

# Synthesis, characterization and electrochemistry of the novel metalloporphyrazines annulated with tetrathiafulvalene having pentoxycarbonyl substituents

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**ABSTRACT:** Three novel tetrathiafulvalene-annulated metalloporphyrazines with electron-withdrawing pentoxycarbonyl groups at the periphery were synthesized *via* the cyclotetramerization of dipentyl 6,7-dicyanotetrathiafulvalene-2,3-dicarboxylate in the presence of corresponding metal salts (Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, Cu(OAc)<sub>2</sub>·2H<sub>2</sub>O, and NiCl<sub>2</sub>) and in pentanol. Molecular structures were fully characterized by <sup>1</sup>H NMR, FT-IR, UV-vis, MALDI-TOF mass spectra and elemental analysis. These newly synthesized macrocyclic dyes were sufficiently stable in air during the purification process and also in further experiments. Electron-withdrawing substituents reduced the ability of tetrathiafulvalene groups to form radical cations. Solution electrochemical data showed one reductive and three oxidative processes within a -2000 mV to +2200 mV potential window. The four couples observed were assigned to Pz<sup>-2</sup>/Pz<sup>-3</sup> (I), TTF<sup>•+</sup>/TTF (II), TTF<sup>+2</sup>/TTF<sup>•+</sup> (III) and Pz<sup>-1</sup>/Pz<sup>-2</sup> (IV).

**KEYWORDS:** tetrathiafulvalenedinitrile, metalloporphyrazines, electrochemistry, tetramerization, aggregation.

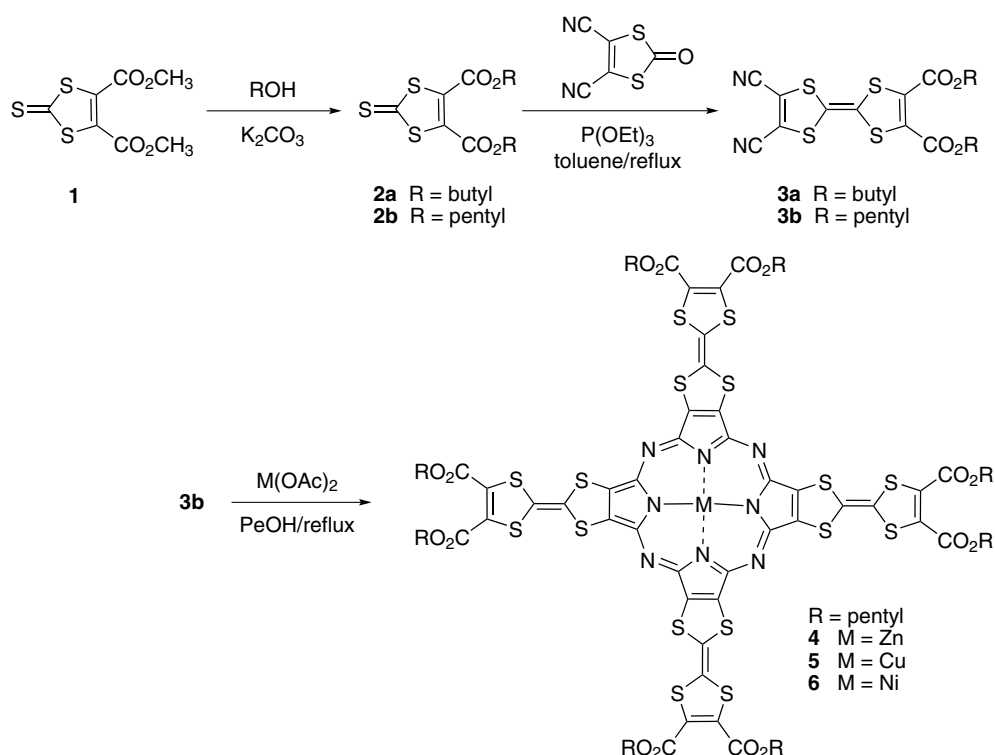
## INTRODUCTION

Porphyrins and phthalocyanines (Pcs) represent a major class of dyes and are applied extensively in biological systems and in material science because of their unique molecular assembly properties and excellent optical and electrical properties [1,2]. A lot of work has been done on the modification of the Pcs and porphyrins so that they may be used for various applications [3–5]. For example, substituted Pcs containing hydrocarbon chains and/or crown ether (CE) units self-assembled into highly organized columnar aggregates are used for one-dimensional charge and ion transport [6].

