

Supporting Information

Physicochemical Investigation of the Panchromatic Effect on β -Substituted Zn^{II} Porphyrinates for DSSCs: The Role of the π Bridge between a Dithienylethylene Unit and the Porphyrinic Ring.

Gabriele di Carlo, Alessio Orbelli Biroli, Francesca Tessore, Maddalena Pizzotti, Patrizia Romana Mussini, Anna Amat, Filippo De Angelis, Alessandro Abbotto, Vanira Trifiletti, Riccardo Ruffo

Syntheses

[2-((4-((E)-2-(5-((E)-2-(3,4-dihexylthiophen-2-yl)vinyl)-3,4-dihexylthiophen-2-yl)vinyl)phenyl)ethynyl)-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinate] Zn^{II} (**5**)

Aldehyde **4** (80 mg, $6.4 \cdot 10^{-2}$ mmol) and phosphonate **16** (52 mg, $7.6 \cdot 10^{-2}$ mmol) were introduced under nitrogen in 2.6 mL of dry and deaerated THF in a Schlenk tube. Then tBuOK (19 mg, $16.9 \cdot 10^{-2}$ mmol) is added portionwise and the reaction mixture was allowed to react at room temperature for 3 hours. The organic phase was reduced under vacuum; the mixture was extracted with CH_2Cl_2 , washed with acidulated water and dried over Na_2SO_4 . After solvent removal the crude obtained is purified by column chromatography (silica gel, Hexane/AcOEt 96:4) leading to **6** as purple powder (99.2 mg, 87% yield).

1H -NMR (400 MHz, $CDCl_3$, $25^\circ C$): δ = 9.33 (d, 1H), 9.03-8.96 (m, 5H), 8.77-8.75 (m, 1H), 8.12 (m, 8H), 7.85 (s, 1H), 7.81 (s, 3H), 7.45-7.41 (m, 2H), 7.33-7.30 (m, 2H), 7.07-7.01 (m, 2H), 6.92 (d, 1H, $J_{trans} = 15.7$ Hz), 6.91 (d, 1H, $J_{trans} = 15.7$ Hz), 6.81 (s, 1H), 2.72-2.63 (m, 6H), 2.57-2.51 (m, 2H), 1.58-1.48 (m, 72H), 1.42-1.38 (m, 38H), 0.99-0.95 ppm (m, 12H).

[2-((4-((E)-2-(5-((E)-2-(5-formyl-3,4-dihexylthiophen-2-yl)vinyl)-3,4-dihexylthiophen-2-yl)vinyl)phenyl)ethynyl)-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinate] Zn^{II} (**6**)

Compound **5** (99.2 mg, $5.6 \cdot 10^{-2}$ mmol), dissolved in dry DCE (370 μ L) and anhydrous DMF (8.6 μ L, $11.2 \cdot 10^{-2}$ mmol) were introduced under nitrogen atmosphere in a Schlenk tube. POCl₃ (6.3 μ L, $6.7 \cdot 10^{-2}$ mmol) is added dropwise at 0°C, then the mixture was refluxed for 18 h. After cooling to room temperature, 256 μ L of an aqueous solution of NaOH (1.25 M) was added dropwise and the mixture was vigorously stirred for 2 h. The solution was finally extracted with CH₂Cl₂ and the organic phase dried over Na₂SO₄. Removal of the solvent and column chromatography (silica gel, Hexane/ CH₂Cl₂ 1:1) gave aldehyde **10** as purple powder (58.8 mg, 58% yield).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 10.04 (s, 1H), 9.19 (s, 1H), 8.97-8.86 (m, 5H), 8.75-8.73 (m, 1H), 8.16-8.11 (m, 8H), 7.87-7.83 (m, 4H), 7.46-7.43 (m, 2H), 7.35-7.31 (m, 4H), 7.05 (d, 1H, $J_{\text{trans}} = 15.6$ Hz), 6.97 (d, 1H, $J_{\text{trans}} = 15.6$ Hz), 2.57-2.51 (m, 2H), 2.72-2.63 (m, 6H), 1.59-1.50 (m, 72H), 1.44-1.39 (m, 38H), 1.02-0.95 ppm (m, 12H).

