

Supplementary Materials: Synthesis and Characterization of Ethylenedithio-MPTTF-PTM Radical Dyad as a Potential Neutral Radical Conductor

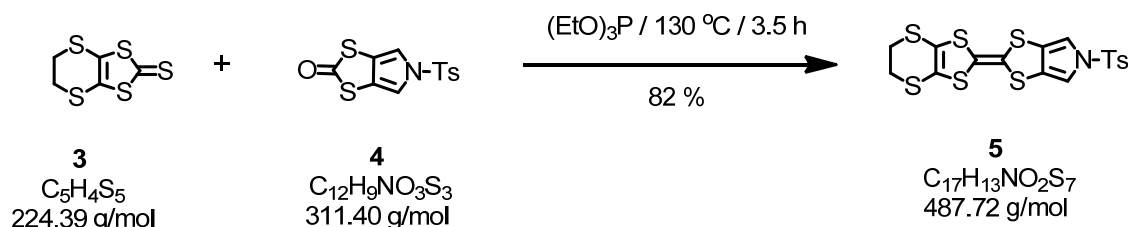
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1. General Methods for Synthesis and Characterization

All reagents and solvents employed for the syntheses were of high purity grade and were purchased from Sigma-Aldrich Co. (Saint Louis, MO, USA) and Merck (Darmstadt, Germany). Dry solvents were used in the chemical reactions and in the cyclic voltammeteries. $^1\text{H-NMR}$ spectra were recorded using a Bruker Avance 250, 400, or 500 instruments and Me_4Si as an internal standard. Infrared spectra were recorded with Spectrum One FT-IR Spectroscopy instrument and UV/Vis/NIR spectra were measured using Cary 5000E Varian. ESR spectra were performed with a Bruker ESP 300 E equipped with a rectangular cavity T102 that works with an X-band (9.5 GHz). The solutions were degassed by argon bubbling before the measurements. LDI/TOF MS were recorded in a Bruker Ultraflex LDI-TOF spectrometer. Cyclic voltammetry measurements were obtained with a potentiostat 263a from EG & G Princeton Applied Research in a standard 3 electrodes cell. The IR-NIR spectra have been collected with a Bruker FT-IR IFS-66 spectrometer equipped with a Hyperion microscope. The spectral resolution is about 2 cm^{-1} for both spectrometers. The manipulation of the radicals in solution was performed under red light.

2. Synthesis and Characterization

2.1. Synthesis of 5



Anhydrous $(\text{EtO})_3\text{P}$ (40 mL) was heated to $130\text{ }^\circ\text{C}$ before the thione **3** (1.10 g, 4.90 mmol) and the ketone **4** (0.99 g, 3.18 mmol) were added. After stirring the reaction mixture at $130\text{ }^\circ\text{C}$ for 10 min, an additional portion of **3** (1.08 g, 4.81 mmol) was added, whereafter the reaction mixture was heated at $130\text{ }^\circ\text{C}$ for 3.5 h. The reaction mixture was cooled to room temperature, whereupon cold MeOH (50 mL, $-18\text{ }^\circ\text{C}$) was added. Leaving the mixture overnight at $-18\text{ }^\circ\text{C}$ producing a yellow precipitate, which was filtered off and washed with cold MeOH ($3 \times 20\text{ mL}$, $-18\text{ }^\circ\text{C}$). The yellow solid was dissolved in CH_2Cl_2 (500 mL) and Celite 545 (40 mL) was added, before the solvent was removed in vacuo. The resulting residue was purified by column chromatography (silica gel: 1. CH_2Cl_2 /petroleum ether (b.p. $60\text{--}80\text{ }^\circ\text{C}$) 1:1, 2. CH_2Cl_2) and the broad yellow band was collected and concentrated to give the title compound **5** as a yellow powder containing traces of grease. Yield (1.27 g, 82%). M.p. $> 250\text{ }^\circ\text{C}$.

$^1\text{H-NMR}$ (CDCl_3) (Compound **5** is very insoluble in most organic solvents preventing a useful $^{13}\text{C-NMR}$ spectrum to be obtained) $\delta = 2.41$ (s, 3H), 3.29 (s, 4H), 6.93 (s, 2H), 7.30 (d, 2H, $J = 8.3$ Hz), 7.72 (d, 2H, $J = 8.3$ Hz).

