### Tetraaryl Zn<sup>II</sup> Porphyrinates Substituted at β-Pyrrolic Positions as Sensitizers in Dye-Sensitized Solar Cells: A Comparison with *meso*-Disubstituted Push–Pull Zn<sup>II</sup> Porphyrinates

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Abstract: A facile and fast approach, based on microwave-enhanced Sonogashira coupling, has been employed to obtain in good yields both mono- and, for the first time, disubstituted pushpull Zn<sup>II</sup> porphyrinates bearing a variety of ethynylphenyl moieties at the  $\beta$ pyrrolic position(s). Furthermore, a comparative experimental, electrochemical, and theoretical investigation has been carried out on these β-monoor disubstituted Zn<sup>II</sup> porphyrinates and meso-disubstituted push-pull Zn<sup>II</sup> porphyrinates. We have obtained evidence that, although the HOMO-LUMO energy gap of the meso-substituted push-pull dyes is lower, so that charge transfer along the push-pull system therein is easier, the  $\beta$ -mono- or disubstituted push-pull porphyrinic dyes show comparable or better efficiencies when acting as sensitizers in DSSCs. This behavior is apparently not attributable to more intense B and Q bands, but rather to more facile charge injection. This is suggested by the DFT electron distribution in a model of a  $\beta$ monosubstituted porphyrinic dye interacting with a TiO<sub>2</sub> surface and by the positive effect of the  $\beta$  substitution on the incident photon-to-current conversion efficiency (IPCE) spectra, which show a significant intensity over a broad wavelength range (350–650 nm).

**Keywords:** cyclic voltammetry • density functional calculations • porphyrins • push-pull systems • solar cells In contrast, meso-substitution produces IPCE spectra with two less intense and well-separated peaks. The positive effect exerted by a cyanoacrylic acid group attached to the ethynylphenyl substituent has been analyzed by a photophysical and theoretical approach. This provided supporting evidence of a contribution from chargetransfer transitions to both the B and Q bands, thus producing, through conjugation, excited electrons close to the carboxylic anchoring group. Finally, the straightforward and effective synthetic procedures developed, as well as the efficiencies observed by photoelectrochemical measurements, make the described  $\beta$ -monosubstituted Zn<sup>II</sup> porphyrinates extremely promising sensitizers for use in DSSCs.

#### Introduction

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Dye-sensitized solar cells (DSSCs) have emerged as an innovative and competitive alternative to conventional solar cells based on silicon, due to their potential low cost and interesting conversion efficiencies.<sup>[1]</sup> Until recently, the most efficient DSSCs were mainly based on polypyridyl ruthenium complexes as dyes,<sup>[2]</sup> reaching up to 11 % light conversion efficiency.<sup>[3]</sup> However, the poor absorption of these dyes in the near-infrared region of the solar spectrum and the relatively high cost and environmental issues of ruthenium complexes encouraged the search for more efficient and possibly cheaper dyes.

Inspired by the process of solar energy collection by the photosynthetic cores of bacteria and plants, which incorporate a porphyrinic center as a light-harvesting chromophore, porphyrinic structures have been considered as interesting dyes and some of them have been synthesized and investigated for applications in DSSCs.<sup>[1,4]</sup> Porphyrins, by virtue of their strong electronic absorption bands up to the near-infrared region and their long-lived  $\pi^*$  singlet excited states of

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appropriate LUMO energy, are now viewed as interesting sensitizers for use in DSSCs. In particular, *meso*-disubstituted push-pull Zn<sup>II</sup> porphyrinates, characterized by a strong and directional electron excitation process along the push-pull system, have been extensively investigated.<sup>[4c]</sup> Recently, more than 12 % efficiency has been reached by an optimally engineered *meso*-disubstituted push-pull Zn<sup>II</sup> porphyrinate acting as a light-harvesting dye.<sup>[5]</sup> Although some *meso*-disubstituted push-pull Zn<sup>II</sup> porphyrinate as dyes in recent years, display interesting light-conversion efficiencies,<sup>[4c]</sup> their syntheses require multiple steps and are characterized by very low overall yields.<sup>[6,7]</sup>

β-Substituted tetraaryl Zn<sup>II</sup> porphyrinates, which incorporate a tetraaryl porphyrinic core as a starting material, are synthetically more attractive, since this core can be easily obtained by means of a one pot reaction between pyrrole and the appropriate aryl aldehyde. Moreover, the attachment to this core of an appropriate functionalization bearing a carboxylic group, for instance after selective bromination of the  $\beta$ -pyrrolic position, can be achieved by a one-step reaction. Recently, a new synthesis of Zn<sup>II</sup> porphyrinates substituted at the  $\beta$ -pyrrolic position by an ethynyl moiety was reported, based on a modified Horner-Emmons condensation, giving overall yields ranging from moderate to high.<sup>[8]</sup> Further advantages may be cited: firstly, the more sterically hindered architecture of a tetraaryl porphyrinic core should ensure a lower degree of  $\pi$ -stacking aggregation of the dve when adsorbed on TiO<sub>2</sub>, and secondly, enhanced solubility in most common organic solvents should facilitate the purification process, allowing the production of very pure porphyrinic dyes.

Surprisingly, relatively few reports have been published on DSSCs based on  $\beta$ -substituted tetraaryl Zn<sup>II</sup> porphyrinates as dyes,<sup>[1,4,9]</sup> although light-conversion efficiencies for such systems of up to 7.1% have been reported.<sup>[10]</sup> Moreover, to the best of our knowledge,  $\beta$ -disubstituted pushpull tetraaryl Zn<sup>II</sup> porphyrinates have never been synthesized and investigated as dyes for use in DSSCs, most probably due to synthetic difficulties.

An electron-transfer process induced by light absorption, from the tetraaryl porphyrinic core to an ethynylaryl moiety bearing a strong electron-acceptor group attached at the  $\beta$ pyrrolic position, was first highlighted by some of us as part of a nonlinear optical investigation.<sup>[11]</sup> Further evidence of such electron transfer from the tetraaryl porphyrinic core to the carboxylic group of an ethynylaryl moiety linked to the  $\beta$ -pyrrolic position was subsequently provided by spectroscopic and computational studies,<sup>[12]</sup> thus suggesting that  $\beta$ substituted porphyrinic structures of this kind may serve as interesting light sensitizers in DSSCs. This evidence, together with the promising light-conversion efficiencies hitherto reported for some DSSCs involving β-substituted tetraaryl Zn<sup>II</sup> porphyrinates as dyes,<sup>[10]</sup> and the rather simple synthesis of such systems,<sup>[3,12]</sup> prompted us to investigate a series of  $\beta$ substituted [tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate] Zn<sup>II</sup> species. It was anticipated that these would show increased solubility in organic solvents and a significant

degree of steric hindrance that would prevent aggregation of the dye when adsorbed on TiO<sub>2</sub>.<sup>[13]</sup> Specifically, we have investigated the effects on the DSSC efficiency of the presence of one, or two adjacent, carboxylic acid groups or of a cyanoacrylic acid group on the ethynylphenyl substituent in the  $\beta$  position anchoring the dye on the TiO<sub>2</sub> surface. The effects on the electrochemical properties and absorption spectra produced by the presence of different groups on the  $\beta$ -ethynylphenyl moiety have also been experimentally investigated and their electronic origin has been studied by means of DFT and TDDFT calculations.

Moreover, we have devised a new synthetic procedure, by which several issues associated with the synthesis of  $\beta$ -disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates involving two opposite  $\beta$  positions of the porphyrinic ring may be circumvented. Application of this procedure provides a facile synthesis of such push-pull porphyrinic structures that, as far as we are aware, have not been synthesized previously.

Finally, we have compared the light-conversion efficiencies, under the same fabrication conditions, of DSSCs based on the various synthesized  $\beta$ -monosubstituted Zn<sup>II</sup> porphyrinates or  $\beta$ -disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates, as well as those based on the corresponding *meso*-disubstituted push-pull Zn<sup>II</sup> porphyrinates that have previously been reported as efficient dyes for use in such cells.<sup>[4c]</sup>

#### **Results and Discussion**

Synthesis: Partridge et al.<sup>[8]</sup> have recently reported a modified Horner-Emmons condensation for the synthesis of several tetraaryl Zn<sup>II</sup> porphyrinates bearing an ethynyl group at the  $\beta$ -pyrrolic position. Their synthetic route involved a condensation reaction between a 2-formylporphyrin and highly reactive halo-phosphonates to give various halo-vinyl groups, followed by an elimination reaction to obtain an ethynyl substituent at the  $\beta$ -pyrrolic position. Although this protocol gave the products in moderate to high yields, it is not compatible with various functional groups, such as carboxylic or cyanoacrylic acids. Thus, syntheses of such derivatives would require additional steps, making them more expensive and laborious. Therefore, for the synthesis of a series of tetraaryl Zn<sup>II</sup> porphyrinates substituted at the βpyrrolic position, as investigated in this work (Figure 1), we have devised and optimized a synthetic route based on microwave-enhanced Sonogashira coupling. Traditional coupling reactions between various ethynylaryl derivatives and the tetraaryl  $Zn^{II}$  porphyrinate brominated at the  $\beta$ -pyrrolic position have previously been reported to proceed with relatively low yields<sup>[11,14]</sup> (Scheme 1).

We therefore first optimized the procedure for bromination of the porphyrinic core, obtaining in good yields (around 50–60%) both the monobromo (**3a**) and the dibromo (**2a**) intermediates. The functionalization process involves an initial complexation step of the core, furnishing in quantitative yield the  $Zn^{II}$  porphyrinate **1a**, which is more reactive, in this specific case, than the corresponding free

10724 -



Figure 1. Zn<sup>II</sup> porphyrinates investigated in this work.

base for the following bromination reaction. This latter step was accomplished by refluxing 1a in CCl<sub>4</sub> and adding 1.1 or 1.8 equiv of N-bromosuccinimide in order to obtain larger quantities of 3a or 2a, respectively. This is a quite remarkable result, since the bromination of tetraaryl Zn<sup>II</sup> porphyrinates has been investigated for many decades, and generally only low yields have been reported owing to the formation of a series of different β-brominated products.<sup>[15]</sup> However, it must be pointed out that we have been unable, purely on the basis of <sup>1</sup>H NMR characterization, to discriminate between dibromination at the 2,12- or 2,13 positions, although we have clear chromatographic and <sup>1</sup>H NMR evidence that mainly one dibrominated product was obtained (Figure S1 in the Supporting Information). In the following, the  $\beta$ -dibrominated tetraaryl Zn<sup>II</sup> porphyrinate **2a** refers to the more symmetrical [2,12-dibromo-5,10,15,20-tetrakis(3,5di-*tert*-butylphenyl)porphyrinate]Zn<sup>II</sup>.