[2-((4-((E)-2-(5-((E)-2-(5-((E)-2-carboxy-2-cyanovinyl)-3,4-dihexylthiophen-2-yl)vinyl)-3,4-dihexylthiophen-2-yl)vinyl)phenyl)ethynyl)-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinate]Zn^{II} (Dye 1)

In Schlenk tube cyanoacetic acid (8.3 mg, $9.7 \cdot 10^{-2}$ mmol), dissolved in 1 mL of CH₃CN, and 10 μ L of piperidine were added under nitrogen atmosphere over a stirred solution of aldehyde **6** (58.8 mg, $3.2 \cdot 10^{-2}$ mmol) in 2 ml CHCl₃, thus the mixture was refluxed overnight. Afterwards, the solvent was evaporated under reduced pressure, the crude was taken up with CH₂Cl₂ and washed with water. Finally the organic phase was dried with Na₂SO₄ and the product was purified by column chromatography (silica gel, CH₂Cl₂/CH₃OH 95/5), obtaining pure **1** as a purple powder (39 mg, 65% yield).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 9.19 (s, 1H), 8.97-8.86 (m, 5H), 8.75-8.73 (m, 1H), 8.40 (s, 1H), 8.16-8.11 (m, 8H), 7.87-7.83 (m, 4H), 7.45 (d, 2H, $J = 8.3$ Hz), 7.33 (d, 2H, $J = 8.3$ Hz), 7.32 (d, 1H, $J_{\text{trans}} = 15.4$ Hz), 7.25 (d, 1H, $J_{\text{trans}} = 15.4$ Hz), 7.10 (d, 1H, $J_{\text{trans}} = 15.4$ Hz), 6.96 (d, 1H, $J_{\text{trans}} = 15.4$ Hz), 3.24 (m, 2H), 2.71-2.67 (m, 4H), 1.93 (m, 2H), 1.62-1.30 (m, 110H), 1.02-0.94 ppm (m,

12H). MS-FAB(+) m/z: 1875 [M+H]⁺; elemental analysis calcd (%) for Chemical Formula: C₁₂₄H₁₅₃N₅O₂S₂Zn: C 79.43, H 8.22, N 3.73; found C 79.74, H 8.20, N 3.74

[2-ethynyl-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) (8)

The compound **8** was synthesized by enhanced microwave Sonogashira coupling starting from [2-Bromo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl) porphyrinate] Zn(II), proceeding as reported in our previous work.⁸

Pd(PPh₃)₄ (11.2 mg, 1.0·10⁻² mmol), **7** (117.1 mg, 9.7·10⁻² mmol), freshly distilled NEt₂H (12mL), anhydrous DMF (4mL) and ethynyltrihexylsilane (299 mg, 9.7·10⁻¹ mmol) were introduced in a dry Schlenk tube and degassed with four freeze-pump-thaw cycles at -78°C. The mixture was then transferred under nitrogen flow in a microwave quartz vessel, and CuI (2.8 mg, 1.5·10⁻² mmol) was added. The mixture was allowed to react in the microwave cavity at 120°C for 1 hr, then the solvent was evaporated *in vacuo*. The crude was purified by flash chromatography (hexane/THF 98:2), leading to [2-ethynyl(trihexyl)silane-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn(II) as a purple solid (86.3 mg, 62% yield). The ethynyl terminal group was finally deprotected by treatment with Tetra-*n*-butylammonium fluoride (TBAF) in THF, as reported in literature,¹⁵ and the pure compound **8** (48.5 mg, 70% yield) was obtained by flash chromatography (hexane/CH₂Cl₂ 8:2).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 9.19 (s, 1H), 8.94-8.82 (m, 7H), 8.06 (s, 4H), 8.01 (s, 2H), 7.91 (s, 2H), 7.80 (s, 1H), 7.77 (s, 3H), 3.17 (s, 1H), 1.54 (s, 36H), 1.52 (s, 18H), 1.50 ppm (s, 18H).