Various tetrathiafulvalene (TTF)-modified Pcs and porphyrins have been developed since the first report

of a symmetrically-functionalized Pc with eight (TTF) units appeared in 1996 [7–19]. These compounds exhibited interesting optical and electrical properties such as photoinduced electron transfer followed by fluorescence. This behavior results from the combination of Pc or porphyrin units and TTF units into a single molecule. The unique redox properties of TTF is characterized by a sequential and reversible oxidation to a radical cation (TTF<sup>•+</sup>) and a dication (TTF<sup>+2</sup>) [20–22]. Interestingly, a tetra(thiafulvalene-crown-ether) phthalocyanine was found to self-assemble into helical tapes (nanometers in width and micrometers in length) and showed potentially novel electronic and structural properties [23]. Although TTF annulated macrocycles have received less attention, they are believed to be more attractive candidates for various applications than ensembles of TTF and Pcs or porphyrins linked by spacers because they can self-assemble into various organized aggregates [24–29]. Normally, Pcs or porphyrins that are directly annulated

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**Scheme 1.** Synthetic route for tetrathiafulvalene-annulated metalloporphyrazines (**4–6**)

with four TTF units do not show luminescence because of the presence of fused electron-donating TTF units. Their fluorescent forms can, however, be achieved if the TTF units are oxidized using various chemical oxidants or an electrochemical method. Hence they could be regarded as electro-switchable fluorescent molecules. Electro-switched luminescence has been observed in a mono TTF-annulated porphyrin and tetrakis-TTF-Pc molecules [25–26, 30]. The synthesis of tetrakis-TTF-porphyrin resulted in a mixture of the neutral porphyrin and its corresponding radical cation. We have recently also reported the synthesis of novel porphyrazines (Pzs) annulated with four TTF units that also contain electron-donating alkylthio groups. These molecules spontaneously form TTF group radical cations during the separation process [31]. This hindered an accurate assessment of their photophysical and electrochemical properties.

To investigate the effect of peripheral substituents on the stability of TTF annulated Pzs we introduced electron-withdrawing pentoxycarbonyl groups onto TTF annulated Pzs. Three novel TTF-annulated Pz dyes, as shown in Scheme 1, were thus synthesized and we evaluated their photophysical and electrochemical properties.

## EXPERIMENTAL

### General

NMR spectra were recorded in CDCl<sub>3</sub> with a Bruker AV-300 Spectrometer (300 MHz for <sup>1</sup>H and 75 MHz for

<sup>13</sup>C), and chemical shifts were referenced relative to tetramethylsilane ( $\delta_H/\delta_C = 0$ ). The UV-vis spectra were recorded on a Hitachi U-3010 spectrophotometer in CHCl<sub>3</sub> ( $c = 2 \times 10^{-5}$  M). Mass spectrometry was performed on a Hewlett Packard 1100-HPLC/MSD instrument (APCI mode). HRMS data were obtained by a JEOL JMS SX 102A apparatus. MALDI-TOF-MS data were obtained by a Shimadzu AXIMA-CFR<sup>TM</sup> plus mass spectrometry, using a 1,8,9-anthracenetriol (DITH) matrix. Cyclic voltammetry was carried out on a Potentiostat/Galvanostat 273A instrument in CH<sub>3</sub>CN-CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M Bu<sub>4</sub>PF<sub>6</sub> as supporting electrolyte and the scan rate was 100 mV.s<sup>-1</sup>. Counter and working electrodes were made of Pt and Glass-Carbon, respectively, and the reference electrode was calomel electrode (SCE). IR spectra were recorded on a Shimadzu FT-IR 1730 instrument (KBr pressed disc method). Mass spectrometry was performed on a Hewlett Packard 1100-HPLC/MSD instrument. The ESR spectra were recorded using a FA200GEOL spectrometer at 25 °C. Crystal data were measured on a Rigaku SCXmini diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) by  $\omega$  scan mode at 293(2) K.

### Synthesis

All reagents and solvents were of commercial quality and distilled or dried when necessary using standard procedures. All reactions were carried out under argon atmosphere. Starting materials **1** [32], 4,5-dicyano-1,3-dithiol-2-one [33] and **2a** [34] were prepared according to methods described in referenced literature.

**Dipentyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (2b).** A mixture of **1** (1000 mg, 4 mmol) and K<sub>2</sub>CO<sub>3</sub> (100 mg,

0.15 mmol) in 10 mL pentanol was stirred for 72 h at room temperature. Methanol produced was removed uninterruptedly under reduced pressure. The reaction mixture was concentrated in vacuum to yield yellow oil, which was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/P.E. = 1:1, *R<sub>f</sub>* = 0.74) to give pure **2b** as yellow oil. Yield 1160 mg (80.3%). <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 0.94 (3H, s, -CH<sub>2</sub>-CH<sub>3</sub>), 1.37 (4H, s, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.73 (2H, t, *J* = 6.6 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-), 4.30 (2H, t, *J* = 6.6 Hz, -O-CH<sub>2</sub>-). <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>C</sub>, ppm 13.92 (-CH<sub>2</sub>-CH<sub>3</sub>), 22.23 (-CH<sub>2</sub>-CH<sub>3</sub>), 27.87 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 27.96 (-CH<sub>2</sub>-CH<sub>2</sub>-), 67.44 (O-CH<sub>2</sub>-), 138.36 (C=C), 157.56 (C=O), 207.44 (C=S). MS (APCI): *m/z* 362.0448 (calcd. for [M + H]<sup>+</sup> 363.53).

**Dialkyl 2,3-dicyanotetrathiafulvalenes-6,7-dicarboxylate (3a-3b).** According to literature procedure [34], an equimolar mixture of 4,5-dicyano-1,3-dithiol-2-one (2 mmol) and **2** (2 mmol) in 60 mL toluene was added dropwise to a refluxing mixture of 10 mL P(OEt)<sub>3</sub> and 20 mL toluene. The mixture was refluxed for 1 h. After cooling to room temperature, the solvent was removed in vacuum and the red oily residue obtained was chromatographed on a silica gel column (CH<sub>2</sub>Cl<sub>2</sub>/P.E. = 1/1, v/v) to afford dark red solid **3**. Compound **3a**: recrystallization from petroleum ether gave **3a** as dark red needles. Yield 122 mg (13.6%), mp 66–67 °C. Anal. calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>: C, 47.56; H, 3.99; N, 6.16. Found: C, 47.55; H, 3.71; N, 6.00. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 0.96 (3H, t, *J* = 7.2 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.34–1.47 (2H, m, -CH<sub>2</sub>-CH<sub>3</sub>), 1.64–1.73 (2H, m, -CH<sub>2</sub>-CH<sub>2</sub>-), 4.26 (2H, t, *J* = 6.6 Hz, -O-CH<sub>2</sub>-CH<sub>2</sub>-). <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>C</sub>, ppm 13.62 (-CH<sub>2</sub>-CH<sub>3</sub>), 18.99 (-CH<sub>2</sub>-CH<sub>3</sub>), 30.27 (-CH<sub>2</sub>-CH<sub>2</sub>-), 67.07 (COO-CH<sub>2</sub>-CH<sub>2</sub>-), 101.94 (C-CN), 108.85 (NC-C=C-CN), 118.71 (-S-C=C-S-), 121.10 (S-C=C-S-), 131.76 (OOC-C=C-COO-), 158.64 (-C-COO-). IR (KBr pellets): ν<sub>max</sub>, cm<sup>-1</sup> 2959 (C-H), 2870 (C-H), 2216 (C≡N), 1734 (C=O), 1705 (C=O), 1579, 1294, 1252, 1026. MS (APCI): *m/z* 477.0 (calcd. for [M + Na]<sup>+</sup> 477.61). Compound **3b**: recrystallization from petroleum ether gave **3b** as a dark red needles. Yield 214 mg (22.2%), mp 64.7 °C. Anal. calcd. for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>: C, 49.77; H, 4.59; N, 5.80. Found: C, 49.55; H, 4.73; N, 5.57. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 0.92 (3H, t, *J* = 3.0 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.35 (4H, br, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.70 (2H, br, -CH<sub>2</sub>-CH<sub>2</sub>-), 4.25 (2H, t, *J* = 6.6 Hz, -CH<sub>2</sub>-COO-). <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>C</sub>, ppm 13.95 (-CH<sub>2</sub>-CH<sub>3</sub>), 22.23 (-CH<sub>2</sub>-CH<sub>3</sub>), 27.84 (-CH<sub>2</sub>-CH<sub>2</sub>-), 28.81 (-CH<sub>2</sub>-CH<sub>2</sub>-), 67.36 (COO-CH<sub>2</sub>-CH<sub>2</sub>-), 101.97 (C-CN), 108.88 (NC-C=C-CN), 118.72 (-S-C=C-S-), 120.93 (-S-C=C-S-), 131.79 (OOC-C=C-COO-), 158.64 (-C-COO-). IR (KBr pellets): ν<sub>max</sub>, cm<sup>-1</sup> 2954 (C-H), 2860 (C-H), 2210 (C≡N), 1740 (C=O), 1701 (C=O), 1290, 1224. MS (APCI): *m/z* 483.0 (calcd. for [M + H]<sup>+</sup> 483.66).

