Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Comparing the self-assembly processes of two redox-active exTTF-based regioisomer ligands

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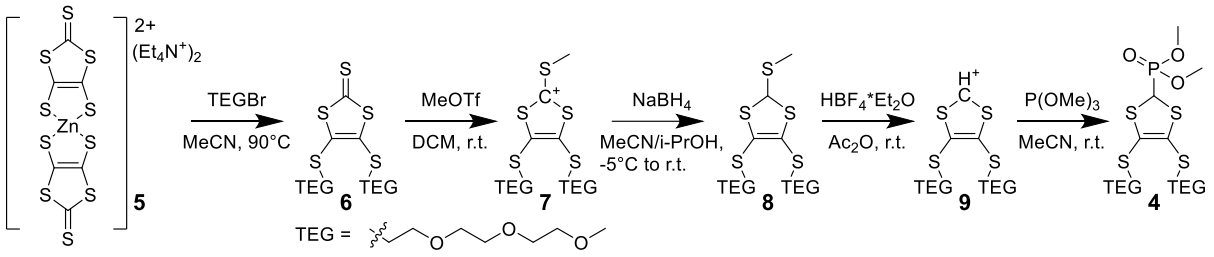
Instrumentation

NMR spectra were recorded on Bruker Avance III 300 spectrometer at room temperature or 298 K (^{1}H DOSY NMR). NMR chemical shifts are given in ppm (δ) relative to Me_4Si with solvent resonances used as internal standards (^{1}H), or external H_3PO_4 solution (^{31}P). ^{1}H DOSY NMR spectra were analyzed with MestReNova (v 14.0) software. FAB-HRMS spectra were recorded on JEOL JMS-700 MStation using a positive-ion mode. Ultra high resolution mass measurements were performed on a FT ICR-MS – 7T (Solarix 2xR, Bruker) with ESI source in positive ion mode. Cyclic voltammetry experiments were carried out on a BioLogic SP-150 potentiostat, Pt or Cgr working electrode, Pt counter electrode and Ag wire reference electrode (calibration using Fc as an internal reference).

Experimental procedures and characterizations

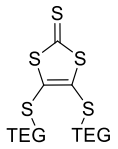
Chemicals

Complexes **5**[1] and Pd(dppf)OTf_2,[2] compounds **1**[3] and **3**[4] were synthesized using procedures described in the literature. All reagents were commercial reagent grade and were used without further purification. For synthesis and crystallizations, analytical grade solvents were used.



Scheme S1. *Synthesis of compound **4***

Synthesis of compound 6

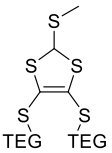


4,5-Bis((2-(2-(2-methoxyethoxy)ethoxy)ethyl)thio)-1,3-dithiole-2-thione (**6**)

In a 100 mL 3-neck flask charged with 5.36 g (7.45 mmol) of bis(tetraethylammonium)bis(1,3-dithiole-2thione-4,5-dithiol)zincate (**5**) was added acetonitrile (40 mL), and the solution was degassed with argon for 10 min. Then 5.45 g (5 mL, 24.01 mmol, 3.2 equiv.) of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane was added. The reaction was stirred at reflux for 3 h. Then, the solution was concentrated and 50 mL of methylene chloride was added. The resulting white precipitate was filtered through a thin layer of silica. The organic layer was washed with 2 x 100 mL. of water, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with ethyl acetate as eluent to afford compound **6** (7.90 g, 96%) as a red liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71 (t, *J* = 6.4 Hz, 4H), 3.64 (s, 8H), 3.67 – 3.60 (m, 4H), 3.56 – 3.53 (m, 4H), 3.38 (s, 6H), 3.07 (t, *J* = 6.4 Hz, 4H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 211.06, 136.57, 71.94, 70.64, 70.60, 69.87, 59.06, 36.14. FAB-HRMS: found: 490.0635, calculated: 490.0646.

Synthesis of compound 8

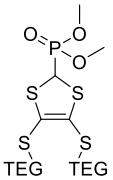


4,5-Bis((2-(2-(2-methoxyethoxy)ethoxy)ethyl)thio)-2-(methylthio)-1,3-dithiole (**8**)

In a 250 mL flask charged with 5.50 g (10.85 mmol) of compound **6**, was added 25 ml of methylene chloride, and the solution was degassed with argon for 5 min. Then, 1.91 g (1.32 mL, 11.66 mmol, 1.07 equiv.) of methyl trifluoromethanesulfonate was added and the reaction was stirred at r.t. overnight. The solution was concentrated and the resulting residue rinced with 5 ml of diethyl ether and dried under vacuum. To the obtained intermediate compound **7** (7.49 g, red liquid) were added 70 mL of acetonitrile and 30 ml of isopropyl alcohol. The solution was cooled to -5 °C and $NaBH_4$ was added as a solid portion by portion until the bubbling stopped. The solution was stirred for 3 h at r.t.. Then, the mixture was concentrated and the residue was dissolved in ethyl acetate. The organic layer was washed with 2 x 50 mL of water, dried over $MgSO_4$ and concentrated to afford compound **8** (5.50 g, 95 %) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (s, 1H), 3.69 – 3.64 (m, 4H), 3.66 (s, 12H), 3.57 – 3.54 (m, 4H), 3.32 (s, 6H), 3.16 – 3.07 (m, 2H), 2.96 – 2.87 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 125.04, 71.96, 70.58, 70.16, 59.08, 57.38, 35.15, 14.00. FAB-HRMS: found: 506.0952, calculated: 506.0959.