[(*E*)-2-((5-(2-(5-formyl-3,4-dihexylthiophen-2-yl)vinyl)-3,4-dihexylthiophen-2-yl)ethynyl)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn^{II} (9)

The intermediate **8** (48.5 mg, 4.2·10⁻² mmol), dissolved in freshly distilled NEt₃ (1.5 mL) and anhydrous THF (1.5 mL), was introduced in a dry Schlenk tube. PdCl₂(PPh₃)₂ (4.4 mg, 0.6·10⁻²

mmol) and iodide intermediate **14** (60 mg, $8.4 \cdot 10^{-2}$ mmol) were added and the mixture degassed with four freeze-pump-thaw cycles at -78°C . Finally, CuI (1.2 mg, $0.4 \cdot 10^{-2}$ mmol) was added and the mixture was refluxed for 18 hr. The solvent was evaporated *in vacuo* and the crude was purified by column chromatography (silica gel, hexane/AcOEt = 98/2), leading to coupling product **9** as a purple powder (45 mg, 63% yield).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ = 9.72 (s, 1H), 9.25 (s, 1H), 9.03 (d, 4H), 8.99 (d, 1H), 8.84 (d, 1H), 8.16-8.11 (m, 8H), 7.92 (s, 1H), 7.87-7.84 (m, 3H), 7.33 (d, 1H, $J_{\text{trans}} = 15.5$ Hz), 7.08 (d, 1H, $J_{\text{trans}} = 15.5$ Hz), 2.89 (t, 2H), 2.75 (m, 4H), 2.66 (t, 2H), 1.59-1.55 (m, 72H), 1.43-1.40 (m, 38H), 1.06-0.93 ppm (m, 12H).

[(*E*)-2-((5-(2-(5-((*E*)-2-carboxy-2-cyanovinyl)-3,4-dihexylthiophen-2-yl)vinyl)-3,4-dihexylthiophen-2-yl)ethynyl)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate] Zn^{II}
(Dye 2)

In Schlenk tube cyanoacetic acid (6.7 mg, $7.9 \cdot 10^{-2}$ mmol), dissolved in 1 mL of CH_3CN , and 10 μL of piperidine were added under nitrogen atmosphere over a stirred solution of aldehyde **9** (45 mg, $2.6 \cdot 10^{-2}$ mmol) in 2 ml CHCl_3 , thus the mixture was refluxed overnight. Afterwards, the solvent was evaporated under reduced pressure, the crude was taken up with CH_2Cl_2 and washed with water. Finally the organic phase was dried with Na_2SO_4 and the product was purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ 95/5), obtaining pure **2** as a purple powder (28 mg, 61% yield).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ = 9.21 (s, 1H), 9.99 (d, 4H), 8.93 (d, 1H), 8.80 (d, 1H), 8.85 (s, 1H), 8.09-8.01 (m, 8H), 7.88 (s, 1H), 7.80-7.77 (m, 3H), 7.30 (d, 1H, $J_{\text{trans}} = 15.3$ Hz), 7.11 (d, 1H, $J_{\text{trans}} = 15.3$ Hz), 2.87-2.67 (m, 8H), 1.62-1.28 (m, 110H), 0.95-0.88 ppm (m, 12H). MS-FAB(+) m/z : 1772 $[\text{M}+\text{H}]^+$; elemental analysis calcd (%) for Chemical Formula: $\text{C}_{116}\text{H}_{147}\text{N}_5\text{O}_2\text{S}_2\text{Zn}$: C 78.58, H 8.36, N 3.95; found C 78.87, H 8.34, N 3.96

[2-((*E*)-2-(5-((*E*)-2-(3,4-dihexylthiophen-2-yl)vinyl)-3,4-dihexylthiophen-2-yl)vinyl)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn^{II} (11**)**

2-formyl-porphyrin **10** (60 mg, 5.2·10⁻² mmol) and phosphonate **16** (42 mg, 6.2·10⁻² mmol) were introduced under nitrogen in 2.5 mL of dry and deaerated THF in a Schlenk tube. Then tBuOK (15 mg, 13.5·10⁻² mmol) is added portionwise and the reaction mixture was allowed to react at room temperature for 2 hours. The organic phase was reduced under vacuum; the mixture was extracted with CH₂Cl₂, washed with acidulated water and dried over Na₂SO₄. After solvent removal the crude obtained is purified by column chromatography (silica gel, Hexane/CH₂Cl₂ 8:2) leading to **11** as purple powder (78 mg, 90% yield).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 9.09-9.01 (m, 6H), 8.96 (d, 1H), 8.20 (s, 2H), 8.16 (s, 4H), 8.07 (s, 2H), 7.91 (s, 1H), 7.85 (s, 3H), 7.39 (d, 1H, J_{trans} = 15.3 Hz), 7.14 (d, 1H, J_{trans} = 15.5 Hz), 7.05 (d, 1H, J_{trans} = 15.5 Hz), 6.86 (s, 1H), 6.58 (d, 1H, J_{trans} = 15.3 Hz), 2.81-2.76 (m, 2H), 2.81-2.76 (m, 2H), 2.68-2.64 (m, 4H), 2.62-2.58 (m, 2H), 1.62-1.52 (m, 72H), 1.44-1.42 (m, 38H), 0.99-0.95 ppm (m, 12H).