$\text{C}_{17}\text{H}_{13}\text{NO}_2\text{S}_7$ Calculated: C 41.87 H 2.69 N 2.87 S 46.01

Found: C 42.39 H 2.73 N 2.77 S 45.40

$\text{C}_{17}\text{H}_{13}\text{NO}_2\text{S}_7 + \frac{1}{2} \text{CH}_2$ Calculated: C 42.40 H 3.05 N 2.83 S 45.27

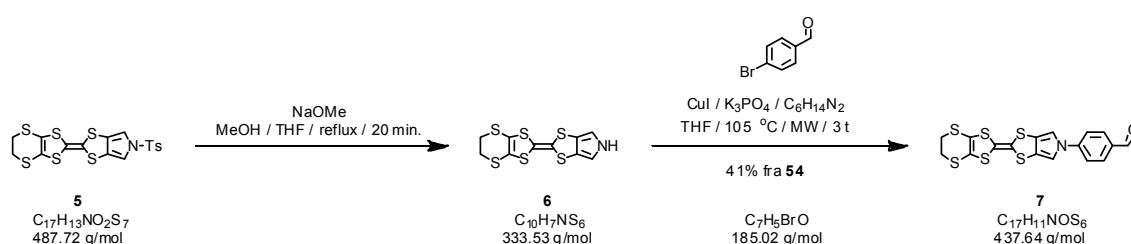
MS (ESI): $m/z = 486$ (M^+)

HiRes-FT ESI-MS: $\text{C}_{17}\text{H}_{13}\text{NO}_2\text{S}_7^+$ Calculated $m/z = 486.8991$

$\text{C}_{17}\text{H}_{13}\text{NO}_2\text{S}_7^+$ Found $m/z = 486.8987$

IR (KBr): $\nu/\text{cm}^{-1} = 3125; 2919; 1595; 1371; 1225; 1188; 1171; 1090; 1054$

2.2. Synthesis of **7**



A solution of the MPTTF compound **5** (0.390 g, 0.800 mmol) in a mixture of anhydrous THF (50 mL) and anhydrous MeOH (50 mL) was degassed (N_2 , 20 min.), before a solution of NaOMe in MeOH (25% *w/w*, 1.85 mL, 8.1 mmol) was added. The reaction mixture was heated under reflux for 20 min and then allowed to cool down to room temperature. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (500 mL). This mixture was washed with H_2O (3×200 mL) and dried (MgSO_4) before the solvent was removed in vacuo to produce a yellow solid containing **6**, which was used in the next reaction without further purification.

The crude product containing the MPTTF compound **6**, 4-bromobenzaldehyd (0.681 g, 3.68 mmol), CuI (0.315 g, 1.65 mmol), and K_3PO_4 (0.548 g, 2.58 mmol) was dissolved in anhydrous THF (20 mL) and degassed (N_2 , 20 min) before \pm trans 1,2 diaminocyclohexane (0.40 mL, 0.38 g, 3.3 mmol) was added. The reaction mixture was heated to 105 °C under microwave (MW) irradiation for 3 h and then cooled to room temperature before the solvent was removed in vacuo. The crude product was dissolved in CH_2Cl_2 (500 mL) and washed with H_2O (3×250 mL). The aqueous phases were combined and extracted with CH_2Cl_2 (16×250 mL). The combined organic phases were dried (MgSO_4) and Celite 545 (20 mL) was added, before the solvent was removed in vacuo. The resulting residue was purified by column chromatography (silicagel: 1. EtOAc, 2. CH_2Cl_2) and the broad yellow band was collected and concentrated to give a yellow powder, which was recrystallized from PhMe (400 mL) and washed with cold PhMe (0 °C, 50 mL) providing the title compound **7** as an orange powder. Yield (0.143 g, 41%). M.p. > 250 °C.

$^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{SO}$) (Compound **7** is very insoluble in most organic solvents preventing a useful $^{13}\text{C-NMR}$ spectrum to be obtained): $\delta = 7.66$ (s, 2H), 7.77 (s, 2H), 7.98 (s, 2H), 9.97 (s, 1H, CHO), the signal from the four CH_2 protons are obscured under the water signal present in the NMR solvent.

