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SYNTHESIS, PHOTOPHYSICAL AND ELECTROCHEMICAL PROPERTIES OF A D-σ-A ENSEMBLE DERIVED FROM PORPHYRAZINE AND TETRATHIAFULVALENE

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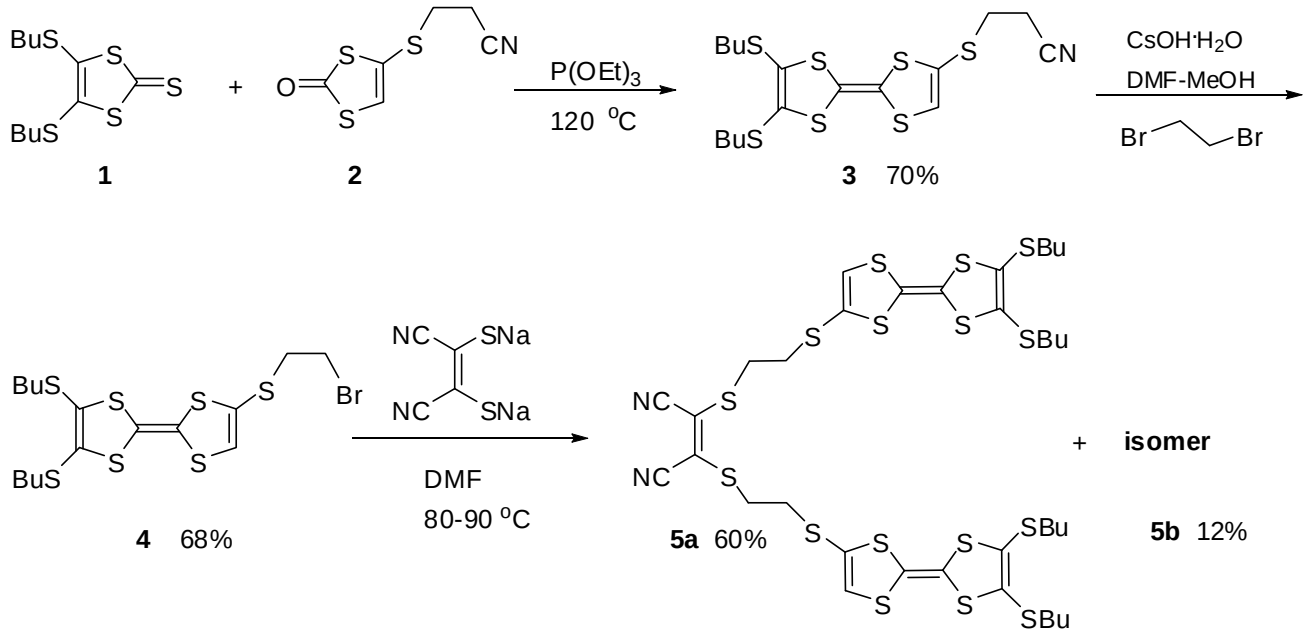
Abstract – Cis/trans 1,2-dicyanoethylenes bearing tetrathiafulvalene units linked by a ethylenedithio spacer were prepared. The cis isomer was converted to eight tetrathiafulvalene unit substituted magnesium porphyrazine upon a metal-templated cyclotetramerization with magnesium propoxide in propanol. The dicyanoethylenes and target compound were characterized by EA, NMR, and MALDI-TOF mass and photophysical and Electrochemical properties were discussed.

Construction of ensembles composed of covalently linked electron donor and acceptor moieties is currently a challenge in the field of supramolecular chemistry and material science. Typical examples of this type of ensemble are the polyads derived from tetrathiafulvalene (TTF) drivatives and macrocyclic tetrapyrroles (phthalocyanine, porphyrin, and porphyrazine). The investigations of the electronic interaction in such system are very useful in understanding electron transfer of D-σ-linker-A molecules (D-σ-A). In the previous studies, the phthalocyanine (Pc) and porphyrin derivatives substituted with one, two, four, or eight TTF units and directly annulated with one or four TTF units at peripheral position have been prepared and their electron transfer behaviors were investigated.[1-3] In most cases, it has been demonstrated that the fluorescence from Pcs or porphyrins are efficiently quenched by the TTF unit regardless of its covalently substituted or directly annulated forms as a consequence of inter- or intramolecular electron transfer between the macrocycle and TTF. Similarly, silicon Pcs-TTF hybrids show weaker luminescence due to quenching of the Pc emission by electron transfer from the axially linked TTF groups.[4] On this account, they could be regarded as electro-switched fluorescent molecules because their fluorescent form can be achieved easily through the oxidation of TTF using various chemical oxidants or an electrochemical method. However, in the case of tetrakis-TTF-annulated