[2-((*E*)-2-(5-((*E*)-2-(5-formyl-3,4-dihexylthiophen-2-yl)vinyl)-3,4-dihexylthiophen-2-yl)vinyl)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn^{II} (12**)**

Intermediate **11** (78 mg, 4.6·10⁻² mmol), dissolved in dry DCE (307 μL) and anhydrous DMF (7.1 μL, 6.7·10⁻² mmol) were introduced under nitrogen atmosphere in a Schlenk tube. POCl₃ (5.2 μL, 5.6·10⁻² mmol) is added dropwise at 0°C, then the mixture was refluxed for 18 h. After cooling to room temperature, 206 μL of an aqueous solution of NaOH (1.25 M) was added dropwise and the mixture was vigorously stirred for 2 h. The solution was finally extracted with CH₂Cl₂ and the organic phase dried over Na₂SO₄. Removal of the solvent and column chromatography (silica gel, Hexane/ CH₂Cl₂ 7:3) gave aldehyde **12** as purple powder (46 mg, 60% yield).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 10.07 (s, 1H), 8.98 (s, 1H), 8.93 (d, 4H), 8.90 (d, 1H), 8.85 (d, 1H), 8.19 (s, 2H), 8.14 (m, 4H), 8.06 (s, 2H), 7.88 (s, 1H), 7.88 (s, 1H), 7.85 (s, 1H), 7.84 (s,

2H), 7.40 (d, 2H, $J_{\text{trans}} = 15.4$ Hz), 6.99 (d, 1H, $J_{\text{trans}} = 15.4$ Hz), 6.60 (d, 1H, $J_{\text{trans}} = 15.4$ Hz), 2.93 (t, 2H), 2.93 (t, 2H), 2.76 (t, 2H), 2.67 (m, 4H), 1.60-1.34 (m, 110H), 0.99-0.91 ppm (m, 12H).

[2-((*E*)-2-(5-((*E*)-2-(5-((*E*)-2-carboxy-2-cyanovinyl)-3,4-dihexylthiophen-2-yl)vinyl)-3,4-dihexylthiophen-2-yl)vinyl)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn^{II}
(Dye 3)

In Schlenk tube cyanoacetic acid (4.6 mg, $5.4 \cdot 10^{-2}$ mmol), dissolved in 1 mL of CH₃CN, and 10 μ L of piperidine were added under nitrogen atmosphere over a stirred solution of aldehyde **12** (46 mg, $2.7 \cdot 10^{-2}$ mmol) in 3 ml CHCl₃, thus the mixture was refluxed overnight. Afterwards, the solvent was evaporated under reduced pressure, the crude was taken up with CH₂Cl₂ and washed with water. Finally the organic phase was dried with Na₂SO₄ and the product was purified by column chromatography (silica gel, CH₂Cl₂/CH₃OH 95/5), obtaining pure **3** as a purple powder (37 mg, 77% yield).

¹H-NMR (400 MHz, CDCl₃, 25°C): $\delta = 9.06$ (s, 1H), 9.01 (d, 4H), 8.97 (d, 1H), 8.91 (d, 1H), 8.45 (s, 1H), 8.16 (s, 2H), 8.11 (m, 4H), 8.03 (s, 2H), 7.84 (s, 1H), 7.80 (s, 3H), 7.34 (d, 2H, $J_{\text{trans}} = 15.4$ Hz), 7.00 (d, 1H, $J_{\text{trans}} = 15.4$ Hz), 6.61 (d, 1H, $J_{\text{trans}} = 15.4$ Hz), 2.73-2.63 (m, 8H), 1.63-1.47 (m, 72H), 1.36-1.29 (m, 38H), 0.96-0.88 ppm (m, 12H). MS-FAB(+) m/z : 1774 [M+H]⁺; elemental analysis calcd (%) for Chemical Formula: C₁₁₆H₁₄₉N₅O₂S₂Zn: C 78.49, H 8.46, N 3.95; found C 78.77, H 8.49, N 3.97

