powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = –2.31 (s, 2 H, N*H*), 0.62 (s, 9 H, 3 C*H*$_3$Si), 7.13–7.18 (m, 6 H, Ar*H*), 7.41–7.48 (m, 30 H, Ar*H*), 8.03–8.07 (m, 6 H, Ar*H*), 8.92 (s, 4 H, Ar*H*), 9.02 (d, *J* = 6.0 Hz, 2 H, Ar*H*), 9.67 (d, *J* = 6.0 Hz, 2 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.51 (*CH*$_3$Si), 98.79 (alkyne), 121.09 (Ar*C*), 121.37 (Ar*C*), 121.51 (Ar*C*), 123.51 (Ar*C*), 125.08 (Ar*C*), 129.66 (Ar*C*), 135.57 (Ar*C*), 135.67 (Ar*C*), 135.74 (Ar*C*), 139.41 (Ar*C*), 147.80 (Ar*C*), 147.97 (Ar*C*) ppm. IR (film): $\tilde{\nu}$ = 3329, 3059, 3036, 2953, 2143, 1593, 1491, 1281, 1157, 849, 754 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 303.5 (4.52), 439 (4.71), 537 (3.78), 580 (4.07), 668.5 (3.67) nm. MS (MALDI-TOF, dithranol): *m*/*z* = 1135.5 [M]$^+$.

5,10,15-Tris[(4-diphenylamino)phenyl]-20-(trimethylsilylethynyl)-porphyrinatozinc(II) (16): $Zn(OAc)_2$ (335 mg, 1.83 mmol) was added to a solution of porphyrin **15** (190 mg, 0.17 mmol) in CH_2Cl_2 (75 mL) and MeOH (25 mL). The mixture was stirred at room temperature for 30 min, after which the solvents were evaporated in vacuo, and the residue was extracted with CH_2Cl_2 and washed with MeOH to give compound **16** (200 mg, quant.) as a dark green solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.65 (s, 9 H, 3 C*H*$_3$Si), 7.13–7.19 (m, 6 H, Ar*H*), 7.42–7.50 (m, 30 H, Ar*H*), 8.04–8.08 (m, 6 H, Ar*H*), 9.02–9.06 (m, 4 H, Ar*H*), 9.12 (d, *J* = 6.0 Hz, 2 H, Ar*H*), 9.78 (d, *J* = 6.0 Hz, 2 H, Ar*H*) ppm. IR (film): $\tilde{\nu}$ = 3340, 3051, 2924, 2137, 1589, 1489, 1333, 1281, 997, 854, 754, 692 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 307 (4.20), 445 (4.71), 569.5 (3.59), 618.5 (3.64) nm. MS (MALDI-TOF, dithranol): *m*/*z* = 1197.4 [M]$^+$.

5,10,15-Tris[(4-diphenylamino)phenyl]-20-(4-carboxyphenylethynyl)porphyrinatozinc(II) (4): TBAF (1 M in THF; 0.64 mL, 0.64 mmol) was added to a solution of compound **16** (192 mg, 0.16 mmol) in dry THF (30 mL) at 0 °C, and the mixture was stirred at room temperature for 15 min. The reaction was quenched with H_2O, and the mixture was extracted with CH_2Cl_2. Without any further purification, the deprotected derivative was redissolved in dry THF (20 mL) and Et_3N (10 mL), and 4-iodobenzoic acid (80 mg, 0.32 mmol) was added. The mixture was deoxygenated by bubbling argon through it for 15 min, after which $AsPh_3$ (98 mg, 0.32 mmol) and $Pd_2(dba)_3$ (37 mg, 0.04 mmol) were added, and the reaction mixture was stirred at reflux for 1 h. The solvents were then evaporated, and the residue was extracted with CH_2Cl_2. After purification by column chromatography (CH_2Cl_2 followed by CH_2Cl_2/MeOH, 10:1) and washing with MeOH, porphyrin **4** was obtained (170 mg, 85%) as a dark green solid. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 7.10–7.15 (m, 6 H, Ar*H*), 7.39–7.49 (m, 30 H, Ar*H*), 8.07 (t, *J* = 9.0 Hz, 6 H, Ar*H*), 8.16 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 8.26 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 8.93–8.97 (m, 4 H, Ar*H*), 9.09 (d, *J* = 6.0 Hz, 2 H, Ar*H*), 9.83 (d, *J* = 6.0 Hz, 2 H, Ar*H*), 10.82 (br. s, 1 H, COO*H*) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 306 (4.73), 446 (5.26), 527 (3.56), 571 (4.11), 622 (4.36) nm. HRMS (MALDI-TOF, dithranol): calcd. for $C_{83}H_{55}N_7O_2Zn$ 1245.3709; found 1245.3703.