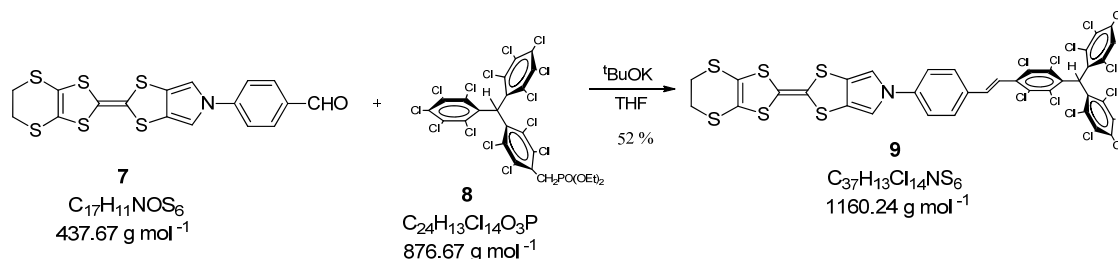
$^1\text{H-NMR}$ (CDCl_3): $\delta = 3.31$ (bs, 4H), 7.00 (bs, 2H); 7.44 (bs, 2H), 7.94 (bs, 2H), 9.98 (s, 1H).

$\text{C}_{17}\text{H}_{11}\text{NOS}_6$ Calculated: C 46.66 H 3.20 N 2.53 S 43.95

Found: C 46.58 H 3.16 N 2.64 S 43.78

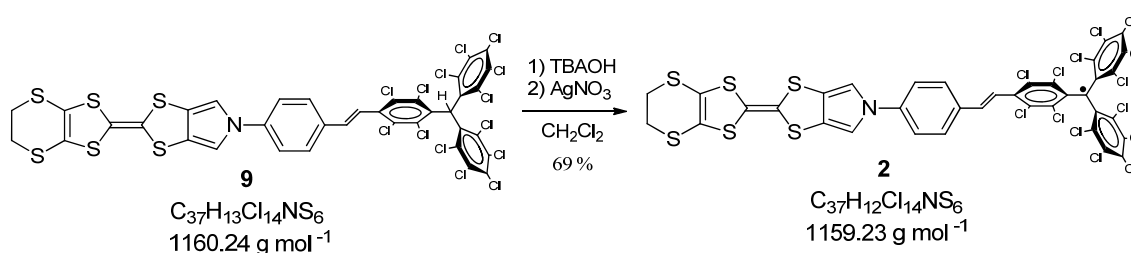
MS (ESI): $m/z = 436(M^+)$
 HiRes-FT ESI-MS: $C_{17}H_{11}NOS_6 +$ Calculated $m/z = 436.9165$
 $C_{17}H_{11}NOS_6^+$ Found $m/z = 436.9140$
 IR (KBr): $\nu/cm^{-1} = 2921; 2844; 1690; 1600; 1584; 1519; 1492; 1391; 1311; 1172$

2.3. Synthesis of 9



A solution of the phosphonated PTM derivative **8** (219 mg, 0.25 mmol) was dissolved in anhydrous THF (50 mL) under strict inert conditions and cooled down to -78°C . Potassium *tert*-butoxide (84 mg, 0.75 mmol) was added and the reaction mixture was stirred for 20 min to form the yellow-orange ylide. Subsequently, compound **7** (120 mg, 0.27 mmol) was added and the reaction mixture was allowed up to room temperature and then stirred for 3 d. Then the reaction mixture was extracted with CH_2Cl_2 (150 mL) washed with H_2O (75 mL), and dried (MgSO_4) before the solvents were evaporated under reduced pressure. Finally, the product was purified by column chromatography (silicagel: ether/hexane 1:1) to obtain compound **9** as a light yellow powder. Yield (150 mg, 52%). Characterization: $^1\text{H-NMR}$ (400 MHz, CD_3SO): $\delta = 7.75$ (d, 2H, $J = 8.6$ Hz), 7.58 (d, 2H, $J = 8.6$ Hz), 7.55 (s, 2H), 7.22 (d, 1H, $J = 16.6$ Hz), 7.13 (d, 1H, $J = 16.6$ Hz); 6.94 (s, 1H); 3.41 (s, 4H). FT-IR: $\nu/cm^{-1} = 2922$ (w), 2851 (w), 2743 (w), 1603 (m, $\text{CH}=\text{CH}$), 1519 (s), 1486 (w), 1461 (w), 1365 (w), 1337 (w), 1311 (s), 1298 (s), 1187 (m), 1138 (m), 1038 (m), 967 (m), 934 (m), 875 (w), 808 (s), 748 (m), 719 (w), 685 (w), 669 (s). LDI-TOF (positive mode): m/z (amu/ e^-): 1158.944 (M^+); (negative mode): m/z (amu/ e^-): 1158.845 (M^-). Cyclic voltammetry (Bu_4NPF_6 0.1 M in CH_2Cl_2 as electrolyte): $E^{\text{ox}1/2} = +0.425$ V; $E^{\text{ox}2/2} = +0.925$ V. M.p.: 220°C .

