

Supporting information

Efficiency Improvement Using Bis(trifluoromethane) Sulfonamide Lithium Salt as chemical additive in Porphyrin Based Organic Solar Cell

Susana Arrechea^{a,b}, Ana Aljarilla^a, Pilar de la Cruz^a, Emilio Palomares^{c,d*}, Ganesh D. Sharma^{e*}, Fernando Langa^{a*}

Universidad de Castilla-La Mancha. Institute of Nanoscience, Nanotechnology and Molecular Materials (INAMOL), Campus de la Fábrica de Armas, 45071-Toledo. Spain. Tel: 34 9252 68843. E-mail: Fernando.Langa@uclm.es

^bEscuela de Ingeniería Química, Facultad de Ingeniería, Universidad de San Carlos de Guatemala. Guatemala.

^cInstitute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Avda. Països Catalans, 14, Tarragona, E-43007, Spain. E-mail: epalomares@ICIQ.ES epalomares@ICIQ.ES

^dICREA. Passeig Lluís Companys, 23. Barcelona. E-08010. Spain.

^eDepartment of Physics, The LNM Institute of Information Technology (Deemed University), Rupa ki Nagal, Jamdoli, Jaipur (Raj.) 302031, India, E-mail: gdsharma273@gmail.com

Table of contents

1. Experimental details	S2
2. Synthetic Procedures	S3
3. ¹H -NMR, ¹³C-NMR, FT-IR and MALDI-TOF or MS spectra	S5
4. Thermogravimetric analysis	S11
5. Absorption spectra	S12
6. Cyclic and Osteryoung Square Wave Voltammetry plots of 1a and 1b	S13
7. Optimized geometries of 1a and 1b	S16

1. Experimental details

Synthetic procedures were performed under Argon atmosphere, in dry solvent unless otherwise noted. All reagents and solvents were reagent grade and were 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. ^1H -NMR spectra were obtained on Bruker TopSpin AV-400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl_3 , 7.27 ppm). ^{13}C -NMR chemical shifts (δ) are reported relative to the solvent residual peak (CDCl_3 , 77.0 ppm). UV-Vis measurements were carried out on a Shimadzu UV 3600 spectrophotometer. For extinction coefficient determination, solutions of different concentration were prepared in CH_2Cl_2 (HPLC grade) with absorption between 0.1-1 of absorbance using a 1 cm UV cuvette. The emission measurements were carried out on Cary Eclipse fluorescence spectrophotometer. Mass spectra (MALDI-TOF) were recorded on a VOYAGER DETM STR mass spectrometer using dithranol as matrix and a ULTRAFLEX III mass spectrometer using DCTB+PMMANa2100 as matrix. Melting points are uncorrected.

The molecular geometries and frontier molecular orbitals of these new dyes have been optimized by density functional theory (DFT) calculations at the B3LYP/6-31G* level using Gaussian03W.^{S1} Cyclic voltammetry was performed in ODCB-acetonitrile (4:1) solutions. Tetrabutylammonium perchlorate (0.1 M as supporting electrolyte) were purchased from Acros and used without purification. Solutions were deoxygenated by argon bubbling prior to each experiment, which was run under argon atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode ($\varnothing = 2$ mm) and a platinum wire counter electrode. An Ag/AgNO_3 (0.01 M in CH_3CN) electrode was used as reference and checked against the ferrocene/ferrocenium couple (Fc/Fc^+) before and after each experiment.

The thermal stability was evaluated by TGA on a Mettler Toledo TGA/DSC Starte System under nitrogen, with a heating rate of 10 $^\circ\text{C}/\text{min}$. Heating of crystalline samples leads to melting of the solids, but no recrystallization was observed.

S1. Gaussian 03, Revision D.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, 2004.

2. Synthetic Procedures.

Synthesis of 4. Under Argon atmosphere, cycles of vacuum and argon atmosphere were done to a solution of porphyrin **2**^{S2} (0.25 mmol, 243 mg), **3**^{S3} (0.5 mmol, 341 mg), Pd₂(dba)₃ (0.6 eq, 0.15mmol, 137 mg) and AsPh₃ (3.8 eq, 0.95 mmol, 290 mg). Then, a freshly distilled Et₃N (45 mL/mmol, 11 mL) in 58 mL of dried and degasified THF (230 mL/mmol,) were added. The product **4** was purified by column chromatography (silica gel, hexane:CH₂Cl₂, 1:1), it was obtained as a green solid (0.13 mmol, 270 mg, 51%). ¹H-NMR (400 MHz, CDCl₃) δ/ppm: 9.94 (s, 2H), 9.60 (d, 4H, *J* = 4.5 Hz), 8.86 (d, 4H, *J* = 4.5 Hz), 7.71 (t, 2H, *J* = 8.5 Hz), 7.38 (d, 2H, *J* = 15.5 Hz), 7.12 (d, 2H, *J* = 15.5 Hz), 7.01 (d, 4H, *J* = 8.5 Hz), 3.87 (t, 8H, *J* = 6.1 Hz), 3.12 (t, 3H, *J* = 7.4 Hz), 2.88 (t, 3H, *J* = 7.3 Hz), 2.77 (t, 3H, *J* = 7.3 Hz), 2.69 (t, 3H, *J* = 7.3 Hz), 1.97 (m, 4H), 1.71-1.55 (m, 16H), 1.48-1.34 (m, 52H), 1.01-0.84 (m, 36H), 0.53 (m, 14H), 0.41 (m, 6H), 0.24 (m, 8H). ¹³C-NMR (100 MHz, CDCl₃) δ/ppm: 181.9, 159.9, 153.1, 151.3, 150.5, 148.1, 147.0, 142.8, 141.9, 136.9, 134.8, 132.0, 130.3, 129.9, 123.6, 120.7, 119.5, 118.8, 115.9, 105.2, 101.5, 100.5, 89.8, 68.6, 32.3, 31.9, 31.7, 31.6, 31.6, 31.2, 31.0, 30.8, 29.8, 29.5, 29.4, 28.6, 27.6, 27.2, 26.5, 24.9, 22.8, 22.7, 22.6, 22.0, 14.2, 14.2, 14.11, 14.10, 13.5. MALDI-TOF MS (*m/z*): calculated for C₁₃₀H₁₇₆N₄O₆S₄Zn: 2081.18; found: 2082.29 (M+1). FT-IR (ATR) ν/cm⁻¹: 2952, 2925, 2854, 2335, 2171, 1652, 1616, 1589, 1502, 1454, 1400, 1375, 1340, 1292, 1247, 1220, 1205, 1122, 1097, 1060, 997, 931, 823, 792, 765, 744, 723, 709.

