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Review

The synthesis and properties of unsymmetrical porphyrazines annulated with a tetrathiafulvalene bearing two tetraethylene glycol units

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1. Introduction

Phthalocyanines (Pc's) have attracted significant attention for many years because of their two-dimensional, π -electron conjugation, manifold structural variety, high thermal and chemical stability, as well as unique electrical, optical, magnetic, catalytic, mesogenic and film formation properties for various applications [1–4]. Structurally, both Pc and porphyrazine (Pz) are isoelectronic with porphine but Pz's have received comparatively little attention in comparison to functionalized porphyrins (Pr's) and Pc's [3,5–14]. In general, the functional groups attached directly at the β -positions of rings in the Pz core are more strongly coupled to the macrocycle core than are those attached at the β -position of rings in the Pc core and, therefore, exert a greater effect on the physical properties of the compound [15]. In this context, the attachment of various substituents at the periphery of Pz's allow fine-tuning of the resulting compound's solubility, redox and electronic properties. Although various symmetrical Pzs have been studied [4,16–25], there has been only a few reports concerning unsymmetrical Pz's [26–28], mainly because they are difficult to synthesize and purify. In recent years, there has been growing interest in the properties of unsymmetrically Pcs as they display second- and third-order

ABSTRACT

A dicyano-tetrathiafulvalene precursor was prepared by the cross-coupling reaction of 4,5-dicyano-1,3dithiol-2-one with 4,5-bis(3,6,9,12-tetraoxatridecylthio)-1,3-dithiol-2-thione. A Mg(II) template cyclization of the precursor with excess 2,3-bis(methylthio)maleonitrile gave the unsymmetrical magnesium porphyrazine, which was easily converted to the metal-free derivative by treatment with acetic acid in the dark. The metal-free porphyrazine was converted to the corresponding zinc porphyrazine in 75% yield. The products were fully characterized using spectroscopic data and elemental analysis. They were soluble in common organic solvents; solution electrochemical, UV–Vis and ESR data revealed that all porphyrazines formed an electron transfer complex with 7,7,8,8-tetracyanoquinodimethan and 2,3,5,6tetrafluoro-7,7,8,8-tetracyanoquinodimethane.

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nonlinear optical properties in solution, high thermal stability, mesogenic behavior, Langmuir–Blodgett film formation and semiconducting properties [29–35]. Recently, the present authors have reported three series of symmetrical Pzs bearing tetrathiafulvalene (TTF) units, including Pzs annulated directly with four TTF units and linked TTF units, with either a tetrathia-18-crown-6 ether or ethylenedithio functions [36–38]. Symmetrical Pzs bearing multi-TTF units display good electron donating properties and give rise to octa- or hexadeca- radical cationic species bearing TTF moieties.

It is well known that both porphyrinic macrocycles and tetrathiafulvalene derivatives are semiconductors [39]. To study the effect of combining a Pz ring with TTF moieties on the redox behavior of conjugated molecules, this paper concerns the synthesis, photophysical and electron donating characteristics of a single TTF moiety bearing two tetraethylene glycol units attached to the Pz ring (Scheme 1).

2. Experimental

All reagents and solvents were of commercial quality and were either distilled or dried as necessary using standard procedures. All reactions were carried out under an Argon atmosphere. NMR spectra were recorded using a Bruker AV-300 Spetrometer (300 MHz for ¹H and 75 MHz for ¹³C), and chemical

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Scheme 1. Synthetic route of unsymmetrical porphyrazines (7-9).

shifts were referenced to tetramethylsilane ($\delta_{\rm H}/\delta_{\rm C} = 0$). UV–vis spectra were recorded on a Hitachi U-3010 spectrophotometer in CHCl₃ ($c = 2 \times 10^{-5}$ M), mass spectrometry was performed using a Hewlett Packard 1100-HPLC/MSD (EI mode) and HRMS data were obtained using a Thermo MAT95XP high resolution mass spectrometer (EI mode). MALDI-TOF-MS data were obtained using a Shimadzu AXIMA-CFR plus mass spectrometry employing a 1,8,9-anthracenetriol (DITH) matrix. Cyclic voltammetry was carried out on a Potentiostat/Galvanostat 273A instrument using a mixture of CH₂Cl₂-CH₃CN (4:1, V/V), 0.1 M Bu₄PF₆ as supporting electrolyte, employing a 100 mV⁻¹ scan rate The counter and working electrodes were made of Pt and Glass-Carbon, respectively, and the reference electrode was a calomel electrode (SCE). IR spectra were recorded on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. Electron spin resonance (ESR) was measured using a JEOL JES FA-200 spectrometer in CH₂Cl₂. Bis (tetraethylammonium)bis((1,3-dithiole-2-thione-4,5-dothiol)) zincate salt 1 and the ketone 4 were prepared according to procedures described in the literature [40,41]. 3,6,9,12-Tetraoxatrideccyl toluene-p-sulfonate was prepared according to the literature [42].

