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Modulating the electronic properties of asymmetric push–pull and symmetric Zn(II)-diarylporphyrinates with *para* substituted phenylethynyl moieties in 5,15 *meso* positions: A combined electrochemical and spectroscopic investigation

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ABSTRACT

Push–pull Zn(II)-porphyrinates have recently shown attracting performances as light harvesting systems in dye-sensitized solar cells (DSSCs). To fully exploit their intrinsically high efficiency it is important to finely tune their HOMO and LUMO levels, which can be achieved by proper choice of the push and pull substituents. Of course such target-oriented molecular design requires the availability of reliable relationships between molecular structure and electronic properties; therefore we have carried out a combined electrochemical, spectroscopic and computational investigation on a wide, systematic range of Zn(II)-porphyrinates 5,15 *meso* substituent with phenylethynyl linkers, including a first symmetric series carrying on the opposite terminals the same substituent ($-N(CH_3)_2$, $-OCH_3$, $-COOCH_3$, -COOH, $-NO_2$); and a second push–pull one, with the terminal positions carrying one donor and one acceptor group belonging to the series above. Moreover, two suitably modified porphyrins allowed evaluation of the effects of (i) the presence or absence of the phenyl group in the linker between the porphyrin core and the acceptor group, and (ii) the effect of perfluorination on the same phenyl group. A rationalization scheme is proposed encompassing the whole porphyrin set, affording *inter alia* interesting clues on the different localization of the redox centres and effective conjugation between the porphyrin core and the side chains as a function of the molecular design.

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1. Introduction

Porphyrins are extremely versatile molecular architectures with a widespread potential in the field of organic electronics, including emissive and optoelectronic applications [1–5] and recently also of organic photovoltaic cells [6–11] on account of their interesting photophysical properties, tunable through a variety of substituents which can be linked to the *meso* or β pyrrolic positions of the porphyrinic ring. Moreover porphyrins are characterized by good thermal and chemical stabilities.

Some of us have investigated the synthesis and second-order non linear optical (NLO) properties of metal

10,20-diphenylporphyrins, carrying in the 5,15 *meso* positions a *para* substituted phenyl ring connected by a triple bond to the porphyrin ring [12,13].

These metal porphyrins act as a push–pull system by introduction of an electron donor group on one aromatic ring and an electron acceptor group on the other one, as first reported by Therien and coworkers [14–16]. The large quadratic hyperpolarizability [12–16] and the significant two-photon absorption [17,18] of this family of push–pull metal porphyrins have been attributed mainly to a directional charge transfer process along the push–pull system, origin of a quite strong Q absorption band corresponding to the transition from the donor HOMO to the acceptor LUMO level, as reported for the first time by some of us by a TDDFT investigation [19]. Moreover, also transitions between energy levels localized mainly on the porphyrin ring, origin of the very strong B absorption band at about 450 nm, are contributing to the hyperpolarizability, although to a less extent [19].

Starting from the evidence of the presence of various strong charge transfer processes in this family of push-pull metal

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Fig. 1. A synopsis of the investigated Zn(II)-porphyrinates.

porphyrins, interest for their application as dyes in DSSCs (Dye-Sensitized Solar Cells) has raised in the last years. Several push-pull Zn(II)-porphyrinates of this family have been synthesized and investigated, all of them featuring: (a) one or more carboxylic groups as electron acceptor groups on one aromatic ring, ensuring efficient anchoring on the TiO₂ layer, and (b) phenylethynyl moieties as π -spacers between the porphyrin core and the terminal acceptor carboxylic or donor groups. Many of these push-pull Zn(II)-porphyrinates show attractive performances when acting as dyes in DSSCs [20–26]. To fully exploit the efficiency of these porphyrins as light harvesting dyes it is necessary to match specific requirements, such as a LUMO energy level higher than that of the TiO₂ conduction band and a HOMO energy level lower than the energy of the electrolytic redox couple I^{-}/I_{3}^{-} [7,27–31]. This can be achieved by tuning the HOMO-LUMO levels in particular by proper choice of the donor groups of the push-pull system. In order to produce rational guidelines for this choice, a convenient experimental approach appears to be the electrochemical systematic characterization of an exhaustive series of Zn(II)-porphyrinates, either asymmetrically (push-pull) or symmetrically substituted in 5,15 meso positions affording reliable comparison not only of HOMO-LUMO energy gaps (which can be also theoretically or experimentally evaluated by electron absorption spectroscopy) but also of the origin of the electronic effects, introduced by different donor or acceptor groups, acting on the HOMO and LUMO energy levels, critical for the design of the appropriate porphyrinic dye.

In order to follow this approach we have investigated, by cyclic voltammetry and electronic absorption spectroscopy with the support of a TDDFT theoretical study, two series of 10,20-diaryl Zn(II)-porphyrinates carrying in 5,15 *meso* positions *para* substituted phenylethynyl linkers (Fig. 1) namely:

- a first series of five symmetric porphyrinic architectures (1–5), carrying in the 5,15 meso positions the same para substituted phenylethynyl moiety, where the substituents are -N(CH₃)₂, -OCH₃, -COOCH₃, -COOH, -NO₂, *i.e.* regularly ranging from a strong donor to a strong acceptor group;
- a second one of four *asymmetric push-pull* porphyrinic architectures (6-9), carrying in the 5,15 meso positions one donor and one acceptor group belonging to the series above;
- finally, two suitably modified porphyrinic architectures in order to evaluate the effect of the absence of the phenyl ring in the ethynyl linker between the porphyrinic core and the acceptor COOEt group (3'), and of the perfluorination of the phenyl ring carrying the COOH group, thus producing an increased acceptor effect (6').

The aryl substituent in position 10,20 is the 3,5-di-*tert*butylphenyl ring with the exception of **7**, where the substituent is a simple phenyl ring.

2. Experimental

2.1. Synthesis

All reagents and solvents were purchased from Sigma–Aldrich and used as received except for Et_3N and Et_2NH (freshly distilled over KOH) and THF (freshly distilled from Na/benzophenone under nitrogen atmosphere). Silica gel (Geduran Si 60, 63–200 μ m) was purchased from Merck.

Glassware has been flame-dried under vacuum before use when it was necessary.

Zn(II)-porphyrinates **1**, **2**, **3**, **3**′, **4**, **5** and **9** have been synthesized following the specific procedures reported in Appendix A.

[5,15-Diiodo-10,20-bis(3,5-di-tert-butylphenyl)porphyrinate]-Zn(II) [32], [5,15-dibromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrinate]Zn(II) [33], [5-(4'-carboxy-phenylethynyl)-15-(4"-N,N-dimethylamino-phenylethynyl)-10,20-bis(3,5-di-tert-butylphenyl)porphyrinate]Zn(II) (6) [32], [5-(4'-carboxy-2',3',5',6'tetrafluorophenylethynyl)-15-(4"-N,N-dimethylamino-phenylethynyl)-10,20-bis(3,5-di-tert-butylphenyl)porphyrinate]Zn(II) (6') [32], [5-(4'-N,N-dimethylamino-phenylethynyl)-15-(4"-nitrophenylethynyl)-10,20-(diphenyl)porphyrinate]Zn(II) (7) [13] and [5-(4'-carboxy-phenylethynyl)-15-(4"-methoxy-phenylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) (8) [32] were prepared following the syntheses reported in literature. All the compounds have been characterized by ¹H and ¹⁹F NMR spectra recorded on a Bruker Avance DRX-400 in CDCl₃, CDCl₃ with a drop of pyridine- d_5 or in THF- d_8 (Cambridge Isotope Laboratories, Inc.) as solvent.

2.2. Electronic absorption spectra

Electronic absorption spectra were recorded in diluted THF solutions at room temperature by a Jasco V-530 spectrometer. The "onset" optical energy gaps were evaluated by the edge corresponding to the intersection between the negative tangent line in the inflection point of the lowest energy absorption band and the tangent line to a linear portion of the absorption tail.

2.3. Electrochemistry

The voltammetric studies have been performed in a 4 cm^3 cell, on ~0.0005 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_2 bubbling. The ohmic drop has been compensated by the positive feedback technique [34].

Deaeration is here more critical than usual, because most reduction peaks in our series of Zn(II)-porphyrinates fall in close proximity of oxygen reduction, a process which, moreover, porphyrins efficiently catalyse.

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 $0.05-2 V s^{-1}$, with ohmic drop compensation; scans were performed both starting in positive and negative directions, in order to check possible electrode poisoning effects by subsequent processes, which however proved not to be our case (see the detailed CV patterns reported for each porphyrin in the Supporting Material (Part C), where peaks coincide irrespective of the starting direction and width of the potential scan). Differential pulse voltammetry (DPV) curves (step potential: 5 mV, modulation amplitude: 50 mV) were also recorded for each compound, as a support to CV peak inspection, enhancing the porphyrin signals with respect to the background. Moreover, in the absence of surface poisoning as in the present case, comparison of DPV scans in positive and negative direction (cyclic DPV, CPDV [35,36]), evidences electron transfer reversibility (the more reversible a given electron transfer process, the more similar the corresponding peaks obtained in the positive and negative DPV scans).