porphyrin, the synthesis resulted in a mixture of the neutral porphyrin and its corresponding radical cation.[5] Recently, we have also reported the novel porphyrazines (Pzs) annulated with four TTF units having electron-donating butylthio groups.[6] But, they spontaneously generated the corresponding radical cation of TTF groups during separation process. This electron transfer process hindered us to assess accurately its photophysical and electrochemical properties.

In order to stabilize the system, we incorporated the porphyrazine ring with TTF units by a ethylenedithio linker to synthesize a D-σ-A polyad derived from a porphyrazine and eight peripheral TTF units and studied their photophysical and electrochemical properties.

The cross-coupling reaction of **1** and **2** in the triethyl phosphite at 120 °C under Ar gave 6,7-dibutylthio-2-(2-cyanoethylthio) tetrathiafulvalene **3** in good yield as a red solid. Compound **3** was deprotected by treatment with cesium hydroxide in a mixture of DMF and MeOH and the derived thiolate ion was reacted with excess 1,2-dibromoethane to yield compound **4** which was subsequently converted into key intermediates cis/trans isomeric 1,2-dicyanoethylenes **5a** and **5b** bearing tetrathiafulvalene units linked by a ethylenedithio spacer by reaction with disodium maleonitrile 2,3-dithiolate in DMF (Scheme 1).

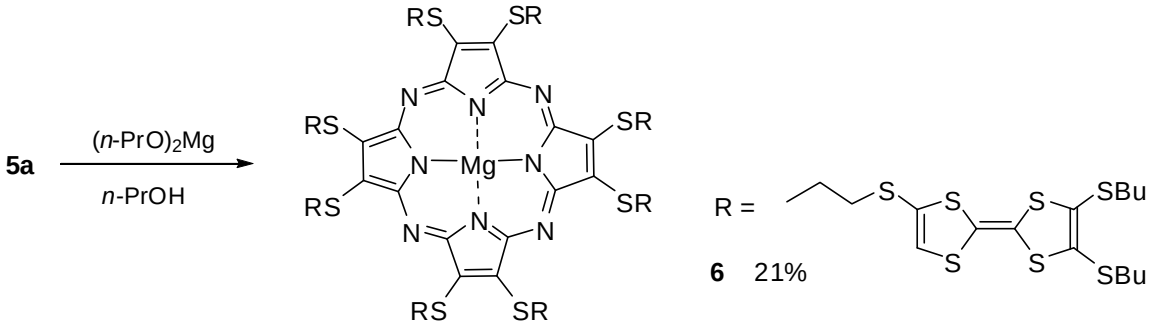


Scheme 1

The MALDI-TOF mass spectra of **5a** and **5b** showed peaks at m/z 1017.9030 (M^+) and 1018.9048 (M^+ + 1), respecvely, corresponding to M^+ (1017.9192) of **5a** and **5b**. The IR spectrum of **5a** (a red oil) shows the C≡N stretching vibration at 2205 cm^{-1}, while the stretching vibration of **5b** (a deep grey solid) appered at 2230 cm^{-1}. In the ^1H NMR spectra measured in $CDCl_3$, the peaks of -SCH_2- of **5a** and **5b**, which is closed to cyano group, appeared at 3.36 ppm and 3.34 ppm, respectively. In view of the facts mentioned

above, **5a** and **5b** could be assigned as *cis* isomer and trans isomer, respectively. This results are similar to the 2,3-dimethylthiofumaronitrile and 2,3-dimethylmaleonitrile.[7]

Target compound **6** was prepared by a magnesium templated macrocyclization of **5a** in propanol in 21% yield (Scheme 2). As expected, compound **6** was sufficiently stable for purification and for further