5-(3,4-Dimethoxycarbonylphenylethynyl)-10,15,20-tris[(4-diphenylamino)phenyl]porphyrin (17): TBAF (1 M in THF; 0.27 mL, 0.27 mmol) was added to a solution of compound **16** (81 mg, 0.068 mmol) in dry THF (10 mL) at 0 °C, and the mixture was stirred at room temperature for 15 min. The reaction was quenched with H_2O, and the mixture was extracted with CH_2Cl_2. Without any further purification, the deprotected derivative was redissolved in dry THF (10 mL) and Et_3N (5 mL), and 4-bromophthalate

(40 mg, 0.14 mmol) was added. The mixture was deoxygenated by bubbling argon through it for 15 min, after which $AsPh_3$ (41 mg, 0.13 mmol) and $Pd_2(dba)_3$ (15 mg, 0.016 mmol) were added, and the reaction mixture was stirred at reflux for 1 h. The solvents were then evaporated and the residue was extracted with CH_2Cl_2. After purification by column chromatography (hexane/THF, 4:1), compound **17** was obtained (71 mg, 80%) as a dark green solid. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 3.93 (s, 3 H, COOCH_3), 3.98 (s, 3 H, COOCH_3), 7.11–7.16 (m, 6 H, Ar*H*), 7.40–7.47 (m, 30 H, Ar*H*), 8.00 (d, J = 9.0 Hz, 1 H, Ar*H*), 8.05–8.13 (m, 6 H, Ar*H*), 8.26 (dd, J = 1.6, 8.0 Hz, 1 H, Ar*H*), 8.36 (d, J = 3.0 Hz, 1 H, Ar*H*), 8.94–8.97 (m, 4 H, Ar*H*), 9.10 (d, J = 3.0 Hz, 2 H, Ar*H*), 9.82 (d, J = 6.0 Hz, 2 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, [D$_8$]-THF): δ = 49.95 (COOCH_3), 52.00 (COOCH_3), 114.40 (alkyne), 122.02 (Ar*C*), 122.65 (Ar*C*), 123.95 (Ar*C*), 125.53 (Ar*C*), 130.17 (Ar*C*), 130.40 (Ar*C*), 130.80 (Ar*C*), 131.97 (Ar*C*), 132.51 (Ar*C*), 133.32 (Ar*C*), 133.69 (Ar*C*), 134.63 (Ar*C*), 136.34 (Ar*C*), 137.74 (Ar*C*), 139.63 (Ar*C*), 148.26 (Ar*C*), 148.83 (Ar*C*), 150.70 (Ar*C*), 151.59 (Ar*C*), 153.04 (Ar*C*), 167.28 (C=O) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 304.5 (4.47), 451.5 (5.00), 573 (3.74), 630 (4.05) nm. MS (MALDI-TOF, dithranol): m/z = 1317.4 [M]$^+$.

5-(3,4-Dicarboxyphenylethynyl)-10,15,20-tris[(4-diphenylamino)phenyl]porphyrin (5): A mixture of compound **17** (58 mg, 0.044 mmol) and NaOH (0.5 M; 2.3 mL, 1.15 mmol) in THF (4 mL) and MeOH (1.6 mL) was heated at reflux for 20 min. It was then cooled to room temperature, extracted with CH_2Cl_2, and purified by reverse-phase column chromatography (H_2O/THF, 1:1) to give porphyrin **5** (34 mg, 60%) as a dark green solid. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 7.34–7.40 (m, 23 H, Ar*H*), 7.44–7.50 (m, 16 H, Ar*H*), 8.05 (t, J = 9.0 Hz, 6 H, Ar*H*), 8.85–8.89 (m, 4 H, Ar*H*), 9.00 (d, J = 6.0 Hz, 2 H, Ar*H*), 9.76 (d, J = 6.0 Hz, 2 H, Ar*H*) ppm. UV/Vis ($CHCl_3$): λ_{max} (logε) = 303 (3.90), 445 (4.04), 577 (3.28), 629 (3.36) nm. HRMS (MALDI-TOF, dithranol): calcd. for $C_{84}H_{55}N_7O_4Zn$ 1289.3607; found 1289.3602.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra and MALDI-TOF mass spectra for all new compounds are included, together with fluorescence and square-wave voltammetry spectra for porphyrins **1**–**5**.

Acknowledgments

Financial support from the Spanish Ministerio de Ciencia e Innovación (MICINN) and the Ministerio de Educación y Ciencia (MEC) (CTQ-2011-24187/BQU, PIB2010US-00652, CONSOLIDER-INGENIO 2010 CDS 2007-00010, Nanociencia Molecular, PLE2009-0070), and from Comunidad de Madrid (CAM) (MADRISOLAR-2, S2009/PPQ/1533) is acknowledged.

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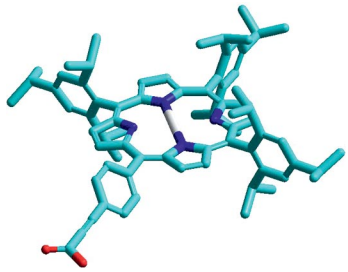
Received: January 23, 2013
Published Online: ■

Porphyrin Dyes

The synthesis of two series of unsymetrically functionalized porphyrins, bearing either 2,4,6-triisopropylphenyl or triphenylamino substituents at three of the four *meso* positions, is described. The electronic features of these new compounds have been investigated by UV/Vis and electrochemical measurements to determine their potential as dyes for dye-sensitized solar cells.



Keywords: Porphyrinoids / Dyes / Electronic structure / Redox chemistry / Structure–activity relationships