(*E*)-5-(2-(3,4-dihexyl-5-iodothiophen-2-yl)vinyl)-3,4-dihexylthiophene-2-carbaldehyde (14)

The aldehyde **13** (100 mg, $1.8 \cdot 10^{-2}$ mmol) dissolved in 4 mL of CHCl₃ was introduced in a dry Schlenk tube under nitrogen atmosphere. A solution of N-Iodosuccinimide (45 mg, $2.0 \cdot 10^{-2}$ mmol) dissolved in acetic acid (2 mL) was added dropwisely at 0°C. After that the mixture was stirred overnight at room temperature and concentrated, and the residue was diluted with CH₂Cl₂ (10 mL). The organic phase was washed with water, neutralized with K₂CO₃, dried over Na₂SO₄ and

evaporated to dryness. The residue was purified by chromatography on silica gel (eluent: CH₂Cl₂/hexane) leading to **14** as a yellow powder (120 mg, 98% yield).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 9.99 (s, 1H, CHO), 7.20 (d, 1H, J_{trans} = 15.6 Hz), 6.89 (d, 1H, J_{trans} = 15.6 Hz), 2.86 (m, 2H), 2.67-2.58 (m, 4H), 2.51 (m, 2H), 1.62-1.28 (m, 32H), 0.93-0.90 ppm (m, 12H).

1s) Lee, C.-W.; Lu, C.-W.; Lan, C.-M.; Huang, Y.-L.; Liang, Y.-R.; Yen, W.-N.; Liu, Y.-C.; Lin, Y.-S.; Diao, E. W.-G; Yeh, C.-Y. Novel Zinc Porphyrin Sensitizers for Dye-Sensitized Solar Cells: Synthesis and Spectral, Electrochemical, and Photovoltaic Properties. *Chemistry – A European Journal* **2009**, *15*, 1403-1412.