Scheme 2

experiments, and which was soluble in the usual organic solvents except for alcohols solvents. The ^{1}H NMR spectrum of **6** recorded in $CDCl_3$ at 25 °C showed only the broadened signals, which could be explained by considering that slow tumbling results from aggregation in concentrated solutions.[5] In contrast, compound **6** showed clearer signals for the butylthio groups when the spectrum was measured at 50 °C.[3d] The UV-vis spectrum of **6** in a mixture of $CHCl_3$ and MeCN showed one very broadened Q-band at 678 nm (ε = 58000) In the ultraviolet region, the B-band (or Soret band) of the Mg-Pz ring leads to superimposed bands with the absorption of TTF.[1a] Broadening of the Q- and B-bands should be attributed to n→π* transitions of nonbonding electrons of peripheral S and N atoms and overlapping of B-band.[8] To investigate the ability of compound **6** as an electron donor, the doping experiment was conducted using excess 7,7,8,8-tetra-cyanoquinodimethane (TCNQ) in a mixture of $CHCl_3$ and MeCN. This doping mixture produced two new absorption bands at 747 nm and 847 nm which corresponds to the SOMO–LUMO transition of the cation radical species of the TTF moieties (Figure 1a).[2,9] The MALDI-TOF MS of **6** observed at *m*/*z* = 4101.6263 supports proposed formula for this structure. The elemental analysis conforms desired compond **6**.

The electrochemical characterization of compounds **5a-b** and **6** were carried out by using cyclic voltammetry in $CHCl_3$ (Figure 1b). The cyclic voltammogram of **5a** shows two quasi-reversible redox wave at $E^1_{1/2}$ = 0.744 V and $E^2_{1/2}$ = 1.142 V. Compound **5b** was much alike to the case of **5a**. This confirmed further that **5a** and **5b** are the cis/trans isomers. Compund **6** shows oxidation processes at E_{pa} = -0.693 V (I), +0.563 V (II), + 0.938 V and +1.218 versus SCE. The four couples observed were assigned to Pz^{-2}/Pz^{-3} (I), $TTF^{+\bullet}$/TTF (II), TTF^{+2}/ $TTF^{+\bullet}$ (III) and Pz^{-1}/Pz^{-2} (IV).[10] Processes I and IV are

irreversible in term of the ratio of anodic to cathodic peak currents. Processes II and III are quasi-reversible because the anodic to cathodic peak currents are near unity even though that ΔE values

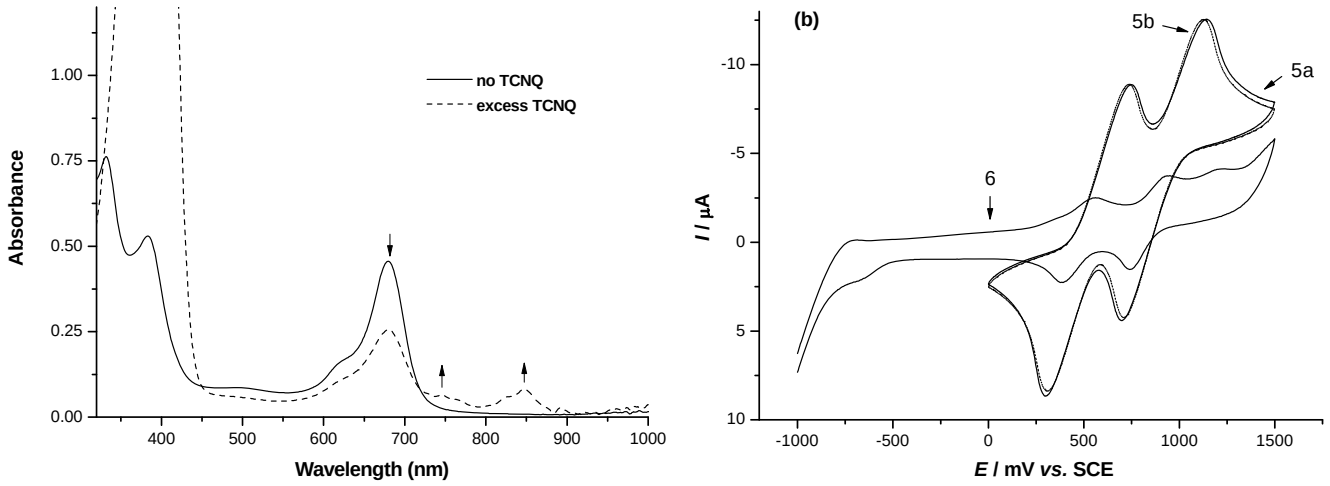


Figure 1. (a) UV-vis spectra of **6** in a mixture $CHCl_3$-MeCN (3:1, v/v) at 20 °C no TCNQ (solid line) and addition of excess TCNQ (dotted line); (b) Cyclic voltammograms of **5a**, **5b** and **6**, in 0.1 M tetrabutylammonium hexafluorophosphate in $CHCl_3$ at 0.1 V s^{-1}, Pt electrode.

for II (ΔE = 0.194 V) and III (ΔE = 0.194 V) were greatly beyond the 0.060 V scope. It is apparent that the TTF unit of compound **6** was easier to oxidize than the precursor **5a** due to the disappearance of the electron-withdrawing cyano groups.

