

meso-Substituted Porphyrin with Benzo[1,2-*b*:4,5-*b'*]dithiophene Moieties

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Dedicated to Prof. Dr. Dr. h.c. Oscar I. Koifman on the occasion of the 70th anniversary of his birth

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*We report on the synthesis and detailed characterization of novel A4-type porphyrins (free-base and Zn(II)) substituted at the four meso positions by benzo[1,2-*b*:4,5-*b'*]dithiophene moieties. In comparison with their common phenyl meso-substituted analogues, these thienyl-substituted porphyrins display, in particular, much broader Soret band with extended absorption up to 500 nm.*

Keywords: *meso*-Porphyrin, benzodithiophene, thienyl-porphyrin.

мезо–Тетракис(бензо[1,2-*b*:4,5-*b'*]дитиофенил)порфирин

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*Описывается синтез и дана подробная характеристика новых порфиринов А4-типа (свободного основания и его Zn^{II} комплекса), замещенных бензо[1,2-*b*:4,5-*b'*]дитиофенильными группами по четырем мезо-положениям. По сравнению с их фенилзамещенными аналогами, в ЭСП тиенил-замещенных порфиринов наблюдается уширенная полоса Соре, простирающаяся до 500 нм.*

Ключевые слова: мезо-Порфирин, бензодитиофен, тиенил-порфирин.

Introduction

Porphyrins are a large family of highly π -delocalized conjugated macrocycles inspired by natural photosynthetic systems, such as chlorophyll pigments or heme. In particular, they display extraordinary and peculiar optical, photophysical and electrochemical properties, which can be tuned by changing the peripheral substituents and/or central metal ion. Porphyrins substituted at the *meso*-positions by five-

membered ring heteroaraomatic groups are a particular class of molecules that display particular properties rather different than their typical and common (*meso*)phenyl-substituted analogues. For instance, in thienyl-substituted porphyrins, the smaller size of a thiophene five-membered ring makes possible a larger conjugation with the porphyrin macrocycle than for phenyl groups (typically considered orthogonal to the porphyrin plane), which results in important changes of their electrochemical and photophysical properties.^[1] In

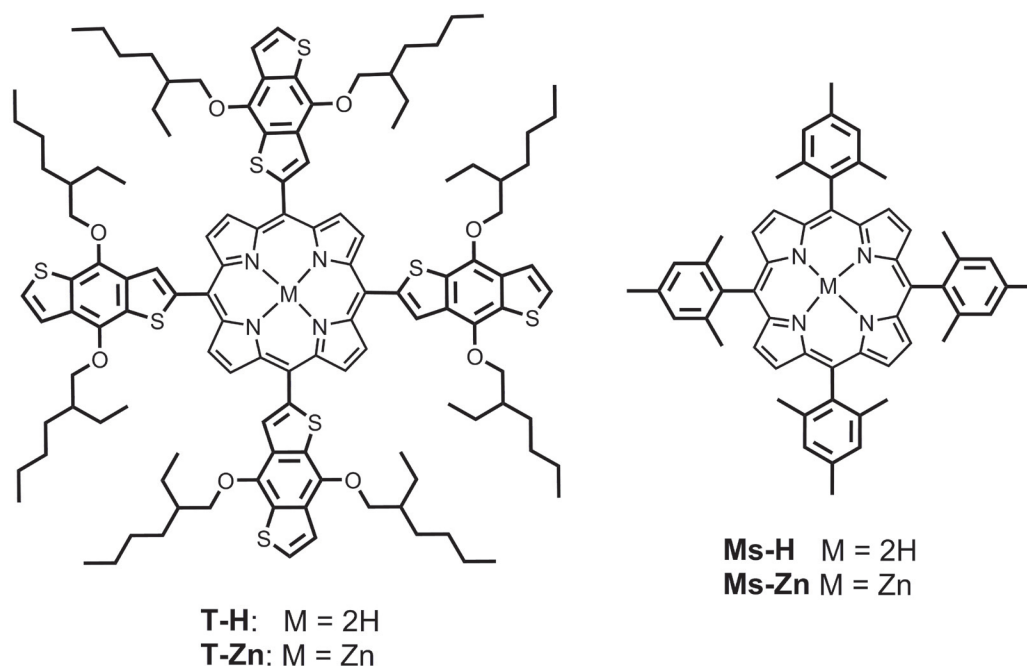


Figure 1. Molecular structures of tetrakis(BDT)porphyrins and benchmark tetrakis(mesityl)porphyrins.

particular, these kinds of porphyrins are known to display broadening and/or redshifts of their absorption bands. Despite their potential interests, this class of porphyrin is less known, and has been less studied.