To maximize the yield of the classical Sonogashira coupling,<sup>[16]</sup> a microwave-assisted synthetic approach has been applied to circumvent the low reactivity of 3a, in which bromine atoms are attached at the  $\beta$ -pyrrolic positions of [tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn<sup>II</sup>. By reactions of **3a** with appropriate ethynylphenyl reagents, we obtained in good yields (40–65%) a series of  $\beta$ -ethynylphenyl monosubstituted Zn<sup>II</sup> porphyrinates **1**, **3**, and **4** (Scheme 1).

The Sonogashira couplings were carried out by adding **3a** and the requisite ethynylphenyl reagent to a mixture of *N*,*N*-dimethylformamide and diethylamine (or triethylamine), and then adding catalytic amounts of  $[Pd(PPh_3)_4]$  and CuI. The reaction mixture was then subjected to microwave-irradiation for 1 h at 120 °C according to a previous report on the Sonogashira coupling of several aryl-halogenated substrates.<sup>[17]</sup> In this way, we were able to attach ethynyl groups at the highly crowded  $\beta$ -pyrrolic position of Zn<sup>II</sup> porphyrinates.

In a previous study, Yeh et al.<sup>[14]</sup> reported the synthesis of **1** in just 30% yield by refluxing a solution of **3a** and 4-ethynylbenzoic acid in a mixture of THF and triethylamine for 24 h in the presence of a catalytic amount of  $[Pd_2(dba)_3]$  and four equivalents of AsPh<sub>3</sub>. Our microwave-enhanced meth-



Scheme 1. i) NBS,  $CCl_4$ , 5 h, reflux; ii) 4-ethynylbenzoic acid,  $[Pd(PPh_3)_4]$ , CuI, HNEt<sub>2</sub>/DMF (3:1), 1 h, MW (120°C); iii) 4-ethynylbenzoic acid, 4-ethynylyl-*N*,*N*-dimethylaniline,  $[Pd(PPh_3)_4]$ , CuI, HNEt<sub>2</sub>/DMF (3:1), 1 h, MW (120°C); iv) dimethyl ester of 4-ethynylphthalic acid,  $[Pd(PPh_3)_4]$ , CuI, HNEt<sub>2</sub>/DMF (3:1), 1 h, MW (120°C); v) NaOH in THF/CH<sub>3</sub>OH/H<sub>2</sub>O (1:1:0.1) 1 h, reflux; vi) 4-ethynylbenzaldehyde,  $[Pd(PPh_3)_4]$ , CuI, HNEt<sub>2</sub>/DMF (3:1), 1 h, MW (120°C); viii) 2-cyanoacetic acid, piperidine,  $CH_3CN/CHCl_3$ , 16 h (80°C); viii) 4-ethynylbenzaldehyde, 4-ethynyl-*N*,*N*-dimethylaniline,  $[Pd(PPh_3)_4]$ , CuI, HNEt<sub>2</sub>/DMF (3:1), 1 h, MW (120°C):

odology has provided access to **1** without recourse to  $AsPh_3$ , with a significant reduction in the reaction time to 1 h and an increased yield of up to 65%.

In conclusion, we have been able to synthesize dyes 1, 3, and 4 in good overall yields by a simple and efficient threestep synthetic procedure. Moreover, starting from 2a and applying the same three-step process, we have also synthesized the hitherto unknown β-disubstituted push-pull tetraaryl  $Zn^{II}$  porphyrinates 2 and 5 (Figure 1). Compounds 2 and 5 were obtained in acceptable yields (25% and 23%, respectively) by one pot reactions carried out by treating solutions of 2a in N,N-dimethylformamide and diethylamine (or triethylamine) with equimolar amounts of both 4-ethynyl-N,N-dimethylaniline and 4-ethynylbenzoic acid or 4-ethynylbenzaldehyde, under conditions similar to those described above for the synthesis of 1, 3, and 4 (see Experimental Section). A similar one pot synthetic methodology has previously been reported by some of us<sup>[7]</sup> for the synthesis of meso-disubstituted push-pull Zn<sup>II</sup> porphyrinates. It has now been extended to the synthesis of β-disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates, confirming its applicability as

an easy and simple means of obtaining porphyrinic push-pull structures.

The related *meso*-disubstituted push-pull  $Zn^{II}$  porphyrinates **6**, **7**, and **8** were synthesized starting from [5,15-diiodo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate] $Zn^{II}$  (**6a**), which was prepared as previously reported in the literature.<sup>[7]</sup> As summarized in Scheme 2, **6** and **8** were obtained by the above-described one-step procedure, while **7** was prepared by the traditional multi-step synthesis (see Experimental Section).<sup>[7]</sup>

Energy levels and electronic distributions of molecular orbitals: We carried out a computational DFT and TDDFT investigation on all of the  $Zn^{II}$  porphyrinates considered in this work in order to compare the energies and electronic distributions of their ground- and excited-state levels. A similar theoretical investigation was recently reported for **1** and in particular for **4**.<sup>[12]</sup>

Figure 2 shows a schematic energy diagram with particular emphasis on the HOMO–LUMO energy gaps for **1–8**. Iso-density plots of the electronic distributions for the first three



Scheme 2. ix) 4-Ethynylbenzoic acid, 4-ethynyl-*N*,*N*-dimethylaniline,  $[Pd(PPh_3)_4]$ , CuI, NEt<sub>3</sub>, THF, 24 h, 70°C; x) 1-ethynyl-3,4-carboxymethylbenzene,  $[PdCl_2(PPh_3)_2]$ , CuI, HNEt<sub>2</sub>, THF, 24 h, 70°C; xi) 4-ethynyl-*N*,*N*-dimethylaniline,  $[Pd_2(dba)_3]/PPh_3$ , CuI, NEt<sub>3</sub>, THF, 24 h, 70°C; xii) LiOH/H<sub>2</sub>O, THF, 24 h, RT; xiii) (*E*)-2-cyano-3-(4-ethynylphenyl)acrylic acid, 4-ethynyl-*N*,*N*-dimethylaniline,  $[Pd(PPh_3)_4]$ , CuI, NEt<sub>3</sub>, THF, 24 h, 70°C; xii) 4-ethynyl-*N*,*N*-dimethylaniline,  $[Pd(PPh_3)_4]$ , CuI, NEt<sub>3</sub>, THF, 24 h, 70°C; xii) 4-ethynyl-*N*,*N*-dimethylaniline,  $[Pd(PPh_3)_4]$ , CuI, NEt<sub>3</sub>, THF, 24 h, 70°C; xii) 4-ethynyl-*N*,*N*-dimethylaniline,  $[Pd(PPh_3)_4]$ , CuI, NEt<sub>3</sub>, THF, 24 h, 70°C; xii) 4-ethynyl-*N*,*N*-dimethylaniline,  $[Pd(PPh_3)_4]$ , CuI, NEt<sub>3</sub>, THF, 24 h, 70°C; xii) 4-ethynyl-*N*,*N*-dimethylaniline,  $[Pd(PPh_3)_4]$ , CuI, NEt<sub>3</sub>, THF, 24 h, 70°C.



Figure 2. Energy levels of the main occupied/unoccupied molecular orbitals of 1 on  $TiO_2$  and of all of the  $Zn^{II}$  porphyrinates investigated. The LUMO of the dye is mainly located on the LUMO+7 and LUMO+12 of 1 on  $TiO_2$ , the contributions being 23 % and 45 %, respectively.

occupied HOMOs and unoccupied LUMOs are shown in Figure 3.

It can be seen that the  $\beta$ -monosubstituted tetraaryl Zn<sup>II</sup> porphyrinate **4** shows significant variations in both the HOMO and LUMO energy levels with respect to **1** and **3**. The HOMO–LUMO energy gap decreases from 2.59 and 2.57 eV for **1** and **3**, respectively, to 2.33 eV for **4**. This can be attributed to a decrease in the LUMO energy level for the latter, due to the presence of the cyanoacrylic acid group, allowing a lower-energy HOMO–LUMO electron excitation. The HOMO–LUMO energy gap appears to be unaffected by the addition of a second adjacent carboxylic acid group on the phenyl ring of the ethynylphenyl substituent, as in **3** (Figure 2).

The key assumption underpinning the four-orbital Gouterman model is that in tetraaryl  $Zn^{II}$  porphyrinates the HOMO and HOMO-1 are near-degenerate and the LUMO and LUMO+1 are degenerate.<sup>[18]</sup> In **1**, **3**, and even **4**, substitution at the  $\beta$  position does not markedly affect the relative energies of the two HOMOs, but the degeneracy of the two LUMOs is broken. This is especially so for **4**, for which the difference between the LUMO and LUMO+1 energy levels is around 0.5 eV due to the lower energy and concomitantly increased electron density located on the  $\beta$ ethynylphenyl substituent characterizing the LUMO (Figures 2 and 3). Moreover, the LUMO+2, which is far away in

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10727



Figure 3. Isodensity plots (cut-off 0.03), as computed by a DFT approach using THF solution, of the electronic distributions of the first occupied/unoccupied orbitals of 1–8.

energy from the LUMO+1 in the Gouterman model, becomes closer, particularly in the case of **4**, due to the significant electron density on the  $\beta$ -ethynylphenyl substituent.<sup>[12]</sup> These deviations from the Gouterman model are much less significant for **1** and **3** (Figures 2 and 3). It thus appears that the presence of an electron-withdrawing group such as cyanoacrylic acid on the substituent in the  $\beta$  position leads to a significant departure from the Gouterman model due to the stabilization of both the LUMO and LUMO+2.<sup>[12]</sup>

Compared to the corresponding  $\beta$ -monosubstituted tetraaryl Zn<sup>II</sup> porphyrinates **1** and **4**, the HOMO and LUMO energy levels of the  $\beta$ -disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates **2** and **5** show shifts towards less negative energies of the HOMOs, leading to significant decreases in the HOMO-LUMO energy gaps (2.30 eV for **2** versus 2.59 eV for **1**; 2.06 eV for **5** versus 2.33 eV for **4**). This can be ascribed to high electron densities located on the push–pull ethynylphenyl substituent bearing the dimethylamino group (Figures 2 and 3).