Synthesis of 1a. To a solution of **4** (0.05 mmol, 110 mg) in 4 mL of dried CH₂Cl₂ (25 mL/mmol), 3-ethylrhodanine (0.53 mmol, 85 mg) and 3 drops of piperidine were added. The reaction mixture was stirred at reflux for 18 h and quenched by the addition of water and extracted with CHCl₃ (3 x 150 mL). The combined organic extract was dried over anhydrous MgSO₄ and filtered. The solvent was removed by rotary evaporation. The product was purified by column chromatography (silica gel, hexane:CHCl₃, 1:1) and recrystallized with CH₂Cl₂:MeOH. **1a** was obtained as a green solid (69 mg, 0.03 mmol, 59% yield). ¹H-NMR (400 MHz, CDCl₃) δ/ppm: 9.61 (d, 4H, *J* = 3.6 Hz), 8.86 (d, 4H, *J* = 3.6 Hz), 7.97 (s, 2H), 7.72 (t, 2H, *J* = 8.2 Hz), 7.32 (d, 2H, *J* = 15.5 Hz), 7.17 (d, 2H, *J* = 15.5 Hz), 7.02 (d, 4H, *J* = 8.2 Hz), 4.25 (q, 4H, *J* = 6.6 Hz), 3.88 (t, 8H, *J* = 6.2 Hz), 3.14 (m, 4H), 2.83-2.72 (m, 14H), 1.99 (m, 6H), 1.70-1.33, (m, 58H), 0.97-0.83 (m, 32H), 0.53-0.41 (m, 25H), 0.24 (m, 8H). ¹³C-NMR (100 MHz, CDCl₃)

S2. S. J. Lee, K. L. Mulfort, X. Zuo, A. J. Goshe, P. J. Wesson, S. T. Nguyen, J. T. Hupp, D. M. Tiede, *J. Am. Chem. Soc.*, **2008**, *130*, 836-838.

S3. (a) L. Pellejà, R. Domínguez, A. Aljarilla, J. N. Clifford, P. de la Cruz, F. Langa, E. Palomares, *ChemElectroChem*, **2014**, *1*, 1126-1129; (b) S. Arrechea, A. Molina-Ontoria, A. Aljarilla, P. de la Cruz, F. Langa, L. Echegoyen, *Dyes and Pigments*, **2015**, *121*, 109-117; (c) G. Morán, S. Arrechea, P. de la Cruz, V. Cuesta, S. Biswas, E. J. Palomares, G. D Sharma, F. Langa, *J. Mater. Chem. A*, **2016**, Accepted Manuscript DOI: 10.1039/C6TA04369K.

δ /ppm: 192.7, 167.7, 160.1, 151.5, 151.0, 150.7, 148.4, 145.8, 142.8, 142.5, 137.6, 132.2, 130.8, 130.5, 130.1, 124.1, 122.7, 120.8, 119.2, 119.0, 116.1, 105.4, 101.7, 100.8, 90.1, 68.8, 40.1, 32.1, 32.0, 31.9, 31.8, 31.8, 31.7, 31.4, 31.2, 31.0, 30.0, 29.6, 29.5, 28.8, 27.9, 27.6, 27.3, 25.1, 22.9, 22.9, 22.8, 22.2, 14.42, 14.38, 14.30, 14.28, 13.7, 12.5. MP: $>300^{\circ}\text{C}$. MALDI-TOF MS (m/z): calculated for $\text{C}_{141}\text{H}_{188}\text{N}_6\text{O}_6\text{S}_8\text{Zn}$: 2367.15; found: (M^+) 2367.14. FT-IR (ATR) ν/cm^{-1} : 2951, 2923, 2856, 2331, 2173, 1702, 1567, 1504, 1456, 1392, 1324, 1234, 1205, 1130, 1095, 997, 923, 879, 827, 792, 765, 721.

Synthesis of 1b. To a solution of **4** (0.05 mmol, 110 mg) in 2 mL of dried CHCl_3 were allowed to react with malonitrile (0.15 mmol, 9.9 mg). The reaction mixture was stirred at reflux for 18 h and quenched by the addition of water and extracted with CHCl_3 (3 x 150 mL). The combined organic extract was dried over anhydrous MgSO_4 and filtered. The solvent was removed by rotary evaporation. The product was purified by column chromatography (silica gel, CHCl_3) and recrystallized with CH_2Cl_2 :MeOH. **1b** was obtained as a green solid (80 mg, 0.03 mmol, 73% yield). ^1H -NMR (400 MHz, CDCl_3) δ /ppm: 9.60 (d, 4H, $J = 4.6$ Hz), 8.87 (d, 4H, $J = 4.6$ Hz), 7.80 (s, 2H), 7.72 (t, 2H, $J = 8.5$ Hz), 7.42 (d, 2H, $J = 15.5$ Hz), 7.15 (d, 2H, $J = 15.5$ Hz), 7.02 (d, 4H, $J = 8.5$ Hz), 3.87 (t, 8H, $J = 6.3$ Hz), 3.13 (t, 3H), 2.82-2.71 (m, 9H), 2.05-1.98 (m, 6H), 1.68-1.26 (m, 68H), 0.96-0.86 (m, 32H), 0.53-0.41 (m, 22H), 0.24 (m, 8H). ^{13}C -NMR (100 MHz, CDCl_3) δ /ppm: 159.9, 156.0, 151.4, 150.6, 149.4, 148.4, 147.3, 144.2, 141.6, 136.9, 132.1, 130.3, 130.0, 128.3, 125.6, 120.8, 120.6, 118.0, 116.1, 115.7, 114.3, 105.22, 102.2, 100.4, 89.8, 73.1, 68.7, 31.9, 31.7, 31.6, 31.5, 31.0, 30.8, 29.5, 29.4, 28.6, 24.9, 22.8, 22.6, 22.0, 14.2, 14.1, 14.0, 13.4. MP: $>300^{\circ}\text{C}$. MALDI-TOF MS (m/z): calculated for $\text{C}_{136}\text{H}_{176}\text{N}_8\text{O}_4\text{S}_4\text{Zn}$: 2177.20; found: (M^+) 2177.19. FT-IR (ATR) ν/cm^{-1} : 2951, 2923, 2856, 2217, 2167, 1589, 1556, 1506, 1456, 1340, 1288, 1247, 1207, 1093, 998, 927, 827, 792, 721, 711.