Recently, sulfur-containing fused polycyclic heteroaromatic compounds, containing three or more fused rings, have raised particular expectations as semiconductive organic materials for optoelectronics or photovoltaics. Among them, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) displays remarkable properties such as high-field effect mobility and -conductivity, easy tuneable low-band gap and molecular energy level control.^[2-8] In this context, we report on the synthesis and characterisation of two tetrakis BDT-*meso*-substituted porphyrins, **T-H** (free-base) and **T-Zn** (zinc; see Figure 1). The *meso*-phenyl analogues, tetrakis(mesityl)porphyrins **Ms-H** (free-base) and **Ms-Zn** (Zinc) have been used as benchmarks to compare the UV-Vis absorption properties.

Experimental

Materials

Synthetic procedures were carried out under an inert argon atmosphere, in dry solvents unless otherwise noted. All dry solvents (anhydrous grade) were purchased at SDS, used without purification, dried over molecular sieves (3 Å), and flushed under argon atmosphere, prior to use. THF was freshly distilled from sodium benzophenoneketyl prior to use. All chemicals were purchased from Aldrich and used without further purification. Chromatographic purifications were performed using silica gel 60 SDS (particle size 0.040-0.063 mm). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. MS experiments were performed by the Servicio interdepartamental de Investigación (SIdI) at the universidad autonoma univesity de Madrid. . MALDI-TOF MS/HRMS spectra were recorded on a Bruker Reflex III

spectrometer with a laser beam operating at 337 nm. ¹H (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a Bruker AC-300 equipment; chemical shifts (δ) are given in ppm relative to the residual solvent peak of the deuterated solvent, and coupling constants (*J*) are given in Hz. UV-Vis spectra were recorded on a JASCO V-660 instrument.

Synthesis

meso-Tetrakis(2,4,6-trimethylphenyl) free-base porphyrin (**Ms-H**) was prepared according to the Lindsey's method, and the corresponding metallated analogue *meso*-tetrakis(2,4,6-trimethylphenyl) Zn(II) porphyrin (**Ms-Zn**) by metalation with Zn(OAc)₂ in a refluxing mixture of CHCl₃ and MeOH (9:1). Spectral and analytical data have been already extensively reported in the literature.^[9]

Compound 1. The synthesis of this compound was previously reported elsewhere in the literature.^[2,4] ¹H NMR (CDCl₃, 300 MHz) δ_H ppm: 7.56 (d, ³*J* = 5.5 Hz, 2H), 7.40 (d, ³*J* = 5.5 Hz, 2H), 4.27 (d, ³*J* = 5 Hz, 4H), 1.90 (m, ³*J*_{app} ≈ 6 Hz, 2H), 1.86-1.54 (m, 8H), 1.54-1.43 (m, 80H), 1.12 (t, ³*J* = 7.5 Hz, 6H), 1.05 (t, ³*J* = 7.5 Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ_C ppm: 144.6, 131.4, 129.9, 125.8, 120.2, 75.9 (OCH₂), 40.7, 30.5, 29.2, 23.9, 23.1, 14.1 (CH₃), 11.3 (CH₃). MS (FAB+, *m*-NBA): *m/z* (%) found 222.0 (82) [M-2(ethylhexyl)]⁺, 334.1 (12) [M-(ethylhexyl)+H]⁺, 446.2 (100) [M]⁺. HRMS, exact mass (FAB+, *m*-NBA + PEGH): *m/z* calcd for C₂₆H₃₈O₂S₂ [M]⁺: 446.2313; found 446.2303. Data are consistent with those reported in the literature.

Compound 2. In an argon flushed Schlenk flask, a 2.5 M commercial solution of *n*-BuLi in hexanes (0.43 mL, 1.075 mmol) was added drop by drop by syringe to a solution of **1** (433 mg, 0.97 mmol) in dry THF (8 mL) at -78 °C under argon. The mixture was stirred for 1.5h at the addition temperature (meanwhile, the colour of the mixture progressively turned from light yellow to deep dark brown). Next, dry DMF (0.3 mL, 3.87 mmol) was added dropwise and the mixture was stirred at -60 °C for 1.5h before allowing to warm slowly to room temperature within 1h. Finally, few drops of a saturated NH₄Cl aqueous solution were added to quench the