The presence in **5** of a cyanoacrylic acid group produces, as in **4**, a loss of the degeneracy between the LUMO and LUMO+1 due to a decrease in the energy of the former. A decrease in the energy of the LUMO+2 brings it closer to the LUMO+1. It must be pointed out that the HOMO-2, which does not have a spatial analogue in the Gouterman model, is largely substituent-based in **1**, **3**, and **4**, but in **2** and **5** does not show a similar electron density on the "pull" ethynylphenyl substituent bearing the carboxylic or cyanoacrylic acid group (Figure 3).

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The HOMO–LUMO energy gaps of the  $\beta$ -disubstituted push–pull tetraaryl Zn<sup>II</sup> porphyrinates **2** and **5** were found to be higher than those of the corresponding *meso*-disubstituted push–pull Zn<sup>II</sup> porphyrinates **6** and **8** (2.02 eV for **6** versus 2.30 eV for **2**; 1.84 eV for **8** versus 2.06 eV for **5**), since the latter show both much higher HOMO energy levels and significantly less negative LUMO energies. Moreover, the presence on the phenyl ring of the "pull" ethynylphenyl substituent of a cyanoacrylic acid group as in **8**, instead of a carboxylic acid group as in **6**, produces a decrease in the HOMO–LUMO energy gap from 2.02 eV to 1.84 eV, with a concomitant significant perturbation of the energy levels of **6** since the HOMO–1, HOMO–2 and the LUMO+1, LUMO+2 become near-degenerate (Figure 2).

The LUMOs of 1, 3, and 4 are characterized by some electron density located on the "pull" ethynylphenyl substituent in the  $\beta$  position, particularly in the case of 4 bearing a cyanoacrylic acid group. In the LUMO+2 and HOMO-2, more significant electron density is located on this "pull" substituent in the  $\beta$  position. As a consequence, the HOMO $\rightarrow$ LUMO and particularly the HOMO $\rightarrow$  LUMO+2 electron transitions are associated with electron transfer from the porphyrinic core to the "pull" ethynylphenyl substituent, as suggested previously,<sup>[11,12]</sup> while the HOMO-2 $\rightarrow$ LUMO electron transition produces, except in 4, an unexpected electron transfer from the porphyrinic core.

In the  $\beta$ -disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates **2** and **5**, the electron density of the HOMO is located on the "push" ethynylphenyl substituent bearing the dimethylamino group. While the LUMO of **2** is mainly located on the porphyrinic core with a minor contribution from the "pull" ethynylphenyl substituent, the presence of the cyanoacrylic acid group in **5** leads to a LUMO almost entirely located on the substituent. The LUMO+1 of both compounds is located on the porphyrinic core, while a significant electron density in the LUMO+2 of **2** and, to a lesser extent of **5**, is located on the "pull" ethynylphenyl substituent.

For the *meso*-disubstituted push-pull **6** and **7**, the LUMO+2 is characterized by a significant electron density on the "pull" ethynylphenyl substituent, while in the LUMO the electron density located on the "pull" ethynylphenyl substituent is insignificant.

In **8**, compared to **6** and **7**, both the LUMO and LUMO+1 are associated with a significant electron density located on the "pull" ethynylphenyl substituent, due to the presence of the cyanoacrylic acid group, as previously observed for  $\beta$ -disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates. In contrast to **6** and **7**, however, the LUMO+2 is entirely located on the porphyrinic core.

In conclusion,  $\beta$ -mono- and push-pull disubstitution of the porphyrinic ring produces a marked deviation from the Gouterman simple model of the energy levels, which is most pronounced for a push-pull structure and in the presence of a cyanoacrylic acid group. The latter acts mainly on the HOMO-LUMO energy gap by decreasing the energy of the LUMO, in both the  $\beta$ -monosubstituted porphyrinate **4** and the  $\beta$ -disubstituted push-pull porphyrinate **5**. It also decreases the energy of the LUMO+2, bringing the latter closer to the LUMO+1, which is not affected by the presence of the cyanoacrylic acid group, being centered on the porphyrinic ring. Hence, the original degeneracy of the LUMO and LUMO+1 levels of the Gouterman model is destroyed, but a new near-degeneracy is introduced by the approach of the LUMO+1 and LUMO+2 levels. Regarding the electronic distributions, the presence of a "push" substituent shifts the electron distribution of the HOMO towards the substituent, while the presence of a cyanoacrylic acid group significantly increases the electron distributions of the LUMO and the LUMO+1 towards the "pull" substituent and the anchoring group, thus suggesting more facile electron injection into the semiconductor.

To gain insight into the interaction between the Zn<sup>II</sup> porphyrinates, acting as electron-donor dyes, and the TiO<sub>2</sub> semiconductor, we also performed DFT calculations on 1 adsorbed on the surface of an approximately  $2 \times 2$  nm TiO<sub>2</sub> cluster.<sup>[20]</sup> To the best of our knowledge, the only previous theoretical study modeling a porphyrinic dye/TiO<sub>2</sub> interaction has been that recently performed by He et al.<sup>[21]</sup> using a very simple semiconductor model. Our DFT investigation of this joint system has shown that the LUMOs are mainly located on the semiconductor. The first LUMOs to make a significant contribution in 1 are the LUMO+7 and the LUMO+12, contributing 23% and 45%, respectively (Figure 4(a)). The LUMO+7 of this joint system is found 0.13 eV below the LUMO of the isolated 1, not interacting with the  $TiO_2$ , while the LUMO+12 is computed to lie at essentially the same energy as that of the isolated **1**.

The density of states (DOS) for the first 100 unoccupied states has been described using a Gaussian convolution with  $\sigma$ =0.2 for the whole joint system as well as the projection of the electronic states of **1** and of the semiconductor states (Figure 4(b)).

As can be seen, in the low-energy range, below -3.10 eV, no contribution from 1 to the joint DOS of the system is apparent; only the unoccupied orbitals of the semiconductor manifold contribute to the total DOS. The DOS of 1, when linked to  $TiO_2$ , is mainly located between -3.00 and -2.40 eV; at -2.79 eV, at which the LUMO+12 is located, the accumulated contributions from the LUMO to the LUMO+12 account for the entire electron density on the LUMO of the isolated dye 1. Above the LUMO+12, there is a series of orbitals that make small contributions to 1 up to the LUMO+30 at -2.58 eV, which is almost entirely located on 1 (99%). The broadening of the partial DOS for dye 1 suggests quite strong coupling between the LUMO of 1 and the TiO<sub>2</sub> manifold of unoccupied states, which, together with the good alignment of the energy levels, is suggestive of efficient electron injection from 1 to the semiconductor.<sup>[20]</sup>

Experimental and calculated electronic absorption spectra and experimental emission spectra: Electronic absorption spectra of  $\beta$ -monosubstituted tetraaryl Zn<sup>II</sup> porphyrinates 1,



Figure 4. a) Electronic distributions of the LUMO+7 and LUMO+12 of the TiO<sub>2</sub> system, where the LUMO of the dye **1** is mainly located, with contributions of 23% and 45%, respectively. b) Density of unoccupied states for **1**@TiO<sub>2</sub>; total: black line, TiO<sub>2</sub>: dotted line; dye: dash-dot-dash line. The inset shows an expansion of the partial density of states on **1**.

3, and 4,  $\beta$ -disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates 2 and 5, and *meso*-disubstituted push-pull Zn<sup>II</sup> porphyrinates 6, 7, and 8, each in THF solution, are presented in Figures S2 and S3 in the Supporting Information. The corresponding optical data, both experimental and computed by TDDFT calculations, are summarized in Table 1.

The  $\beta$ -mono- or disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates 1–5 in THF solution show the typical absorption spectra of porphyrinic systems, with a strong B absorption band at about 430-460 nm and two weaker Q absorption bands at about 566-577 and 604-616 nm, as expected for a decrease in the porphyrin microsymmetry as considered in the "Gouterman four-orbital simple model".<sup>[18]</sup> Porphyrinate 4, and more especially 5, bearing a cyanoacrylic acid group, show a red-shifted shoulder of a broad B band (Figures S2 and S3), which may be rationalized in terms of a significant departure from the "Gouterman four-orbital simple model" due to the presence of an electron-withdrawing group on the ethynylphenyl substituent, which, as previously suggested,<sup>[11,12]</sup> is the origin of the broadening of the B band. The computed absorption spectra are consistent with this hypothesis since, for both 4 and 5, three transitions close in energy and intensity in the region of the B band (410510 nm) are computed, giving rise to a broad band in this spectral region, in contrast to a single B band for **1**, **2**, and **3** (Table 1).

Zn<sup>II</sup> porphyrinates 1–3 show comparable energies of the B bands, but the two Q bands of 2, characterized by a push– pull architecture, are slightly red-shifted (by about 7–9 nm) with respect to those of 1 and 3, due to a major contribution from the HOMO $\rightarrow$ LUMO transition and to a lower HOMO–LUMO gap (Table 1). On the other hand, 5 shows significant red-shifts of both the B and Q bands, due to the push–pull structure and the presence of the electron-with-drawing cyanoacrylic acid group, which significantly destabilizes/stabilizes the HOMO/LUMO set (Figures S2 and S3; Table 1).

If we consider the configuration interactions that give rise to the B and Q bands, we notice that in **1** and **3** it is mainly the HOMO, HOMO–1, and LUMO+1, characterized by close energy levels (Figure 2) and an electron density mainly located on the porphyrinic core and LUMO, with a limited electron density on the ethynylphenyl substituent (Figure 3), that contribute to the pertinent transitions, in full agreement with the "Gouterman four-orbital model". The electronic transition HOMO–2→LUMO contributes only marginally to the B band (Table 1). Since the HOMO–2 of **1** and **3** shows a significant electron density located on the ethynylphenyl substituent (Figure 3), the B band of these dyes is apparently associated with a small degree of charge transfer from the substituent to the porphyrinic core, which is at variance with the simple "Gouterman four-orbital model".