Synthesis of compound 4

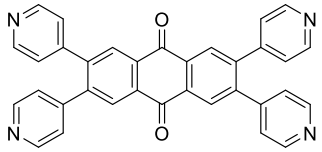


Dimethyl (4,5-bis((2-(2-(2-methoxyethoxy)ethoxy)ethyl)thio)-1,3-dithiol-2-yl)phosphonate (**4**)

In 250 mL flask charger with 5.60 g (11.05 mmol) of compound **8**, was added 25 ml of acetic anhydride. The solution was degassed with argon for 30 min and 1.97 g (1.67 mL, 12.16 mmol, 1.1 equiv.) of HBF_4*Et_2O were added. The reaction was stirred for 2 h at r.t.. The solution was then concentrated and the residue rinced with 25 ml of Et_2O and dried under vacuum to afford intermediate compound **9**. Then, 100 mL of acetonitrile was added and the resulting solution was degassed with argon for 30 min. Then, 2.00 g (13.34 mmol) of NaI and 1.65 g (1.57 mL, 13.33 mmol) of $P(OMe)_3$ were added, and the reaction was stirred under argon for 3 h. The solution was then concentrated and the resulting solid dissolved in 100 ml of methylene chloride. The organic layer was washed with 3 x 50 mL of water and 50 mL of brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel with ethyl acetate as eluent to afford compound **3** (2.32 g, 36 %) as a red liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (d, *J* = 5.8 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.79 – 3.63 (m, 16H), 3.56-3.54 (m, 4H), 3.37 (s, 6H), 3.13 – 3.04 (m, 2H), 2.98 – 2.89 (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 125.63, 71.94, 70.57, 70.46, 70.05, 59.06, 54.79, 41.36 (d, $J^{(13C-31P)}$ = 161 Hz), 35.30. ^{31}P NMR (121.6 MHz, $CDCl_3$) δ 18.51. (FAB-HRMS: found: 568.1054, calculated: 568.1058.

Synthesis of compound 5

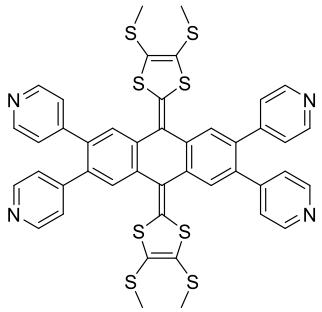


2,3,6,7-tetra(pyridin-4-yl)anthracene-9,10-dione (**2**)

In a 250 mL Schlenk flask charged with 910 mg (1.08 mmol) of 2,3,6,7-tetrabromoanthracene-9,10-dione **1** and 1.28 g (10.40 mmol, 9.6 equiv.) of 4-pyridylboronic acid was added 140 mL of toluene, 50 mL of ethanol and a solution of K_2CO_3 (4.80 g in 4 ml of water). The mixture was degassed with argon for 1 h. Then, 800 mg (0.69 mmol, 0.64 equiv.) of tetrakis(triphenylphosphine)palladium (0) was added, the mixture was degassed for 15 min and stirred under argon at 90°C for 12 hours. The solution was concentrated and 50 ml of methylene chloride was added. The residue was filterer and concentrated. The residue was purified by column chromatography on silica gel with methylene chloride to methylene chloride / methanol (v/v 92/8) as eluent to afford compound **2** (245 mg, 27 %) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, *J* = 6.5 Hz, 8H), 8.44 (s, 4H), 7.17 (d, *J* = 6.5 Hz, 8H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 181.62, 150.20, 146.39, 143.82, 133.22, 129.77, 124.06. FAB-HRMS: found: 516.1585, calculated: 516.1586.

Synthesis of ligand L2Me

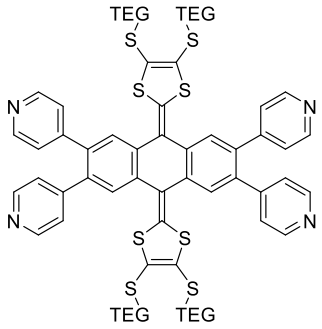


Ligand **L2Me**

In a 50 mL Shlenck flask charged with 221 mg (0.72 mmol) of phosphonate **3**, was added 4 mL of anhydrous THF and the solution was cooled to -78 °C. Then, 280 µL of *n*-BuLi (0.70 mmol, 0.97 equiv., 2.5 M) was added and the solution was stirred at -70 °C for 1 h. Then, 150 mg of **2** (0.29 mmol, 0.4 equiv.) in 10 mL of anhydrous THF was cannulated into the reaction media and the reaction was warmed up to r.t. overnight. Then, the solution was concentrated and 50 ml of methylene chloride was added. The organic layer was washed with 2 x 30 mL of water, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on alumina with methylene chloride to methylene chloride / methanol (v/v 99/1) as eluent to afford ligand **L2Me** (151 mg, 60 %) as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 6.5 Hz, 8H), 7.65 (s, 4H), 7.11 (d, *J* = 6.5 Hz, 8H), 2.42 (s, 12H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 149.89, 147.92, 135.75, 135.08, 134.70, 127.41, 126.67, 124.51, 120.99, 19.36. FAB-HRMS: found: 872.0396, calculated: 872.0393.