reaction (the colour of the mixture turned immediately to bright yellow. The reaction mixture was diluted in hexanes (50 mL), then successively dried over MgSO_4 , filtrated and solvents evaporated. The crude product was purified by column chromatography on SiO_2 , eluent Hexanes/ CH_2Cl_2 6:4, to afford **2** (318 mg, 0.67 mmol) in a 69 % yield, as a deep-yellow viscous oil. UV-Vis (CH_2Cl_2) λ_{max} nm (ϵ , $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 278 (25000), 329 (16300), 418 nm (8900). ^1H NMR (CDCl_3 , 300 MHz) δ_{H} (ppm): 10.07 (s, 1H; CHO), 8.13 (s, 1H; Ar-*H* BDT), 7.46 (br s, 2H; 2 Ar-*H* BDT), 4.25 (d, $^3J=5.5$ Hz, 2H; OCH_2), 4.15 (d, $^3J=5.5$ Hz, 2H; OCH_2), 1.87-1.30 (m, 18H; CH/CH_2), 1.08-0.90 (m, 12H; 4CH_3). ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} ppm: 184.2 (CHO), 147.1, 144.4, 142.4, 134.9, 131.4, 131.2, 130.0, 129.6, 128.3, 120.3, 76.3 (OCH_2), 76.0 (OCH_2), 40.6, 30.3, 29.1 (two signals), 23.7, 23.0 (two signals), 14.0 (CH_3), 11.2 (CH_3). MS (FAB⁺, *m*-NBA): *m/z* (%) found 249.9 (100) ($[\text{M}-2(\text{ethylhexyl})+2\text{H}]^+$), 474.0 (71) $[\text{M}]^+$, 475.0 (53) $[\text{M}]^+/\text{[M+H]}^+$. HRMS (FAB⁺, *m*-NBA + PEGH): *m/z* calc for $\text{C}_{27}\text{H}_{38}\text{O}_3\text{S}_2$ $[\text{M}]^+$: 474.2262; found 474.2274.

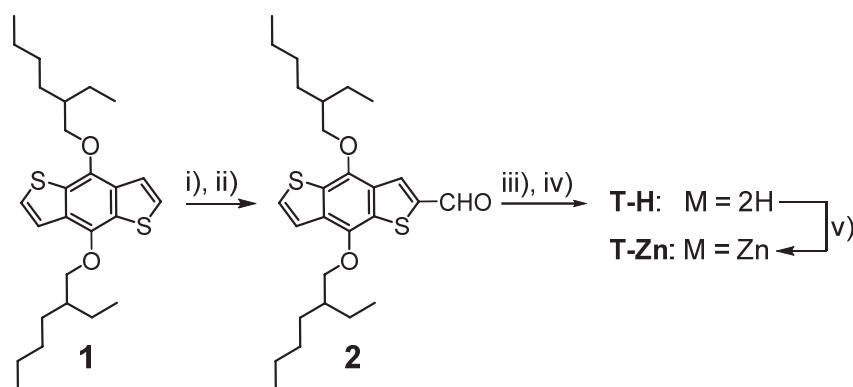
Porphyrin (T-H). In an argon flushed flask, compound **2** (102 mg, 215 μmol) and a 221 mM solution of pyrrole in CHCl_3 (1 mL, 221 μmol) were dissolved under argon in CHCl_3 containing 0.75% EtOH (20 mL). The solution was degassed vigorously by bubbling argon for 15 min with a needle/septum. Next, a commercial 79.3 mM solution of $\text{BF}_3\cdot\text{Et}_2\text{O}$ in CHCl_3 (1 mL, 79.3 μmol) was introduced with a syringe and the resulting reddish solution stirred at room temperature under argon for 6h. Subsequently, DDQ (146 mg, 643 μmol) was added and the mixture stirred at room temperature for an additional hour. Finally, few drops of Et_3N were added to the mixture to neutralize the acidity of the medium. The mixture was filtered through a plug of SiO_2 (CH_2Cl_2) and then the solvents evaporated. Purification by column chromatography on SiO_2 (CHCl_3 /hexanes, 6:4) afforded **T-H** (68 mg, 32.5 μmol) in 59 % yield as a dark-purple brownish solid. UV-Vis (CH_2Cl_2) λ_{max} nm (ϵ , $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 286 (74600), 354 (74700), 421 (225000), 530 (27800), 573 (13800), 597 (13300), 661 (3600). ^1H NMR (CDCl_3 , 300 MHz) δ_{H} ppm: 9.33 (s, 8H; 8 β -pyrrolic), 8.38 (s, 4H; 4Ar-*H* BDT), 7.73 (d, $^3J=5.6$ Hz, 4H; 4Ar*H* BDT), 7.57 (d, $^3J=5.6$ Hz, 4H; 4Ar*H* BDT), 4.49 (d, $^3J=6$ Hz, 8H; 4OCH_2), 4.47 (d, $^3J=6$ Hz, 8H; 4OCH_2), 2.00-1.24 (m, 72H; $8\text{CH}+32\text{CH}_2$ chains), 1.08 (t, $^3J=7.5$ Hz, 12H; 4CH_3), 1.03 (t, $^3J=7.5$ Hz, 12H; 4CH_3), 0.93 (t, $^3J=7$ Hz, 12H; 4CH_3), 0.84 (t, $^3J=7$ Hz, 12H; 4CH_3), -2.36 (s, 2H; NH). ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} ppm: 145.0, 143.4, 142.0, 132.1, 131.6, 131.3, 130.6, 127.6, 126.4, 120.7, 112.8, 76.4 (OCH_2), 76.2 (OCH_2), 40.8, 30.5, 30.4, 29.3, 29.2, 23.9, 23.9, 23.1, 23.0, 14.1 (CH_3), 14.0 (CH_3), 11.4 (CH_3), 11.3 (CH_3). MS (MALDI-TOF, DCTB): *m/z* (%) found 2086.9 (48), 2087.9 (87), 2088.9 (100), 2089.9 (73), 2090.9 (43), $[\text{M}]^+$. HRMS (FAB⁺, DCTB+PEGNa 2000): *m/z* calc for $\text{C}_{124}\text{H}_{158}\text{N}_4\text{O}_8\text{S}_8$ $[\text{M}]^+$: 2086.9840; found 2086.9837.