Whereas 1 and 3 depart only slightly from this model, a much greater discrepancy is evident when we consider the configuration interactions that give rise to the B and Q bands of 4, bearing a cyanoacrylic acid group. In 4, the HOMO, HOMO-1, and LUMO+1 still show an electron density mainly located on the porphyrinic core, but the LUMO shows an increased electron density located on the ethynylphenyl substituent, as do the HOMO-2 and LUMO+2 (Figure 3). In this case, the HOMO-2 participates through a strong contribution of 70% to the main transition of the B band computed at 451 nm (Table 1). In this case, however, the involvement of the HOMO-2 does not imply an electron transfer from the "pull" ethynylphenyl substituent to the porphyrynic core, since the LUMO is also located on the "pull" substituent. On the other hand, the LUMO+2, which becomes suitably close in energy to the LUMO and LUMO+1 to be significantly involved in the configuration interactions, is involved in the three calculated B absorption transitions at 410 nm (23% contribution from the transition HOMO→LUMO+2), 451 nm (21% contribution from the transition HOMO $-1 \rightarrow LUMO+2$ ), and 509 nm (23% contribution from the transition HOMO-1 $\rightarrow$ LUMO+2). Moreover, the LUMO is also involved in the B band calculated at 451 nm (70% HOMO $-2 \rightarrow$ LUMO). It also transpired that transitions involving the LUMO are more relevant for 4 than for 1 or 3, if we consider the configuration interactions giving rise to the transitions involving the two Q bands of 4 calculated at 580 nm (71%

10730 -

Dye	Abs. B bands $\lambda_a$ (nm) [log $\varepsilon$ ] 438 [5.37]	Computed Abs. B bands <sup>[a]</sup> $\lambda_a$ (nm) [intensity (a.u.)]		Abs. Q bands $\lambda_{a}$ (nm) [log $\varepsilon$ ]	Computed Abs. Q bands <sup>[a]</sup> $\lambda_a$ (nm) [intensity (a.u.)]		Em. Bands $\lambda_e$ (nm)
1		453 [1.18]	$(40\% \text{ H-1}\rightarrow\text{L})$ $(35\% \text{ H}\rightarrow\text{L+1})$	566 [4.20]	562 [0.04]	(49% H-1→L) (47% H→L+1)	617 667
			$(19\% \text{ H-}2 \rightarrow \text{L})$	604 [3.90]	575 [0.08]	$(72 \% H \rightarrow L)$ (26 % H-1 $\rightarrow$ L+1)	
2	439 [5.18]	456 [1.85]	$(40 \% \text{ H-}2 \rightarrow \text{L})$ $(34 \% \text{ H-}1 \rightarrow \text{L+}1)$ $(21 \% \text{ H-}3 \rightarrow \text{L})$	573 [4.15]	546 [0.09]	$(33\% \text{ H-}2\rightarrow\text{L})$ $(22\% \text{ H-}1\rightarrow\text{L})$ $(22\% \text{ H-}1\rightarrow\text{L+}1)$	627 679
			× /	613 [3.94]	626 [0.76]	(92% H→L)	
3	438 [5.49]	455 [1.88]	$(40 \% \text{ H-1} \rightarrow \text{L})$ $(36 \% \text{ H} \rightarrow \text{L+1})$	566 [4.31]	562 [0.04]	$(50\% \text{ H-1}\rightarrow\text{L})$ $(47\% \text{ H}\rightarrow\text{L+1})$	618 668
			$(13\% \text{ H-2}\rightarrow\text{L})$	604 [4.02]	578 [0.09]	$(74\% \text{ H} \rightarrow \text{L})$ (24% H-1 $\rightarrow$ L+1)	
4	438 [5.30]	410 [1.17]	$(42 \% \text{ H-1} \rightarrow \text{L+1})$ $(23 \% \text{ H} \rightarrow \text{L+2})$	568 [4.37]	580 [0.32]	$(71 \% \text{ H-1} \rightarrow \text{L})$ $(21 \% \text{ H} \rightarrow \text{L+1})$	617 669
		451 [1.07]	(70 % H-2 $\rightarrow$ L) (21 % H-1 $\rightarrow$ L+2)	606 [4.21]	617 [0.16]	(90% H→L)	
	460 (sh)	509 [0.75]	$\begin{array}{c} (38\% \text{ H} \rightarrow \text{L+1}) \\ (27\% \text{ H-1} \rightarrow \text{L}) \\ (23\% \text{ H-1} \rightarrow \text{L+2}) \end{array}$				
5	449 [5.11]	414 [1.01]	$(56 \% \text{ H-2} \rightarrow \text{L+2})$ $(18 \% \text{ H-1} \rightarrow \text{L+1})$	577 [4.36]	556 [0.12]	$(57\% \text{ H} \rightarrow \text{L+2})$ $(19\% \text{ H} \rightarrow \text{L+1})$	626 683
		450 [0.64]	$(63 \% \text{ H-}3 \rightarrow \text{L})$ $(30 \% \text{ H-}2 \rightarrow \text{L+}1)$		569 [0.13]	$(36\% \text{ H-}2\rightarrow\text{L})$ $(15\% \text{ H}\rightarrow\text{L+}1)$	
	464 (sh)	497 [1.07]	$\begin{array}{c} (49\% \text{ H-}1 \rightarrow \text{L+}2) \\ (21\% \text{ H-}2 \rightarrow \text{L+}1) \\ (21\% \text{ H-}2 \rightarrow \text{L}) \end{array}$	616 [4.25]	683 [0.74]	$(15\% \text{ H-}1\rightarrow\text{L})$ $(94\% \text{ H}\rightarrow\text{L})$	
6	456 [5.23]	428 [1.59]	(59% H-1→L+1) (15% H→L+2)	671 [4.69]	697 [1.37]	(94% H→L)	680
7	451 [5.32]	432 [1.85]	(64 % H-1 $\rightarrow$ L+1) (12 % H-2 $\rightarrow$ L)	662 [4.61]	708 [1.43]	(96% H→L)	668
8	458 [5.26]	460 [1.38]	$(44 \% \text{ H-1} \rightarrow \text{L+2})$ $(44 \% \text{ H-2} \rightarrow \text{L+1})$	668 [4.58]	764 [1.69]	(98% H→L)	688

Table 1. Experimental and computed electronic absorption spectra and experimental emission spectra in THF solution of the  $Zn^{II}$  porphyrinates investigated in this work.

[a] The composition of the transitions involved in each computed absorption band is reported in parentheses.

HOMO $-1 \rightarrow$ LUMO) and in particular at 617 nm (90% HOMO $\rightarrow$ LUMO) (Table 1).

In summary, charge-transfer processes from the porphyrinic core to the ethynylphenyl substituent and, to a lesser extent, in the opposite sense, may make significant contributions to both the B and Q bands. This implies that the electronic properties of the substituents on the phenyl ring of the ethynylphenyl substituent in the  $\beta$  position affect both the extent and direction of the charge-transfer associated with the B and Q absorption bands. While for **1** and **3** both the B and Q bands originate from electronic transitions mainly located on the porphyrinic core, for **4** the transitions contributing to the B and Q bands may largely involve orbitals with a significant electron density located on the ethynylphenyl substituent in the  $\beta$  position, so that the "Gouterman four-orbital simple model" is strongly perturbed.

In the push-pull  $Zn^{II}$  porphyrinates **2** and **5**, the HOMO energy levels show, as expected, an electron density located

on the "push" ethynylphenyl substituent bearing the dimethylamino group. In **2**, only the LUMO+2 level shows a high electron density located on the "pull" ethynylphenyl substituent, while for both the LUMO and LUMO+1 the electron density is mainly located on the porphyrinic core (Figure 3). Since, as for **1** and **3**, the electronic transition HOMO $\rightarrow$ LUMO+2 does not contribute at all to either the B or Q bands (Table 1), it follows that the classical chargetransfer process along the push–pull system is not so relevant. Moreover, the configuration interactions that give rise to the B band of **2** only involve transitions located within the porphyrinic core (Table 1 and Figure 3).

In the case of **5**, however, the configuration interactions of both the B and Q bands involve orbitals such as the LUMO and LUMO+2, with high electron density located on the ethynylphenyl substituent bearing the cyanoacrylic group (Figure 3). As a consequence, **5** shows significant push-pull character. In fact, the notable contributions from

transitions involving charge transfer between the "push" and "pull" substituents, such as HOMO -- LUMO (94%) and HOMO $\rightarrow$ LUMO+2 (57%), to the calculated absorption Q bands at 683 and 556 nm, respectively, confirm a significant charge-transfer process along the push-pull system (Table 1). Moreover, the evidence for a significant contribution to the B absorption band of charge-transfer transitions such as HOMO-2 $\rightarrow$ LUMO+2 (56% for the band calculated at 414 nm), HOMO-1→LUMO+2 (49% for the band calculated at 497 nm), and HOMO-2→LUMO (21% for the band calculated at 497 nm) supports the view that charge-transfer processes also contribute significantly to the calculated B bands. Therefore, the excited states associated with the B and more particularly the Q bands should largely correspond to the transfer of electrons to the "pull" ethynylphenyl substituent in the  $\beta$  position bearing the anchoring cyanoacrylic acid group, favoring electron injection into the TiO<sub>2</sub>.

When we consider, for comparison, the *meso* push–pull  $Zn^{II}$  porphyrinates **6**, **7**, and **8**, we observe strong red-shifts of both the B band (by about 17, 12, and 19 nm, respectively) and the single Q band (by about 58, 49, and 55 nm, respectively), with respect to the corresponding  $\beta$ -disubstituted push–pull  $Zn^{II}$  porphyrinate **2** and to a lesser extent **5** (Figure S3 and Table 1), as expected for a stronger push–pull system.<sup>[19,22]</sup> Although the intensity of the B band is not too different, the single Q bands of **6–8** are markedly more intense than the two Q bands of **2** and **5** (Figure S3 and Table 1).

As when comparing 1 and 3, the presence in 7 of two adjacent carboxylic acid groups located on the phenyl ring of the "pull" phenylethynyl substituent produces insignificant effects on both the B and Q bands, with only a slight increase in the intensity of the B band when compared to that of 6 (Figure S3 and Table 1). In 6–8, the HOMO is characterized by a high electron density located on the "push" ethynylphenyl substituent bearing the dimethylamino group, as is the HOMO-2 (Figure 3). Moreover, for both 6 and 7, the electron density located on the "pull" ethynylphenyl substituent is much larger in the LUMO+2 than in the LUMO. Since in 6 the HOMO $\rightarrow$ LUMO+2 charge-transfer transition contributes only marginally to the calculated B band at 428 nm (15%) and in 7 the HOMO-2 $\rightarrow$ LUMO charge-transfer transition contributes even less to the calculated B band at 432 nm (12%), it follows that, despite the push-pull structure, in 6 and particularly in 7 the B band mainly originates from transitions involving the porphyrinic core.