Synthesis of ligand L2TEG

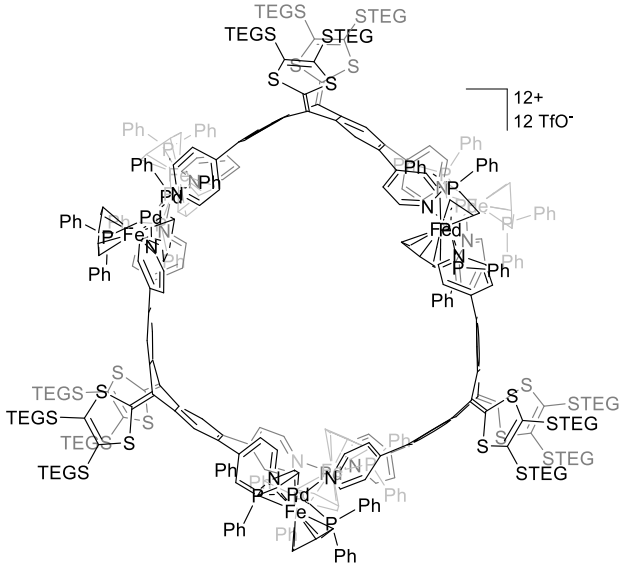


Ligand **L2TEG**

In a 50 mL Shlenck flask charged with 330 mg (0.72 mmol) of phosphonate **4**, was added 4 mL of anhydrous THF and the solution was cooled to -78 °C. Then, 280 µL of *n*-BuLi (0.70 mmol, 0.97 equiv., 2.5 M) was added and the solution was stirred at -70 °C for 1 h. Then, 150 mg of **2** (0.29 mmol, 0.4 equiv.) in 10 mL of anhydrous THF was cannulated into the reaction media and the reaction was warmed up to r.t. overnight. Then, the solution was concentrated and 50 ml of methylene chloride was added. The organic layer was washed with 2 x 30 mL of water, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on alumina with methylene chloride to methylene chloride / methanol (v/v 99/1) as eluent to afford ligand **L2TEG** (176 mg, 65 %) as an orange sticky solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 6.5 Hz, 8H), 7.65 (s, 4H), 7.11 (d, *J* = 6.5 Hz, 8H), 3.74 – 3.64 (m, 12H), 3.71 – 3.61 (m, 32H), 3.54 – 3.50 (m, 8H), 3.35 (s, 12H), 3.03 (td, *J* = 6.5 Hz, 1.3 Hz, 8H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 150.05, 148.03, 135.92, 135.16, 134.51, 127.45, 127.023, 124.64, 120.75, 72.06, 70.74, 70.68, 70.11, 59.19, 35.81. FAB-HRMS: found: 568.1054, calculated: 568.1058.

Synthesis of metalla-structure $Pd_6(L2TEG)_3^{12+}$



$Pd_6(L2TEG)_3^{12+}$

A mixture of ligand **L2TEG** (3 mg, 3.44 µmol) and *cis*-Pd(*dppf*)$(OTf)_2$ (6.59 mg, 6.88 µmol, 2 equiv.) in CH_3NO_2 (1 mL) was stirred for 5 min at room temperature. The red solution was analyzed without any purification.

^{1}H NMR (300 MHz, CD_3NO_2) δ 8.52 (d, *J* = 6.5 Hz, 24H), 8.21 – 8.15 (m, 24H), 7.95 – 7.83 (m, 72H), 7.73 – 7.68 (m, 24H), 7.31 (s, 12H), 7.01 (d, *J* = 6.5 Hz, 24H), 4.98 (s, 12H), 4.81 (s, 12H), 4.72 (s, 24H), 4.67 (s, 12H), 3.60 (t, *J* = 6.8 Hz, 24H), 3.48 – 3.37 (m, 96H), 3.21 (s, 36H), 3.07 – 2.96 (m, 24H). ^{31}P NMR (122 MHz, CD_3NO_2) δ 33.78.