3. ^1H -NMR, ^{13}C -NMR, FT-IR and MALDI-TOF MS spectra

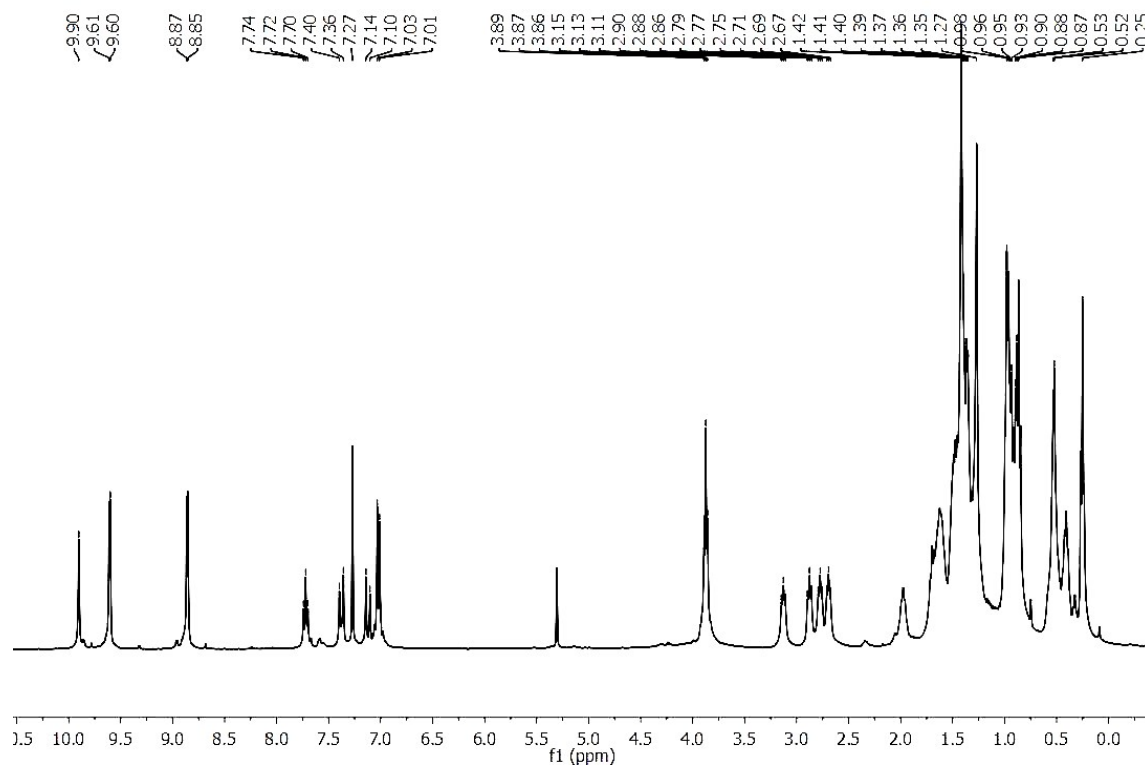


Figure S1. ^1H -NMR spectrum (400 MHz, CDCl_3) of 4.

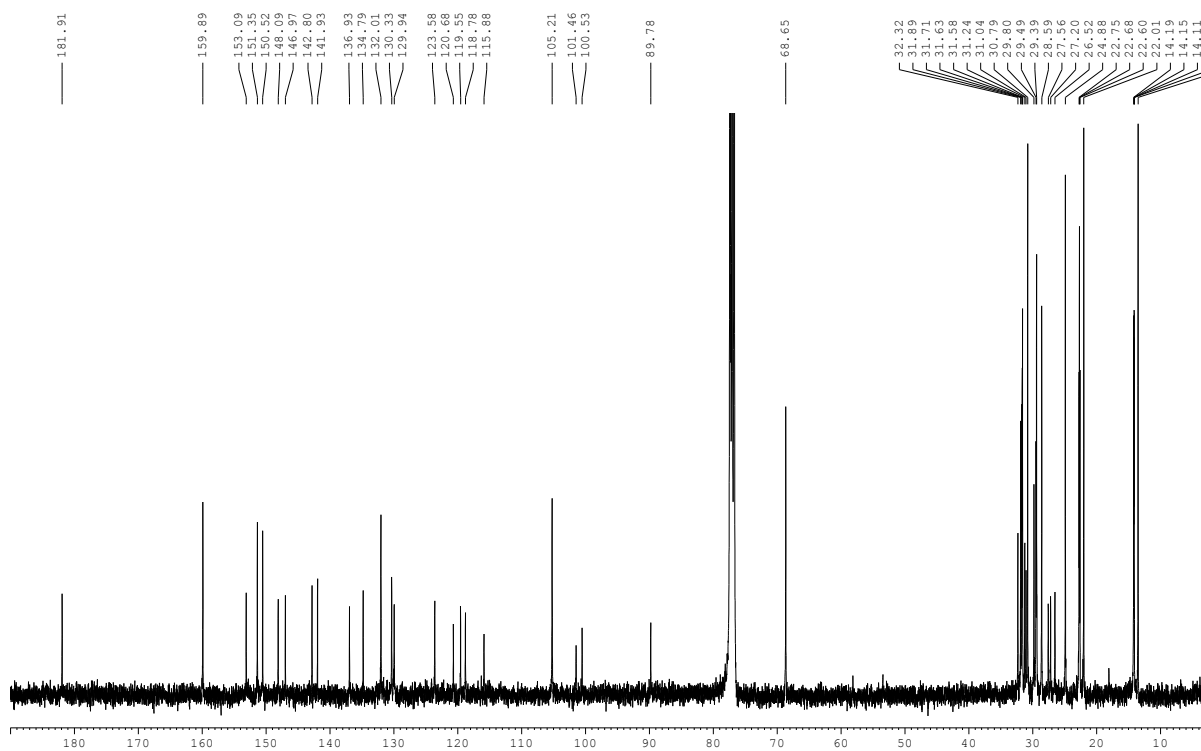
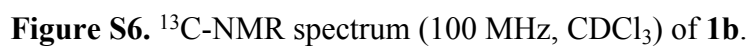
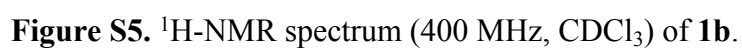