The working electrode was a glassy carbon one (AMEL, diameter = 1.5 mm) cleaned by synthetic diamond powder (Aldrich, diameter = 1 μ m) on a wet cloth (Struers DP-NAP); the counter electrode was a platinum disk or wire; the operating reference electrode was an aqueous saturated calomel electrode, but the potentials were ultimately referred to the Fc⁺/Fc couple (the intersolvental redox potential reference currently recommended by IUPAC [37,38]) by both external and internal standardization. To prevent water and chloride leakage into the working solution a compartment filled with the operating medium and ending with a porous frit was interposed between the reference electrode and the cell.

2.4. DFT and TDDFT calculations

DFT ground state optimized geometries and energies of dyes **1–5** and **3**' were obtained by using the B3LYP exchange correlation functional [39] along with a 6-31G* basis set. For sake of simplicity the *tert*-butyl substituents of the phenyl rings have been replaced by hydrogen atoms.

TDDFT excited state calculations were performed on the DFT optimized geometries at the same B3LYP/6-31G* level of theory, both *in vacuo* and in water solution.

Although a TDDFT approach coupled with a GGA exchange correlation functional and relatively large basis set has proven to provide reliable agreement between predicted and experimentally observed vertical excitation energies and other spectroscopic properties in porphyrin derivatives [40–43], some of us have shown in previous papers [13,19,32] that B3LYP, also adopted by other researchers [44–46], gives very good results for push–pull 5,15 *meso*-substituted Zn(II)-porphyrinates; in particular, B3LYP has been found sufficient to study the charge transfer character of Q bands by TDDFT calculations [43].

The lowest 10 excitation energies were calculated, spanning approximately 3.5 eV. All the calculations have been performed by the Gaussian 03 program package [47]. The nonequilibrium C-PCM solvation model was employed for TDDFT calculations in solution [48,49].

3. Results and discussion

3.1. Syntheses

The Zn(II)-porphyrinates investigated in this work are reported in Fig. 1, which includes:

- the series of *symmetric* Zn(II)-porphyrinates, **1–5**;
- the series of *asymmetric push-pull* Zn(II)-porphyrinates, **6-9**;
- the symmetric Zn(II)-porphyrinate **3**′, to be compared to **3** in order to evaluate the effect of the absence of the phenyl ring in the ethynyl linker;
- the asymmetric, push–pull Zn(II)-porphyrinate **6**′, to be compared to **6** in order to evaluate the effect of perfluorination of the phenyl ring carrying the COOH group.

Syntheses of all the Zn(II)-porphyrinates investigated were carried out by the Sonogashira coupling [50], starting from the 5,15-diiodo or 5,15-dibromo Zn(II)-porphyrinates. For **6**, **6**′, **7** and **8** synthetic procedures previously reported in literature were followed [13,32], while for the remaining Zn(II)-porphyrinates the syntheses are reported in Appendix A. In particular, symmetric Zn(II) porphyrinates **1**, **2**, **3**, **3**′ and **5** were synthesized starting from the 5,15-diiodo Zn(II)-porphyrinate by a one-step reaction with the donor or the acceptor phenyl ethynyl moiety, whereas the push–pull Zn(II)-porphyrinate **9** was synthesized by a two-step method starting from the 5,15-dibromo Zn(II)-porphyrinate, by introducing first the donor and then the acceptor phenyl ethynyl moiety, following the procedure reported by Therien and coworkers [14]. Finally **4** was obtained by hydrolysis of **3** with LiOH in a THF/H₂O mixture.

3.2. Electronic absorption spectra

The electronic absorption spectra of all the Zn(II)-porphyrinates investigated, recorded in THF solution and normalized with respect to the maximum absorption peak, are collected in Fig. 2; details on the absorption maxima and onset wavelengths are reported in Table 1.

All spectra feature the two absorption bands, typical of metal porphyrins, one very strong centred at about 450 nm (Soret or B band) and one quite strong centred in the 650–700 nm range (Q band); in some cases a weaker band appears, also as a shoulder, in this latter range (Fig. 2). The B band corresponds mainly to the singlet $S_0 \rightarrow S_2$ transition, centred on the porphyrin core, while the Q band corresponds mainly to the singlet $S_0 \rightarrow S_1$ charge-transfer transition between the HOMO–LUMO levels [19].

The increased push–pull character of the asymmetric Zn(II)porphyrinates, resulting from increasing strengths of the electron donor or electron acceptor groups or of both, can be expressed in terms of Hammett parameters, which follows the sequence 8 < 9 < 6 < 7, with a regular red-shift of both B and Q bands (see Table 1).

On the contrary, the symmetric Zn(II)-porphyrinates display nearly constant wavelengths of both B and Q bands with the exception of **1** and **5** (actually the two opposite limiting cases in the sequence of the Hammett parameters) (Table 1) featuring, in particular **1**, a remarkable red shift of both bands which could be tentatively attributed to quadrupolar contributes, [51] because of the known ambivalent behaviour, both donor or acceptor, of the porphyrinic ring [52].

Moreover it can be noticed that the increase of the peak widths of the B band appear to regularly account for the symmetric or asymmetric character: in the symmetric series the B bands are quite sharp, albeit widening in the two limiting cases **1** and **5** (strongest electron donor and acceptor substituents, respectively), while in

Table 1

Onset and maximum absorption wavelengths of Zn(II)-porphyrinates **1–5**, **6–9**, **3'** and **6'**, together with the corresponding calculated values of optical energy gaps. Zn(II)-porphyrinates are reported in increasing order of the sum of Hammett σ_p parameters [56] for the two substituents in 5,15 *meso* positions, with the exception of **3'** and **6'**. E_g values are highlighted in bold character.

#	Substituents	$\Sigma \sigma_{ m p}$	B band				Q band				
			Onset		Max		Onset		Max		
				$\lambda_{\rm B}/{\rm nm}$	$E_{\rm g}/{\rm eV}$	$\lambda_{\rm B}/{\rm nm}$	$E_{\rm g}/{\rm eV}$	λ_Q/nm	$E_{\rm g}/{\rm eV}$	λ_Q/nm	$E_{\rm g}/{\rm eV}$
1	p-C ₆ H ₄ NMe ₂	p-C ₆ H ₄ NMe ₂	-1.66	487	2.55	467	2.66	703	1.77	678	1.83
2	p-C ₆ H ₄ OMe	p-C ₆ H ₄ OMe	-0.54	469	2.65	451	2.75	675	1.84	658	1.89
3	p-C ₆ H ₄ COOMe	p-C ₆ H ₄ COOMe	0.90	467	2.66	452	2.75	680	1.83	660	1.88
4	p-C ₆ H ₄ COOH	p-C ₆ H ₄ COOH	0.90	468	2.65	451	2.75	678	1.83	659	1.88
5	p-C ₆ H ₄ NO ₂	p-C ₆ H ₄ NO ₂	1.56	481	2.58	458	2.71	697	1.78	669	1.86
6	p-C ₆ H ₄ NMe ₂	p-C ₆ H ₄ COOH	- 0.38 ^a	486	2.55	456	2.72	698	1.78	671	1.85
7	p-C ₆ H ₄ NMe ₂	$p-C_6H_4NO_2$	-0.12	496	2.50	459	2.70	710	1.75	677	1.83
8	p-C ₆ H ₄ OMe	p-C ₆ H ₄ COOH	0.49	470	2.64	451	2.75	677	1.83	659	1.88
9	p-C ₆ H ₄ OMe	$p-C_6H_4NO_2$	0.83	478	2.60	459	2.70	691	1.80	667	1.86
3′	p-COOEt	p-COOEt	0.90	458	2.71	440	2.82	664	1.87	644	1.93
6′	p-C ₆ H ₄ NMe ₂	p-C ₆ F ₄ COOH	- 0.11 ^a	494	2.51	454	2.73	707	1.76	673	1.84

^a The difference between the two $\Sigma \sigma_p$ entries results from a +0.27 contribution accounting for the perfluorinated C₆F₅ ring [56].

the asymmetric series the B bands are significantly larger, and their width regularly increases with increasing push-pull character. It is worthwhile noticing also that the only spectrum of an asymmetric Zn(II)-porphyrinate of width comparable to those of the symmetric series is **8**, characterized by a weak push-pull asymmetric character.

This trend of the peak widths can be extended also to the Q band widths, albeit it is less conspicuous. Interestingly the ratio of the peak intensities of the Q band with respect to the B one, defined as $\varepsilon_Q/\varepsilon_B$, shows some specific and peculiar trends namely (Fig. 3):



Fig. 2. A synopsis of the normalized electronic absorption spectra of the Zn(II)porphyrinates **1–5**, **6–9**, **3'** and **6'**. Inset: focusing on the Q bands.



Fig. 3. Ratio of the peak intensities of the Q band with respect to the B one, defined as ϵ_Q/ϵ_B , for Zn(II)-porphyrinates **1–5**, **6–9** and **3**', **6**'.