2.4. Synthesis of 2



Tetrabutylammonium hydroxide (1.0 M in methanol, 60 μL , 0.060 mmol) was added to a solution of compound **9** (50 mg, 0.043 mmol) in distilled THF (20 mL) and the purple solution was stirred for 2 h. Then AgNO_3 (12 mg, 0.071 mmol) dissolved in MeCN (10 mL) was added and the reaction mixture was stirred for additional 60 min. The solution changes from purple to dark brown and a precipitate of silver (Ag^0) was formed. The reaction mixture was subsequently filtered and the filtrate was evaporated under reduced pressure. Finally, the product was purified by flash column chromatography (silica gel: CH_2Cl_2 /hexane 1:1) affording the radical dyad **2** as a dark reddish-brown powder. Yield (35 mg, 69%). Characterization: FT-IR: $\nu/cm^{-1} = 2952$ (w), 2918 (w), 2853 (w), 1602 (m, $\text{CH}=\text{CH}$), 1519 (s), 1484 (w), 1461 (w), 1430 (w), 1380 (w), 1361 (w), 1333 (m), 1309 (s), 1298 (s), 1257 (m), 1228 (w), 1183 (w), 1155 (w), 1118 (w), 1038 (m), 966 (w), 935 (m), 859 (w), 814 (s), 766 (w), 752 (w), 737 (m), 707 (m), 666 (w), 651 (s). UV-VIS-NIR (CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$, $\epsilon/M^{-1}\cdot\text{cm}^{-1}$): 325 (22269), 370

(22658), 386 (31503), 437 (12011). LDI-TOF (positive mode): m/z (amu/e⁻): 1158.396 (M⁺). Cyclic voltammetry (Bu₄NPF₆ 0.1 M in CH₂Cl₂ as electrolyte): $E^{red_{1/2}} = -0.220$ V; $E^{ox_{1/2}} = +0.510$ V; $E^{ox_{2/2}} = +0.953$ V. ESR (CH₂Cl₂): $g = 2.0025$; $a_H = 1.9$ Hz; $\Delta H_{pp} = 1.1$ Hz. M.p.: 220 °C.