Porphyrin (T-Zn). A solution of **T-H** (33 mg, 15.8 μmol) and $\text{Zn}(\text{OAc})_2$ (20 mg, 109 μmol) in 5 mL of a mixture of CHCl_3 /MeOH (9:1) was heated to reflux for 1.5 h. Solvents were evaporated to dryness, and then the crude was purified by column chromatography on SiO_2 (CHCl_3 /hexanes, 1:1) to afford **T-Zn** (24 mg, 11.1 μmol) in 70 % yield as a dark-pink brownish solid. UV-Vis (CH_2Cl_2) λ_{max} nm (ϵ , $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 293 (46000), 353 (66100), 425 (233700), 561 (35700), 603 (8300). ^1H NMR (CDCl_3 , 300 MHz) δ_{H} ppm: 9.29 (s, 8H; 8 β -pyrrolic), 8.34 (s, 4H; 4Ar-*H* BDT), 7.69 (d, $^3J=5.6$ Hz, 4H; 4Ar*H* BDT), 7.66 (d, $^3J=5.6$ Hz, 4H; 4Ar*H* BDT), 4.46 (d, $^3J=5.4$ Hz, 8H; 4OCH_2), 4.42 (d, $^3J=5.4$ Hz, 8H; 4OCH_2), 1.96-1.16 (m, 72H; $8\text{CH}+32\text{CH}_2$ chains), 1.03 (t, $^3J=7.5$ Hz, 12H; 4CH_3), 0.97 (t, $^3J=7.5$ Hz, 12H; 4CH_3), 0.86 (t, $^3J=7$ Hz, 12H; 4CH_3), 0.78 (t, $^3J=7$ Hz, 12H; 4CH_3). ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} ppm: 151.6 (twice intense: $2\times[4\text{ArH}]$), 145.6, 144.1, 143.9, 132.4, 132.0, 131.8, 131.2, 127.3, 127.1, 120.8, 113.3, 76.5 (OCH_2), 76.3 (OCH_2), 41.5, 31.1, 31.0, 29.8, 29.8, 25.5, 25.2, 24.9, 24.8, 24.7, 24.5, 24.4, 23.5, 23.5, 14.0 (2 signals: $[4+4]\text{CH}_3$), 11.3 (2 signals: $[4+4]\text{CH}_3$).