- the symmetric series shows a nearly constant low ratio $\varepsilon_Q/\varepsilon_B$ of ~0.15, the only exception being clearly provided by **1** which, as above stated, could be justified in terms of quadrupolar contribution [51];
- **3**' presents the lowest ratio because in the absence of the phenyl ring in the linker the electronic properties of the molecule approach that of a non substituted Zn(II)-porphyrinates, generally presenting a very low $\varepsilon_0/\varepsilon_B$ value (≤ 0.10)²;
- the asymmetric push-pull series shows a regular increase of the $\varepsilon_Q/\varepsilon_B$ ratio, at fixed donor group, with increasing strength of the acceptor one; two different straight lines can be perceived for $D = -OCH_3$ and $-N(CH_3)_2$, the second one characterized by much higher values, consistently with the higher donating ability of the amino group and therefore with a higher push-pull character of the porphyrinic architecture.

² In our experience we found the same ratio value in the case of the 5,15 diiodo or dibromo Zn(II)-porphyrinates, but also in the case of the 5-bromo-15-iodo Zn(II)-porphyrinate. Moreover it has been reported [53] for several octaalkyl metal-porphyrinates, unsubstituted in all the *meso* positions, a molar extinction coefficient 10 times higher for the B band than for the Q band in vapor phase absorption spectra.



Fig. 4. Schematic diagram of the HOMO–LUMO energy levels, calculated in water solution, for Zn(II)-porphyrinates **1–5** and **3**′.

From electronic absorption spectra "optical" energy gaps E_g have been calculated by using both either the maximum or the onset wavelengths (Table 1), according to the equations:

$$E_{g,\max}(eV) = \frac{h(Js^{-1}) \times c(ms^{-1})}{\lambda_{\max}(m) \times e(C)} \quad (\text{maxima criterion}) \tag{1a}$$

$$E_{g,onset}(eV) = \frac{h(Js^{-1}) \times c(ms^{-1})}{\lambda_{onset}(m) \times e(C)} \quad (onset criterion)$$
(1b)

For the symmetric series **1–5** the energy gap of both the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions evaluated from the maximum wavelength of the B and in particular of the Q bands respectively, is lower for strong donor ($-NMe_2$) or strong acceptor ($-NO_2$) groups, suggesting, in accordance with the ambivalent donor and acceptor properties of the porphyrinic core [52], a more facile electron transfer to the porphyrinic core ($-NMe_2$) or *vice versa* ($-NO_2$). For the other groups (-OMe, -COOMe, -COOH) the energy gap is slightly higher but quite independent from the donor or acceptor nature of the group, consistently with a less relevant electron transfer process from or to the porphyrinic core.

It was already reported [32] that for the asymmetric Zn(II)porphyrinates **6** and **8** the energy gap of the Q band, corresponding to the HOMO–LUMO transition with a significant electron transfer along the push–pull system, is lower when the donor group is –NMe₂, just confirming the relevant effect of the strength of the donor group. Moreover for the symmetric Zn(II)-porphyrinate **3**' the energy gap of the Q band is higher if compared to **1–5**, suggesting a less relevant electron transfer from the porphyrinic core to the –COOEt group, in the absence of an intermediate phenyl ring in the ethynyl linker.

Finally the fluorination of the aromatic ring carrying the acceptor -COOH group as in **6**' does not produce a relevant effect on the energy gap of both the B and Q bands which is quite similar to that of the non fluorinated Zn(II)-porphyrinate **6** (Table 1).

In order to confirm such analysis of the properties and trends of the electronic absorption spectra we carried out a DFT theoretical investigation on the ground state energy level of the symmetric Zn(II)-porphyrinates **1–5** and **3**′. Such kind of investigation has been already reported for the asymmetric Zn(II)-porphyrinates **6** and **8** [32] and **7** [19].

The DFT computational investigation has given information on the energy of the HOMO and LUMO levels (Fig. 4), together with that of other levels of higher or lower energy (Table B.7 in the Supplementary Material), and on the electron density on the HOMO and LUMO orbitals (Fig. 5).

In agreement with the trends of the absorption spectra (Figs. 2 and 3 and Table 1) the energy gap between the HOMO–LUMO levels is lower for **1** and, although to a lesser extent, for **5**, while it is slightly higher and quite independent from the nature of the donor or acceptor groups for **2**, **3** and **4** (Fig. 4).

Such a picture is clearly in agreement with the higher values of the ratio $\varepsilon_Q/\varepsilon_B$ reported in Fig. 3, since the electron transfer from the HOMO to the LUMO level involves a relevant electron density transfer from the donor ethynyl phenyl moiety carrying the $-NMe_2$ strong donor group to the porphyrinic core for **1** (Fig. 5) and a less significant electron density transfer from the porphyrinic core to the ethynyl phenyl moiety carrying the nitro strong acceptor group for **5** (Fig. 5), in accordance with the suggested ambivalent acceptor/donor properties of the porphyrinic core is much less relevant for **2**, **3** and **4**, having less strong donor or acceptor groups respectively (see Fig. 5).

For asymmetric Zn(II)-porphyrinates **6** and **7** we have a strong electron density transfer along the push–pull system mainly when the donor group is $-N(CH_3)_2$, due to the large electron density centred on the ethynyl phenyl moiety carrying the donor group (HOMO level) while the acceptor LUMO level is centred mainly on the ethynyl phenyl moiety carrying the carboxylic group [32].

Therefore in the asymmetric architectures the HOMO or LUMO energy levels do not significantly involve the porphyrinic core, while for the HOMO (**3**, **4**, **5**) and for the LUMO (**1**, **2**) levels of the symmetric architectures the contribution of the porphyrinic core is relevant.

Finally for the symmetric Zn(II)-porphyrinate **3**′, lacking the phenyl ring in the ethynyl linker, the HOMO–LUMO energy gap is higher so that the electron density transfer (Fig. 5) from the porphyrinic ring (HOMO level) to the ethynyl moiety carrying the —COOEt group (LUMO level), is much less relevant in agreement with the energy and intensity trend of its electronic absorption spectrum (Table 1 and Fig. 3).

In order to confirm the above suggestions raised by the DFT investigation we have carried out also a TDDFT computational investigation, explicitly calculating the systems' excited states, thus allowing a complete definition of the electronic origin of the B and Q bands.

The computed excitation energies and oscillator strengths of the optical transitions calculated *in vacuo* and in solution taking into consideration the lowest 10 excitation states are reported in Table B.8 in the Supplementary Material.

In particular a quite good agreement between theoretical and experimental values was found for the Q band, for which the major contribution of the HOMO–LUMO transition was confirmed, according to the trend of Table 2.

For both **1** and **5** the calculated values of λ_{max} and *f* of the absorption Q band are higher if compared to the values for **2**, **3** and **4**, in full agreement with the experimental trends of Table 1 and Fig. 3.

For **3**' the calculated values of λ_{max} and *f* of the Q band are at higher energy and of lower intensity still in agreement with the experimental findings (Table 1 and Fig. 3), as a consequence of a lower HOMO–LUMO contribution to the Q band, due to the lack of the phenyl ring in the ethynyl linker.

Finally the TDDFT calculations have shown that for the Zn(II)-porphyrinates **1** and **5**, in addition to two very close major strong transitions at about 400–410 nm characterizing the B band, two close transitions of minor but still relevant intensity at about 470–490 nm are found (Figures B.1 and B.6 and Tables B.1 and B.6 in the Supplementary Material), which correspond to the broad absorption band found in the experimental spectra.



Fig. 5. Electron density plots of the HOMO and LUMO levels of Zn(II)-porphyrinates 1-5 and 3' calculated in water solution (isodensity value = 0.02).

In the case of **2**, **3**, **4** and **3**′ we still have two very close major transitions at about 435–445 nm (Figures B.2, B.3, B.5, B.4 and Tables B.2, B.3, B.5 and B.4 in the Supplementary Material) but transitions at lower energy as in **1** and **5** are lacking. All these transitions mainly involve the electronic density of the porphyrinic core and excited states of higher energy.

3.3. Electrochemical characterization

All Zn(II)-porphyrinates investigated in this work have been electrochemically characterized by both cyclic voltammetry (CV) and differential pulse voltammetry (DPV), the latter affording significant enhancement of the faradaic signal *vs* capacitive background ratio, a useful tool considering the moderate solubility and large size and sterical hindrance, implying low diffusion coefficients, of the Zn(II)-porphyrinates investigated.

The investigation was carried out in DMF+0.1 M TBAP, which ensures sufficient solubility for all the Zn(II)-porphyrinates investigated together with a satisfactory potential window for both reduction and oxidation processes.