3. ¹H-NMR of 9

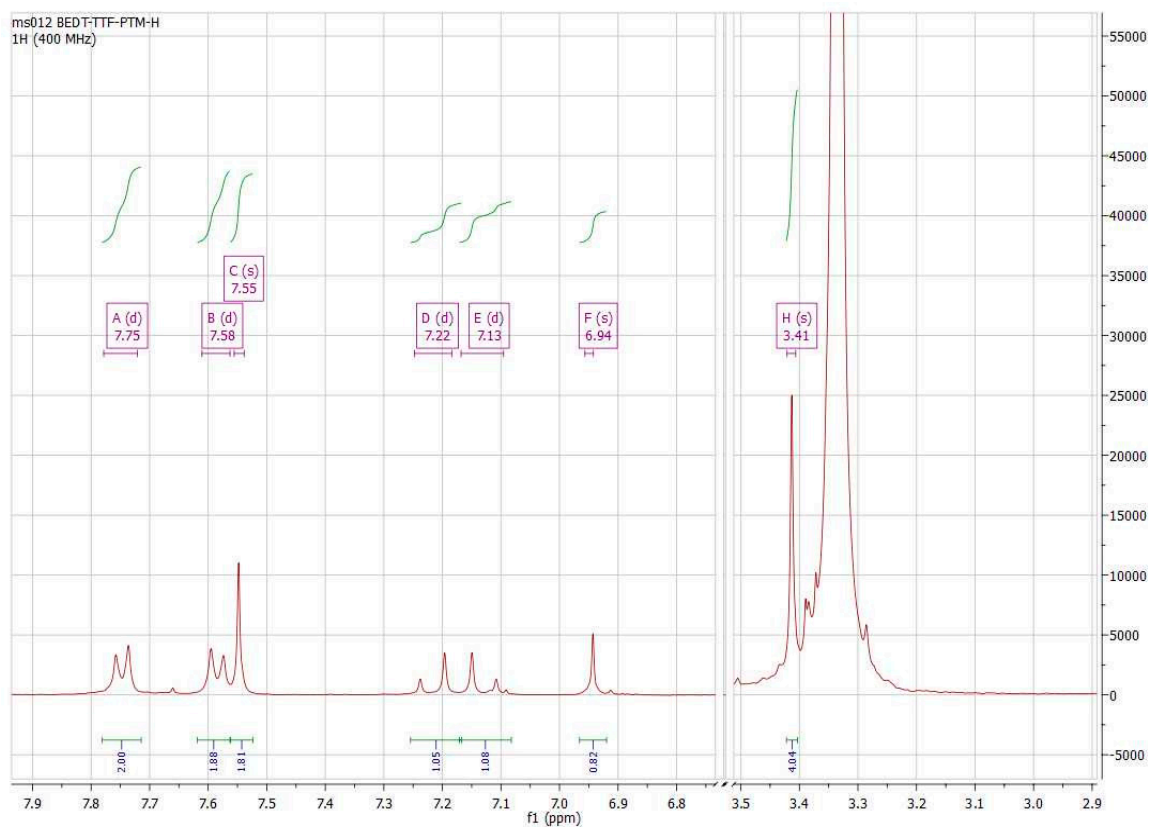


Figure S1. ¹H-NMR spectrum of dyad 9.

4. FT-IR of 9 and 2

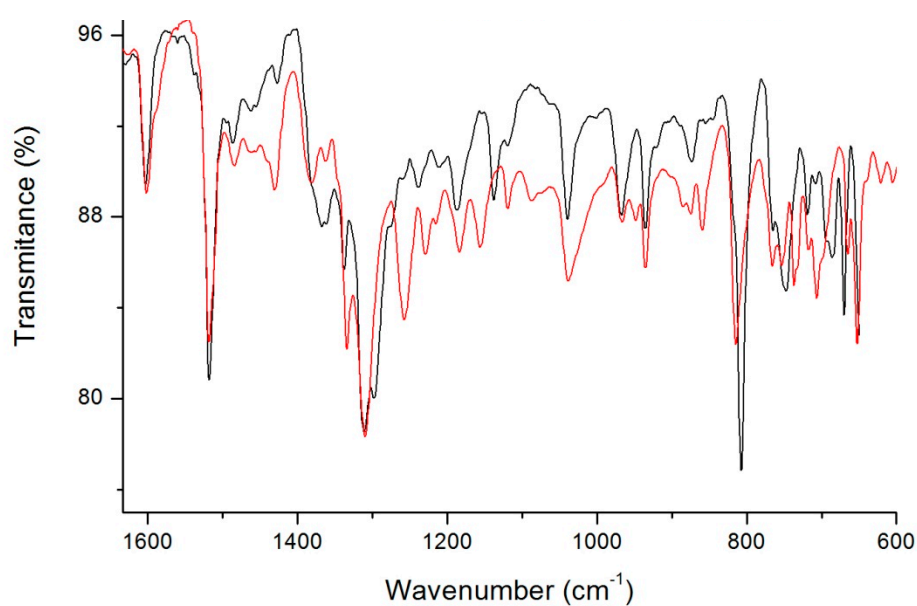


Figure S2. FT-IR spectra of dyads 9 (black line) and 2 (red line).