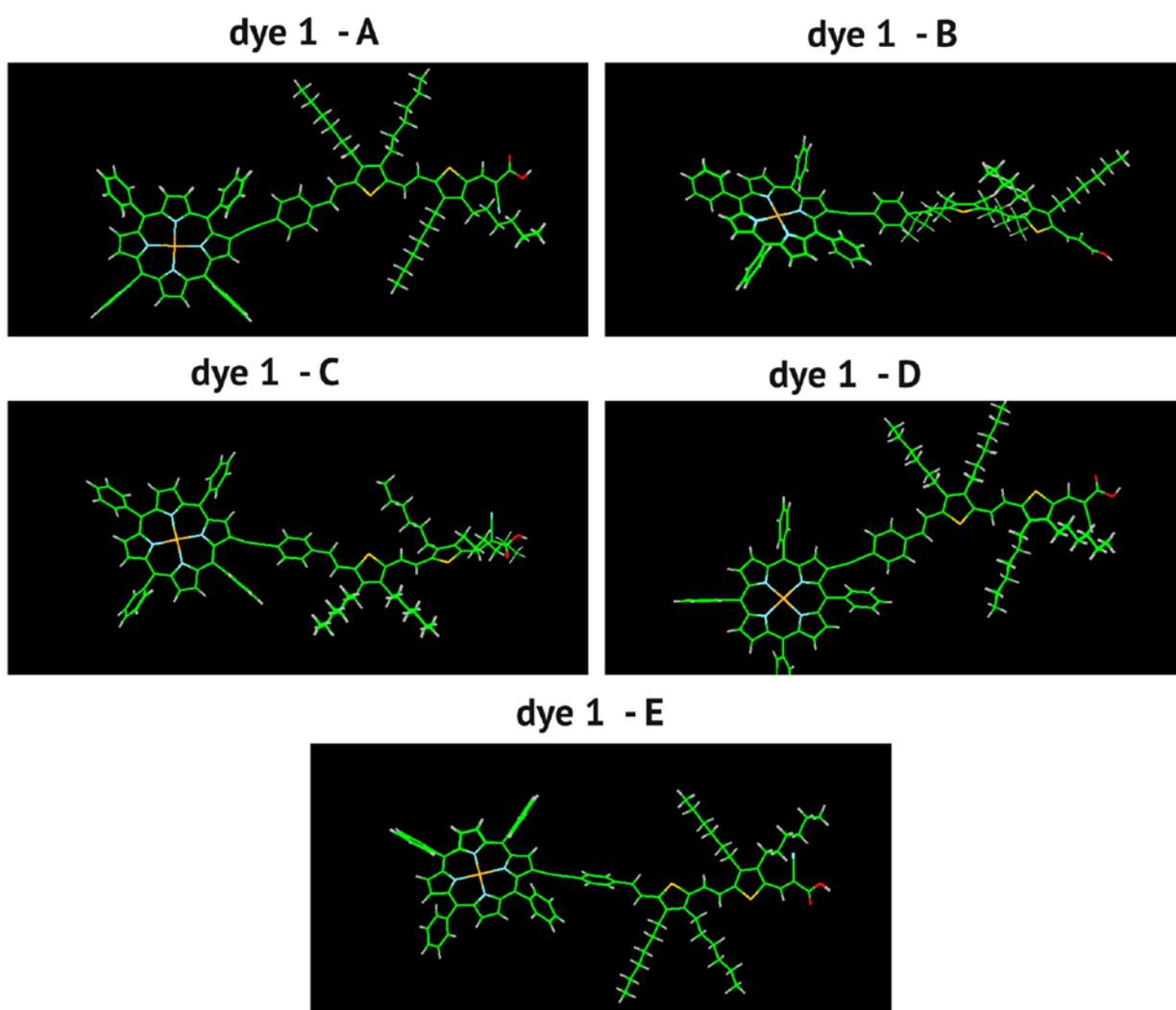


Figure 1S. Studied conformers for dye 1.

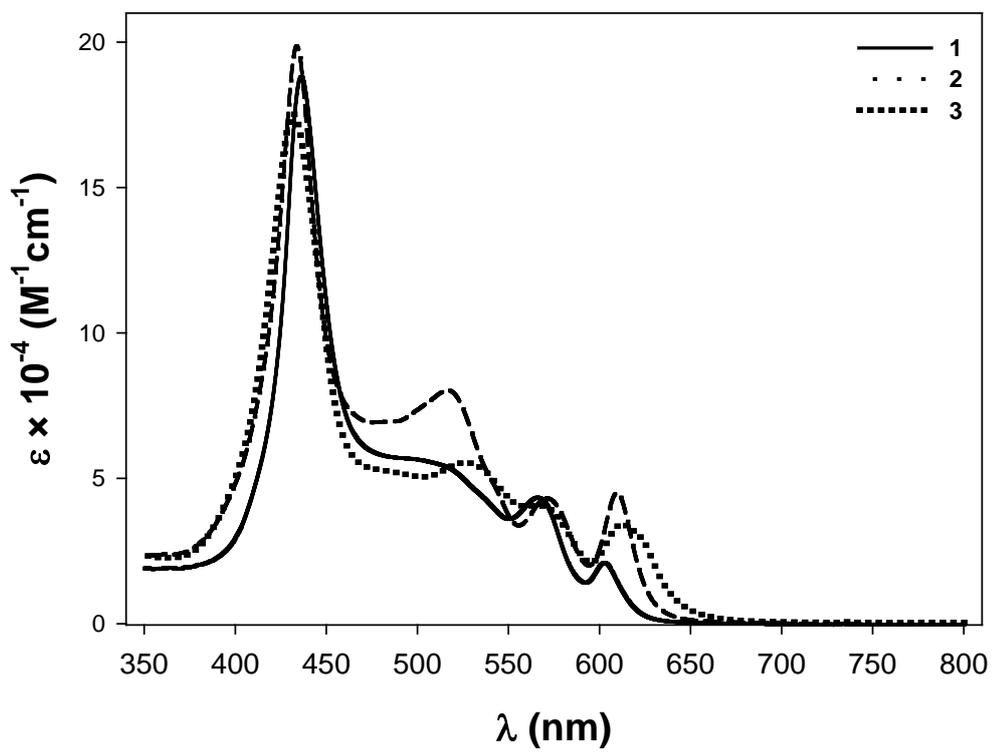


Figure 2S. Electronic absorption spectra in THF solution of **1-3**.