Figure S2. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 4.



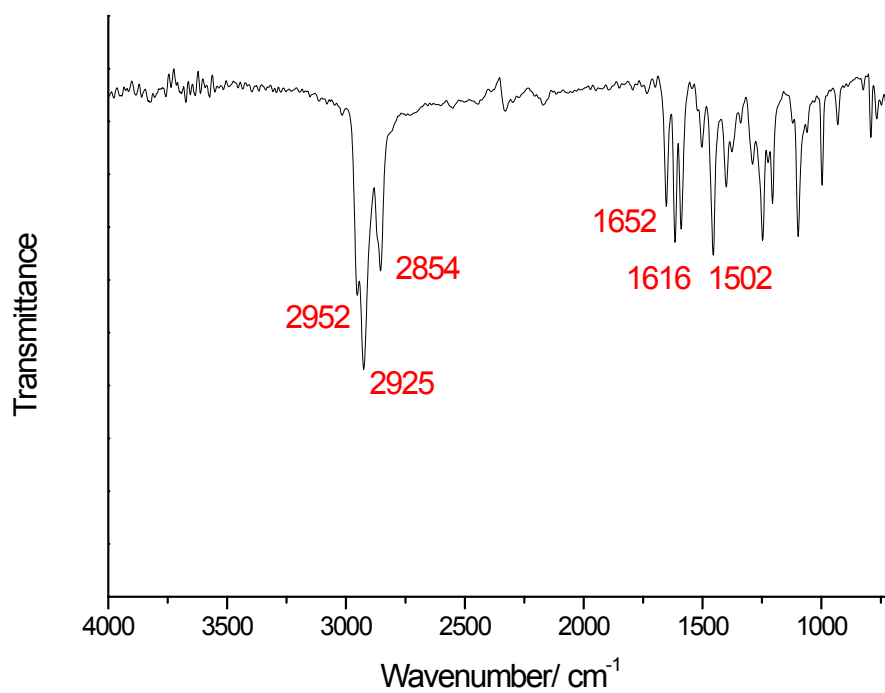


Figure S7. FT-IR spectrum of **4** (NaCl window).

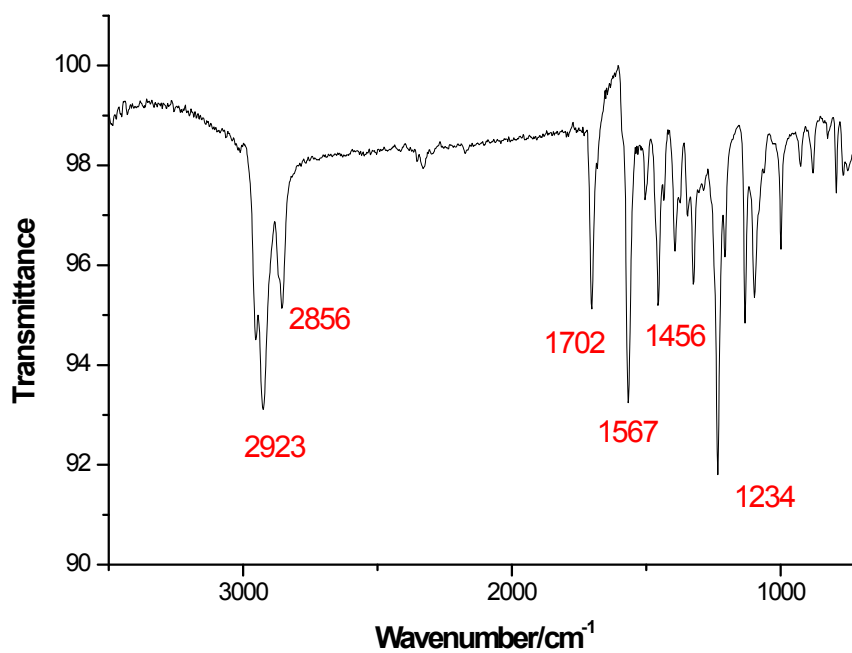


Figure S8. FT-IR spectrum of compound **1a** (NaCl window).