In **8**, however, bearing a cyanoacrylic acid "pull" group, the LUMO and LUMO+1, but not the LUMO+2, show high electron density located on the "pull" ethynylphenyl substituent (Figure 3). In this case, both the HOMO $\rightarrow$  LUMO (98%) and HOMO-2 $\rightarrow$ LUMO+1 (44%) transitions contribute significantly to the calculated Q and B bands at 764 and 460 nm, respectively (Table 1), as expected for a significant degree of charge transfer along the push-pull system.

In summary, the presence of the cyanoacrylic acid group produces significant conjugation effects on both the energy levels and electronic distributions of orbitals involved in transitions that contribute to both the B and Q bands of  $Zn^{II}$  porphyrinate **4** when compared to **1** and **3**, of **5** when compared to **2**, and of **8** when compared to **6** and **7**. In particular, for all of these  $Zn^{II}$  porphyrinates, both the B and Q bands show increased charge-transfer character, with electron transfer to the "pull" substituent anchored on the TiO<sub>2</sub>.

Finally, it must be pointed out that when the push-pull system involves the 2,12- (or 2,13-)  $\beta$  positions of two opposite pyrrolic rings, as in 2 and 5, the conjugation between the "push" and "pull" substituents increases on going from 2 to 5, but it remains less significant than that in 6, 7, or 8, in which the push-pull system involves the 5,15-meso positions of a 10,20-diaryl porphyrinic core (Table 1; Figures 2 and 3). Hence, for the *meso*-5,15- push-pull Zn<sup>II</sup> porphyrinates 6, 7, and particularly 8, the porphyrinic ring acts as an efficient linker between the "pull" and "push" substituents, whereas, for the  $\beta$ -disubstituted push-pull Zn<sup>II</sup> porphyrinate 2, and to a lesser extent 5, the porphyrinic ring is less efficient as a linker. All of the investigated Zn<sup>II</sup> porphyrinates show a significant fluorescence; the emission spectra of 1-5 in THF solution show two emission bands at around 620 and 680 nm, with the emission at higher energy always stronger, in accordance with the emission spectra reported for structurally similar tetraarvl Zn<sup>II</sup> porphyrinates substituted at the  $\beta$ -pyrrolic position.<sup>[11,9a]</sup> The emission bands of **1–5** have rather similar energies (Table 1), with only small redshifts for 2 and 5, as expected for some push-pull character, while 6, 7, and 8 show only one emission band, at roughly the same energy, as previously reported for such meso pushpull structures.<sup>[7]</sup>

Electrochemical investigation: The electrochemical properties of the  $\beta$ -substituted or disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates 1–5 and of the *meso*-disubstituted push– pull  $Zn^{II}$  porphyrinates 7 and 8 have been investigated by cyclic voltammetry (CV). We also studied the dimethyl esters of 3 and 7, designated as 3b (Scheme 1) and 7b, respectively. Normalized CV patterns obtained at 0.2 Vs<sup>-1</sup> on a glassy carbon (GC) electrode in DMF + 0.1 M TBAP (tetrabutylammonium perchlorate) are presented in Figures S5 (a, b) and S6 in the Supporting Information. The corresponding key features are summarized in Table 2, together with the electrochemical and DFT computed HOMO and LUMO energies and, for the sake of comparison, the corresponding HOMO→LUMO energy gaps. The electrochemical properties of the *meso*-disubstituted push-pull Zn<sup>II</sup> porphyrinate 6 have already been fully investigated by some of us,<sup>[23]</sup> and its normalized CV pattern is included in the Supporting Information and its key features in Table 2 for the sake of comparison.

At least two oxidation and two reduction peaks were observed for all of the studied  $Zn^{II}$  porphyrinates in the potential window investigated, all of them being reversible or quasi-reversible from both the electrochemical and chemical

10732 -

	Experimental									Compu	uted	
				$\begin{array}{l} E^{\bullet}_{Ia} \\ [V] (Fc^+   Fc) \end{array}$	$\begin{array}{l} E^{\bullet}_{IIa} \\ [V] (Fc^+ Fc) \end{array}$		L [eV]	H [eV]	H-L gap [eV]	L [eV]	H [eV]	H-L gap [eV]
1	-2.32	-2.13	-1.738	0.382	0.63		-3.06	-5.18	2.12	-2.78	-5.37	2.59
2	-2.23	-1.92	-1.674	0.307	0.46		-3.13	-5.11	1.98	-2.83	-5.14	2.30
3		-2.14	-1.752	0.339	0.60		-3.05	-5.14	2.09	-2.81	-5.38	2.57
3b		-2.05	-1.68	0.37	0.63		-3.12	-5.17	2.05			
4		-2.10	-1.695	0.324	0.63		-3.11	-5.12	2.02	-3.08	-5.42	2.33
5		-2.03	-1.655	0.298	0.48		-3.15	-5.10	1.95	-3.09	-5.15	2.06
6		-2.07	-1.515	0.227	0.36	0.51	-3.29	-5.03	1.74	-2.96	-4.98	2.02
7	-2.49	-2.05	-1.56	0.17	0.40		-3.24	-4.97	1.73	-3.01	-5.00	1.99
7b			-1.46	0.21	0.35	0.47	-3.34	-5.01	1.67			
8	-2.38	-1.89	-1.50	0.20	0.44		-3.30	-5.00	1.70	-3.18	-5.01	1.84

Table 2. Key CV features of the investigated  $Zn^{II}$  porphyrinates, and HOMO and LUMO energy levels derived therefrom. Oxidation peaks localized on the dimethylamino groups are italicized. HOMO and LUMO energy levels have been calculated in THF solution by the DFT approach.

points of view. As a consequence, CV peak analysis could be conveniently conducted in terms of formal potentials  $E^{\circ'} = (E_{\text{rev,a}} - E_{\text{rev,c}})/2$  (approaching standard potentials  $E^{\circ}$  but neglecting activity coefficients). The experimental  $E^{\circ'}$  values also provide the most reliable means of calculating the electrochemical HOMO and LUMO energy levels and the HOMO–LUMO energy gap (Table 2) according to the following equations:<sup>[23]</sup>

$$E_{\text{LUMO}} (\text{eV}) = -\text{e} \times \left[ (E^{\circ'}{}_{\text{Ic}}/\text{V}(\text{Fc}^+|\text{Fc}) + 4.8 \text{ V}(\text{Fc}^+|\text{Fc} \text{ vs zero}) \right]$$
(1)

$$E_{\text{HOMO}} (\text{eV}) = -\text{e} \times \left[ (E^{\circ\prime}{}_{\text{Ia}}/\text{V}(\text{Fc}^{+}|\text{Fc}) + 4.8 \text{ V}(\text{Fc}^{+}|\text{Fc} \text{ vs zero}) \right]$$
(2)

where Fc<sup>+</sup>/Fc is the ferrocenium/ferrocene redox couple adopted as a reference for intersolvental comparison of electrode potentials.<sup>[24]</sup>

The presence of a dimethylamino group, as in **2**, **5**, **6**, **7**, **7b**, and **8**, consistently results in a first oxidation peak at a significantly lower positive potential (easier oxidation), with a second oxidation peak closely following. This feature, which is in accordance with observations made previously by some of  $us^{[23,25]}$  and by other research groups<sup>[11,26]</sup> for a series of  $Zn^{II}$  porphyrinates bearing one substituent with a dimethylamino group, can be explained in terms of the first oxidation peak being localized on the dimethylamino group with the second involving oxidation of the porphyrinic core.

If we compare the  $Zn^{II}$  porphyrinates having the same push-pull system attached at the 2,12- $\beta$  or the 5,15-meso positions, respectively, that is, **2** versus **6** and **5** versus **8**, we notice a significantly larger gap between the first oxidation and first reduction peaks for **2** and **5** (0.24–0.25 V), corresponding to a larger electrochemical HOMO-LUMO energy gap (Table 2), as confirmed by DFT calculations (Figure 2). This confirms that for a push-pull system attached at the 2,12- $\beta$ -pyrrolic positions the HOMO-LUMO energy gap is widened and therefore there is less efficient charge transfer. Moreover, both the first oxidation and first reduction peaks for *meso* push-pull  $Zn^{II}$  porphyrinates, such as 6, 7, and 8, appear at significantly milder potentials (less positive and less negative, respectively), compared to those for 2 and 5. The difference is more remarkable for the first reduction peaks (2 versus 6: 0.15 V; 5 versus 8: 0.14 V) than for the first oxidation peaks (2 versus 6: 0.08 V; 5 versus 8: 0.10 V), the latter being localized on the dimethylamino group (Table 2).

Comparison of the CV patterns of a  $\beta$ -disubstituted pushpull tetraaryl Zn<sup>II</sup> porphyrinate and a  $\beta$ -monosubstituted tetraaryl Zn<sup>II</sup> porphyrinate (2 versus 1 or 5 versus 4) shows that in the presence of the competing dimethylamino redox site, as in 2 and 5, implying localization of the first oxidation on the "push" substituent, the second oxidation involving the porphyrinic core shifts to slightly more positive potentials. This is consistent with a Coulombic repulsive interaction with the charge being generated in the first oxidation step.

In the absence of the dimethylamino group, and therefore of a push-pull system (as in 1, 3, 3b, and 4), the  $E^{\circ'}{}_{Ia}-E^{\circ'}{}_{Ic}$ gap becomes larger (Table 2), approaching (as for 3, 3b, and 4) or reaching (as for 1) the boundaries of the well-known Kadish relationship,<sup>[27,28]</sup> which holds for symmetrical tetraphenylporphyrin (TPP) and diphenylporphyrin (DPP) templates when the porphyrinic electronic core is not significantly perturbed by the substitution:

$$E^{\circ'}{}_{\rm Ia} - E^{\circ'}{}_{\rm Ic} = 2.25 \pm 0.15 \, \rm V \tag{3}$$

It is noteworthy that this larger gap is not only a result of the positive shift of the first oxidation peak in the absence of the dimethylamino group, but also of the negative shift of the first reduction peak (Table 2). The second Kadish relationship, typical of the above templates, concerning the difference between first and second reduction peaks:

$$E^{\circ'}{}_{\rm Ic} - E^{\circ'}{}_{\rm IIc} = 0.42 \pm 0.03 \, \rm V \tag{4}$$

also appears to be satisfied by **1**, **3**, and **4** and approached by **3b** (Table 2).