Results and Discussion

Synthesis

The synthesis of the BDT-porphyrins **T-H** and **T-Zn** are depicted in Scheme 1. The starting building block **1**, is composed of a central BDT core, armed with two ethylhexyloxy chains at the [3,4]positions of the central benzo moiety. These lateral chains are known to be of high importance to avoid aggregation between BDT molecules, and confer high solubility in organic media. Moreover, in the final structure, they are also expected to avoid π - π stacking aggregation between porphyrin macrocycles. Compound **1** was described previously, and synthesized according to the literature.^[2,4] The next key-step was the mono and regioselective functionalization at the α -position of one thiophene moiety. This could be achieved successfully by treatment with a slight excess of *n*-BuLi (1.1 eq) in THF at low temperature, to afford the major and *in-situ* generated, mono lithiated intermediate. Subsequent reaction with DMF afforded, after hydrolysis, compound **2** in good yield (69 %). Next, the free-base porphyrin **T-H** was prepared by condensation of aldehyde **2** (1 eq), mesitaldehyde with pyrrole in CHCl_3 under $\text{BF}_3\cdot\text{OEt}_2$ acid-catalyzed conditions, followed by oxidation with DDQ (2,3-dichloro-5,6-dicyano-



Scheme 1. Reagents and conditions: i) *n*-BuLi (1.1 eq), THF, -78 °C, 1.5 h; ii) DMF, -78 °C to RT, 1.5 h followed by $\text{NH}_4\text{Cl}/\text{H}_2\text{O}$, RT, 5 min (2: 69 %); iii) Pyrrole (1 eq), $\text{BF}_3\cdot\text{OEt}_2$, CHCl_3 , 6 h then iv) DDQ, RT, 1h (**T-H**: 59 %); v) $\text{Zn}(\text{OAc})_2$, CHCl_3 /MeOH (9:1), reflux 1.5 h (**T-Zn**: 70 %).

1,4-benzoquinone) at RT, under the classical conditions optimized by Lindsey.^[10,11] **T-H** was obtained in excellent yield (59 %). Finally, metalation of the free base porphyrin **T-H** with an excess of Zn(OAc)₂ afforded the Zn(II) porphyrin **T-H** in 70 % yield.

Characterisation

All compounds were characterised by NMR and UV-Vis spectroscopy, MS and HRMS spectrometry. The MALDI-TOF spectra of **T-H** and **T-Zn** are depicted in Figure 2. Both porphyrins displayed the expected molecular ion peak, corresponding to the mono-charged species [M]⁺.

Next, the porphyrins were characterised and investigated by ¹H and ¹³C NMR spectroscopy (Figures 3 and 4). The monosubstitution pattern in compound **2**, led to the loss of equivalency of the two thiophene moieties, and as well of the two ethylhexyl chains, which appear magnetically non-equivalent to each other. This can be clearly seen over the methoxy protons region in the ¹H NMR spectrum (two doublets), and over the methoxy carbons region in the ¹³C NMR where two distinct signals can be observed. Moreover, all aromatic carbons of the BDT skeleton appear non-equivalent, displaying ten distinct signals in the NMR spectrum, in agreement with its molecular structure. This asymmetric pattern is conserved in the porphyrins **T-H** and **T-Zn**, for which the BDT subunits display an AB system for the H_A and H_B protons, a single singlet for the H_C protons, and two distinct doublets for the H₃ and H_a methoxy protons. It is worth to notice that meanwhile the NMR spectra of **T-H** were perfectly well-defined in CDCl₃ solutions, those of **T-Zn** were quite broad and ill-defined. In [D₈]-THF the spectra of **T-Zn** became perfectly well-resolved, with sharp signals. This witness the tendency (although very low) of

T-Zn to undergo π-π stacking in CDCl₃ solution at high-concentration (>15 mM). In contrast, **T-H** still displayed perfectly well-defined NMR spectra in CDCl₃ solutions at concentration as high as 40 mM. As a characteristic feature of free base porphyrin, the highly shielded NH protons appear as unique singlet signal at -2.36 ppm in the ¹H NMR spectrum of **T-H**, due to fast tautomerism at RT.^[12,13] Interestingly, the four BDT subunits appear magnetically equivalent to each other in the NMR spectra of the two porphyrins, which witnesses free-rotation of the BDT subunits around the porphyrin plane. In the ¹³C NMR spectra of **T-Zn**, twelve signals are observed in the aromatic carbons region with one signal twice intense, which are in agreement with the thirteen expected signals for the four sets of thirteen non-equivalent aromatic carbons. In **T-H** only eleven over the thirteen expected signals were observed in the ¹³C NMR spectra. It is common and known in free-base porphyrin that the tertiary carbons at the α and β-position of the N atoms (¹³C-12 and ¹³C-11, respectively) have long relaxation time, which most often result in very broad signals that could not be detected.