2.1. Synthesis of 13-iodo-2,5,8,11-tetraoxatridecane(2)

A mixture of 3,6,9,12-tetraoxatrideccyl toluene-*p*-sulfonate (3.21 g, 8.8 mmol) and Nal (6.6 g, 44 mmol) in dry acetone was stirred and heated to reflux under N₂ for 2 h. Upon cooling the reaction mixture was filtered and extracted with methylene chloride (3×30 mL). The combined extracts were washed with water (3×30 mL), dried (MgSO₄), and evaporated to furnish a pale yellow coloured oil. The crude product was purified by silica gel column chromatography using ethyl acetate/petroleum ether (100:1) as the eluent to give a colorless oil. Yield: 2.15 g (77%). ¹H NMR (CDCl₃), 3.26 (t, 2H, CH₂–I, J = 6.9 Hz), 3.39 (s, 3H, CH₃–O), 3.55 (t, 2H, CH₂–OCH₃, J = 4.2 Hz), 3.67 (s, 10H, CH₂–O), 3.76 (t, 2H,

CH₂–O, J = 6.9 Hz). MS (ESI), (m/z): 318 [M]⁺. HRMS (FAB) Anal. calcd. for C₉H₁₉IO₄: 318.0328. Found: m/z 318.0350.

2.2. 4,5-Bis(2,5,8,11-tetraoxatridecan-13-ylthio)-1,3dithiole-2-thione(**3**)

A solution of bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol)-zincate salt (1) (340 mg, 0.47 mmol) and 13-iodo-2,5,8,11-tetraoxatridecane (2) (760 mg, 2.3 mmol) in CH₃CN (15 mL) was stirred under reflux for 1.5 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated under vacuum and the oily residue obtained was chromatographed on a silica gel column (ethyl acetate/petroleum ether, 4:1) to afford compound **3** as a yellow coloured oil. Yield: 415 mg, (76%). ¹H NMR (CDCl₃), 3.07 (t, 4H, CH₂–S, *J* = 6.6 Hz), 3.37 (s, 6H), 3.54 (t, 4H, CH₂–O, *J* = 4.2 Hz), 3.64–3.66 (m, 20H, CH₂–O), 3.71 (t, 4H, CH₂–O, *J* = 6.6 Hz). HRMS (FAB) Anal. calcd. for C₂₁H₃₈O₈S₅: 578.1170. Found: *m*/*z* 578.1158.

2.3. 2-(4,5-Dicyano-1,3-dithio-2-ylidene)-4,5-bis(2,5,8,11tetraoxatridecan-13-ylthio)-1,3-dithiole(**5**)

A solution of compound **3** (810 mg, 1.4 mmol) and compound **4** (235 mg, 1.4 mmol) in toluene (45 mL) was added dropwise to a refluxing mixture of P(OEt)₃ (15 mL) and toluene (100 mL). The ensuing mixture was refluxed for 1 h; after cooling to room temperature, the solvent was removed under vacuum and the oily residue obtained was chromatographed on a silica gel column (ethyl acetate/petroleum ether, 4:1) to afford compound **5** as dark red coloured oil. Yield: 125 mg (13%). IR (NaCl disk): 2872, 2216, 1452, 1352, 1267,1107, 1022. ¹H NMR (CD₃CN), 3.04 (t, 4H, CH₂–S, J = 6.6 Hz), 3.30 (s, 6H, CH₃–O), 3.47 (t, 4H, CH₂–O, J = 3.9 Hz), 3.49–3.56 (m, 24H, CH₂–O), 3.65 (t, 4H, CH₂–O, J = 6.3 Hz). HRMS (FAB) Anal. calcd. for C₂₆H₃₈N₂O₈S₆: 698.0952. Found: *m/z* 697.9507.