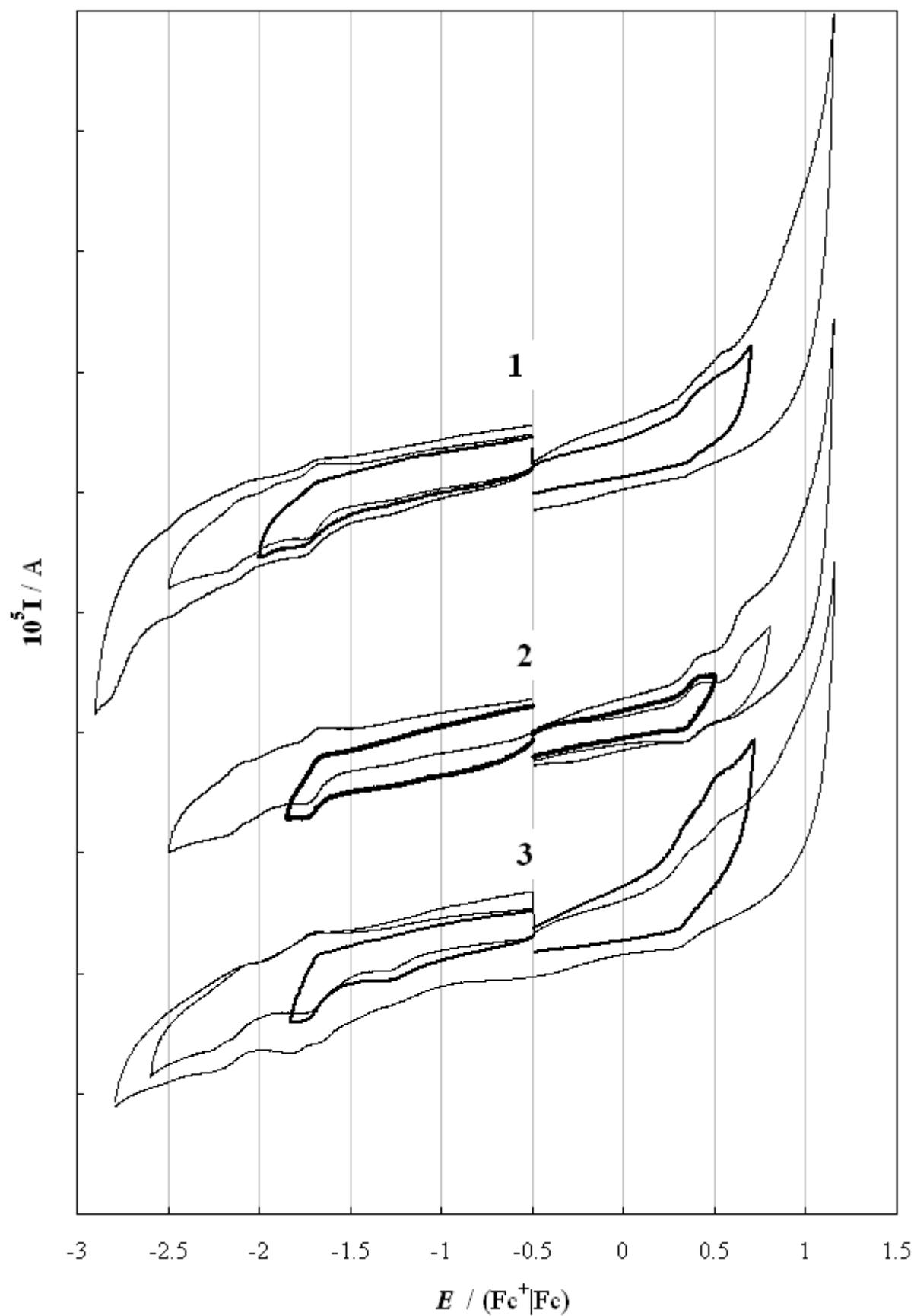


Figure 3S. CV features of porphyrinates **1–3** in DMF + 0.1 M TBAP, at 0.2 V s^{-1} scan rate, with ohmic drop compensation.