Synopses of CV and DPV patterns are provided in Fig. 6 (symmetric series **1–5**), 7 (**3** *vs* **3**') and 8 (asymmetric push–pull series **6–9** and **6**'). Relevant oxidation and reduction peaks are accounted for in terms of (a) onset potential, (b) formal potential, and (c) peak (maximum) potential (Table 3), corresponding to the three current approaches to the calculation of electrochemical HOMO and LUMO energy levels, ultimately referred to the absolute value of the normal hydrogen electrode (NHE) as critically assessed in a

Table 2

Calculated properties of the Q band of symmetric Zn(II)-porphyrinates 1–5 and 3'.

fundamental review paper [54]:

$$E_{\text{LUMO}}(\text{eV}) = -e \times \left[(E_{\text{onset, Ic}}/\text{V}(\text{Fc}^+|\text{Fc}) + 4.8 \text{V}(\text{Fc}^+|\text{Fc} vs \text{ zero}) \right]$$
(onset criterion) (2a)

$$E_{\text{LUMO}}(\text{eV}) = -e \times \left[(E_{\text{lc}}^{\circ} / \text{V}(\text{Fc}^+ | \text{Fc}) + 4.8 \,\text{V}(\text{Fc}^+ | \text{Fc} \, vs \, \text{zero}) \right]$$
(formal potential criterion) (2b)

$$E_{\text{LUMO}}(\text{eV}) = -e \times \left[(E_{\text{p,Ic}}/\text{V}(\text{Fc}^+|\text{Fc}) + 4.8 \text{V}(\text{Fc}^+|\text{Fc} vs \text{ zero}) \right]$$
(maxima criterion) (2c)

$$E_{\text{HOMO}}(\text{eV}) = -e \times \left[(E_{\text{p,Ia}}/\text{V}(\text{Fc}^+|\text{Fc}) + 4.8 \text{V}(\text{Fc}^+|\text{Fc} \, vs \, \text{zero}) \right]$$
(maxima criterion) (3a)

$$E_{\text{HOMO}}(\text{eV}) = -e \times \left[(E_{\text{Ia}}^{\circ'} / \text{V}(\text{Fc}^+ | \text{Fc}) + 4.8 \,\text{V}(\text{Fc}^+ | \text{Fc} \, vs \, \text{zero}) \right]$$
(formal potential criterion) (3b)

$$E_{\text{HOMO}}(\text{eV}) = -e \times [(E_{\text{onset},\text{la}}/\text{V}(\text{Fc}^+|\text{Fc}) + 4.8 \text{V}(\text{Fc}^+|\text{Fc} \nu s \text{ zero})]$$
(onset criterion) (3c)

where *e* denotes the electron charge.

Table 3

A synopsis of reduction and oxidation potentials (onset, formal and peak maxima ones) for the Zn(II)-porphyrinates investigated. The data have been obtained working in DMF+0.1 TBAP, obtained with GC electrodes and referred to the ferricinium/ferrocene reference redox couple. Also the corresponding calculated values of HOMO and LUMO level energies and HOMO–LUMO gaps energies are reported. Data are ordered in increasing order of sum of Hammett σ_p parameters [56] for the two substituents in 5,15 *meso* positions. *E*_g values are highlighted in bold character.

#	Substituents	$\Sigma \sigma_{ m p}$	Onset criterion ^a						Formal potential criterion					
				$\frac{E_{\rm lc}/\rm V}{\rm (Fc^+ Fc)}$	E _{la} /V (Fc ⁺ Fc)	E _{LUMO} /eV	E _{HOMO} /eV	Eg/eV	$\frac{E_{\rm lc}^{\circ'}/{\rm V}}{({\rm Fc}^{+} {\rm Fc})}$	$\frac{E_{la}^{\circ'}}{(Fc^+ Fc)}$	$E_{\rm LUMO}/{\rm eV}$	E _{HOMO} /eV	Eg/eV	
1	p-C ₆ H ₄ NMe ₂	p-C ₆ H ₄ NMe ₂	-1.66	-1.46	0.072	-3.34	-4.87	1.53	-1.59	0.144 0.23 ^b	-3.21	-4.94 -5.03 ^c	1.73 1.82	
2	p-C ₆ H₄OMe	p-C ₆ H₄OMe	-0.54	-1.42	0.249	-3.38	-5.05	1.67	-1.54	0.288	-3.26	-5.09	1.82	
3	n-C ₆ H₄COOMe	p-C ₆ H₄COOMe	0.90	-1.32	0.341	-3.48	-5.14	1.67	-1.45	0.448	-3.35	-5.25	1.90	
4	n-C ₆ H₄COOH	p-C ₆ H₄COOH	0.90	-1.34	0.351	-3.46	-5.15	1.69	-1.42	0.453	-3.38	-5.25	1.88	
5	$n - C_6 H_4 NO_2$	$p - C_6 H_4 N O_2$	1 56	-1.20	0 366	-3.60	-5.17	1.57	-1 39	0.450	-3.41	-5.25	1.84	
-	F -042	F -042							-1.62 ^b		-3.18 ^c		2.07	
6	p-C ₆ H ₄ NMe ₂	p-C ₆ H ₄ COOH	-0.38	-1.40	0.158	-3.41	-4.96	1.55	-1.51	0.230	-3.29	-5.03	1.74	
7	n-CaH (NMea	$n_{\rm C}$ H $NO_{\rm D}$	0.12	1 20	0.164	3 51	4.96	1.46	1 30	0.30	3 /1	-5.10	1.67	
,	p-C61141010122	p-C61141002	-0.12	-1.29	0.104	-5.51	-4.90	1.40	-1.39 1.49b	0.235	-3.41	-5.05 5.18°	1.02	
0	n C H OMo	» С Ц СООЦ	0.40	1.24	0.270	2.56	5 17	1 61	1 47	0.55	-3.32	-5.10	1.00	
0	$p - C_6 \Pi_4 O M c$	р-с ₆ п ₄ сооп	0.49	-1.24	0.370	-3.50	-5.17	1.01	-1.47	0.454	-3.33	-5.25	1.33	
5	p-C61140101E	p-C ₆ H ₄ NO ₂	0.85	-1.20	0.551	-3.32	-5.15	1.01	-1.30 1.40b	0.591	-3.42	-5.19	1.//	
									-1.49		-5.51-		1.00	
3′	p-COOEt	p-COOEt	0.90	-1.15	0.488	-3.65	-5.29	1.64	-1.25	0.614	-3.55	-5.41	1.86	
6′	$p-C_6H_4NMe_2$	p-C ₆ F ₄ COOH	-0.11	-1.38	0.099	-3.42	-4.90	1.48	-1.46	0.142	-3.34	-4.94	1.60	
										0.33 ^b		-5.12 ^c	1.76	
#	Substituents		$\Sigma \sigma_{ m p}$		Peak maxima criterion									
					$\frac{E_{\rm p,lc}/\rm V}{\rm (Fc^+ Fc)}$	$\frac{E_{\rm p,Ia}}{\rm (Fc^+ Fc)}$	$E_{\rm LUMO}/{\rm eV}$	$E_{\rm HOMO}/\epsilon$	V	E _g /eV	$E_{\rm p,Ic} - E_{\rm p,IIc}/V$	E _{p,Ia}	$-E_{\rm p,IIa}/{\rm V}$	
1	p-C ₆ H ₄ NMe ₂	p-C ₆ H ₄ NMe ₂	-1.66		-1.621	0.170	-3.18	-4.97		1.79	0.52	0.12	2	
					-2.144 ^b	0.289 ^b		-5.09 ^c		1.91				
2	p-C ₆ H ₄ OMe	p-C ₆ H ₄ OMe	-0.54		-1.565 -2.089	0.359	-3.24	-5.16		1.92	0.52			
3	<i>p</i> -C ₆ H ₄ COOMe	p-C ₆ H ₄ COOMe	0.90		-1.427	0.464	-3.37	-5.26		1.89	0.49			
					-1.917 ^b									
4	<i>p</i> -C ₆ H ₄ COOH	p-C ₆ H ₄ COOH	0.90		-1.466 -1.843 ^b	0.470	-3.33	-5.27		1.94	0.38			
5	$p-C_6H_4NO_2$	$p-C_6H_4NO_2$	1.56		-1.426	0.507	-3.37	-5.31		1.93	0.25			
	-	-			-1.673 ^b		-3.13 ^c			2.18				
6	$p-C_6H_4NMe_2$	p-C ₆ H ₄ COOH	-0.38		-1.549	0.267	-3.25	-5.07		1.82	0.54	0.14	ł	
	•	•			-2.090^{b}	0.409 ^b		-5.21 ^c		1.96				
7	p-C ₆ H ₄ NMe ₂	$p-C_6H_4NO_2$	-0.12		-1.386	0.260	-3.41	-5.06		1.65	0.15	0.16	5	
	1 0 1 2	1 0 . 2			-1.536 ^b	0.421 ^b	-3.26 ^c	-5.22 ^c		1.96				
8	p-C ₆ H₄OMe	p-C ₆ H₄COOH	0.49		-1.465	0.490	-3.34	-5.29		1.96	0.59			
	1 0 7				-2.050 ^b					-				
9	p-C ₆ H₄OMe	p-C ₆ H ₄ NO ₂	0.83		-1.400	0.426	-3.40	-5.23		1.83	0.12	0.26	5	
-	r -01.401110	F -01.41.02	0.00		-1.518 ^b	0.685 ^b	-3.28 ^c	-5.48°		1.94		5.20		
3′	p-COOEt	p-COOEt	0.90		-1.270 -1.672 ^b	0.651	-3.53	-5.45		1.92	0.40			
6′	n-CaH (NMea	n-C-F-COOH	0.11		1 /072	0 100	3 30	5.00		1 70	0.46	0.16	:	
5	P-C6114110102	p C614COUT	-0.11		-1.953 ^b	0.355 ^b	-3.30	-5.16 ^c		1.85	0.40	0.10	,	

^a Onset parameters are given only for first oxidation and first reduction peaks since they are not always available for the subsequent ones.

^b Potentials corresponding to the second reduction or oxidation process.