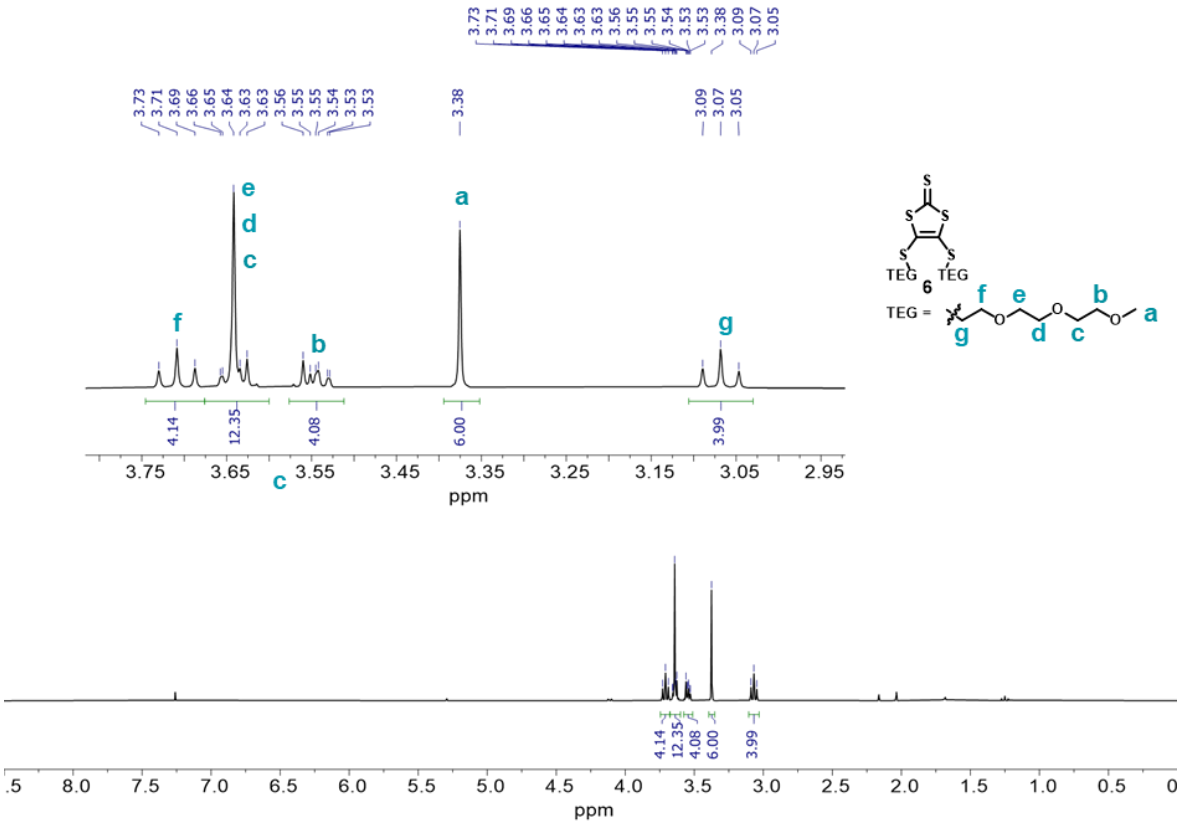


Figure S1. ^{1}H NMR of **6** in $CDCl_3$.

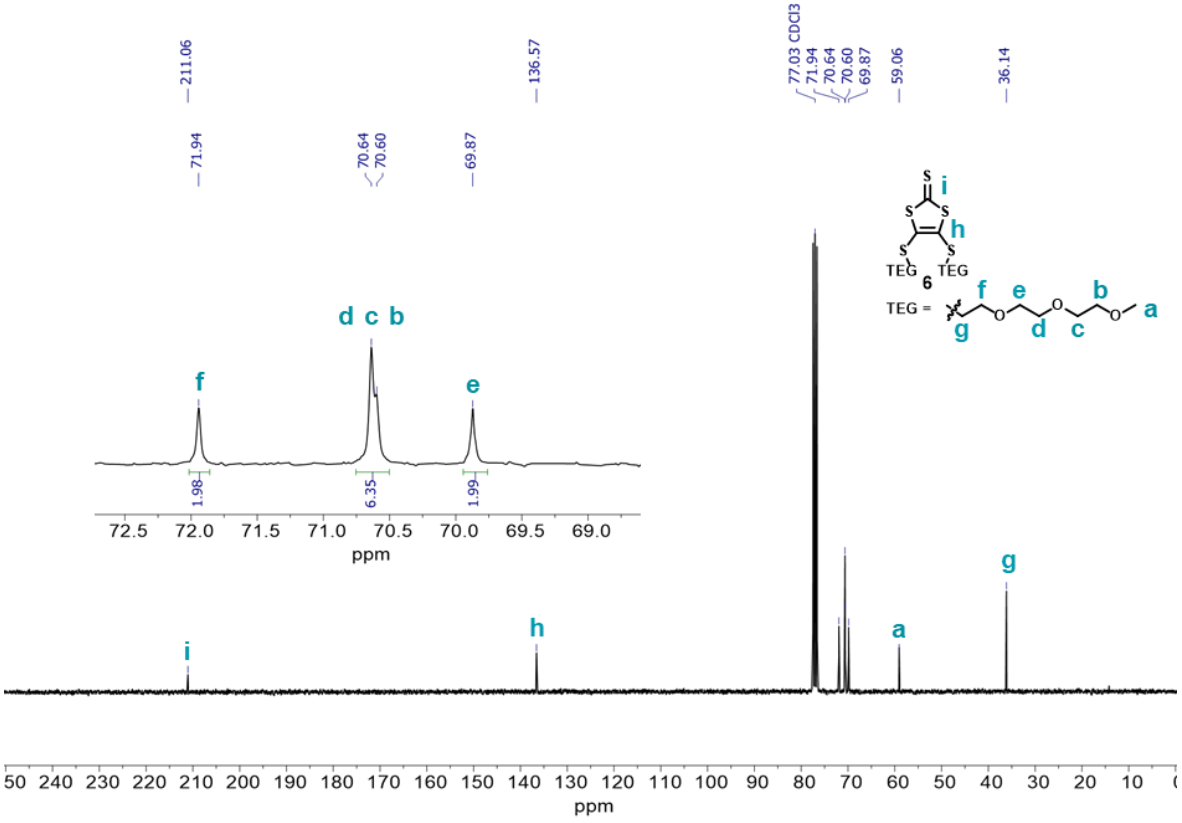


Figure S2. ^{13}C NMR of **6** in $CDCl_3$.