In summary, we first synthesized a D-σ-A polyad derived from a porphyrazine and eight peripheral TTF units. Synthesis of the dicyanoethylenes resulted in the mixture of the cis/trans isomers. The cis isomer converted to target compond **6** upon macrocyclization. As expected, compound **6** was sufficiently stable for purification and for further experiments. Doping of **6** with TCNQ in the mixture of $CHCl_3$ and MeCN (3:1, v/v) resulted in the appearance of two new CT absorption bands centered at λ_{max} = 747 and 847 nm in the absorption spectrum. The demetallization and metal-exchanging of compound **6** are under investigation.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded with a Bruker AV-300 spectrometer, and chemical shifts were referenced relative to tetramethylsilane. The UV-vis spectra were taken on a Hitachi U-3010 spectrophotometer. The mass spectral data were obtained by a Hewlett Pachard 1100-HPLC/MSD instrument. MALDI-TOF-MS data were obtained by a Shimadzu AXIMA-CFR^{TM} *plus* spectrometer, using a 1,8,9-anthracenetriol (DITH) matrix. Cyclic voltammetry was carried out on a Potentiostat/Galvanostat 273A instrucment employing 0.1M Bu_4NPF_6 as the supporting electrolyte in chloroform, with sweep speed of 100 mv/s. Counter and working electrdes were made of platinum and

Glass-Carbon (GCE, 4.00 mm diameter), respectively, and the reference electrode was calomel electrode (SCE). Starting materials **1** and **2** were prepared according to reference.[11]

6,7-Bis(buthylthio)-2-(2-cyanoethyl)thiotetrathiafulvalene (3): A suspension of compound **1** (252 mg, 0.8 mmol) and **2** (82 mg, 0.4mmol) in freshly distilled $P(OEt)_3$ (5 mL) under Ar was stirred at 120 °C for 3 h and then the reaction mixture cooled to rt. The $P(OEt)_3$ was removed in vacuum and the reside was purified by column chromatography on silica gel with CH_2Cl_2 and pet. ether (1:1, v/v) as an eluent to afford a red solid. The solid was recrystallized from MeCN-EtOH to gave **3** as orange needles; yield 131 mg (70.1 %); mp 42-44 °C. ^{1}H NMR ($CDCl_3$): δ 0.93 (t, *J* = 7.2 Hz, 6H), 1.38-1.53 (m, 4H), 1.59-1.67 (m, 4H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.83 (t, *J* = 7.2 Hz, 4H), 3.00 (t, *J* = 7.2 Hz, 2H), 6.56 (s, 1H); MS (APCI) *m/z* (%) = 466 (M^+ + 1, 100). Anal. Calcd for $C_{17}H_{23}NS_7$: C, 43.83; H, 4.98; N, 3,01. Found: C, 43.90; H, 4.89; N, 3,12.

2-(2-Bromoethylthio)-6,7-bis(buthylthio)tetrathiafulvalene (4): To a solution of **3** (165 mg, 0.35 mmol) in dry DMF (25 mL) was added a solution of CsOH • H_2O (118 mg, 0.7 mmol) in anhydrous MeOH (5 mL) over a period of 45 min. The mixture was stirred for an additional 30 min and 1,2-dibromoethane (658 mg, 3.5 mmol) was injected to the mixture in 45 min. The solution was stirred overnight. After seperation by column chromatography on silica gel with CH_2Cl_2/pet. ether (60-90 °C) (1:3, v/v) as eluant, **4** was obtained as an orange solid; yield 124 mg (68 %); mp 37-38 °C. ^{1}H NMR ($CDCl_3$): δ 0.93 (t, *J* =7.3, 6H), 1.42-1.50 (m, 4H), 1.62-1.67 (m, 4H), 2.83 (m, 4H), 3.12 (t, *J* = 7.7Hz, 2H), 3.49-3.55 (t, *J* = 7.7Hz, 2H), 6.47 (s, 1H); MS (APCI), m/z (%) = 520 (M^+ + 1, 100); Anal. Calcd for $C_{16}H_{23}BrS_7$: C, 36.98; H, 4.46. Found: C, 37.11; H, 4.49.