Finally, the porphyrin **T-H** and **T-Zn**, and the benchmarks **Ms-H** and **Ms-Zn** were characterised by UV-Vis spectroscopy in CH₂Cl₂ solutions (Figure 5). All porphyrins display the characteristic absorption bands of porphyrin; a Soret (B-band) at around 420-450 nm, and Q-bands between 500-700 nm. The free-base porphyrins **T-H** and **Ms-H**, display the four Q-bands characteristic of four-fold degenerated transitions (Q_x, Q_y) of D_{2h}-symmetrical free-base porphyrins, while **T-Zn** and **Ms-Zn**, presents only two Q-bands as observed for higher D_{4h}-symmetrical metallo Zn(II) porphyrins. The highest energy transitions bands in the UV region correspond to the absorption of the BDT subunits in **T-H** and **T-Zn**. In comparison with their phenyl-

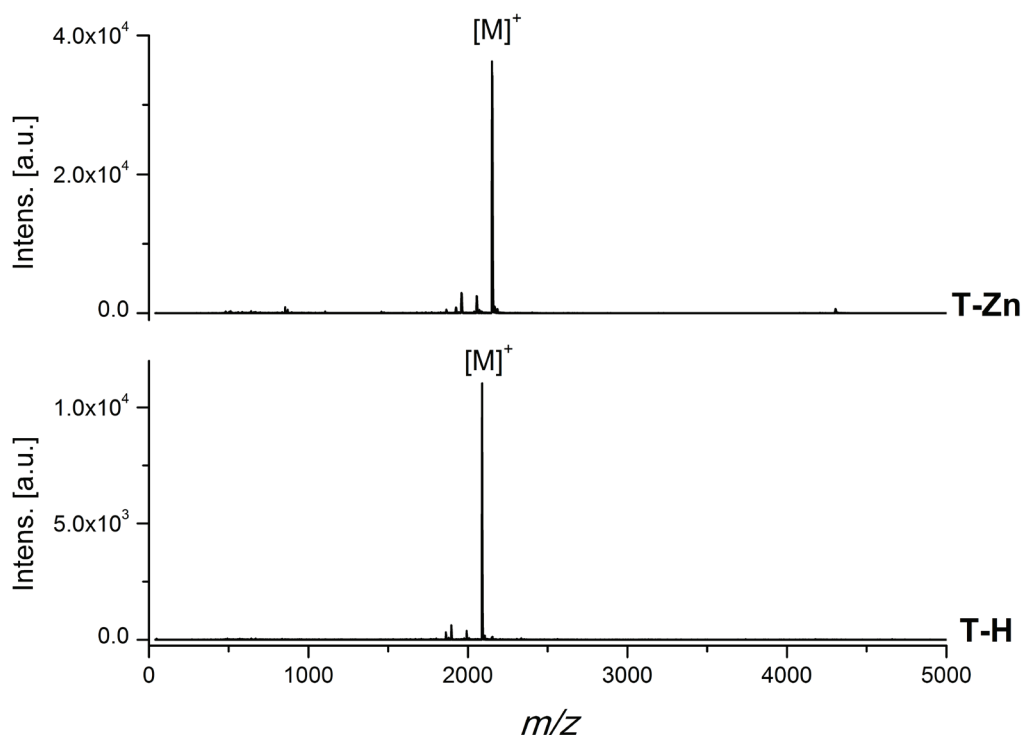


Figure 2. MALDI-TOF mass spectrum of **T-H** (bottom trace) and **T-Zn** (upper trace).