5. Cyclic Voltammetry of 9 and 2

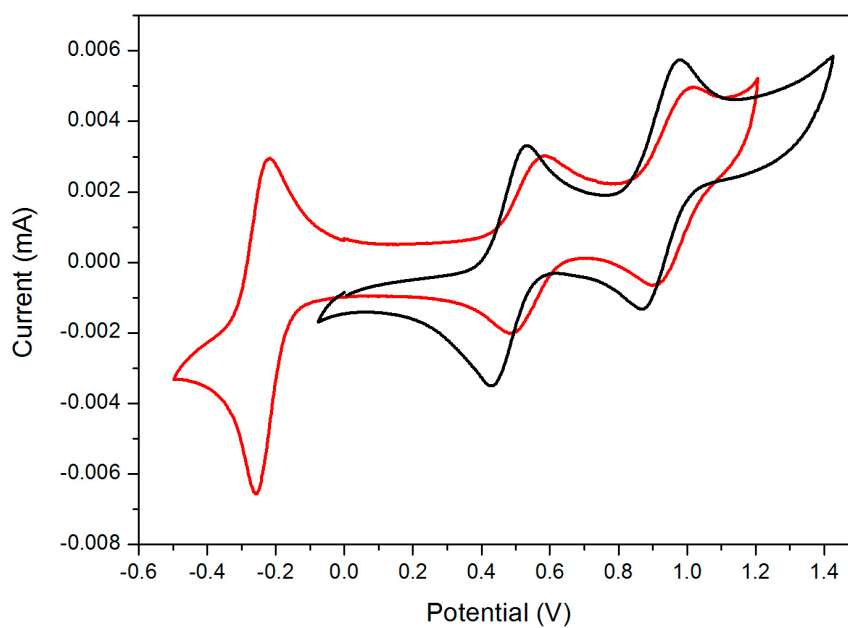


Figure S3. Cyclic voltammograms of dyads 9 (black line) and 2 (red line) in CH_2Cl_2 versus Ag/AgCl