{**2,3,7,8,12,13,17,18-tetrakis[6,7-bis(alkyl-oxy-carbonyl)tetrathiafulvalene]porphyrazines**} **M(II)** (**M** = **Zn** for **4**, **Cu** for **5** and **Ni** for **6**). A mixture of 97 mg **3b** (0.2 mmol) and the appropriate metal salt (0.1 mmol)

(Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O for **4**, Cu(OAc)<sub>2</sub>·2H<sub>2</sub>O for **5**, anhydrous NiCl<sub>2</sub> for **6**) was heated in 10 mL *n*-pentanol at 145 °C for 4 h. The color of reaction solution changed from dark red to black. The solvent was concentrated in vacuum to give **4** as black powder. The solid obtained was purified on silica gel column chromatography (gradient of CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 1/0 → 50:1, v/v) to give **4**. Compound **4**: reprecipitation from CH<sub>2</sub>Cl<sub>2</sub>-MeOH gave **4** as dark blue powder. Yield 56 mg (56%), mp 260 °C (decomposed). Anal. calcd. for C<sub>80</sub>H<sub>88</sub>N<sub>8</sub>O<sub>16</sub>S<sub>16</sub>Zn: C, 48.14; H, 4.44; N, 5.61. Found: C, 48.32; H, 4.23; N, 5.80. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 0.95 (24H, br, -CH<sub>2</sub>-CH<sub>3</sub>), 1.39 (32H, br, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.68 (16H, br, -CH<sub>2</sub>-CH<sub>2</sub>-), 4.22 (16H, br, -CH<sub>2</sub>-COO-). <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>C</sub>, ppm 13.97 (-CH<sub>2</sub>-CH<sub>3</sub>), 22.39 (-CH<sub>2</sub>-CH<sub>3</sub>), 27.97 (-CH<sub>2</sub>-CH<sub>2</sub>-), 66.66 (COO-CH<sub>2</sub>-CH<sub>2</sub>-), 130–134 (br), 157–160 (br). IR (KBr pellets): ν<sub>max</sub>, cm<sup>-1</sup> 2955–2856 (C-H), 1730 (C=O), 1575, 1462, 1250, 1094. UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub>, nm (log ε) 291 (4.53), 358 (4.52), 605 (4.35). MS (MALDI-TOF): *m/z* 1996.81 (calcd. for [M + H]<sup>+</sup> 1997.05). Compound **5**: reprecipitation from CH<sub>2</sub>Cl<sub>2</sub>-MeOH gave **5** as dark purple powder. Yield 52 mg (52.4%), mp 250 °C (decomposed). Anal. calcd. for C<sub>80</sub>H<sub>88</sub>CuN<sub>8</sub>O<sub>16</sub>S<sub>16</sub>: C, 48.18; H, 4.45; N, 5.62. Found: C, 48.27; H, 4.36; N, 5.54. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 0.92 (24H, br, -CH<sub>2</sub>-CH<sub>3</sub>), 1.35 (32H, br, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.68 (16H, br, -CH<sub>2</sub>-CH<sub>2</sub>-), 4.32 (16H, br, -CH<sub>2</sub>-COO-). <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>C</sub>, ppm 13.92 (-CH<sub>2</sub>-CH<sub>3</sub>), 22.26 (-CH<sub>2</sub>-CH<sub>3</sub>), 27.88 (-CH<sub>2</sub>-CH<sub>2</sub>-), 28.07 (-CH<sub>2</sub>-CH<sub>2</sub>-), 66.73 (COO-CH<sub>2</sub>-CH<sub>2</sub>-), 130–133 (br), 157–160 (br). IR (KBr pellets): ν<sub>max</sub>, cm<sup>-1</sup> 2955–2862 (C-H), 1726 (C=O), 1576, 1460, 1246, 1088. UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub>, nm (log ε) 290 (4.78), 317 (4.76), 567 (4.33), 601 (4.31). MS (MALDI-TOF): *m/z* 1994.44 (calcd. for [M + H]<sup>+</sup> 1995.18). Compound **6**: reprecipitation from CH<sub>2</sub>Cl<sub>2</sub>-MeOH gave **6** as dark purple powder. Yield 24.5 mg (24.6%), mp 250 °C (decomposed). Anal. calcd. for C<sub>80</sub>H<sub>88</sub>N<sub>8</sub>NiO<sub>16</sub>S<sub>16</sub>: C, 48.30; H, 4.46; N, 5.63. Found: C, 48.19; H, 4.45; N, 5.44. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 1.05 (24H, br, -CH<sub>2</sub>-CH<sub>3</sub>), 1.48 (32H, br, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.80 (16H, br, -CH<sub>2</sub>-CH<sub>2</sub>-), 4.25 (16H, br, -CH<sub>2</sub>-COO-). <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>C</sub>, ppm 14.13 (-CH<sub>2</sub>-CH<sub>3</sub>), 22.47 (-CH<sub>2</sub>-CH<sub>3</sub>), 28.08 (-CH<sub>2</sub>-CH<sub>2</sub>-), 29.69 (-CH<sub>2</sub>-CH<sub>2</sub>-), 66.56 (COO-CH<sub>2</sub>-CH<sub>2</sub>-). IR (KBr pellets): ν<sub>max</sub>, cm<sup>-1</sup> 2955–2862 (C-H), 1730 (C=O), 1578, 1642, 1230, 1113. UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub>, nm (log ε) 291 (4.78), 325 (4.79), 557 (4.55), 593 (4.40). MS (MALDI-TOF): *m/z* 1988.49 (calcd. for [M + H]<sup>+</sup> 1989.48).