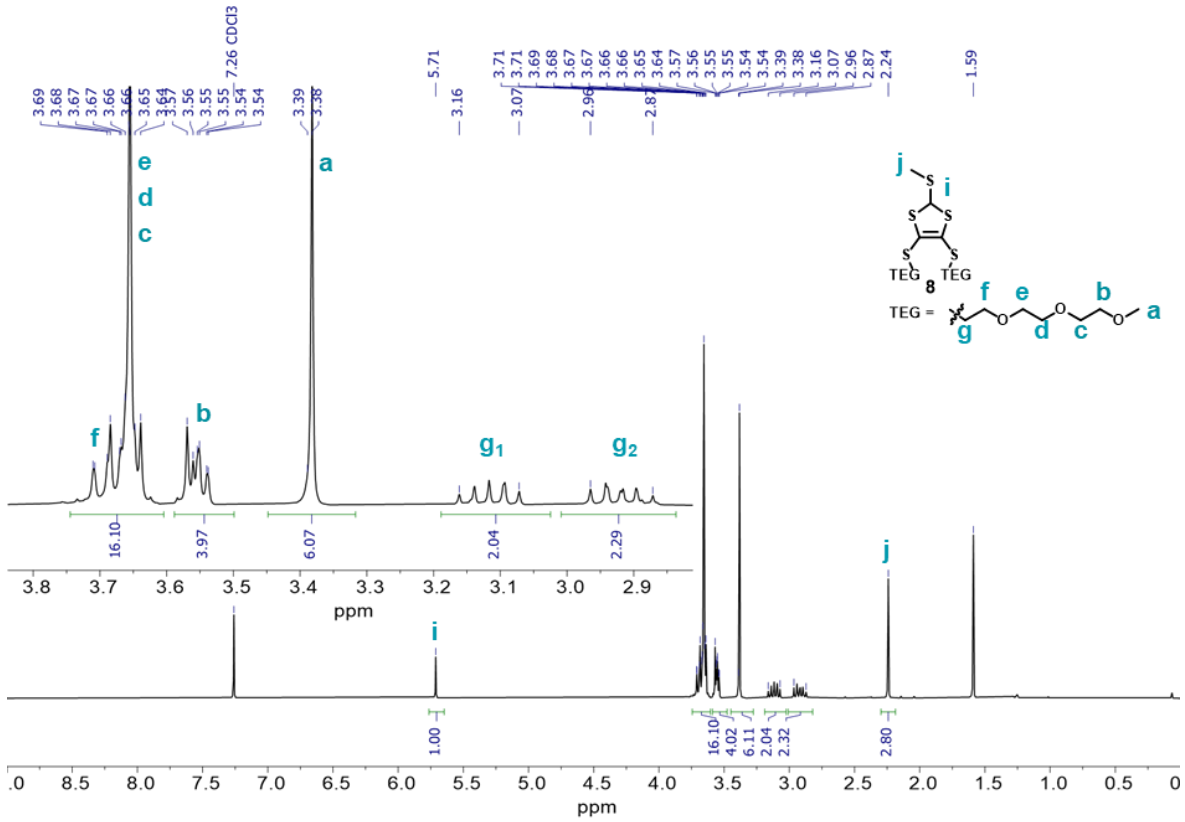


Figure S3. ^{1}H NMR of **8** in $CDCl_3$.