2.4. {2,3-[6,7-Bis(2,5,8,11-tetraoxatridecan-13-ylthio) tetrathiafulvalene] porphyrazi-nato} Mg (II)(7)

A mixture of Mg (179 mg, 7.46 mmol) and I₂ (one small crystal) in *n*-propanol (14 mL) was heated under reflux for 12 h. The suspension was cooled and dinitrile 5 (76 mg, 0.11 mmol) and compound 6 (561 mg, 3.3 mmol) in *n*-propanol (20 mL) were added dropwise and the mixture was further heated under reflux for 24 h. The deep blue coloured suspension was allowed to cool, filtered and the solid washed with methylene chloride. The filtrate was concentrated under vacuum and the residue purified using column chromatography on silica gel (gradient of methylene chloride/ methanol, $100:1 \rightarrow 20:1$) to give a blue coloured solid. Reprecipitation of the solid from methylene chloride/methanol gave 7 as a dark blue powder. Yield: 12 mg (12%), mp >250 °C (by DTA). Anal. Calcd. for C₄₄H₅₆MgN₈O₈S₁₂ (%): C, 42.82; H, 4.57; N, 9.08. Found: C, 42.93; H, 4.59; N, 8.90. R_f = 0.24 (methylene chloride/methanol, 20:1). IR (KBr pellets): 2914, 2864, 1498, 1230, 1205, 1105, 1031, 966. ¹H NMR (CDCl₃), 2.71 (s, 4H, CH₂-S), 2.88 (s, 6H, CH₃-S), 3.03 (s, 6H, CH₃–S), 3.15–3.80 (m, 40H, CH₂–O). UV–vis (CH₃CN): λ_{max}/ nm: $(10^{-5} \varepsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$: 662 (4.67), 375 (4.80). MS (MALDI-TOF), (m/z): 1234.0170 $[M + H]^+$ (calcd. for $[M + H]^+$ 1233.0720).

2.5. 2,3-[6,7-Bis(2,5,8,11-tetraoxatridecan-13-ylthio) tetrathiafulvalene] porphyrazi-ne (**8**)

A solution of magnesium porphyrazine 7 (12.4 mg, 0.01 mmol) in a mixture of acetic acid (0.5 mL) and methylene chloride (0.5 mL)was stirred at room temperature for 72 h and then diethyl ether was added and the resulting suspension adjusted to pH 7 using 1 M NaOH. The organic phase was washed with saturated aq NH₄Cl and water and then dried over MgSO₄. The solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel (methylene chloride/methanol, 60:1) to give a purple coloured solid. Reprecipitation of the solid from methylene chloride/methanol gave 8 as a dark purple powder. Yield: 9 mg (78%), mp 156 °C (Decomp., by DTA). Anal. Calcd. for C₄₄H₅₈N₈O₈S₁₂ (%): C, 43.61; H, 4.82; N, 9.25. Found: C, 43.93; H, 4.66; N, 9.57. $R_{\rm f} = 0.23$ (methylene chloride/methanol, 20:1). IR (KBr pellets): 3406, 2920, 2852, 1231, 1099, 1022. ¹H NMR (CDCl₃), -4.88 (br, 2H, NH), 3.18 (t, 4H, -CH₂S-, J = 6.6 Hz), 3.27 (s, 6H, CH₃-S), 3.35 (s, 6H, CH₃-S), 3.40-3.84 (m, 40H, CH₃-S + CH₂-O). UV-vis (CH₃CN): λ_{max}/nm : (10⁻⁵ ε dm³ mol⁻¹ cm⁻¹): 684 (4.30), 617 (4.43), 525 (4.40), 343 (4.78). MS (MALDI-TOF), (m/z): 1210.1752 (calcd. for [M]⁺ 1210.1026).

2.6. {2,3-[6,7-Bis(2,5,8,11-tetraoxatridecan-13-ylthio) tetrathiafulvalene] porphyrazinato} Zn (II)(**9**)