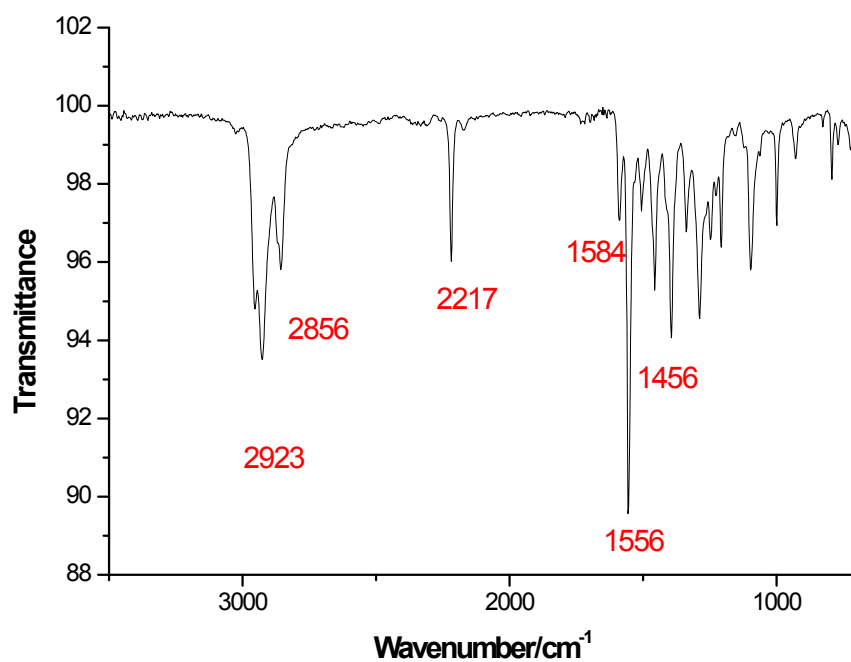


Figure S9. FT-IR spectrum of **1b** (NaCl window).

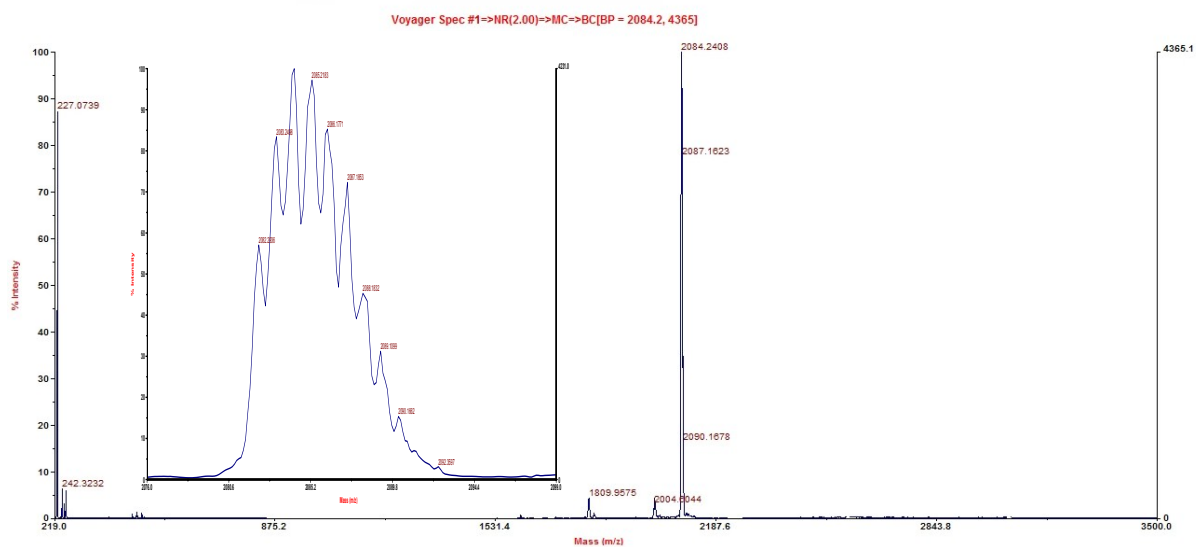


Figure S10. MALDI-MS spectrum of compound **4** (Matrix: Dithranol).

4. Thermogravimetric analysis

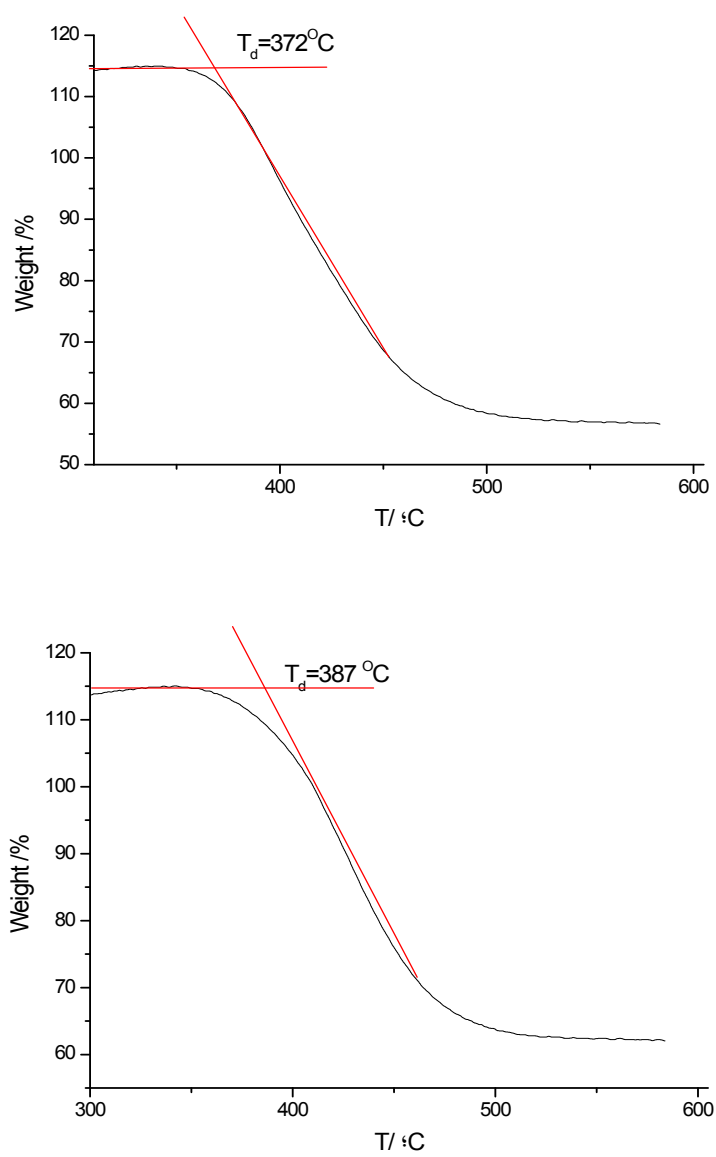


Figure S13. Thermogravimetric analysis of **1a** (up) and **1b** (down).