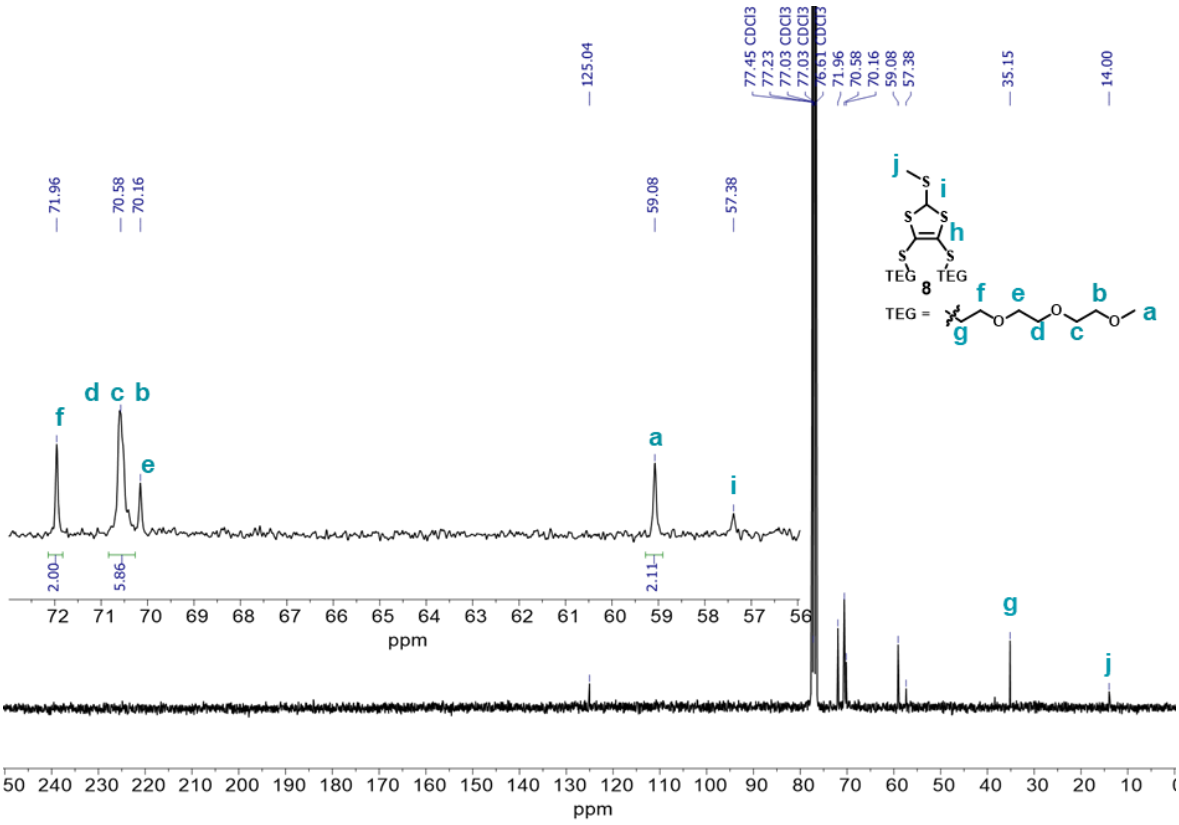


Figure S4. ^{13}C NMR of **8** in $CDCl_3$.

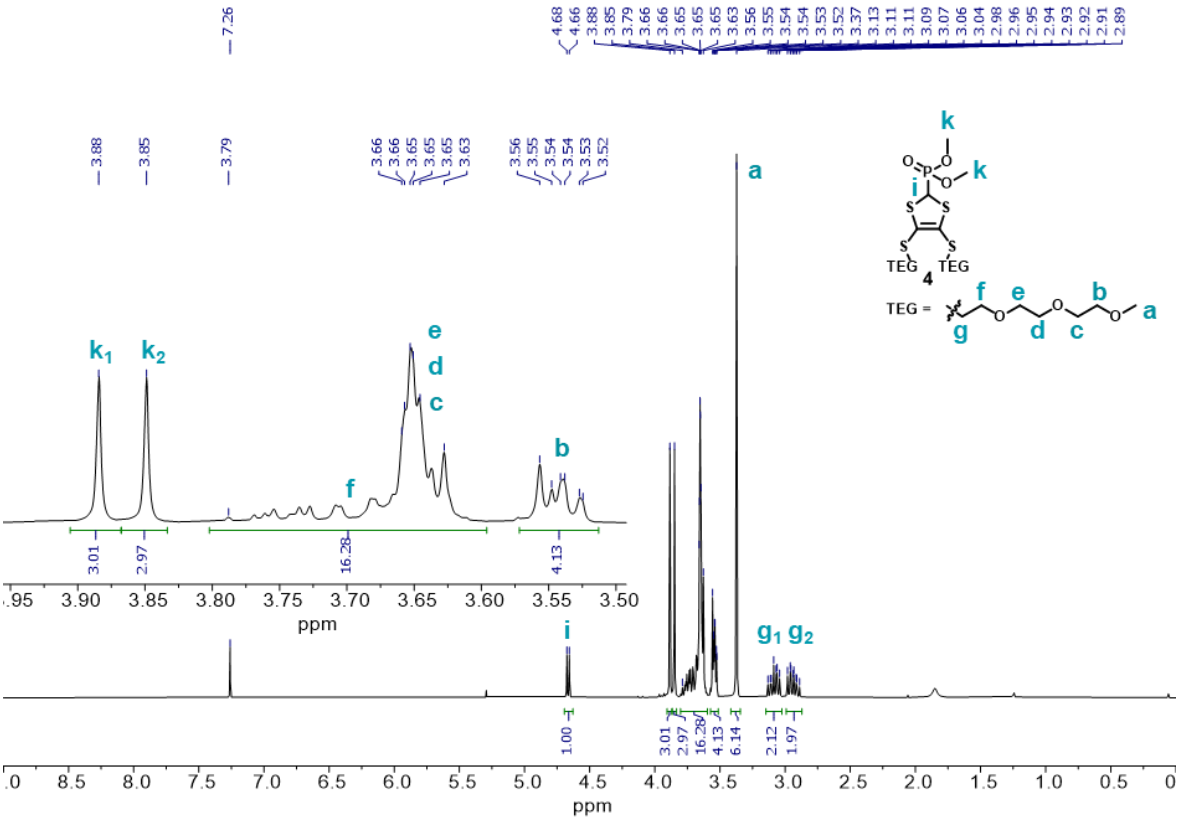


Figure S5. ^{1}H NMR of **4** in $CDCl_3$.