^c Energy level calculated from the potential value corresponding to the second reduction or oxidation process.



Fig. 6. CV (0.2 V s⁻¹ scan rate) and DPV patterns for symmetric Zn(II)-porphyrinates 1-5 in DMF.

The resulting E_{LUMO} and E_{HOMO} levels are reported in Table 3 too. Concerning the choice between the three criteria, as recently discussed in detail by one of us [55], Eonset and Ep values are related to a complex bundle of parameters, depending on the specific reaction mechanism and being influenced by the experimental conditions particularly in the case of electrochemically irreversible electron transfers. On the other hand, the approach based on standard potentials E° (in practice, formal potentials $E^{\circ\prime}$, neglecting activity coefficients), being independent on both scan rate and concentration, and directly related to the process ΔG° , is the safest, most reproducible, best defined, and therefore most significant one; however it is applicable only when all the peaks to be discussed are electrochemically and chemically reversible or quasi reversible. In our case this holds for the first oxidation and reduction peaks, so concerning HOMOs and LUMOs we can consider the values calculated according to this criterion (Table 3, middle section). They appear in excellent consistency with the spectroscopic gaps derived by the Q band (Table 1) both as values and trend, pointing to the same energy levels being involved in the electrochemical and the spectroscopic process. Moreover all HOMO and LUMO energy levels appear to comply with the condition required for DSSC application, *i.e.* all LUMOs are well above the TiO₂ conduction band level (\sim -3.95 eV) [25] and all HOMOs are sufficiently below the I^-/I_3^- couple $(\sim -4.8 \text{ eV})$ [7] excepting perhaps the case of **6**' falling somehow borderline.

Further clues on the nature and localization of the electron transfer processes can be obtained form a detailed analysis of the CV peak position and morphology, which will be made in terms of E_p values, since it allows taking into account second oxidation and/or

reduction peaks (some of which being not reversible) besides the first ones, when necessary.

Looking at Fig. 6a, at least two reduction and one oxidation peak are neatly perceivable for all symmetric Zn(II)-porphyrinates, reversible or quasi reversible chemically (presence of a return peak at least at high scan rates) and electrochemically (fast electron transfer, implied by the nearly constancy of E_p at increasing scan rates v). In the case of **1**, having two $-N(CH_3)_2$ strong donor groups, two close reversible oxidation peaks are perceivable, although they are nearly merging. The voltammetric features of **3'**, when compared to **3** (Fig. 7) point to a significant decrease of chemical reversibility for both the first oxidation and the first reduction electron transfer processes. The CV and DPV of asymmetric push-pull Zn(II)-porphyrinates **6–9** and **6'**, reported in Fig. 8, show two reversible reduction peaks and in most cases two close and nearly merging oxidation peaks.

The series of symmetric Zn(II)-porphyrinates **1–5** and **3**' affords a valuable benchmark in order to evaluate the extent of the electron communication with the porphyrin core along the whole conjugated π system (with concurrent localization of the redox centres), hinging on the evaluation of the effects of the donor or acceptor groups of the ethynyl phenyl moieties linked to 5 and 15 *meso* positions of the porphyrinic ring. A similar approach had previously been followed by Therien et al. [15] although their experiments were significantly impaired by the solvent choice, besides lacking the carboxylic substituent in the form of an acid or an ester, essential for applications of the metal porphyrins in DSSCs.

Zn(II)-porphyrinates from **1** to **5** constitute a series of symmetric electronic structures which, according to the following



Fig. 7. Contrasting CV (0.2 V s⁻¹ scan rate) and DPV patterns for symmetric Zn(II)-porphyrinates 3 and 3' in DMF.

trend from donor to acceptor substituents in *para* position of the phenylethynyl linker:

 $-N(CH_3)_2 > -OCH_3 > -COOCH_3 \approx COOH > -NO_2$

gradually decreases the electron density on the porphyrinic core, as suggested by a regular shift towards more positive values of the

potential of the first oxidation peak corresponding, for **2–5**, to a process involving the oxidation of the electronic core of the ring while for **1** it is the second oxidation peak that correspond to the ring oxidation process (see later and Table 3).

For symmetric Zn(II)-porphyrinates **1** or **5** the $-N(CH_3)_2$ and $-NO_2$ terminal groups can themselves undergo oxidation or reduction processes, respectively, at potentials slightly different from



Fig. 8. CV (0.2 V s⁻¹ scan rate) and DPV patterns for symmetric Zn(II)-porphyrinates 6-9 plus 6' in DMF.



Fig. 9. First and second oxidation E_{Ia} , E_{Ila}) and reduction (E_{Ic} , E_{Ilc}) peak potentials, referred to the Fc⁺|Fc reference redox couple for the Zn(II)-porphyrinates investigated. Symmetric **1–5**: circles; asymmetric push–pull **6–9**: stars; symmetric **3**' without phenyl group: triangles; asymmetric **6**' with a perfluorinated phenyl ring: diamonds. Straight lines are drawn on the points reported as full symbols.

those involving only the porphyrinic core (Table 3) as it occurs for **2–4**. This can result in localization of the first oxidation or reduction process on these groups away from the porphyrinic core, as it will be analysed and discussed more in detail later on.

The substituent effects on the peak potentials for oxidation or reduction processes centred on the porphyrinic core can be conveniently rationalized in terms of the sum of the σ_p Hammett parameters of the electron donor or acceptor groups [56] so that the three peaks, one oxidation and two reduction, exhibit linear relationships vs $\Sigma \sigma_p$, (full circles in Fig. 9 and corresponding straight lines).

The slopes of these Hammett linear plots, which are an indication of the efficiency of the transmission of the electronic inductive effects from the donor or the acceptor substituents to the porphyrinic core acting as redox site, appear to be significant and, meaningfully, nearly equal for the three peaks, confirming that they take place at the same redox site, that is the porphyrinic core, since it is the only redox site common to all the Zn(II)-porphyrinates **1–5** [52]. This evidence confirms the significant efficiency of transmission of the electronic inductive effects by the phenylethynyl linkers to the porphyrinic core. It is worthwhile recalling here a previous comparative test of ours between phenylethenyl and phenylethynyl linkers, showing that triple bonds are more suitable than double ones for the task of ensuring conjugation between the porphyrinic core and the peripheral substituted phenyl groups [52,57].

Concerning this localization of the redox site, we must notice that in the case of **1** carrying two $-N(CH_3)_2$ groups, in which two nearly merging reversible oxidation peaks are observed (Fig. 6), only the second one fits in the Hammett straight line (full circle in Fig. 9). The same feature also holds with all asymmetric Zn(II)-porphyrinates featuring two oxidation peaks and one $-N(CH_3)_2$ group since the second oxidation peak and not the first one lies on the Hammett straight line for **6**, **6**' and **7** (Fig. 9), while, in the case of **9**, featuring two oxidation peaks both of them not concerning $-N(CH_3)_2$ groups, it is the first and not the second that fits in the Hammett straight line. This evidence, in accordance with what reported by some of us and by other research groups [15,52,57], can be explained in terms of the first oxidation peak corresponding to the localized oxidation of the $-N(CH_3)_2$ group while

the second one involves the oxidation of the porphyrinic core. In accordance with such assignment, the DFT computational investigation has confirmed that the electron density of the $-N(CH_3)_2$ group of the phenylethynyl linker lies always, both in symmetric or asymmetric Zn(II)-porphyrinates, on the HOMO level, involved in the first oxidation process. It must be noticed, though, that while this assumption is the only possible in the asymmetric structures **6**, **6**′ and **7** featuring only one $-N(CH_3)_2$ groups, we could also assume that the two nearly merging oxidation peaks may correspond to the oxidations of both the two $-N(CH_3)_2$ groups, as equivalent redox centres slightly interacting through the π conjugated system localized on the 5,15 *meso* positions. Therefore we could assume an oxidation mechanism which involves two oxidation steps as represented in Scheme 1:

- a first oxidation step which must result in the generation of a radical cation localized on one of the two electron rich –N(CH₃)₂ groups; obviously, this structure is in resonance with that with the radical cation localized on the specular –N(CH₃)₂ group;
- once the radical cation is formed, because of the excellent electronic exchange *via* the π system involving the 5,15 *meso* positions [52] and of the electron donor capacity of the other $-N(CH_3)_2$ group, it is possible that it rapidly assumes an alternative resonant structure where the unpaired electron is delocalized on the porphyrinic core, whereas both the $-N(CH_3)_2$ groups are in their quaternary form being positively charged. As a matter of fact this electronic structure is evidently most balanced in term of charge distribution;
- finally since the second oxidation step must involve mainly the porphyrinic core in accordance with the fit of second oxidation peak in the Hammett linear relationship (Fig. 9), both -N(CH₃)₂ groups are oxidized in their quaternary form producing as expected for a direct oxidation of both the two -N(CH₃)₂ groups.

Of course the final doubly positive charged cation is more difficult to oxidize, since in Fig. 6b the peak corresponding to the third oxidation is at a more positive potential and well separated from the previous oxidation peaks.



Scheme 1. Pathway hypothesized for the first and second oxidation processes in Zn(II)-porphyrinate 1.