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These observations are in agreement with TDDFT theoretical interpretation of the experimental absorption spectra, which predicts a weak effect of monosubstitution at the  $\beta$ position, particularly for **1** and **3**, on the energy levels and electronic distributions of the orbitals involving the porphyrinic core.

As regards the effects due to the nature of the "pull" group, switching from a carboxylic acid group to a cyanoacrylic acid group (Table 2) results in slightly less negative first reduction potentials (-1.70 V for 4 versus -1.74 V for 1; -1.66 V for 5 versus -1.67 V for 2; -1.50 V for 8 versus -1.52 V for 6). This trend may be ascribed to an improved conjugation efficiency rather than to a higher inductive effect, since also the first oxidation potentials are at slightly lower values (0.32 V for 4 versus 0.38 V for 1; 0.30 V for 5 versus 0.31 V for 2; 0.20 V for 8 versus 0.23 V for 6).

An interesting observation concerns the Zn<sup>II</sup> porphyrinates bearing two carboxylic acid groups on the phenyl ring of the "pull" ethynylphenyl substituent in the  $\beta$  position. Intriguingly, no significant difference can be perceived between the first reduction potentials of 1 ( $E^{\circ}_{Ic} = -1.74 \text{ V}$ ) and 3 ( $E^{\circ'}_{Ic} = -1.75 \text{ V}$ ), in spite of an expected effect due to the additivity of the Hammett constants of the carboxylic acid group that express its inductive properties.<sup>[29]</sup> Even more impressive is the case of the meso push-pull Zn<sup>II</sup> porphyrinates, that is, 6  $(E^{\circ'}_{Ic} = -1.52 \text{ V})$  and 7  $(E^{\circ'}_{Ic} =$ -1.56 V), since the presence of two carboxylic acid groups results in a slightly less favored reduction. This apparent anomaly might be explained in terms of some interactions, such as reciprocal hydrogen-bonding interactions, between the two adjacent carboxyl groups, weakening their inductive effects. This latter assumption is supported by the observation that the corresponding dimethyl esters 3b and 7b, in which hydrogen-bonding interactions between the two adjacent carboxylic groups are no longer possible, display the expected enhanced electron-attracting inductive effect, with a significant positive shift of the first reduction potential (-1.68 V for 3b versus -1.74 V for 1; -1.46 V for 7b versus)-1.52 V for 6).

Finally, our CV investigation has confirmed the predictions of the DFT calculations, that is, that the  $\beta$ -mono- or disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates **1–5** comply with the energy conditions necessary for their use as dyes in a DSSC, that is, they all have electrochemical LUMO levels at higher energy than that of the TiO<sub>2</sub> conduction band and electrochemical HOMO levels at lower energy than that of the iodine/iodide redox couple (Figure S4 in the Supporting Information).

**Photoelectrochemical investigation**: The  $Zn^{II}$  porphyrinates shown in Figure 1 were evaluated as dyes in DSSCs, prepared with an opaque active 10 µm TiO<sub>2</sub> layer on FTO as a photoanode. The TiO<sub>2</sub> layers on FTO were immersed for 2 h at room temperature in the dark in a solution of the porphyrinic dye in EtOH/THF (9:1). Longer times were tested, but were found not to be beneficial, leading only to modest dye coatings with inferior photovoltaic efficiencies, most probably due to a detrimental slow aggregation of the porphyrinic dye on the  $TiO_2$  surface. Nine different electrolytes were investigated in order to optimize the photovoltaic efficiencies of the DSSCs, varying the solvent and the concentrations of the electrolyte components and additives. The best reproducible efficiencies were obtained using the electrolytes VT3P and VT7 (Table 3). The main difference was

Table 3. Photovoltaic characteristics of DSSCs incorporating 1-8 and of a conventional DSSC containing a benchmark dye.

Dye <sup>[a]</sup>	Electrolyte	$J_{\rm sc}$	$V_{\rm oc}$	FF	PCE
		$[mA cm^{-2}]$	[mV]		[%]
1	VT3P <sup>[a]</sup>	8.9	528	0.65	3.1
2	VT7 <sup>[b]</sup>	11.6	563	0.62	4.1
3	VT7 <sup>[b]</sup>	10.5	586	0.65	4.0
4	VT7 <sup>[b]</sup>	12.9	598	0.60	4.6
5	VT7 <sup>[b]</sup>	14.0	586	0.58	4.7
6	VT7 <sup>[b]</sup>	11.1	600	0.59	3.9
7	VT3P <sup>[a]</sup>	11.7	482	0.53	3.0
8	VT7 <sup>[b]</sup>	13.3	519	0.61	4.2
N719	A6141 <sup>[c]</sup>	15.9	757	0.65	7.8

[a] 0.6 M 1-methyl-3-propylimidazolium iodide, 0.02 M I<sub>2</sub>, and 0.1 M LiI in 3-methoxypropionitrile; [b] 0.6 M 1-methyl-3-propylimidazolium iodide, 0.02 M I<sub>2</sub>, 0.1 M LiI, and 0.05 M 4-*tert*-butylpyridine in 3-methoxypropionitrile; [c] 0.6 M N-butyl-N-methylimidazolium iodide, 0.03 M I<sub>2</sub>, 0.10 M guanidinium thiocyanate, and 0.5 M 4-*tert*-butylpyridine in acetonitrile/valeronitrile (85:15).

the presence of a small amount of 4-*tert*-butylpyridine (TBP) in the latter. We also investigated the effect of the addition of an equimolar amount, with respect to the porphyrinic dye, of chenodeoxycholic acid (CDCA) as a deag-gregating co-adsorbent agent on the photovoltaic efficiencies of the DSSCs.<sup>[30]</sup> Only a slight increase in efficiency was discerned.

The best photovoltaic performances for each porphyrinic dye are listed in Table 3, in comparison to that of the benchmark dye N719, measured with the standard electrolyte A6141<sup>[31]</sup> under the same experimental conditions. The overall conversion efficiencies (PCE) were obtained from the equation:

$$PCE = J_{sc} \times V_{oc} \times FF \tag{5}$$

where  $J_{sc}$  is the short-circuit current density,  $V_{oc}$  is the opencircuit voltage, and FF is the fill factor. Figure 5(a) shows the photocurrent-voltage curves of DSSCs based on the porphyrinic dyes 1, 3, and 4, while Figure 5(b) shows the curves for dyes 2, 5, 6, 7, and 8, characterized by a push-pull system.

In general, the presence of a cyanoacrylic acid group on the "pull" substituent produces a higher photovoltaic efficiency due to higher photocurrent values (Table 3). Moreover, under our experimental conditions, the photovoltaic efficiencies of the DSSCs with  $\beta$ -monosubstituted tetraaryl Zn<sup>II</sup> porphyrinates **1**, **3**, and **4** acting as dyes are quite comparable to those based on  $\beta$ -disubstituted push-pull Zn<sup>II</sup> porphyrinates **2** and **5** (4.1 for **2** versus 3.1 for **1**; 4.6 for **4** 

10734 -

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Figure 5. Current–voltage characteristics of DSSCs incorporating (a) 1, 3, and 4, and (b) 2 and 5-8.

versus 4.7 for 5) or even slightly better than those based on the corresponding push-pull *meso*-disubstituted  $Zn^{II}$  porphyrinates such as 6, 7, and 8 (4.0 for 3 versus 3.0 for 7; 4.6 for 4 versus 4.2 for 8). The latter push-pull porphyrinic systems have been extensively studied and are reported to produce highly efficient DSSCs.<sup>[4c]</sup>

The well-reproducible efficiencies of DSSCs prepared by our experimental protocol for device fabrication incorporating porphyrinic dyes with the same push–pull system linked either through the 2,12- $\beta$ -pyrrolic positions or the 5,15-*meso* positions appeared to be quite consistent (Table 3). This is despite the fact that the latter are characterized by a smaller HOMO–LUMO energy gap (Figure 2) and should therefore show more efficient electron transfer along the push–pull system, and also have a lower LUMO energy level in comparison to push–pull systems with the same "pull" substituent (6 versus 2 and 8 versus 5).

In order to gain a better understanding of the origin of the above trend in the efficiencies of DSSCs based on dyes **1–8**, we investigated the incident monochromatic photon-tocurrent conversion efficiencies (IPCEs). These are indicated



FULL PAPER

Figure 6. Incident monochromatic photon-to-current conversion efficiencies (IPCE) of DSSCs incorporating (a) **2–5**, and (b) **6** and **8**.

in Figure 6(a) for  $\beta$ -monosubstituted **3** and **4** and  $\beta$ -disubstituted push-pull  $Zn^{II}$  porphyrinates 2 and 5. Dyes 4 and 5, characterized by the presence of the electron-withdrawing cyanoacrylic acid group on the "pull" substituent in the  $\beta$ position, exhibit IPCE values higher than 50-60% over a very broad spectral range (350-650 nm). Remarkable plateaus are seen between 400 and 550 nm, at levels of about 80% for 5 and 70% for 4, along with two well-separated peaks, at values of about 75% for 5 and 60-65% for 4, corresponding to the two Q absorption bands at around 550 and 620 nm, respectively. The IPCE spectrum of 2 is also quite high (above 50%) over the same very broad spectral range, but shows a somewhat lower (60-65%) and less extended plateau at around 450 nm, and two well-separated peaks (about 55%) corresponding to the Q absorption bands.

The porphyrinic dye **3** shows an IPCE spectrum with lower values and without a diffuse plateau but with a broad peak (about 60-65%) and two well-separated peaks (about 50-55%) corresponding to the B and Q bands, respectively (Figure 6(a)).

The IPCE spectra of the *meso*-disubstituted porphyrinates **6** and **8**, depicted in Figure 6(b), are quite different, showing, as previously reported for **6**,<sup>[7]</sup> a distinct maximum at about 450 nm corresponding to the B absorption band, IPCE values of around 50–60%, and a less intense peak (IPCE value around 40–50%) at about 670–680 nm corresponding to the single Q band, typical of these push–pull systems. The two maxima are well separated, with IPCE values in the mid-range (530–610 nm) being rather low (around 20–30%). The porphyrinic dye **8**, bearing the acceptor cyanoacrylic acid group, nevertheless shows, as in the case of **5**, higher IPCE values.