1,2-Bis[6,7-bis(buthythio)tetrathiafulvalen-2-ylthioethylthio]-1,2-dicyanoethenes (5a and 5b): A solution of **4** (1.56 g, 3.0 mmol) and disodium maleonitrile 2,3-dithiolate (279 mg, 1.5 mmol) in anhydrous degassed DMF (15 mL) were stirred at 90 °C for overnight under Ar. The solvent was removed in vacuum. MeOH (15 mL) was added to the reaction mixture and the precipitate resulted was collected by suction, and then recrystallized from CH_2Cl_2 to give trans isomer **5b** as deep grey powder; yield 184 mg (12%); mp 53-54 °C. ^{1}H NMR ($CDCl_3$): δ 0.93 (t, *J* = 7.11 Hz, 12H), 1.42-1.50 (m, 8H), 1.62-1.67 (m, 8H), 2.80-2.86 (m, 8H), 3.03(t, *J* = 7.7 Hz, 4H), 3.34 (t, *J* = 7.7 Hz, 4H), 6.54 (s, 2H); MALDI-TOF MS *m/z* (%) = 1017.9030 (M^+ + 1, 100). UV ($CHCl_3$) λ_{max}: 331 (ε = 166000), 373 (e = 105000); IR (KBr) 2230 cm^{-1} ; Anal. Calcd for $C_{36}H_{46}N_2S_{16}$: C, 42.40; H, 4.55; N, 2.75. Found: C, 42.15; H, 4.59; N, 2.88. The filtrate was concentrated in vacuum and the residue was purified by column chromatography on silica gel with CH_2Cl_2/pet. ether (60-90 °C) (1:1, v/v) to give cis isomer **5a** as reddish brown oil; yield 923 mg (60 %). ^{1}H NMR ($CDCl_3$): δ 0.92(t, *J* = 7.2 Hz, 12H), 1.42-1.50 (m, 8H), 1.62-1.67 (m, 8H), 2.79-2.84 (m, 8H), 3.04 (t, *J* = 7.7 Hz, 4H), 3.36 (t, *J* = 7.7 Hz, 4H), 6.52 (s, 2H); MALDI-TOF MS *m/z* (%) = 1017.9048 (M^+, 100); UV ($CHCl_3$) λ_{max}: 331 (ε = 194000); IR (KBr):

2204.64 cm^{-1}; Anal. Calcd for $C_{36}H_{46}N_2S_{16}$: C, 42.40; H, 4.55; N, 2.75. Found: C, 42.07; H, 4.30; N, 2.66.

{2,3,7,8,12,13,17,18,-Octakis[6,7-bis(butylthio)tetrafulvalen-2-ylthioethylthio]porphyrazino}-magnesium (II) (6)

Magnesium (12 mg, 0.5 mmol) metal was dissolved in anhydrous *n*-PrOH at reflux under Ar. To this magnesium propoxide solution was added the compound **5a** (71 mg, 0.07 mmol) and the mixture was refluxed for 12 h under Ar. The solution color changed from purplish red to deep green. The blue mixture was cooled to rt. The dark precipitate was collected by suction and washed with large amounts of $CHCl_3$, The dark grren solid was purified by chromatography on silica gel with CH_2Cl_2/EtOAc (200:1, v/v) to give **6** as dark green solid; yield 15.1mg (21 %); Reprecipitation of **6** from CH_2Cl_2-MeOH gave a dark green powder; mp > 250 °C (decomp). ^{1}H- NMR ($CDCl_3$), δ: 0.89-0.94 (m, 48H), 1.38-1.51 (m, 32H), 1.51-1.70 (m, 32H), 2.65-2.85 (m, 32H), 3.39 (br, 32H), 4.29 (br, 32H), 6.39 (br, 8H); UV-vis ($CHCl_3$) λmax: 678 (ε = 57600), 621(sh, ε = 21500), 382 (ε =66400), 331 (ε = 95400); MALDI-TOF MS *m/z* (%) = 4101.6263 (M^+ + 1, 100), Calcd for $C_{144}H_{184}MgN_8S_{64}$: 4100.6569; Anal. Calcd for $C_{144}H_{184}MgN_8S_{64}$: C, 42.22; H, 4.52; N, 2.73. Found: C, 42.55; H, 4.40; N, 2.60.

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