In the opposite limiting case of the symmetric structure **5**, with a nitro group on both the phenylethynyl moieties, featuring a couple of nearly merging reduction peaks, the first and second reduction process could be significantly localized on the nitro group.

This suggestion is based on the evidence found for regular sequences of substituted aromatic systems, *e.g.* aryl bromides, that the radical anion formed in the first reduction process increasingly becomes more localized in proximity of the very strong electron withdrawing substituents [58], with no solution of continuity, the nitro substituent being the limiting case in the series. Moreover, DFT calculations on the ground state energy level of the neutral Zn(II)-porphyrinate **5** have shown that the reduction process involving the LUMO level, is mainly localized on the nitro group of the phenylethynyl linker (Fig. 5).

Significant electronic effects induced by the donor and acceptor groups of the phenylethynyl moieties on the electronic properties of the porphyrinic core are confirmed by the following evidence.

According to the well known Kadish relationship [59] confirmed by a computational investigation by Zerner and Gouterman [60] the separation between first oxidation and first reduction potentials (corresponding to the electrochemical HOMO–LUMO gap of a porphyrinic simple core) for tetraphenylporphyrin (TPP) and diphenylporphyrin (DPP) templates must range in the interval

$$E_{la}^{\circ'} - E_{lc}^{\circ'} = 2.25 \pm 0.15 \,\mathrm{V} \tag{4}$$

for formal potentials (corresponding to a slightly larger difference, in terms of *peak* potentials).

$$E_{p,la} - E_{p,lc} \approx 2.36 \pm 0.15 \,\mathrm{V}$$
 (5)

It is known that in the presence of purely inductive effects generated by substituents on the porphyrinic core and/or by the presence of a metal ion, both oxidation and reduction potentials should shift in the same direction and to the same extent. Therefore the above gap should remain constant, provided that both oxidation and reduction processes are still centred on the porphyrinic core. It is however reasonable that in our porphyrinic systems the above rule cannot be satisfied in the following two cases:

- (a) when the first oxidation or reduction centres or both do no more coincide with the porphyrinic core as redox site, the separation could become larger or narrower, as a consequence of a shift of the potential of the first oxidation or reduction peak;
- (b) when the effective π conjugation of the porphyrinic architecture is enhanced, the separation between the first oxidation and reduction potentials should decrease, since HOMO rises and LUMO falls implying less positive E_{pa} (easier oxidation) and less negative E_{pc} (easier reduction).

Now, concerning point (b) all of the porphyrinic architectures investigated in this work have a significantly large π conjugated system. This should increase the global effective conjugation and therefore should contribute to decrease the HOMO–LUMO gap, as confirmed by the DFT computational investigation (Fig. 4). Furthermore, concerning point (a), in symmetric and asymmetric Zn(II)-porphyrinates carrying one or two –NMe₂ or –NO₂ groups the first oxidation or reduction centre does not coincide with the porphyrinic core so that in both cases we have a decrease of the gap. This can explain why in the porphyrinic architectures investigated in this work we observed a $E_{p,Ia} - E_{p,Ic}$ difference significantly lower than the above value (5), *i.e.* about 1.85 V (obtained from the difference of the intercepts of the $E_{p,Ia}$ and $E_{p,Ic}$ straight lines in Fig. 9).

This feature is fully consistent, *inter alia*, with the Therien's investigation cited above [15].

Moreover the difference between first and second reduction peak potentials in simple tetraphenylporphyrin and diphenylporphyrin templates must satisfy the Kadish relationship [61–63]:

$$E_{Ic}^{\circ'} - E_{IIc}^{\circ'} = 0.42 \pm 0.03 \, \text{V} \quad (\approx E_{p,Ic} - E_{p,IIc}) \tag{6}$$

Taking into account the symmetric Zn(II)-porphyrinates for which the first two reduction processes are surely localized on the porphyrinic core, *i.e.* 1 and 2, we have found a significantly higher difference, *i.e.* 0.52 V (see Table 3), as a consequence of an efficient π conjugation, resulting in a more efficient separation between negative charges. However it is worthwhile noticing that for increasing strength of electron acceptor substituents the second reduction peaks $E_{p,IIc}$ gradually deviate from the Hammett linear relationship, approaching $E_{p,lc}$, that is the value of the first reduction peak, until they nearly merge as in 5, carrying two nitro groups (Fig. 9). This feature, pointing to two nearly equivalent and independent redox centres in the extreme case 5, is another evidence of the above suggested partial localization of the first negative charge not completely on the porphyrinic core but in increasing proximity of the -NO₂ electron acceptor substituent, so that the introduction of a second negative charge becomes symmetrically localized on the other –NO₂ group, far away from the first one, since this process is more facile from the electrostatic point of view (Fig. 9).

Similar features, namely a slightly larger $E_{p,lc} - E_{p,llc}$ difference of about 0.45–0.52 V are observed for asymmetric Zn(II)-porphyrinates **6** and **8**, respectively, with the exception of Zn(II)-porphyrinates carrying only one nitro group, *e.g.* **7** and **9**, for which the first reduction process is not localized on the porphyrinic core, thus resulting in a much narrower gap of about 0.12–0.15 V (Table 3).

The symmetric Zn(II)-porphyrinate $\mathbf{3}'$ (voltammetric patterns in Fig. 7 and triangle points in Fig. 9) affords by comparison with $\mathbf{3}$ an evaluation of the effects of the absence of the phenyl group in the linker, which appears to be:

- a significant decrease in radical cation and above all radical anion chemical stability: the first reduction peak, neatly observable for 3, is absent for 3' even at high scan rate and also the CV and DPV patterns following the first reduction peak are much more complex and less reversible for 3'. The first oxidation peak, only partially reversible for 3 at 0.2 V s⁻¹ scan rate, but improving at higher scan rates, is nearly irreversible for 3';
- a significant shift of both the first oxidation and the first reduction to higher values of the potential (by about 0.18–0.15 V) for 3' with respect to 3 (Table 3), pointing to the presence of the phenyl ring making the molecule slightly electron richer with the conjugation efficiency remaining nearly the same.

The above approach to the analysis of the CV and DPV patterns and of the values of oxidation and reduction potentials can be conveniently extended to the asymmetric push-pull Zn(II)porphyrinates **6–9**. Their voltammetric features, shown in Fig. 8, are consistent with our former observations because:

a system of two close and nearly merging reversible oxidation peaks is always observed in the presence of a -N(CH₃)₂ group, as for 6 and 7, with 0.14 V and 0.16 V difference between the first and second oxidation peaks, smaller than the difference of 0.26 V between these two oxidation peaks surely centred, in the absence of a -N(CH₃)₂ group on the porphyrinic core, as in 8 and 9 (Table 3). The first oxidation peak in the case of 6 and 7 should correspond, as above suggested by some of us and other research groups, [15,52,57] to an oxidation localized on the -N(CH₃)₂ group, while the second peak should be centred on

the porphyrinic core since only this peak fits the Hammett linear relationship (Fig. 9) obtained taking into account the values of the first oxidation peak involving surely the porphyrinic core, as in the case of asymmetric Zn(II)-porphyrinates not containing a $-N(CH_3)_2$ group such as **8** and **9**.

- A system of two close nearly merging reversible reduction peaks $E_{\rm Ic}$ and $E_{\rm Ilc}$ is always observed in the presence of a nitro group as in **7** and **9** (see Table 3 and Fig. 9). As already mentioned, unlike the symmetric Zn(II)-porphyrinate **5**, it is the second one that better fits the Hammett linear relationship. Accordingly, the first one should be associated to the formation of a radical anion localized on the nitro group, while only the second one to a reduction process centred on the porphyrinic core.
- Finally the trend of CV peaks of the asymmetric Zn(II)porphyrinate **8** is quite consistent with that typical of the symmetric ones (see Fig. 9); it appears also that the absence of strong donor $-N(CH_3)_2$ or acceptor $-NO_2$ groups, **8** hold as for the symmetric ones in the Hammett plots of Fig. 9, which takes into account only oxidation or reduction processes involving the porphyrinic core. It follows that in **8** the push–pull system is so weak that both the oxidation and reduction processes involve mainly the porphyrinic core, not too much perturbed by the push–pull character of the π conjugated system.