The calculated integrated current under the IPCE curves nicely matched the measured photocurrents<sup>[32]</sup> when exposed to a solar simulator using a black tape shading mask  $(0.40 \text{ mm}^2)$  on top of the DSSCs under standard global AM 1.5 solar conditions.<sup>[33]</sup>

It thus appears that the difference between the IPCE spectra of DSSCs based on  $\beta$ -mono or disubstituted pushpull Zn<sup>II</sup> porphyrinates **2–5** and *meso* push-pull disubstituted Zn<sup>II</sup> porphyrinates **6** and **8** is quite significant. In particular, under our experimental conditions, the IPCE peak corresponding to the single rather intense Q absorption band of **6** and **8** was invariably lower in intensity compared to the two peaks corresponding to the two rather weak Q absorption bands of **2–5**. Moreover, while the IPCE spectra of **6** and **8** show distinct peaks at around 450–470 nm corresponding to the B absorption band, those of **2**, **4**, and **5** show intense and rather diffuse plateaus over a wide wavelength range (400–550 nm), particularly in the case of **5**.

Similar IPCE spectra have been reported for DSSCs based on structurally related porphyrinic dyes such as  $\beta$ -monosubstituted tetraaryl Zn<sup>II</sup> porphyrinates with an ethenylphenyl substituent instead of an ethynylphenyl substituent. The presence of a cyanoacrylic acid group on the "pull" substituent, as in **4** and **5**, produces IPCE spectra with values higher than 50% over a broad wavelength range (400–680 nm), with a plateau of about 75% between 430 and 520 nm and two peaks with values around 60–70% corresponding to the two Q bands.<sup>[9a]</sup>

Assuming that the efficiency of light harvesting is close to unity, as reported for many porphyrinic dyes,<sup>[4b]</sup> this evidence would suggest more efficient electron injection into the TiO<sub>2</sub> manifold of unoccupied states when the porphyrinic dye is substituted at the  $\beta$  position, as indicated by previous results.<sup>[4a]</sup>

It is noteworthy that the high IPCE values shown by **4** and **5** are related to the B and Q absorption bands, characterized by a significant contribution from charge-transfer transitions involving, in the excited state, transfer of electrons to the "pull" ethynylphenyl substituent bearing the cyanoacrylic acid group, an excitation process that should facilitate charge-transfer injection to the  $TiO_2$  surface. In fact, when the cyanoacrylic acid group is absent, as in **2** and **3**, while the absorption spectra are rather similar to those of **4** and **5**, the IPCE spectra show lower values. For these dyes, this may be ascribed to the contribution to the B band, and

also in part to the Q bands, of electronic transitions centered on the porphyrinic core, as pointed out in the section devoted to the analysis of the calculated absorption spectra.

This interpretation is also supported by the higher  $J_{sc}$  values of  $\beta$ -substituted DSSCs based on dyes **4** and **5** when compared to those based on dyes **1**, **2**, and **3** (Table 3). It appears that the critical factor in determining injection efficiency in  $\beta$ -substituted DSSCs is the chemical nature of the anchoring group, with the cyanoacrylic acid group exhibiting a better performance than the carboxylic group of a benzoic acid moiety, confirming the findings of a recent report.<sup>[4b]</sup>

The relevance of the injection efficiency in determining the absorbed photon-to-current conversion in the investigated DSSCs is confirmed by the increased IPCE and  $J_{sc}$  values and by the performance of the DSSCs when the "pull" substituent in the  $\beta$  position bears a cyanoacrylic acid group as in **4** and **5** (Figure 6(a) and Table 3). This is despite a concomitant shift towards lower energies of the excited states (Figure 2), which should cause smaller overlap of the LUMOs with the acceptor states of TiO<sub>2</sub>.<sup>[4b]</sup>

In order to confirm a limited difference between  $\beta$ -monoand disubstituted Zn<sup>II</sup> porphyrinates when acting as dyes in DSSCs, we have investigated the electrochemical properties of the best performing porphyrinic dyes **4** and **5** by means of electrochemical impedance spectroscopy (EIS), comparing the data for the  $\beta$ -substituted porphyrinates with those for the corresponding push-pull *meso*-disubstituted porphyrinate **8**. The impedance spectra were analyzed in terms of Nyquist plots (Figure 7), in which the imaginary part of the im-



Figure 7. Electrochemical impedance spectroscopy (EIS) for DSSCs based on porphyrinic dyes **4**, **5**, and **8**. Continuous lines represent the data fitting by using the equivalent circuit shown in the inset.

pedance is plotted as a function of the real part over the frequency range. The equivalent circuit model describing the cell impedance is shown in the inset in Figure 7. Under soft illumination and open-circuit voltage conditions, the recombination resistance ( $R_{\rm rec}$ ), the chemical capacitance ( $C_{\mu}$ ), and the apparent electron lifetime  $\tau_n$  ( $\tau_n = R_{\rm rec}C_{\mu}$ ) were calculated.<sup>[33]</sup> The DSSCs based on **4** and **5** showed similar chemical capacitances, which reflect charge-carrier accumulation on the TiO<sub>2</sub> film and the density of states in the band gap. However, **5** exhibited a slightly higher recombination resistance, which implies an increased electron lifetime and, thus, a more effective suppression of the dark current (Table 4). The *meso* derivative **8** showed the highest recombination resistance, that is, lower recombination losses and dark current, but also the lowest chemical capacitance. The net result was a shorter electron lifetime than in the  $\beta$ -disubstituted Zn<sup>II</sup> porphyrinates.

Table 4. Parameters calculated from EIS data plots of DSSCs incorporating **4**, **5**, and **8**.

Dye	$R_{\rm rec} \left[\Omega {\rm cm}^2\right]$	$C_{\mu}  [\mathrm{F}\mathrm{cm}^{-2}]$	$\tau_{\rm n}  [{ m ms}]$	
4	14.0	$1.3 \times 10^{-3}$	18.2	
5	18.2	$1.2 \times 10^{-3}$	21.8	
8	22.8	$0.8 \times 10^{-3}$	18.2	

### Conclusions

A comparative investigation has been carried out on  $\beta$ -monosubstituted or disubstituted push-pull tetraaryl Zn<sup>II</sup> porphyrinates and *meso*-disubstituted push-pull Zn<sup>II</sup> porphyrinates as sensitizers for use in DSSCs. The aim was to identify possible differences in their photon-to-electron conversion efficiencies and to compare their performances in DSSCs fabricated according to a standard protocol.

In order to facilitate such a comparison, we have devised a new facile synthesis of  $\beta$ -disubstituted push-pull Zn<sup>II</sup> porphyrinates involving two opposite  $\beta$ -pyrrolic positions of the porphyrinic ring, a push-pull porphyrinic system that, to the best of our knowledge, has not hitherto been synthesized.

Through comparative spectroscopic, electrochemical, and theoretical DFT investigations, we have obtained evidence that the HOMO-LUMO energy gap is lower in the case of the meso-disubstituted push-pull porphyrinic dyes, not only when compared to the  $\beta$ -monosubstituted but also the β-disubstituted push-pull porphyrinic dyes. This indicates that the porphyrinic ring is more effective as a linker between the "push" and "pull" ethynylphenyl substituents when the push-pull system involves the 5,15-meso positions (dyes 6, 7, and 8) as opposed to the  $2,12-\beta$ -pyrrolic positions (dyes 2 and 5) of the porphyrinic ring. A more efficient electron transfer by excitation along the push-pull system towards the anchoring carboxylic acid group for dyes 6, 7, and 8 was confirmed by the higher intensity and lower energy of their single Q bands, which originate mainly from the HOMO-LUMO transition, as compared to the rather weak Q bands at lower energy of dyes 2 and 5, which also mainly originate from the HOMO-LUMO transition.

The performances of DSSCs based on  $\beta$ -disubstituted push-pull dyes 2 and 5 were found to be only slightly superior to those of DSSCs based on  $\beta$ -monosubstituted dyes 1 and 4, respectively. Unexpectedly, however, they were also superior to those of DSSCs based on structurally related *meso*-disubstituted push-pull dyes 6 and 8. The DSSCs were fabricated according to a standard protocol in order to allow a valid comparison. Our protocol is probably not optimal, as

suggested by the previously reported higher performances of DSSCs based on N719<sup>[3]</sup> or on the *meso*-disubstituted push-pull porphyrinic dye 6.<sup>[4c]</sup>

The higher efficiency of DSSCs based on dyes with a push–pull system attached at the 2,12- $\beta$  positions of the porphyrinic ring is a rather unexpected result, since electron transfer by excitation along the push–pull system is more efficient when it occurs through the 5,15*-meso* positions, thus suggesting a significant influence of the positioning of the anchoring group.

Moreover, as a general feature, the presence of a cyanoacrylic acid group on the "pull" ethynylphenyl substituent of all of the porphyrinic dyes investigated was found to produce superior DSSC performances, probably due to more efficient electron injection into the  $TiO_2$ , since the cyanoacrylic acid group favors the localization of excited electrons on the "pull" ethynylphenyl substituent bearing the anchoring group.

Interestingly, the IPCE spectra of the  $\beta$ -mono- or disubstituted porphyrinic dyes are more intense, particularly in the presence of a cyanoacrylic acid group, over a broad wavelength range (350–650 nm), while those of the *meso*-disubstituted push–pull porphyrinic dyes are less intense and show the limitation of two well-separated and less intense peaks, corresponding to the B and the single Q bands, with weak IPCE values in the mid-range (530–610 nm) of only 20– 30%.

In fact, DSSCs based on dye **4**, and more especially dye **5**, show an IPCE spectrum with broad and intense coverage over the wavelength range 350–650 nm, similar to that of dyes based on ruthenium complexes such as N719.<sup>[3]</sup> In order to obtain such a broad and intense coverage with porphyrinic dyes substituted at the *meso* positions, the addition of a co-sensitizer<sup>[5]</sup> or the introduction of two thienylene-vinylene units to bridge the porphyrinic ring and the anchoring cyanoacrylic acid group<sup>[34]</sup> is necessary.