The 2H porphyrazine **8** (12 mg, 0.01 mmol) and zinc (II) acetate (3 mg, 0.01 mmol) were added to chlorobenzene (4 mL) and the mixture was heated under reflux, with stirring, under N₂ for 5 h. The reaction mixture was washed with saturated aq NH₄Cl and water and then dried over MgSO₄. The solution was concentrated in vacuo and the residue was purified by column chromatography on silica gel (methylene chloride/methanol, 60:1) to give a blue solid. Reprecipitation of the solid from methylene chloride/methanol gave **9** as a dark blue powder. Yield: 8 mg (75%), mp >250 °C. Anal. Calcd. for C₄₄H₅₆N₈O₈S₁₂Zn (%): C, 41.44; H, 4.43; N, 8.79. Found: C, 41.63; H, 4.46; N, 8.57. *R*_f = 0.24 (methylene chloride/methanol, 20:1). IR (KBr pellets): 3439, 2916, 2850, 1634, 1466, 1419, 1298, 1223, 1107, 1026. ¹H NMR (CDCl₃), 2.72 (s, 4H, -CH₂S–), 2.88 (s, 6H, CH₃–S), 3.03 (s, 6H, CH₃–S), 3.16–3.84 (m, 40H, CH₂–O). UV/vis (CH₃CN): λ_{max}/nm : (10⁻⁵ ε dm³ mol⁻¹ cm⁻¹): 657 (4.67), 369 (4.77).

MS (MALDI-TOF): (m/z): 1273.7125 [M + H]⁺ (calcd. for [M]⁺ 1272.0161).

3. Result and discussion

3.1. Synthesis and characterization

The synthetic routes to target compounds **7–9** are summarized in Scheme 1. The starting material 3, bearing two tetrakis(oxyethylene) chains, was synthesized in 76% yield by the reaction of bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dothiol) zincate (1) with 13-iodo-2,5,8,11-tetraoxatridecane (2). The crosscoupling reaction of **3** with ketone **4** in a mixture of triethyl phosphite and toluene at reflux under Ar gave the key intermediate dicyano TTF derivative 5 in 13% yield. The IR spectrum of 5 shows the typical C \equiv N stretching vibration at 2216 cm⁻¹, which disappears upon tetramerization to the porphyrazines 7-9. A mixed condensation of 30 equiv. of maleonitrile 6 (A) and 1 equiv. of 5 (B) under classic Linstead macrocyclization conditions (magnesium propoxide/n-propanol) produced two porphyrinic products, the desired mono TTF annulated porphyrazine 7 (A₃B) and octakis (methylthio)phthalocyanine (A₄) (Scheme 1). In general, a crossed cyclization of two different maleonitrile derivatives will result in the generation of all six possible porphyrazine products [43]. However, the present synthetic method limits the formation of mixed condensation products (A2B2, A1B3, B4 and ABAB) other than 7 through the use of a large excess of 2,3-bis(methylthio) maleonitrile. Fortunately, the large polarity differrence between the various products enables relatively easy separation of the desired mono TTF annulated porphyrazine 7. Demetallation of 7 with acetic acid gave the free base porphyrazine 8 in 78% yield as a deep purple powder. Upon action of zinc acetate the 2H porphyrazine 8 was converted to Zn-porphyrazine 9 in 75% yield. The compounds **7–9** are soluble in CHCl₃, CH₂Cl₂, benzene, toluene, THF, DMF, DMSO, AcOH and slightly soluble in MeCN, acetone but insoluble in EtOH, MeOH, AcOEt and alkanes. The MALDI-TOF mass spectra of **7–9** featured peaks at m/z 1234.0170 [M + H]⁺, 1210.1752 and 1273.7125 [M + H]⁺, respectively, corresponding to M⁺ (1232.0720) of 7, M⁺ (1210.1026) of 8 and M⁺ (1272.0161) of **9**, respectively. In the ¹H NMR spectrum of **7**–**9**, the characteristic signals relating to the -CH₂O- protons (3.15-3.80 for 7, 3.40–3.84 for 8, 3.16–3.84 for 9) linked with the TTF skeleton and CH₃S- (2.88 and 3.03 for 7, 3.27 and 3.35 for 8, 2.88 and 3.03 for 9) protons linked with the porphyrazine skeleton gave significant resonances characteristic of the proposed structure. In the ¹H NMR spectrum of 8, the typical shielding of the inner core NH protons was observed as broad signals at $\delta = -4.88$ which could be exchanged with D₂O. Elemental analyses of these compounds were in accord with the proposed molecular formulae.