5. Absorption spectra

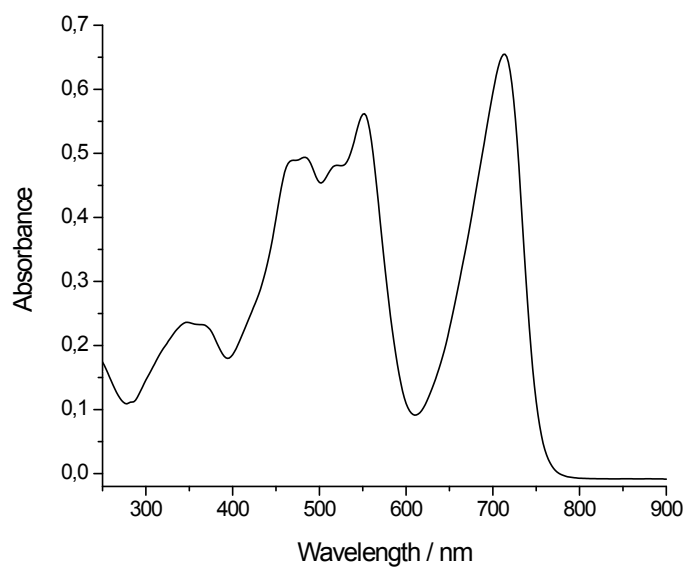


Figure S14. Absorption spectra of compound **1a** in CH_2Cl_2 solution (10^{-5} M).

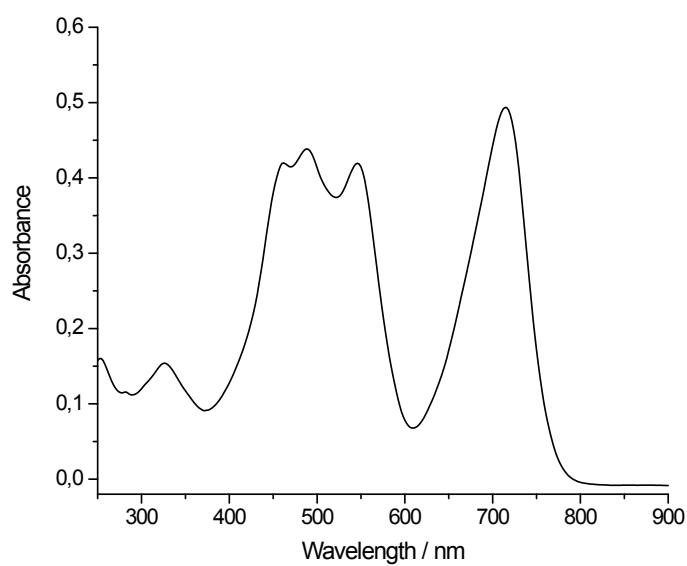
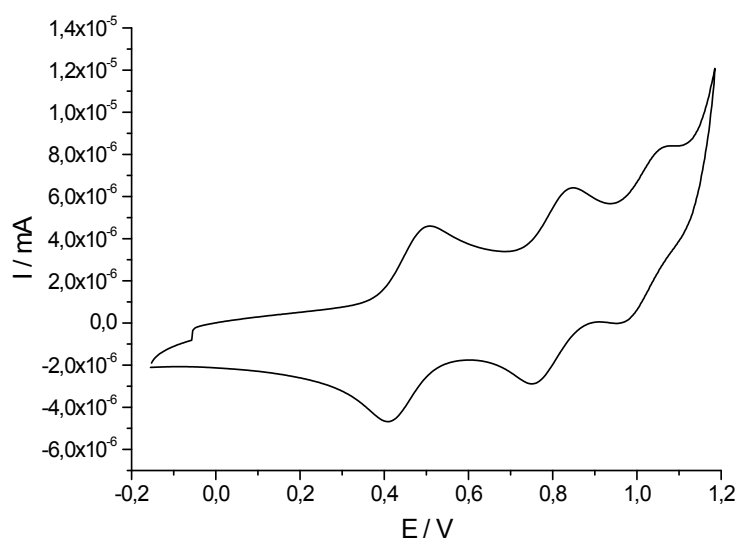
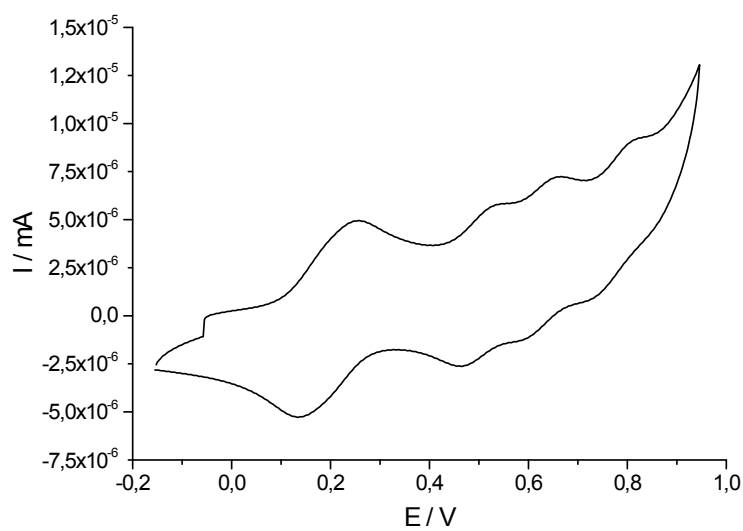


Figure S15. Absorption spectra of compound **1b** in CH_2Cl_2 solution (10^{-5} M).