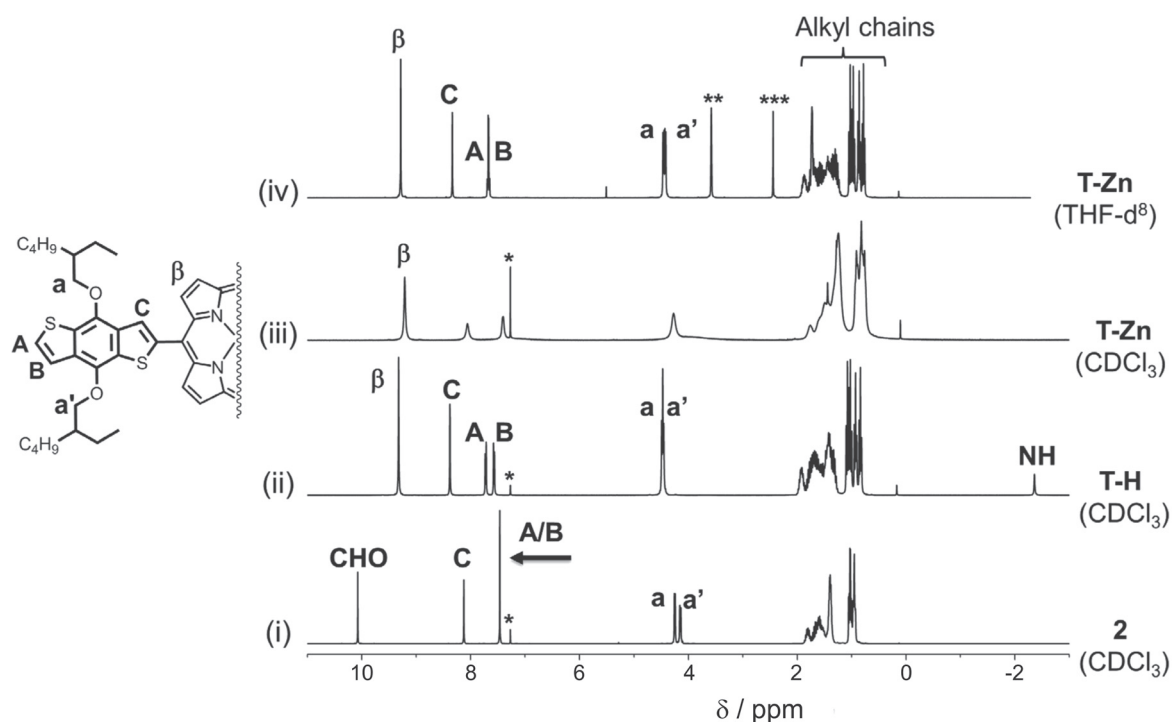


Figure 3. ^1H NMR (300 MHz, 300 K) spectra of (i) compound **2** in CDCl_3 , (ii) **T-H** in CDCl_3 (~[40 mM]), (iii) **T-Zn** in CDCl_3 (~[15 mM]) and (iv) **T-Zn** in $[\text{D}_8]\text{-THF}$ (~[15 mM]) (* denotes the residual solvent peak of CDCl_3 ; ** and *** denote the residual solvent peak and water of $[\text{D}_8]\text{-THF}$, respectively).