## RESULTS AND DISCUSSION

### Synthesis and characterization

The synthesis of target compounds **4–6** is shown in Scheme 1. The first step in the synthetic procedure is the

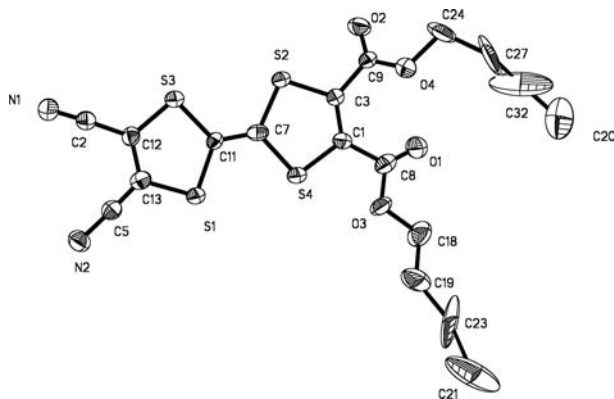


Fig. 1. ORTEP plot of the molecule of **3a**

synthesis of dicyanotetrathiafulvalene **3** that contains electron-withdrawing ester groups. The cross-coupling reaction of 4,5-dicyano-1,3-dithiol-2-one and dialkyl 1,3-dithiol-2-thione-4,5-dicarboxylate (**2a–b**) in a mixture of triethyl phosphite and toluene at reflux and under argon leads to key intermediates 2,3-dicyano-6,7-bis-(pentoxycarbonyl) TTF (**3a–b**) in 14% and 22% yields, respectively.

Red crystals that were suitable for X-ray diffraction analysis of intermediate **3a** was obtained by the slow evaporation of a petroleum ether (30–60 °C) solution of **3a** at room temperature. Compound **3a** crystallizes in a monoclinic space group ( $P2_1/c$ ) and the 1,3-dithiole-4,5-dicarbonitrile unit is almost coplanar with the ester substituent dithiole ring [dihedral angle =  $2.9(2)^\circ$ ] (Fig. 1). In the crystal structure, intermolecular  $S\cdots O$  interactions [ $S3\cdots O2 = 3.013 \text{ \AA}$ ] create dimers between neighboring molecules in the  $ac$  plane. In addition, a weak  $\pi\cdots\pi$  stacking interaction exists between adjacent dithiole rings, with centroid-centroid distances of  $4.075 \text{ \AA}$ , and chains formed along the  $b$  axis (Figs S1–S2, see Supporting information section).

Using the building block **3b**, we synthesized TTF annulated metallo-Pzs (**4–6**) by a metal templated tetramerization in 1-pentanol and obtained yields of 56% for Zn-TTF-Pz **4**, 52% for Cu-TTF-Pz **5** and 15% for Ni-TTF-Pz **6**, respectively. As expected, the TTF annulated Pz dyes were sufficiently stable for purification and for further experiments. The compounds are soluble in common organic solvents such as hexane, benzene, toluene,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , DMF, acetone and THF. The compounds are insoluble in alcohols and DMSO. We were unable to demetallate the metallo-Pzs **4–6** using acidic reaction conditions because the ester groups decomposed [35].