6. Cyclic and Osteryoung Square Wave Voltammetry plots of 1a and 1b

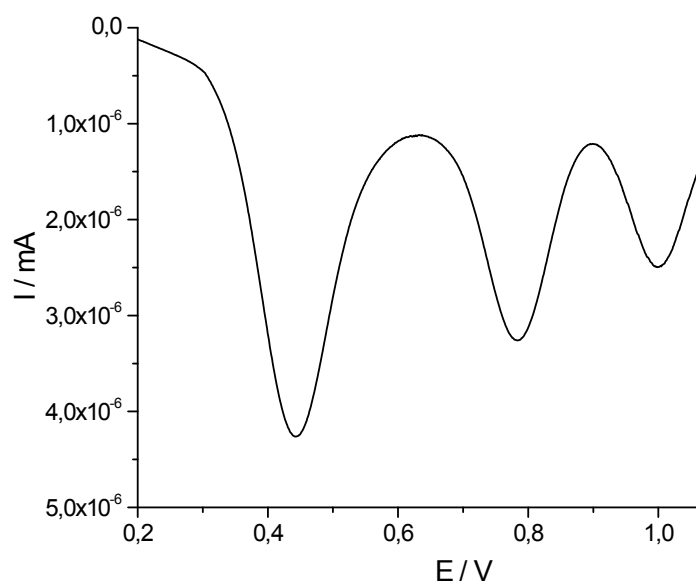


Compound 1a

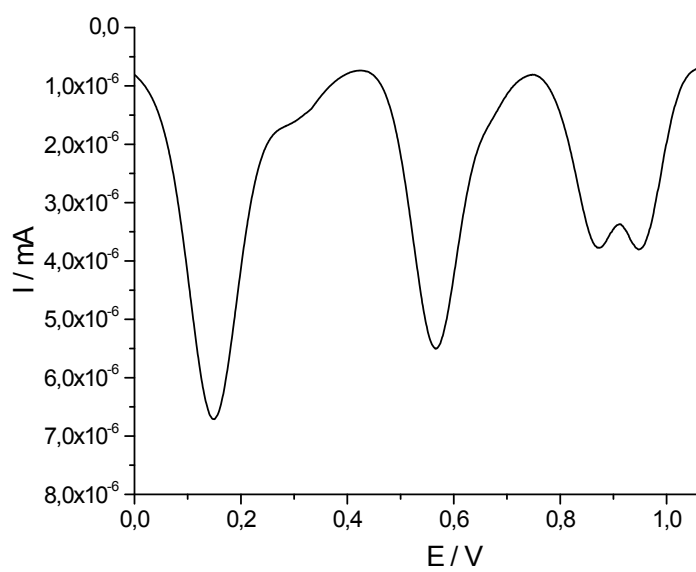


Compound 1b

Figure S16. Cyclic Voltammetry of compound **1a** and **1b** (referred to Fc/Fc⁺).

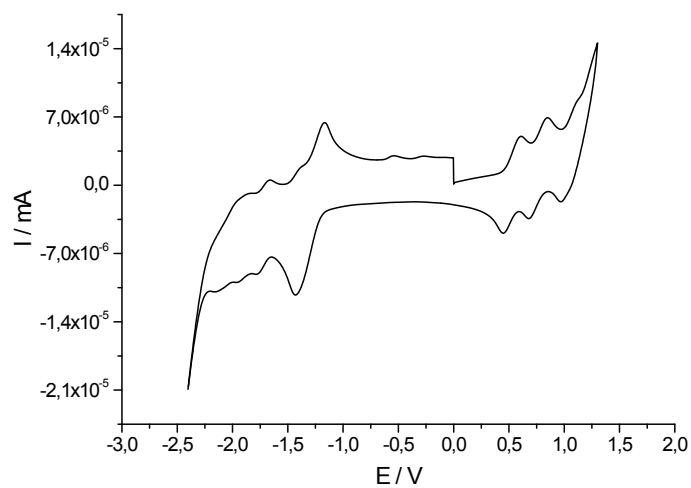


Compound 1a

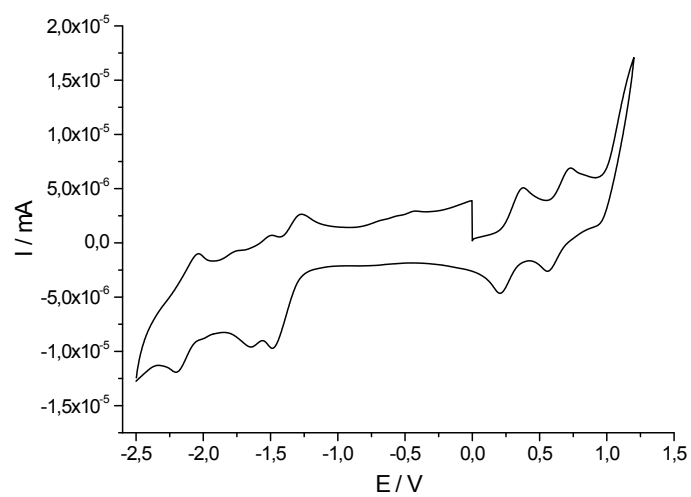


Compound 1b

Figure S17. OSWV of **1a** and **1b** (anodic window), (referred to Fc/Fc⁺).