A comparison between the trend of the CV peaks of the asymmetric Zn(II)-porphyrinate **6** and its fluorinated homologous **6**' (Fig. 8) affords an evaluation of the effects of the perfluorination of the phenyl ring carrying the carboxylic group, that is:

- the two reduction peaks are shifted towards more positive values (Table 3), in accordance with an easier reduction as expected since fluorine atoms set as electron acceptors and therefore should act synergistically to the electron withdrawing effect of the adjacent carboxylic group in order to facilitate the reduction of the oxidized porphyrinic system;
- concerning the first oxidation peak E_{Ia} , one should expect a shift towards more positive values (more difficult oxidation), albeit less than the reduction peaks since the oxidation site, which is $-N(CH_3)_2$ group, as in the case of **6**, is away from the fluorinated aromatic ring. However, in 6' not only the first but also the second oxidation peak remarkably shift towards lower potential values (easier oxidation) (Table 3). This trend could be possibly justified in terms of a π system along the push-pull system partially loosing its planarity upon fluorination of the phenyl group, so that the communication by π conjugation between the electron acceptor moiety and the $-N(CH_3)_2$ donor group is much less facile. In accordance some of us have already shown, by a theoretical DFT approach, that for $\mathbf{6}'$ a planar and a tilted arrangement, with respect to the porphyrin ring, of the fluorinated aromatic ring carrying the -COOH group are energetically comparable [32]. A similar kind of relevant structural effect, has been described by Kadish et al. about the electronic properties of tetraphenyl porphyrins in which the β pyrrole positions are gradually substituted by halogen atoms, resulting in loss of planarity [64]. Since in our series of Zn(II)-porphyrinates only 1, that is a symmetric structure with two donor $-N(CH_3)_2$ groups, is oxidized more easily than 6', it follows that in $\mathbf{6}'$ the behaviour of the $-N(CH_3)_2$ group is more similar to that of a $-N(CH_3)_2$ group not perturbed as 1, by the conjugation effect produced by an antagonist electron acceptor group, as in the case of 6 and 7. It follows that the electron communication along the push-pull system is not relevant for 6'. This intriguing anomaly is consistent with the photoelectrochemical behaviour of 6' when acting as dye in DSSCs [32], pointing to a very low efficiency in comparison with 6; actually, as above mentioned, the experimental value of the HOMO of 6' appears too near

to the I^-/I_3^- couple energy level (-4.94 eV instead of -5.03 eV for **6**, Table 3).

• irreversible multistep processes corresponding to the breakdown of the molecule take place much earlier on both the reduction and the oxidation side (particularly in the latter case).

4. Conclusions

The combined electrochemical, spectroscopic and theoretical investigation of our series of symmetric and push–pull asymmetric Zn(II)-porphyrinates 5,15-*meso* substituted with phenylethynyl linkers affords a rationalization of their electronic properties as a function of the nature of the substituents on the *para* position of the phenyl ring of the linkers.

In the case of moderately electron acceptor (-COOR, -COOH) and/or donor (-OCH₃) substituents the first oxidation or reduction processes are rationalized in terms of predominant inductive effects since their potentials satisfy classical Hammett straight lines holding for both symmetric and asymmetric structures; furthermore, such straight lines are parallel, pointing to both the electron transfer processes being centred mainly on the porphyrinic core. The same also applies to the second reduction process. The difference between first oxidative and reductive potentials (and, concurrently the HOMO-LUMO gap) is quite constant, but lower than that of the classical Kadish relationships, pointing to such porphyrinic structures having a certain amount of global effective conjugation which introduces a perturbation of the electronic core of the porphyrinic ring slightly different from that of TPP or DPP templates considered by Kadish. This evidence confirms inter alia the efficiency of the transfer of the electronic effects by phenylethynyl linkers.

On the contrary, for the symmetric structure the presence of strong electron acceptor or electron donor groups (i.e. -NO2 or $-N(CH_3)_2$, respectively), not only results in a more facile promotion of the first reduction or oxidation process, respectively, but also in peripheral displacement of the first reduction/oxidation site, possibly localized on the acceptor or donor substituent itself (as confirmed by DFT computational investigation on the electron density distribution of the LUMO and HOMO orbital levels), rather than on the porphyrinic core, which appears to be involved only by the second electron transfer. As a consequence for the asymmetric push-pull structure, a higher and asymmetric shrinking of the HOMO-LUMO gap occurs, with the HOMO or LUMO levels being localized respectively on the porphyrinic core. The limiting case is the one featuring both $-NO_2$ and $-N(CH_3)_2$ in an asymmetric push-pull structure, in which both LUMO and HOMO levels appear to be peripherally localized on the $-NO_2$ and $-N(CH_3)_2$ group, respectively, with both first reduction and first oxidation steps highly promoted, affording in the narrowest HOMO-LUMO gap in the series.

Interestingly, peripheral localization of the electronic density of the HOMO and/or LUMO also modulates the intensity ratio of Q and B absorption bands, as a consequence of an increased effective conjugation along the push–pull system.

The presence of the phenyl group besides the ethynyl one in the linker appears to be determining for the chemical stability of the incipient radical anion; it also appears to slightly improve effective conjugation and to make the system slightly electron richer. Perfluorination of this phenyl ring, in a asymmetric push-pull structure, intended to enhance the power of the electron attractor side chain and therefore the push-pull character of the structure, results instead in apparent loss of conjugation, with the electron rich and the electron poor moiety, localized on the 5,15 meso position of the porphyrinic ring, appearing reciprocally independent and not interacting by a significant electron transfer process, an intriguing feature already reported by some of us [32].

Finally the spectroscopic and TDDFT theoretical calculations on the symmetric porphyrinic structures do confirm the ambivalent character of the porphyrinic core, first reported by some of us [52], which act as acceptor with donor $-NMe_2$ groups, and as donor with acceptor $-NO_2$ groups.

The whole set of interpretative/predictive guidelines thus made available will hopefully provide valuable support for targetoriented design and optimization of the synthetic efforts in the current development of highly efficient porphyrinic dyes for DSSC applications.

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Appendix A. Syntheses of Zn(II)-porphyrinates 1, 2, 3, 3', 4, 5 and 9

[5,15-Bis(4'-N,N-dimethylamino-phenylethynyl)-10,20-bis(3,5-di-tert-butylphenyl)porphyrinate]Zn(II), **1**

In a dry Schlenk tube 189.8 mg of [5,15-diiodo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) (0.189 mmol), 17.3 mg of [Pd₂(dba)₃] (0.019 mmol), 19.8 mg PPh₃ (0.075 mmol), 10.8 mg of Cul (0.057 mmol) were deaerated three times with a vacuum–nitrogen cycle and then dissolved with a mixture of 20 ml of THF and 5 ml of Et₂NH previously deaerated with four freeze–pump–thaw cycles at -78 °C. At 70 °C a solution of 41.2 mg of 4-ethynyl-N,N-dimethylaniline (1.5 equiv.) in 5 ml of THF, previously deaerated with three freeze–pump–thaw cycles at -78 °C.

The reaction mixture was stirred under nitrogen atmosphere for 24 h in the dark. Then the solvents were evaporated *in vacuo* and the crude product was purified by column chromatography (SiO₂, n-hexane/THF 8:2) to afford 44.8 mg of pure product (yield 22.9%).

¹H NMR (400.1 MHz, CDCl₃ + py- d_5) δ, ppm: 9.71 (4H, d), 8.87 (4H, d), 8.03 (4H, m), 7.90 (4H, d), 7.79 (2H, m), 6.87 (4H, d), 3.11 (12H, s), 1.55 (36H, s).

MS-FAB(+) m/z: calcd for C₆₈H₇₀N₆Zn 1034, found 1035 [M+H]⁺. UV-vis (THF) λ , nm: 467 (ε = 220,000 M⁻¹ cm⁻¹); 668 (ε = 58,000 M⁻¹ cm⁻¹).

[5,15-Bis(4'-methoxy-phenylethynyl)-10,20-bis(3,5-di-tertbutylphenyl)porphyrinate]Zn(II), 2

In a dry Schlenk tube 123.7 mg of [5,15-diiodo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) (0.123 mmol), 14.2 mg of Pd(PPh₃)₄ (0.012 mmol) and 3.5 mg of Cul (0.018 mmol) were deaerated three times with a vacuum–nitrogen cycle and then dissolved in a mixture of 15 ml of THF and 2.5 ml of Et₂NH, previously deaerated with five freeze–pump–thaw cycles at -78 °C.

Under stirring, in nitrogen atmosphere and at 25 °C, a solution of 25.0 μ l of 4-ethynylanisole (1.6 equiv.) in 5 ml of THF,

previously deaerated with five freeze–pump–thaw cycles at -78 °C, was added dropwise to the reaction. The reaction was left under nitrogen atmosphere for 36 h in the dark. The solvents were removed *in vacuo* and the crude product obtained was purified by column chromatography (SiO₂, *n*-hexane/THF 9:1) to afford 65.1 mg of pure product (yield 52%).

¹H NMR (400.1 MHz, THF-*d*₈) δ, ppm: 9.76 (4H, d), 8.91 (4H, d), 8.15 (4H, m), 8.02 (4H, d), 7.94 (2H, m) 7.16 (4H, d), 3.94 (6H, s), 1.61 (36H, s).

MS-FAB(+) m/z: calcd for C₆₆H₆₄N₄O₂Zn 1008, found 1009 [M+H]⁺.

UV-vis (THF) λ , nm: 451 (ε = 258,000 M⁻¹ cm⁻¹); 658 (ε = 37,000 M⁻¹ cm⁻¹).

[5,15-Bis(4'-carboxymethyl-phenylethynyl)-10,20-bis(3,5-ditert-butylphenyl)porphyrinate]Zn(II), 3

In a dry Schlenk tube 96.5 mg of [5,15-diiodo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) (0.0963 mmol), 5.8 mg of Pd(dba)₂ (0.0101 mmol), 2.7 mg of CuI (0.0143 mmol), 1.35 ml of Et₃N and 5 ml of dry THF were deaerated with four freeze-pump-thaw cycles at $-78 \,^{\circ}$ C.