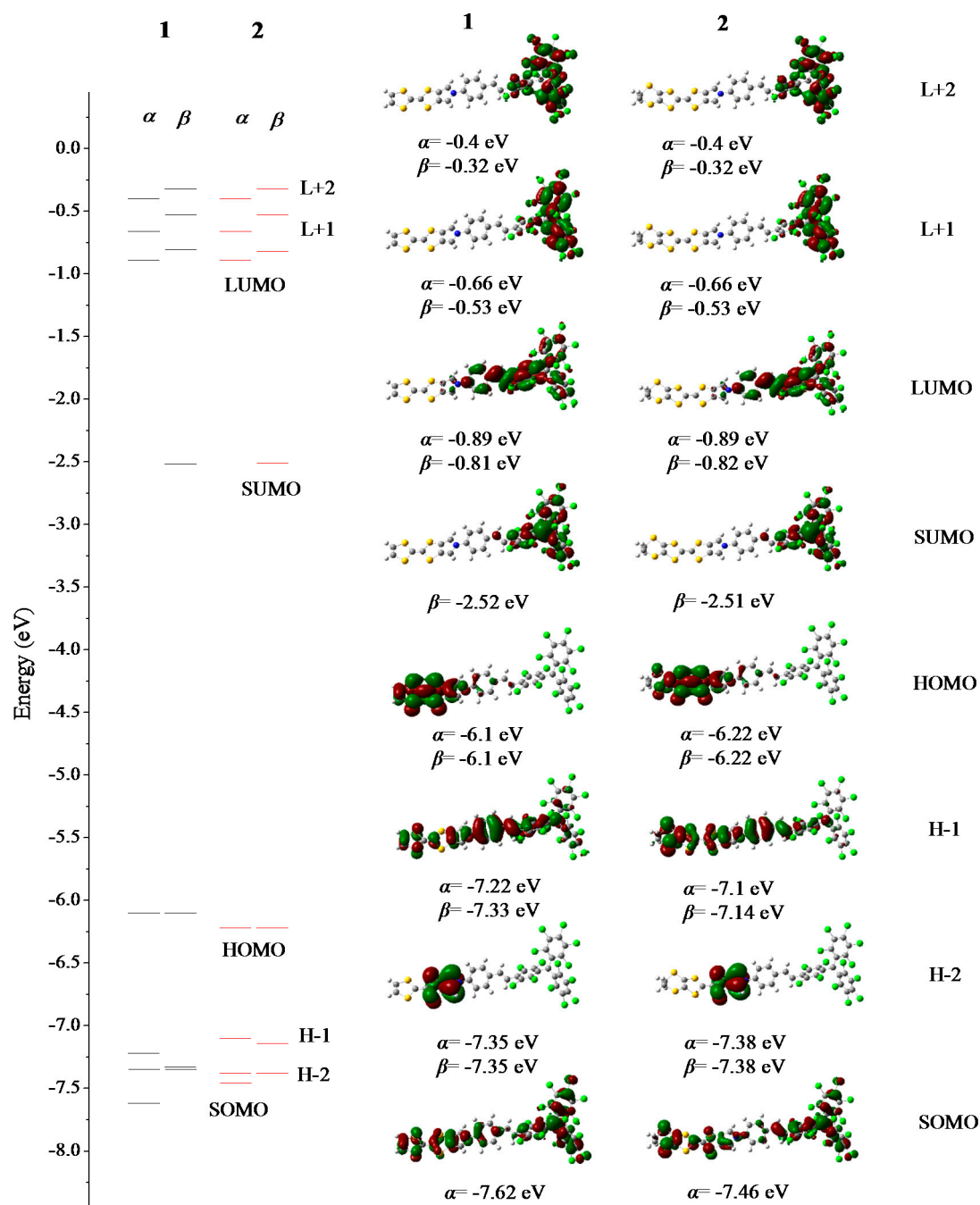


Figure S4. Frontier molecular orbital energy diagrams (left) and topologies (right) for the dyads 1 (black) and 2 (red). The two series of lines represent the orbitals associated to the spin up (α) and spin down (β), respectively.

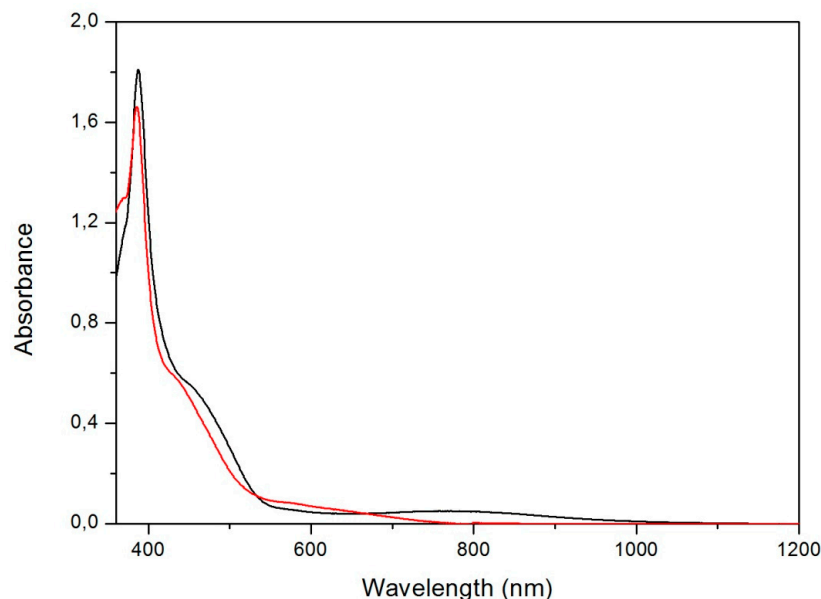


Figure S5. UV-vis-NIR spectra of radical dyad **2** recorded in THF (black line) and **2⁺** which was generated by oxidation of **2** with one equivalent of FeCl₃ (red line).

6. Computational Details

Spin Polarized Density Functional Theory [1] (DFT) calculations have been performed for the dyads **1** and **2**, using the Gaussian 09 package [2]. Geometry optimizations were carried out with the (U)CAM-B3LYP functional [3] and 6-31G* basis set [4], while the effects of the CH₂Cl₂ solvent were introduced by means of the polarizable continuum model [5] (PCM). This approach has been validated in previous works on similar compounds [6].

References

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