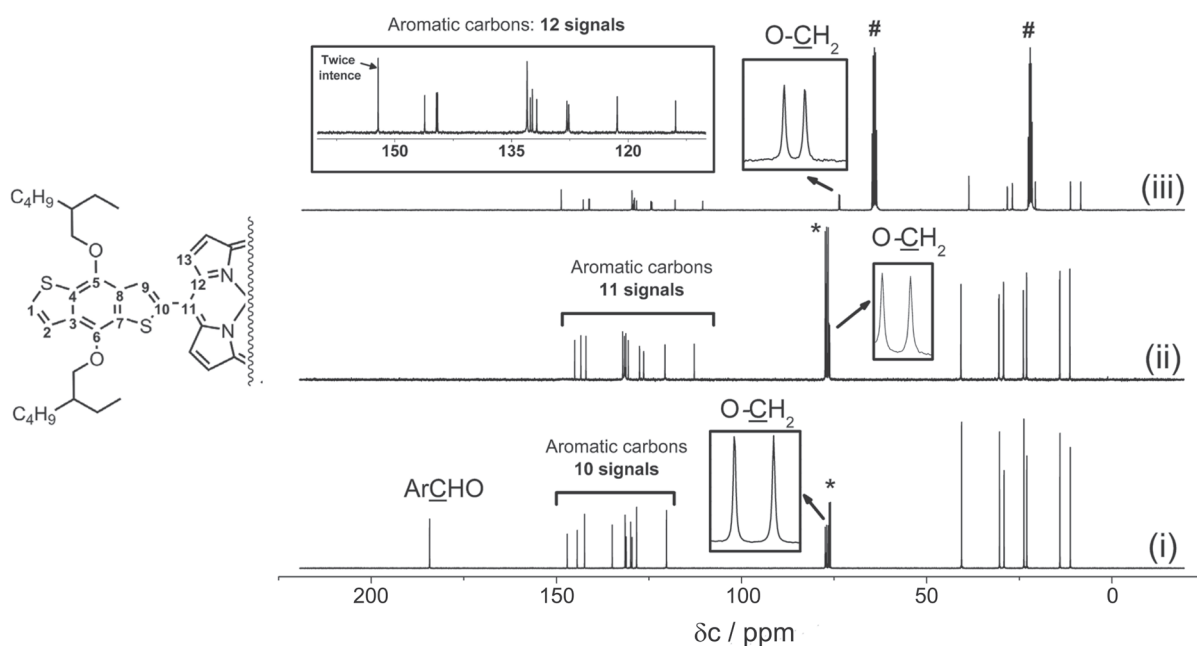


Figure 4. Left: Nomenclature used for ^{13}C NMR; Right: ^{13}C NMR (75 MHz, 300 K) spectra of (i) compound **2** (CDCl_3), (ii) **T-H** (~[40 mM in CDCl_3]), and (iii) **T-Zn** (~[15 mM] in $[\text{D}_8]\text{-THF}$) (* and # denote the signals of the CDCl_3 and of $[\text{D}_8]\text{-THF}$ solvents, respectively).

substituted analogues **Ms-H** and **Ms-Zn**, the Soret band in **T-H** and **T-Zn** appear much broader with lower molar coefficient, and extended to the red region up to near 500 nm. The Q-bands of BDT-porphyrins also appear slightly redshifted, but this time with higher molar coefficients than their mesityl analogues. Upon highly-diluted conditions of

the UV solutions ($C \sim 4\text{-}8 \cdot 10^{-6}$ M), we exclude, at least under this range of concentration, any aggregation phenomena for **T-Zn** and **T-H** (for **T-H** no aggregation was observed by NMR experiments in CDCl_3 solutions up to 40 mM; for **T-Zn**, slight tendency of aggregation seemed to be observed by NMR but at concentration range >15 mM; *i.e.* factor of

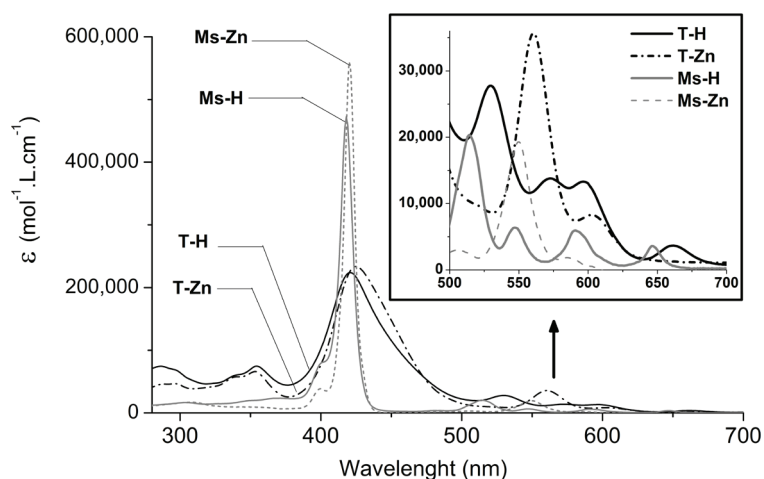


Figure 5. UV-Vis spectra of **T-H**, **T-Zn**, **Ms-H**, and **Ms-Zn** in CH_2Cl_2 solutions ($C \sim 4.8 \cdot 10^{-6}$ M).

dilution of about ~ 2000 from NMR to UV-Vis solutions). Moreover, no broadening of the Q-bands were observed for both **T-Zn** and **T-H**, which also point out that the changes observed in the absorption spectra exclude aggregation phenomena. Thus, the changes observed in the absorption UV-Vis spectra (especially the Soret band) clearly reflect the higher degree of conjugation between the four BDT subunits and porphyrin macrocycle.

Conclusions

Two novel A4-type porphyrins (free-base and Zn(II)) substituted at the four *meso* positions by benzo[1,2-*b*:4,5-*b'*]dithiophene moieties, were synthesised and characterized. These thienyl-substituted porphyrins display broader Soret band, with extended absorption up to 500 nm. One of the main limitations for the use of common porphyrin in electronic or photovoltaic devices, such as phenyl-substituted type, are the small bandwidth and lack of absorption of sunlight in the visible, red, and NIR regions of the solar spectrum. Thus, the peculiar optical properties of this kind of porphyrin are of particular interest, in particular for photovoltaic application, such as DSSC.

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