3.2. Photophysical properties

UV-vis spectra of TTF annulated Pzs **7**–**9** in CH₂Cl₂ are shown in Fig. 1. The electronic absorption spectra of **7** and **9** are very similar to each other and to those reported for other metalloporphyrazine [44]. Both metalloporphyrazine **7** and **9** show an intense and broadened Soret transition $(1a_{2u} \rightarrow 1e_g)$ at 375 and 370 nm, respectively, and an intense broadened Q-band transition $(1a_{1u} \rightarrow 1e_g)$ at 662 and 657 nm, respectively. This broadening obscures the expected "split" of the Q-band, which is normally observed for macrocycles of less than D_{4h} symmetry [15], and is presumably due to overlap of underlying n- π^* transitions that arise from the nonbonding electrons associated with the peripheral S and N atoms. On the other hand the broadening of B-band should be attributed to overlapping with TTF absorption. In general,



Fig. 1. Electronic absorption spectra of 7 (—), 8 (—–) and 9 (- - -) in CH_2Cl_2 $(1\times 10^{-5}~M).$

aggregation processes could also be responsible for the broadening effect. To investigate whether the broadening of the absorption band is due to aggregation or not, the electronic absorption spectra of **7** and **8** at different concentrations were determined in different solvents. The results show that both Q-bands strictly followed the Lambert–Beer law (up to 10 µM), indicating that the broadening of the absorption band arises from the $n-\pi^*$ transitions of heteroatoms. The spectrum of 7 is given as an example (Fig. 2). The electronic absorption spectrum of compound 8 shows a strong near-UV Soret transition at 343 nm, two broadened Q_x and Q_y band transitions at 683 and 617 nm, respectively, and a broad band of lesser intensity centered at 525 nm, which can be assigned to $S(n) \rightarrow \pi^*$ transition [45]. The electronic absorption spectrum of compound 8 is very similar to that reported for other lowsymmetry metallo-free porphyrazine derivatives, where two pyrrole type protons are bonded to the pyrrole ring in the X axial direction [46]. However, the luminescence emission from compounds 7-9 wasn't observed. This quenching is likely to be due to an intermolecular electron transfer interaction between the



Fig. 2. Electronic absorption spectra of 7 at different concentrations in CH_2Cl_2 (1 \times 10⁻⁵ M). The insert plots the Q-band absorbance at 659 nm versus the concentration of 7.

Table 1

Voltammetric data of the target porphyrazines **7–9** in a mixture of CH_2Cl_2 and CH_3CN (4:1, v/v) at 100 mV s⁻¹ scan rate.

Pzs	Ring oxidations $\overline{E_{1/2} (V vs. SCE)^a}$		TTF oxidations $E_{1/2}$ (V vs. SCE) ^a		Ring reductions		ΔE^{b}	
					$E_{1/2}$ (V vs. SCE) ^a			
7	1.25	1.13	0.84	0.44	-0.87	-1.19		1.31
8	1.63 (1.52)	1.29	0.91	0.57	-0.49	-0.98 (-0.77)	-1.76	1.55
9	1.86 (1.54)	1.29	0.84	0.48	-0.83	-1.19 (-1.06)	-1.79	1.33

^a Recorded by differential pulse voltammetry.

^b $\Delta E_{1/2} = \Delta E_{1/2}$ (first oxidation) – $\Delta E_{1/2}$ (first reduction) = HOMO–LUMO gap for metal-free and metallo-porphyrazines having electro-inactive metal.

excited singlet state of the Pz core and TTF unit and the donating effect of six peripheral –SCH₃ groups [47].

3.3. Electron donating properties

The electrochemical characterization of compounds **7–9** was carried out by using cyclic voltammetry in a mixture of CH₂Cl₂-CH₃CN (4:1, v/v). Table 1 lists the assignments of the redox couples, half-wave peak potentials $(E_{1/2})$ and the difference between the first oxidation and reduction processes ($\Delta E_{1/2}$). $\Delta E_{1/2}$ reflects the HOMO-LUMO gap for the target compounds. Fig. 3 shows the cyclic and differential pulse voltammograms of 7 within a -1500 mV to +1500 mV potential window. Compound 7 shows two reduction and three oxidation couples within the potential window of the DCM-ACN/Bu₄PF₆ electrolyte system. The five couples observed were assigned to Pz^{-3}/Pz^{-4} (I), Pz^{-2}/Pz^{-3} (II), $TTF^+ \cdot /TTF$ (III), $TTF^{+2}/TTF^{+} \cdot (IV)$, Pz^{-1}/Pz^{-2} (V) on the basis of results in the literature [35]. Processes I–II and V are irreversible in terms of the ratio of anodic to cathodic peak currents. Processes III-IV, which can be assigned to the simultaneous first and second oxidations of the TTF unit are reversible with an anodic to cathodic peak separation (ΔE) of 0.018 V and 0.042 V, respectively, and the ratio of anodic to cathodic peak currents of near unity. Process V is split into two waves due to electron transfer of aggregated and monomeric species. In fact, the first and second oxidation of the TTF unit occurred 0.230 V and 0.160 V to lower potential than that reported for tetrakis-TTF-annulated porphyrazine [36], which can be attributable to the electron donating effect of six methylthio groups. Metal free Pz 8 shows strong aggregation tendency in