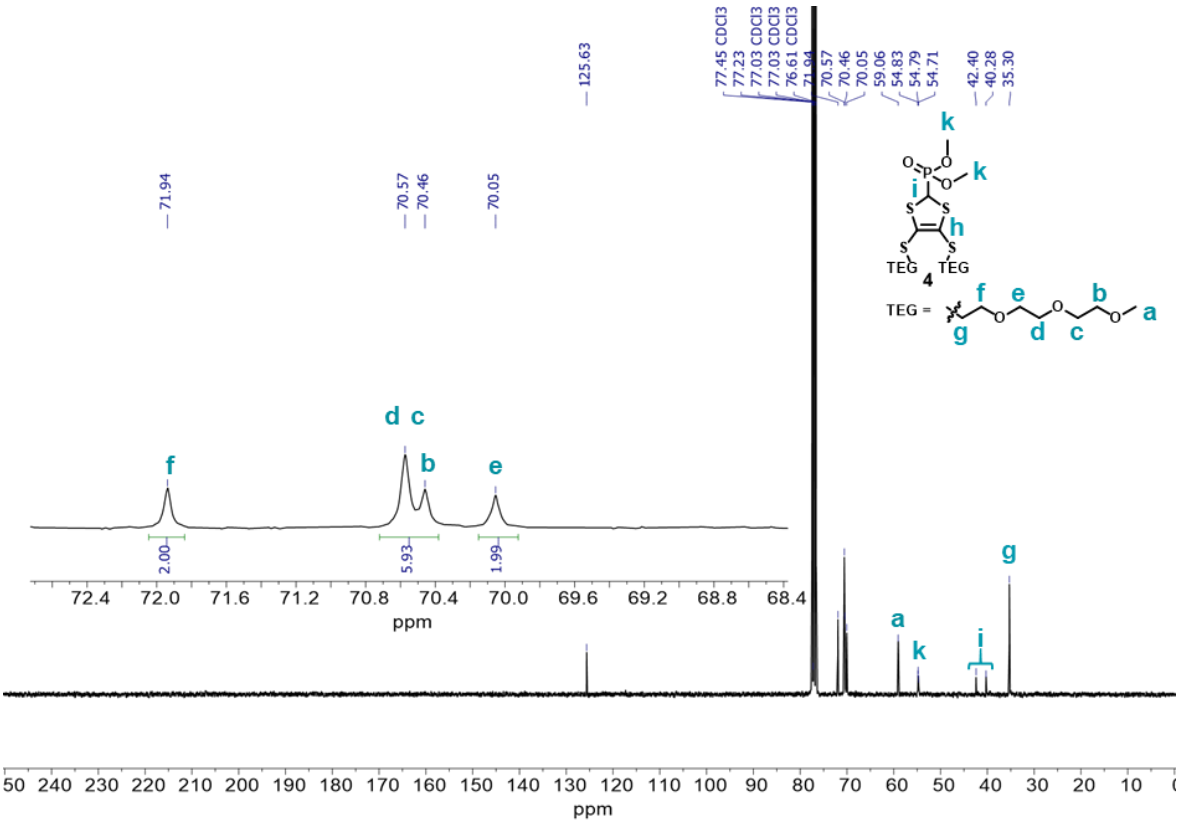


Figure S6. ^{13}C NMR of **4** in $CDCl_3$.