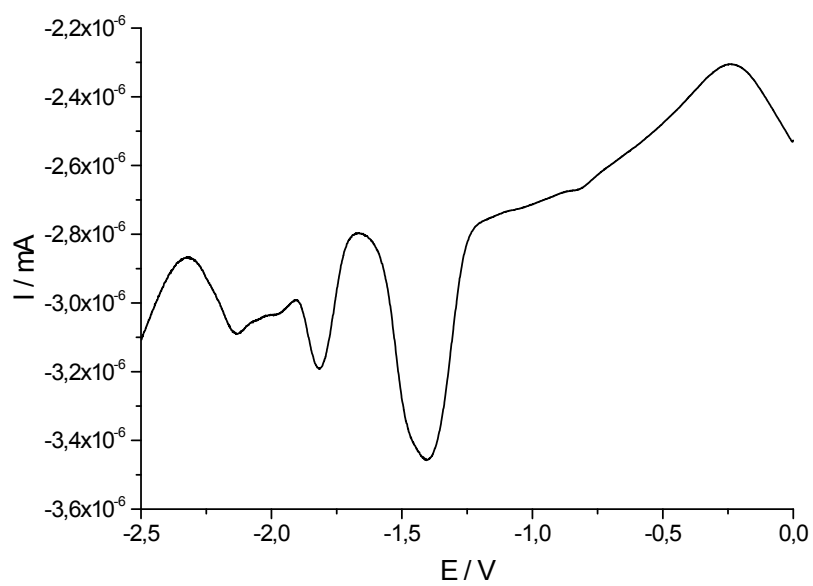


Compound 1a

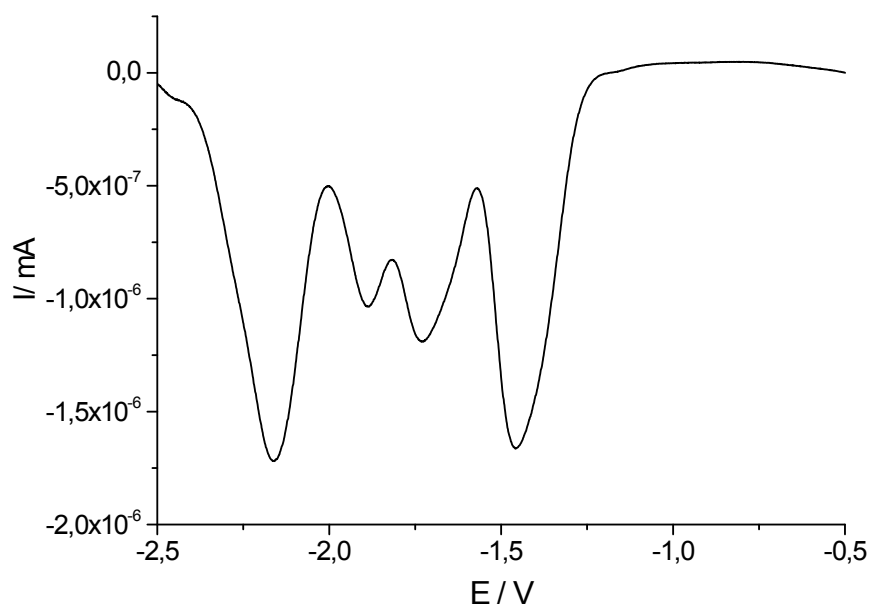


Compound 1b

Figure S18. Cyclic Voltammetry of compound **1a** and **1b** full window (referred to Fc/Fc⁺).



Compound 1a



Compound 1b

Figure S19. OSWV of **1a** and **1b** (cathodic window), (referred to Fc/Fc^+).

7. Optimized geometries of 1a and 1b

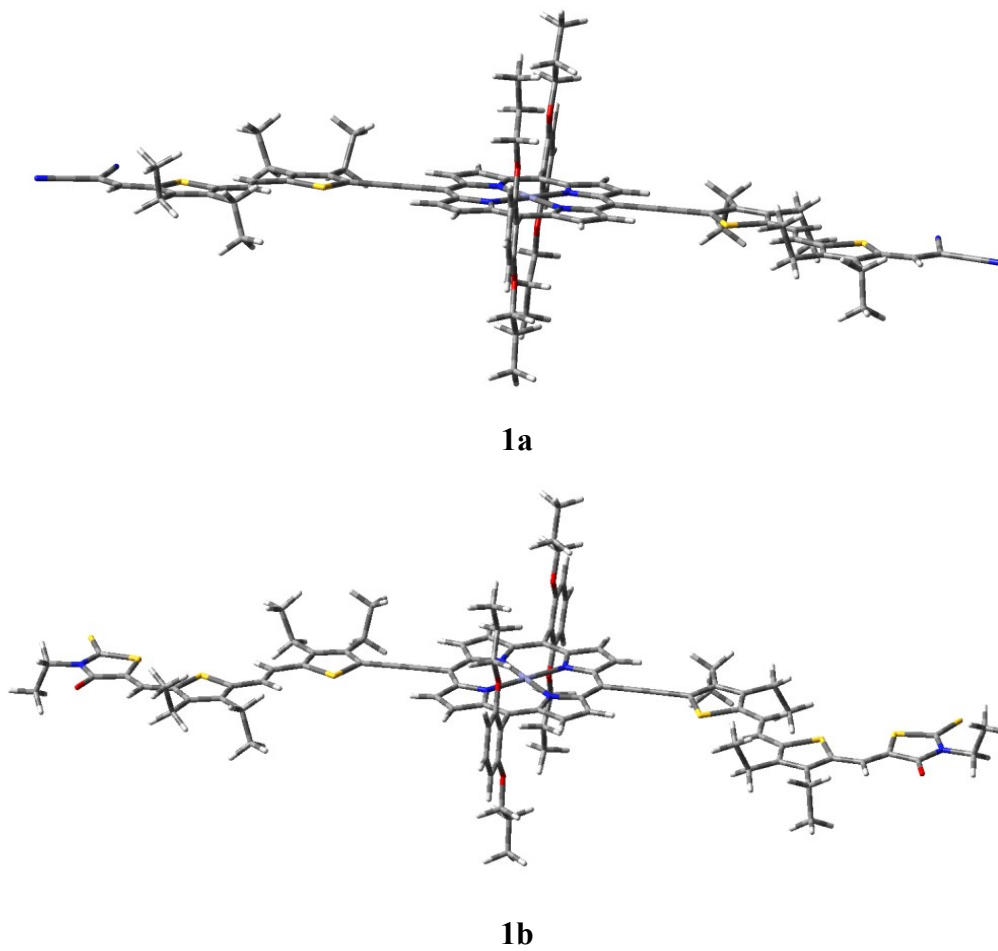


Figure S20. Theoretical optimized geometries of **1a** and **1b**.