In summary, the increased light-harvesting properties arising from  $\beta$  substitution of the porphyrinic ring cannot be ascribed to more intense B and particularly Q bands, but probably to more facile charge injection into the TiO<sub>2</sub> surface, consistent with the DFT electron distribution of the  $\beta$ monosubstituted porphyrinic dye **1** interacting with the TiO<sub>2</sub> surface. Finally, it is worth noting the significant effects on the HOMO–LUMO energy gap, the IPCE spectra, and the performance of the DSSCs exerted by the presence of a cyanoacrylic acid group on the "pull" ethynylphenyl substituent for all of the dyes investigated, confirming the findings of other research groups.<sup>[4b,9b]</sup> In this work, we have investigated in more detail the electronic origin of these effects, as was partially carried out in a recent theoretical study.<sup>[12]</sup>

Our electrochemical and TDDFT investigations have clearly shown that the positive effect produced by the cyanoacrylic acid group is due more to increased conjugation of the "pull" ethynylphenyl substituent with the porphyrinic ring than to an inductive effect. This increased conjugation lowers the energy levels of the LUMO and LUMO+2 (Figure 2), and consequently, upon excitation, increases the electron density in the proximity of the anchoring carboxylic group, as confirmed by the IPCE spectra.

TDDFT calculations have also shown that such an electron transfer involves, upon excitation, not only the Q absorption bands at lower energy but also the B band, confirming the suggestion previously made by some of us to justify the significant photoconversion of the B absorption band of the push–pull porphyrinic dye  $6^{[7]}$  The lower significance of the inductive process is supported by the lack of effect of introducing a second carboxylic acid group on the "pull" ethynylphenyl substituent on the electrochemical, electronic, and photoelectrochemical properties of the investigated porphyrinic dyes.

Finally, our investigation has shown that  $\beta$ -monosubstituted or disubstituted push-pull Zn<sup>II</sup> porphyrinates, obtained by our simple and efficient three-step synthesis, are capable of serving as effective dyes in DSSCs. Indeed, the DSSC performances are comparable to those obtained using *meso* push-pull Zn<sup>II</sup> porphyrinates, which have previously been reported to be the most promising porphyrinic dyes,<sup>[4c]</sup> but which can only be obtained by multi-step syntheses in very low overall yields. Therefore, for technological applications, this work provides an incentive to focus further attention on this promising class of green and stable  $\beta$ -substituted porphyrinic dyes.

#### **Experimental Section**

General: All reagents and solvents used in the syntheses were purchased from Sigma-Aldrich and used as received, except Et<sub>3</sub>N, Et<sub>2</sub>NH (freshly distilled over KOH), THF (freshly distilled from Na/benzophenone under nitrogen atmosphere), and 4-ethynylphthalic anhydride (purchased from ABCR). Silica gels for gravimetric chromatography (Geduran Si 60, 63-200 µm) and for flash chromatography (Geduran Si 60, 40-63 µm) were purchased from Merck. Glassware was flame-dried under vacuum before use when necessary. [5,15-Diiodo-10,20-bis(3,5-di-tert-butylphenyl)porphyrinate]Zn<sup>II[7]</sup> (6a), [5-(4'-carboxyphenylethynyl)-15-(4"-N,N-dimethylaminophenylethynyl)-10,20-bis(3,5-di-tert-butylphenyl)porphyrinate]Zn<sup>II[7]</sup> (6), 4-ethynylbenzoic acid,  $^{[35]}$  and 4-ethynylbenzaldehyde $^{[36]}$  were prepared as reported in the literature. Microwave-assisted reactions were performed using a Milestone MicroSYNTH instrument. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance DRX-400 or a Bruker AMX 300 spectrometer from solutions in CDCl<sub>3</sub> containing, when necessary, a drop of [D<sub>5</sub>]pyridine, or from solutions in [D<sub>8</sub>]THF (Cambridge Isotope Laboratories, Inc.). Mass spectra were obtained on a VG Autospec M246 mass spectrometer with an LSIMS ion source. Electronic absorption spectra were recorded on a JASCO V-530 spectrometer; emission spectra were recorded on a Jobin-Yvon Fluorolog-3 spectrometer equipped with double monochromators and a Hamamatsu-928 photomultiplier tube (PMT) as a detector. Details of the syntheses are reported in the Supporting Information.

**Electrochemical measurements**: Voltammetric studies were performed in a 4 cm<sup>3</sup> cell, using  $5 \times 10^{-4}$ – $1 \times 10^{-3}$  M solutions in dimethylformamide (Aldrich, 99.8%) with 0.1 M tetrabutylammonium perchlorate (TBAP; Fluka) as the supporting electrolyte. The solutions were deaerated by N<sub>2</sub> bubbling. The ohmic drop was compensated for by the positive feedback technique.<sup>[37]</sup> The experiments were carried out using an AUTOLAB PGSTAT potentiostat (EcoChemie, The Netherlands) run by a PC with GPES software. Cyclic voltammetry (CV) investigations were carried out at scan rates typically ranging from 0.05 to 2 V s<sup>-1</sup>, with ohmic drop compensation; differential pulse voltammetry (DPV) curves (step potential: 5 mV, modulation amplitude: 50 mV) were also recorded for each compound as both oxidative and reductive scans. The working electrode was made of glassy carbon (AMEL, diameter 1.5 mm) cleaned with synthetic diamond powder (Aldrich; diameter 1  $\mu$ m) on a wet cloth (STRUERS DP-NAP); the counter electrode was a platinum disk or wire. An aqueous saturated calomel electrode served as the reference, but the potentials were ultimately referred to the Fc<sup>+</sup>/Fc (ferrocenium/ferrocene) couple (the intersolvental redox potential reference currently recommended by IUPAC)<sup>[25,38]</sup> by both external and internal standardization. To prevent leakage of water and chloride into the working solution, a compartment filled with the operating medium and closed with a porous frit was interposed between the reference electrode and the cell.

Preparation of DSSCs: DSSCs were prepared by adapting a procedure reported in the literature.<sup>[31]</sup> FTO glass plates (Solaronix  $7 \Omega sq^{-1}$ ) were cleaned in a detergent solution and in EtOH, and then rinsed with pure water and EtOH. FTO plates were treated with a 40 mm aqueous solution of TiCl<sub>4</sub> for 30 min at 70 °C and then rinsed with water and EtOH. An active monolayer of 10 µm was screen-printed using a 400 nm nanoparticle paste (Dyesol 18NR-AO); the coated films were dried at 125°C for 6 min and then thermally treated under an air flow at 325 °C for 10 min, 450 °C for 15 min, and 500 °C for 15 min. The sintered layer was again treated with 40 mM aqueous TiCl4 at 70 °C, rinsed with EtOH, and heated at 500 °C. After cooling to 80 °C, the TiO2-coated plate was immersed in a 0.2 mm solution of the dye in EtOH/THF (9:1) containing chenodeoxycholic acid (CDCA, 0.2 mM) for 2 h at room temperature in the dark. In the case of the dye N719, the TiO2-coated plate was immersed in a 0.5 mm solution of the dye in EtOH for 20 h. The thickness of the layer was measured by means of a VEECO Dektak 8 Stylus Profiler. The counter electrode was prepared according to the following procedure. A 1 mm hole was made in an FTO plate using diamond drill bits. The electrode was then sequentially cleaned with a detergent solution, 10% HCl, and acetone. After heating at 400°C, the electrode was cooled and a drop of a  $5\!\times\!10^{-3}{}_{\mbox{M}}$  solution of  $H_2PtCl_6$  in EtOH was added. The thermal treatment at 400  $^{\rm o}{\rm C}$  was then repeated. The TiO\_2 electrode with adsorbed dye and Pt counter electrode were then assembled in a sealed sandwich-type cell by heating with a hot-melt ionomer-class resin (Surlyn, 25 um thickness) as a spacer between the electrodes. The electrolyte solution was introduced through the hole by vacuum backfilling and the hole was sealed with Surlyn. A reflective foil was taped to the rear side of the counter electrode to reflect unabsorbed light back to the photoanode.

**Photoelectrochemical measurements**: Photovoltaic J-V curves were obtained using a 500 W xenon light source (ABET Technologies Sun 2000 class ABA Solar Simulator). The power of the simulated light was calibrated to AM 1.5 (100 mW cm<sup>-2</sup>) using a reference Si cell photodiode equipped with an IR cut-off filter (KG-5, Schott) to reduce the mismatch in the region 350–750 nm between the simulated light and the AM 1.5 spectrum. Measurements were made after 3 h and after 1, 3, 5, and 7 days of ageing in the dark. J-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. Incident photon-to-current conversion efficiency (IPCE) spectra were recorded as a function of excitation wavelength in AC mode with a chopping frequency of 1 Hz and a bias of white light (0.3 sun).

**Electrochemical impedance spectroscopy (EIS)**: Impedance spectra were obtained using an EG&G PARSTAT 2263 galvanostat potentiostat. The measurements were performed in the frequency range from 100 kHz to 0.1 Hz using an ac stimulus of 10 mV under 250 Wm<sup>-2</sup> (0.25 sun) illumination under open-circuit conditions (no applied bias voltage).

**Theoretical DFT and TDDFT calculations**: DFT and TDDFT calculations were performed on all of the investigated Zn<sup>II</sup> porphyrinates using Gaussian 09.<sup>[39]</sup> All of the structures were freely optimized in vacuo using B3LYP<sup>[40]</sup> and the 6-311 G\* basis set.<sup>[41]</sup> Single point calculations, including the solvent effects (THF) by means of the CPCM<sup>[42]</sup> conductor-like solvation model, were performed on the optimized structures in order to compute the energies and electronic distributions of the first three occupied/unoccupied molecular orbitals. The absorption spectra were simulated in THF solution by computing the first singlet-singlet excitations; the

# computed spectra were analyzed in terms of the molecular orbital compositions of the main B and Q transitions.

To gain insight into the interactions between the  $Zn^{II}$  porphyrinates and the semiconductor, the adsorption of porphyrin **1** on a TiO<sub>2</sub> surface was also investigated. Following the strategy devised by some of us in a previous investigation,<sup>[43]</sup> a cluster of  $1@(TiO_2)82$  was optimized in the gas phase with the ADF program package<sup>[44]</sup> employing the BPW91 exchange-correlation functional. To take into account the solvent effect, we carried out a single point calculation in THF at the same B3LYP/6-311G\* level of calculation as used for the isolated dyes.

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