Under stirring at room temperature, a solution of 38.4 mg of methyl 4-ethynylbenzoate (0.240 mmol, 2.5 equiv.) in 2.8 ml of THF, previously deaerated with four freeze–pump–thaw cycles at -78 °C, was added *via cannula* under nitrogen atmosphere to the reaction mixture. The reaction was heated at 70 °C for 40 h. The solvents were removed *in vacuo* and the crude product was purified by column chromatography (SiO₂, *n*-hexane/THF 85:15, *R*_f = 0.31) to afford 45 mg of pure product (yield 44%).

¹H NMR (400.1 MHz, CDCl₃ + py- d_5) δ, ppm: 9.68 (4H, d), 8.90 (4H, d), 8.13 (4H, d), 8.00 (4H, s), 7.98 (4H, d), 7.78 (2H, s), 3.91 (6H, s), 1.51 (36H, s).

MS-FAB(+) m/z: calcd for C₆₈H₆₄N₄O₄Zn 1064, found 1065 [M+H]⁺.

UV-vis (THF) λ , nm: 452 (ε =334,000 M⁻¹ cm⁻¹); 660 (ε =48,000 M⁻¹ cm⁻¹).

[5,15-Bis(4'-carboxyethyl-ethynyl)-10,20-bis(3,5-di-tertbutylphenyl)porphyrinate]Zn(II), 3'

In a dry Schlenk tube 95.8 mg of [5,15-diiodo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) (0.0956 mmol), 11 mg of Pd(PPh₃)₄ (0.00956 mmol) and 2.9 mg of CuI (0.0152 mmol), were deaerated three times with a vacuum–nitrogen cycle and then dissolved in a mixture of 17 ml of THF and 4 ml of Et₃N, previously deaerated with five freeze–pump–thaw cycles at -78 °C. Under stirring, in nitrogen atmosphere and at 25 °C, 24 µl of ethyl propiolate (2.5 equiv.) were added dropwise to the reaction. The mixture was allowed to react at 25 °C for 24 h. The solvents were removed *in vacuo* and the crude product obtained was purified by column chromatography (SiO₂, *n*-hexane/THF 9:1) to afford 55.4 mg of pure product (yield 59.5%).

¹H NMR (400.1 MHz, $CDCl_3 + py-d_5$) δ , ppm: 9.66 (4H, d), 8.91 (4H, d), 7.96 (4H, m), 7.78 (2H, m), 4.48 (4H, q), 1.50 (36H, s), 1.48 (6H, t).

MS-FAB(+) m/z: calcd for C₅₈H₆₀N₄O₄Zn 940, found 941 [M+H]⁺. UV-vis (THF) λ , nm: 440 (ε = 260,000 M⁻¹ cm⁻¹); 644 (ε = 24,000 M⁻¹ cm⁻¹).

[5,15-Bis(4'-carboxy-phenylethynyl)-10,20-bis(3,5-di-tertbutylphenyl)porphyrinate]Zn(II), 4

In a one-necked round bottom flask equipped with a magnetic stir bar 20.6 mg of [5,15-bis(4'-carboxymethyl-phenylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) (3)

(0.0193 mmol) were dissolved in 1.7 ml of a 3:1 THF:H₂O mixture; under stirring, 2.6 mg of LiOH (0.106 mmol, 5.5 equiv.) were added. The reaction was left at room temperature for 24 h. The solvents were removed *in vacuo* and the crude product was dissolved in 1 ml of THF and diluted with 10 ml of DCM. The dark green solution was then treated with 10 ml of a 20% aqueous solution of citric acid and left at room temperature overnight under vigorous stirring. Then, the reaction mixture was transferred in a funnel, the phases were separated and the organic phase was washed $3 \times H_2O$ (10 ml), until pH=6–7 was reached. The organic phase was dried over Na₂SO₄, filtered and the solvent was removed *in vacuo*. The title product was obtained in 45% yield (9.1 mg, dark green solid).

¹H NMR (400.1 MHz, THF-*d*₈) δ, ppm: 9.82 (4H, d), 8.97 (4H, d), 8.27 (4H, d), 8.20 (4H, d), 8.16 (4H, s), 7.96 (2H, s), 1.32 (36H, s).

MS-ESI(-) m/z: 1035.3852 [M-H]⁻; 517.1868 [M-2H]²⁻.

UV-vis (THF) λ , nm: 450 (ε = 336,000 M⁻¹ cm⁻¹); 660 (ε = 50,000 M⁻¹ cm⁻¹).

[5,15-Bis(4"-nitro-phenylethynyl)-10,20-bis(3,5-di-tertbutylphenyl)porphyrinate]Zn(II), 5

In a dry Schlenk tube 80.1 mg of [5,15-diiodo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) (0.080 mmol), 29.1 mg of 4-ethynyl-nitrobenzene (2.4 equiv.), 7.3 mg of Pd₂(dba)₃ (0.008 mmol), 13.1 mg of PPh₃ (0.050 mmol) and 5.0 mg of Cul (0.026 mmol) were deaerated three times with a vacuum–nitrogen cycle and then dissolved in a mixture of 20 ml of THF and 5 ml of Et₂NH, previously deaerated with five freeze–pump–thaw cycles at $-78 \,^{\circ}$ C were dissolved in a mixture of 8 ml of THF and 1.3 ml of Et₂NH. Under stirring, the reaction mixture was heated at 70 $\,^{\circ}$ C for 24 h in nitrogen atmosphere. The solvents were removed *in vacuo* and the crude product obtained was purified by column chromatography (SiO₂, *n*-hexane/THF 8:2, *R*_f: 0.22) to afford 8.8 mg of product (yield 11%).

¹H NMR (400.1 MHz, THF-*d*₈) δ, ppm: 9.82 (4H, d), 8.98 (4H, d), 8.50 (4H, d), 8.34 (4H, d), 8.16 (4H, m), 7.97 (2H, m), 1.63 (36H, s). MS-FAB(+) *m*/*z*: calcd for C₆₄H₅₈N₆O₄Zn 1038, found 1038 [M]⁺. UV-vis (THF) λ , nm: 458 (ε = 98,000 M⁻¹ cm⁻¹); 669

[5-Bromo-15-(4'-methoxy-phenylethynyl)-10,20-bis(3,5-di-tertbutylphenyl)porphyrinate [Zn(II)

(ε = 17,000 M⁻¹ cm⁻¹).

In a dry Schlenk tube 108.6 mg of [5,15-dibromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) (0.128 mmol), 14.8 mg of Pd(PPh₃)₄ (0.013 mmol) and 3.6 mg of CuI (0.019 mmol) were deaerated three times with a vacuum–nitrogen cycle and then dissolved in a mixture of 12 ml of THF and 5 ml of Et₂NH, previously deaerated with five freeze–pump–thaw cycles at -78 °C.

Under stirring, in nitrogen atmosphere and at 25 °C, 20 μ l of 4ethynylanisole (1.2 equiv.) was added to the reaction. The reaction was left under nitrogen atmosphere for 24 h. The solvents were removed *in vacuo* and the crude product obtained was purified by column chromatography (SiO₂, *n*-hexane/THF 8.9:1.1, *R*_f = 0.36) to afford 58.3 mg of pure product (yield 47%).

¹H NMR (400.1 MHz, CDCl₃ + py- d_5) δ, ppm: 9.74 (2H, d), 9.64 (2H, d), 8.92 (2H, d), 8.89 (2H, d), 8.02 (4H, m), 7.97 (2H, d), 7.82 (2H, m) 7.10 (2H, d), 3.95 (3H, s), 1.57 (36H, s).

[5-(4'-Methoxy-phenylethynyl)-15-(4''-nitro-phenylethynyl)-10,20-bis(3,5-di-tert-butylphenyl)porphyrinate]Zn(II), 9

In a dry Schlenk tube 58.3 mg of [5-bromo-15-(4'-methoxy-phenylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)por-phyrinate]Zn(II) (0.061 mmol) and 21.1 mg of 4-ethynyl-nitrobenzene (2.3 equiv.) were dissolved in a mixture of 8 ml

of THF and 1.3 ml of Et₂NH. The solution was deaerated with five freeze-pump-thaw cycles at -78 °C. At room temperature and under nitrogen atmosphere 9.0 mg of Pd(PPh₃)₄ (0.008 mmol) and 4.0 mg of Cul (0.021 mmol) were added. Under stirring, the reaction mixture was heated at 75 °C for 24 h. The solvents were removed *in vacuo* and the crude product obtained was purified by column chromatography (SiO₂, *n*-hexane/THF 9:1) to afford 20.4 mg of pure product (yield 33%).

¹H NMR (400.1 MHz, THF- d_8) δ , ppm: 9.79 (4H, m), 8.97 (2H, d), 8.93 (2H, d), 8.48 (2H, d), 8.31 (2H, d), 8.16 (4H, m), 8.04 (2H, d), 7.96 (2H, m) 7.17 (2H, d), 3.95 (3H, s), 1.63 (36H, s).

MS-FAB(+) m/z: calcd for C₆₅H₆₁N₅O₃Zn 1023, found 1024 [M+H]⁺.

UV-vis (THF) λ , nm: 459 (ε = 293,000 M⁻¹ cm⁻¹); 667 (ε = 78,000 M⁻¹ cm⁻¹).

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.electacta.2012.08.039.

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