$^1\text{H}$  NMR spectra of **4–6** in  $\text{CDCl}_3$  displayed four very broad signals which could be explained by considering that slow tumbling results from aggregation in concentrated solutions (Fig. S2) [24, 33]. The MALDI-TOF mass spectra of **4–6** showed peaks at  $m/z = 1996.81$  ( $M^+ = 1996.05$ ) for **4**,  $1994.44$  ( $M^+ = 1994.18$ ) for **5** (Fig. S3) and  $1988.49$  ( $M^+ = 1988.48$ ) for **6**. Results from elemental analysis confirmed the proposed structures of compounds **4–6**.

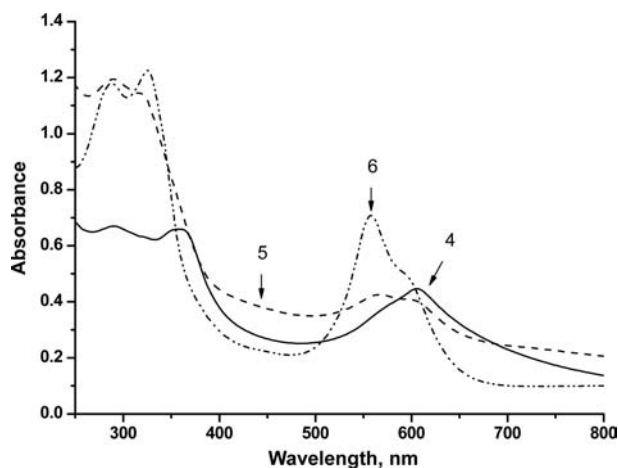
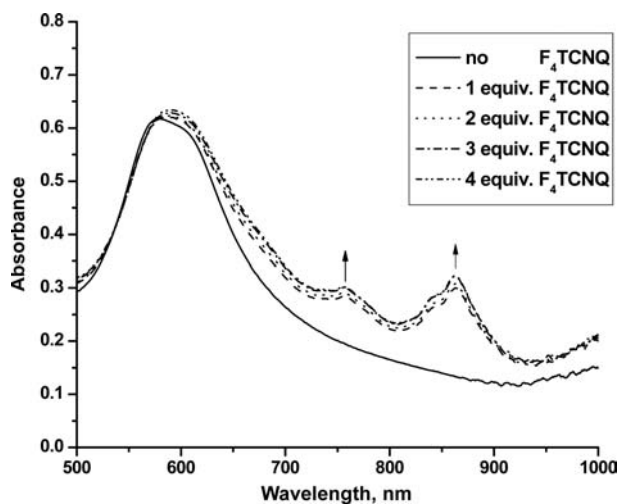


Fig. 2. Absorption spectra of **4–6** in  $\text{CHCl}_3$  ( $2 \times 10^{-5} \text{ M}$ )

### Photophysical properties

UV-vis spectra of TTF annulated Pzs **4–6** in  $\text{CH}_2\text{Cl}_2$  are shown in Fig. 2. Compounds **4–6** show typical Pz electronic spectra, consisting of two strong absorption regions. Broadening of the Q and B bands is attributed to  $n\text{-}\pi^*$  transitions of non-bonding electrons, that are associated with peripheral S and N atoms [36], and also attributed to aggregation of the macrocyclic system. The B band (or Soret band) of metallo-Pz rings in the ultraviolet region for compound **4** arises from deep  $\pi$  LUMO transitions (between  $a_{2u}$  and  $e_g$  orbitals). TTF absorption in this region thus leads to superimposed bands. In the visible region, **4** had an intense Q band at 605 nm with a shoulder at around 574 nm and this corresponds to monomeric and aggregated Pz in chloroform, respectively. The indistinct shoulder band at about 574 nm, arising from the dimer, is attributed to a  $\pi \rightarrow \pi^*$  transition from the HOMO to the LUMO of the Pz $^{2-}$  ring. For **5** the Q band of the dimer at higher energy was centered at 566 nm and the Q band arising from the monomer was at a lower energy and centered at 601 nm as a weak shoulder band. The absorption bands of **6** are similar to those of **5** except that the sharper component of the Q band at higher energy is less intense in **5** and the monomer shoulder band is stronger in **5**. This indicates that there is a higher degree of face-to-face interaction in **6** compared with the interactions in **4** and **5** and this is typical of metallated symmetrically substituted Pzs with  $D_{4h}$  symmetry [37].