Fig. 3. CV of **7** recorded in CH₂Cl₂–CH₃CN (4:1, V/V, 1×10^{-3} M) at 100 mV s⁻¹ scan rate (inset: DPV of **7** at same condition).



1500 1000 500 // a.u. 0 -500 a=2.0015 -1000 g=2.0073 -1500 332 334 336 338 340 342 330 field / KG

Fig. 6. ESR spectrum of the complex of 7 with F₄TCNQ in CH₂Cl₂.

Fig. 4. CV of 8 recorded in CH_2Cl_2 – CH_3CN (4:1, V/V, 0.85 × 10⁻³ M) at 100 mV s⁻¹ scan rate (inset: DPV of 8 at same condition).

concentrated solution, so the redox processes are complex due to the splitting of original waves, which are also induced by electron transfer of aggregated and monomeric species. Three reduction and four oxidation processes are recorded with the complex **8** at -1.76, -0.98 (-0.77), -0.49, 0.57, 0.91, 1.29 and 1.63 (1.52) V vs. SCE at 100 mVs⁻¹ scan rate respectively. The fourth oxidation and the second reduction couples of the complex are split into two peaks due to aggregation of the species (Fig. 4) [48]. Dilution of the solutions of the complex causes the peak current of the waves assigned to the aggregated species to decrease more than that of the monomeric species, supporting the existence of the aggregation—disaggregation equilibrium (Fig. S3). The redox processes of compound **9** is very similar to **8** with small potential shifts due to the different metal center, which also has an aggregation—disaggregation equilibria in solution (Table 1 and Figs. S5 and S6).

In order to address the donor properties of the target compounds, doping studies were conducted using 7,7,8,8-



Fig. 5. Absorption spectra of 7 in CH_2Cl_2 $(1\times10^{-5}$ M) before and after addition of 1 equiv. F_4TCNQ or 50 equiv. TCNQ.

tetracyanoquinodimethane (TCNQ) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) in CH₂Cl₂. For compound 7 doped with 1 equiv. TCNQ in CH₂Cl₂, no CT band was observed in the 600-1000 nm region. But when 7 was doped with 50 equiv. TCNQ or with 1 equiv. F₄TCNQ, two new absorption band were produced around λ_{max} 748–57 nm and 847-66 nm in the UV-Vis spectrum (Fig. 5, Figs. S7 and S8). These new bands correspond to the SOMO-LUMO transition of the cation radical species of the TTF moieties [49]. The formation of the charge-transfer complex between 7 with F4TCNQ in CH₂Cl₂ was also confirmed by the FT-IR and ESR spectra. The FT-IR spectrum of **7** shows the nitrile stretch of the F₄TCNQ radical anion at 2193 $\rm cm^{-1}$ compared to the neutral state of 2222 $\rm cm^{-1}$. In addition a signal in the electron paramagnetic resonance (ESR) spectrum of the complex was centered around g = 2.007and 2.002 at 25 °C, which is in the region characteristic for both a TTF radical cation [50] and a F₄TCNQ radical anion [51]. These results show that some CT takes place between the TTF unit(s) and F₄TCNQ in solution (Fig. 6).

4. Conclusion

In conclusion, we have developed a synthetic route to synthesis of unsymmetrical porphyrazines annulated with a TTF bearing two tetraethylene glycol units. All complexes show an aggregation tendency in concentrated solution, so some redox couples are split into two waves due to electron transfer of aggregated and monomeric species. The ability of compounds **7**–**9** to function as a donor for F₄TCNQ was established, and the formation of charge–transfer complex between **7** with F₄TCNQ was confirmed by the UV–Vis, FT-IR and ESR spectroscopy. The complexation experiment of target compounds with metal cations and synthesis of the longer chain analogues are in progress.

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Appendix. Supplementary data

(1,3-dithiole-2-thione) intermediates. Chemistry A- European Journal 1997; 3(10):1679–90.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2010.03.022.

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