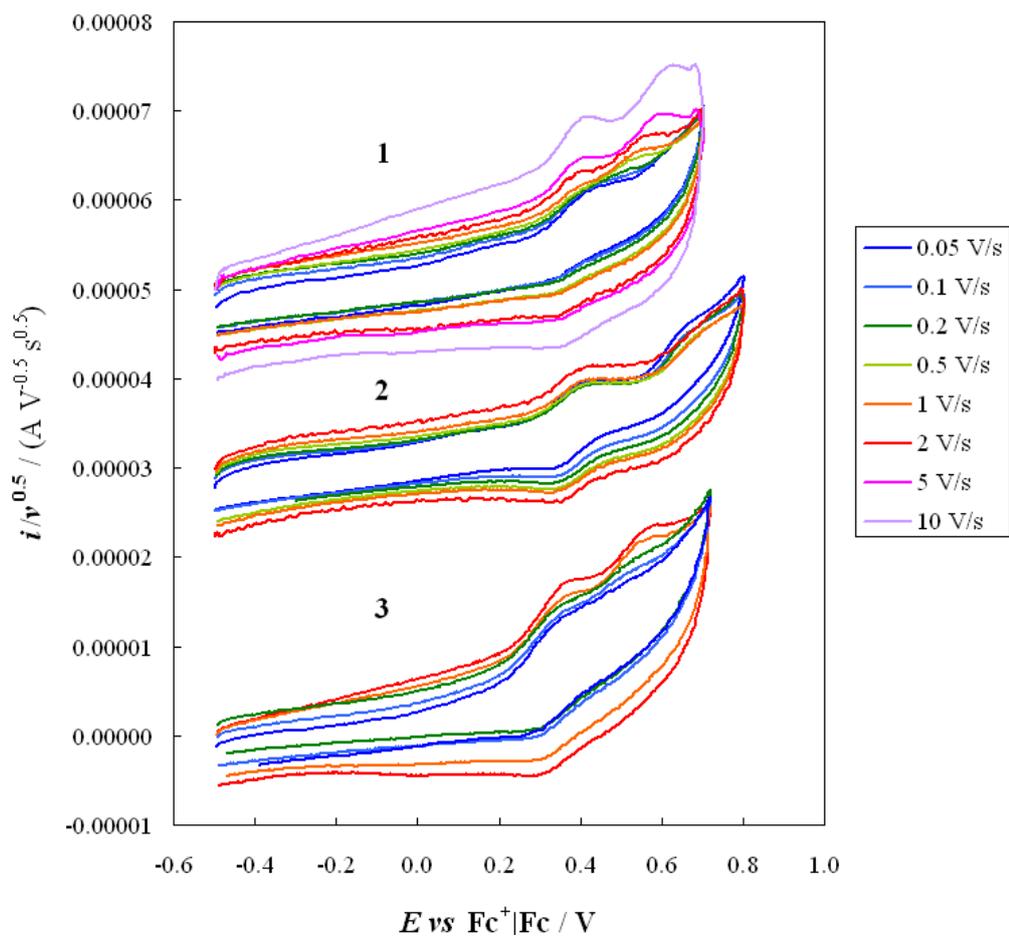


Figure 4S. Scan rate effect on the first oxidation peaks of the investigated molecules, recorded with ohmic drop correction and normalized with respect to $v^{0.5}$.

Table 1S. Experimental and Computed Electronic Absorption Spectra in THF Solution of the Zn^{II}-Porphyrinates 1-3. Comparison between B3LYP and CAM-B3LYP.

Dye	B bands		Comp. B bands		Sharp bands		Comp. Sh. bands		Q bands		Comp. Q bands	
	λ_a (nm) [log ϵ]	λ_a (nm) [Int. (a. u.)]	λ_a (nm) [log ϵ]	λ_a (nm) [Int. (a. u.)]	λ_a (nm) [log ϵ]	λ_a (nm) [Ing (a. u.)]	λ_a (nm) [log ϵ]	λ_a (nm) [Int. (a. u.)]	λ_a (nm) [log ϵ]	λ_a (nm) [Int. (a. u.)]	λ_a (nm) [log ϵ]	λ_a (nm) [Int. (a. u.)]
	Exp.	B3LYP	CAM-B3LYP	Exp.	B3LYP	CAM-B3LYP	Exp.	B3LYP	CAM-B3LYP	Exp.	B3LYP	CAM-B3LYP
1	436 [5.27]	447 [1.21]	418[1.34] 394[1.51]	493 [4.74]	498 [0.15] 524 [0.21]	492 [3.25] --	566 [4.67] 603 [4.36]	545 [0.14] 630 [2.51]	-- 571 [0.19]			
2	434 [5.30]	425 [1.26]	401[1.13] 394[0.86]	511[4.92]	520 [0.23]	457 [2.91]	571 [4.66] 609 [4.67]	549 [0.33] 600 [1.34]	572 [0.17]			
3	432 [5.24]	424 [1.22]	410[0.88] 397[1.35]	527 [4.75]	521 [0.10]	492 [2.54]	566 [4.62] 612 [4.55]	556 [0.22] 630 [1.72]	573 [0.20]			