In order to address the donor properties of target compounds, **4** was selected and doped with TCNQ in  $\text{CH}_2\text{Cl}_2$ . However no CT band was observed at 600–1000 nm region. This might be attributed to the presence of eight strongly electron-withdrawing pentoxycarbonyl groups onto TTF annulated Pzs. Whereas, doping of  $\text{F}_4\text{TCNQ}$  to a  $\text{CH}_2\text{Cl}_2$  solution of **4** ( $2 \times 10^{-5} \text{ M}$ ) resulted in the appearance of two new CT absorption bands, centered on  $\lambda_{\text{max}} = 756 \text{ nm}$  and  $\lambda_{\text{max}} = 863 \text{ nm}$  in the UV-vis spectrum (Fig. 3). These new bands corresponds to the SOMO-LUMO transition of the cation radical species of the TTF moieties [23]. The formation of  $\text{F}_4\text{TCNQ}^\bullet/\text{TTF}^{+\bullet}$  charge-transfer



**Fig. 3.** Absorption spectra of **4** ( $2 \times 10^{-5}$  M) in the  $\text{CH}_2\text{Cl}_2$  after addition of different equiv.  $\text{F}_4\text{TCNQ}$

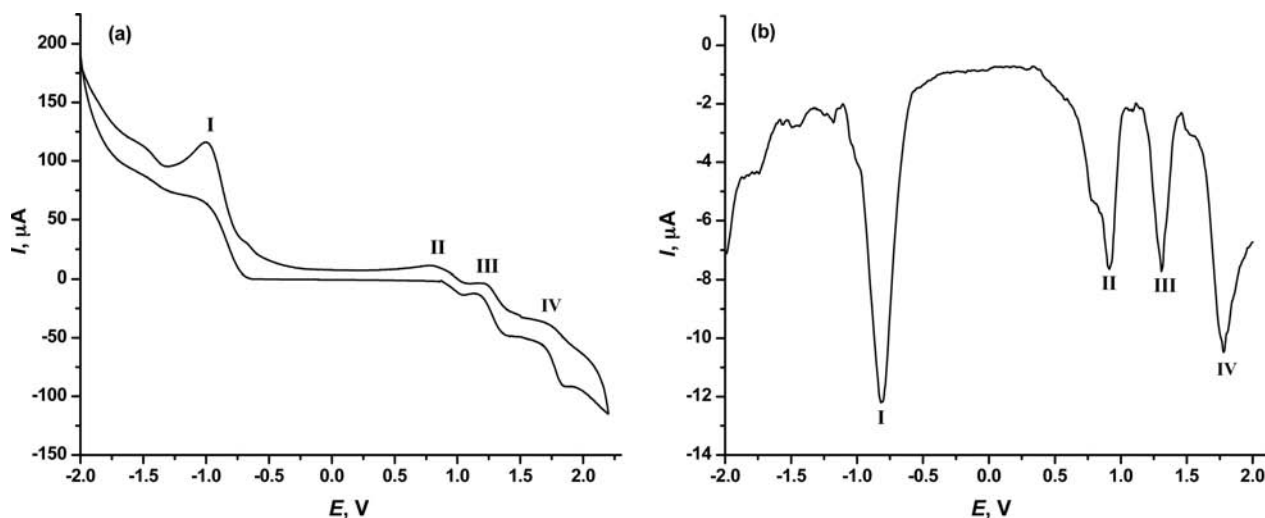
complex in the mixture  $\text{F}_4\text{TCNQ-4}$  (4:1) in  $\text{CH}_2\text{Cl}_2$  was also confirmed by the FT-IR and ESR spectra. A FT-IR spectrum showed the nitrile stretch of the  $\text{F}_4\text{TCNQ}$  radical anion at  $2212\text{ cm}^{-1}$  [38] compared to the neutral state of  $2222\text{ cm}^{-1}$ . In addition, an electron paramagnetic resonance (ESR) spectrum of **4** was centered around

$g = 2.007$  and  $2.002$ , which are in the region characteristic of both a TTF radical cation [39] and a  $\text{F}_4\text{TCNQ}$  radical anion [38]. These results show that in solution some CT takes place between the TTF unit(s) and  $\text{F}_4\text{TCNQ}$  (Fig. S4).

Cyclic voltammetric (CV) studies were performed on compounds **4–6** and their intermediates **3a–b** in a mixture of  $\text{CH}_3\text{CN-CH}_2\text{Cl}_2$ . The data are collected in Table 1. As seen in Table 1, the cyclic voltammograms of **3a–b** reveal that all redox processes are quasi-reversible. Each oxidation wave of the precursor compounds **3a** and **3b** is assigned to a one-electron process. By comparison to tetrathiafulvalene [40], both oxidation peaks were shifted significantly to higher oxidation potentials (1.034 and 1.275 V for **3a** and 1.035 and 1.278 V for **3b**, respectively) because of the electron-withdrawing effect of the cyano and alkoxy carbonyl groups. For the electrochemical characterization of compounds **4–6**, the cyclic voltammograms were indistinct because of aggregation in solution. This behavior has previously been reported in the literature [26, 41]. Differential pulse voltammetry (DPV) provided more detailed information. Figure 4 shows cyclic (a) and differential pulse voltammograms (b) of **4** within a  $-2000\text{ mV}$  to  $+2200\text{ mV}$  potential window. Compound **4** shows redox processes

**Table 1.** Cyclic voltammetric data for M-TTF-Pzs **4–6** and intermediates **3a–b** in a mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  (4:1, v/v)

Compound	$E^1_{1/2}(\Delta E)/\text{V}$	$E^2_{1/2}(\Delta E)/\text{V}$	$E^3_{1/2}(\Delta E)/\text{V}$	$E^4_{\text{pd}}/\text{V}$
TTF <sup>[40]</sup>		0.36	0.77	
<b>3a</b>		1.034 (0.073)	1.275 (0.089)	
<b>3b</b>		1.035 (0.077)	1.278 (0.087)	
<b>4</b>	-0.813 (0.273)	0.914 (0.088)	1.308 (0.150)	1.786
<b>5</b>	-0.802 (0.283)	0.972 (0.106)	1.304 (0.137)	1.784
<b>6</b>	-0.836 (0.283)	0.998 (0.102)	1.313 (0.106)	1.784



**Fig. 4.** Cyclic (a) and differential pulse voltammogram (b) of compound **4** in  $\text{CH}_3\text{CN-CH}_2\text{Cl}_2$  (1:4, v/v) containing  $0.1\text{ M Bu}_4\text{PF}_6$ . Scan rate was  $100\text{ mV}\cdot\text{s}^{-1}$

at  $E_{1/2} = -0.813$  (I),  $0.914$  V (II),  $1.308$  V (III) and  $1.786$  V (IV) vs the SCE and all processes are not completely reversible in terms of  $\Delta E$ , the shift of  $E_p$  at different scanning rates and the ratio of anodic to cathodic peak currents ( $i_{pa}/i_{pc}$ ) [42]. Process I which is assigned to a reduction of the porphyrazine ring system ( $Pz^2/Pz^3$ ) is irreversible because of the excessive anodic to cathodic peak separation ( $\Delta E > 200$  mV) and the difference of anodic to cathodic peak currents. Processes II and III are quasi-reversible because the anodic to cathodic peak currents are near unity while  $\Delta E$  for II and III are 88 mV and 150 mV, respectively. These processes represent the two four-electron oxidation processes of the TTF moieties. Interestingly, **4** shows similar behavior to its phthalocyanine analog [25] with negative shifts in oxidation potentials for the radical cations of TTF (0.12 V). The splitting of the first oxidation wave (process II) arises from the molecular system where the donor moieties interact through conjugation and/or through space. On the other hand, compound **4** is distinct from its phthalocyanine analogs and an irreversible one-electron wave is observed at  $1.786$  V (IV), which is assigned to oxidation of the Pz ring system ( $Pz^1/Pz^2$ ). The redox processes of compounds **5** and **6** are similar to **4** except that their first oxidation waves are not split.

In summary, we developed an efficient synthetic route to the novel porphyrazines that are annulated with tetrathiafulvalene having pentoxycarbonyl substituents. Efficient modulation of macrocycle stability was achieved by the introduction of electron-withdrawing pentoxycarbonyls. Ability of **4** to function as a donor for  $F_4TCNQ$  was established and the formation of TTF $^+$ / $F_4TCNQ^-$  charge-transfer complex was confirmed by the UV-vis, FT-IR and ESR spectral. Compounds **5** and **6** showed similar cyclic voltammetric behavior with one reduction process and three oxidation processes. These were assigned to  $Pz^2/Pz^3$  (I), TTF $^{+*}/TTF$  (II), TTF $^{2+}/TTF^{+*}$  (III) and  $Pz^1/Pz^2$  (IV). The synthesis, self-assembly and film forming properties of TTF-annulated Pzs with longer alkyls and containing oxyethylenes are under investigation.

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### Supporting information

Crystal data and structure of **3a**,  $^1H$ NMR and MALDI-TOF-MS spectra of **5**, and ESR spectrum of **4** (Figs S1–S4, Table S1) are given in the supplementary

material. This material is available free of charge via the Internet at <http://www.worldscinet.com/jpp/jpp.shtml>.

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