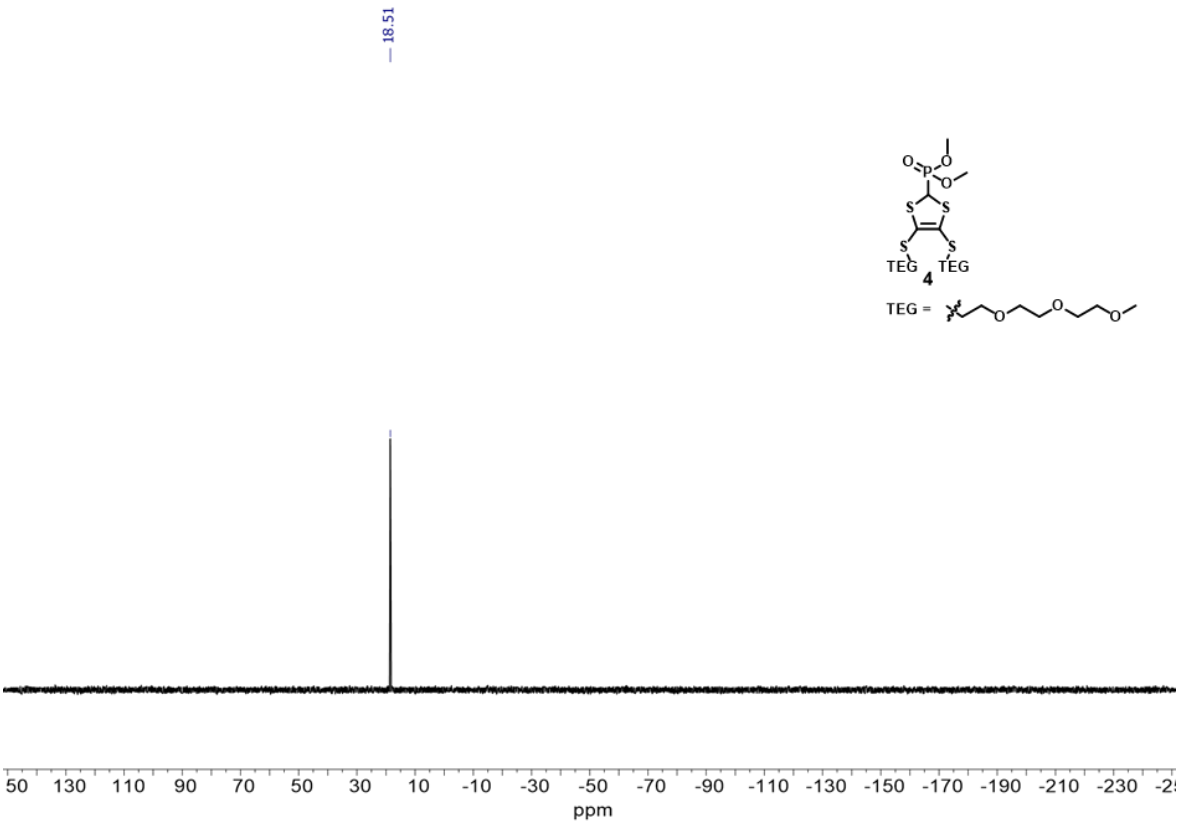


Figure S7. ^{13}P NMR of **4** in $CDCl_3$.

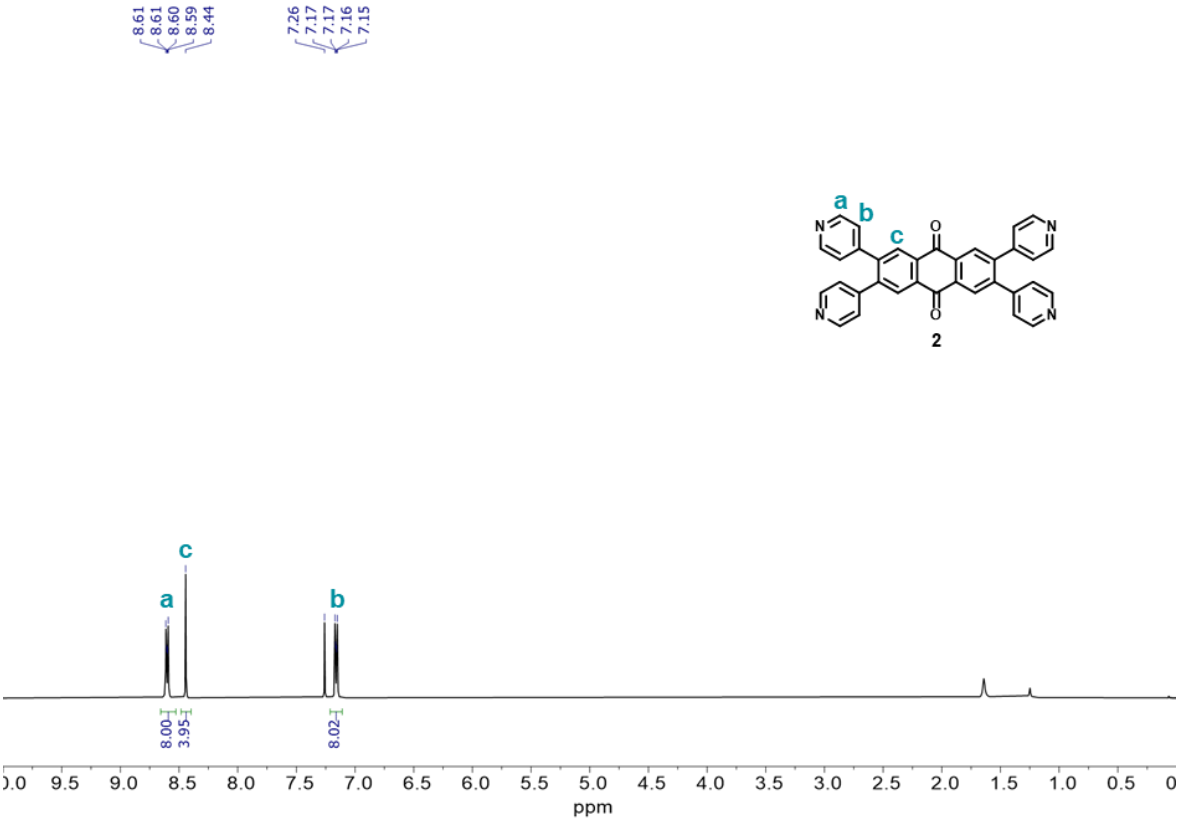


Figure S8. ^{1}H NMR of **2** in $CDCl_3$.

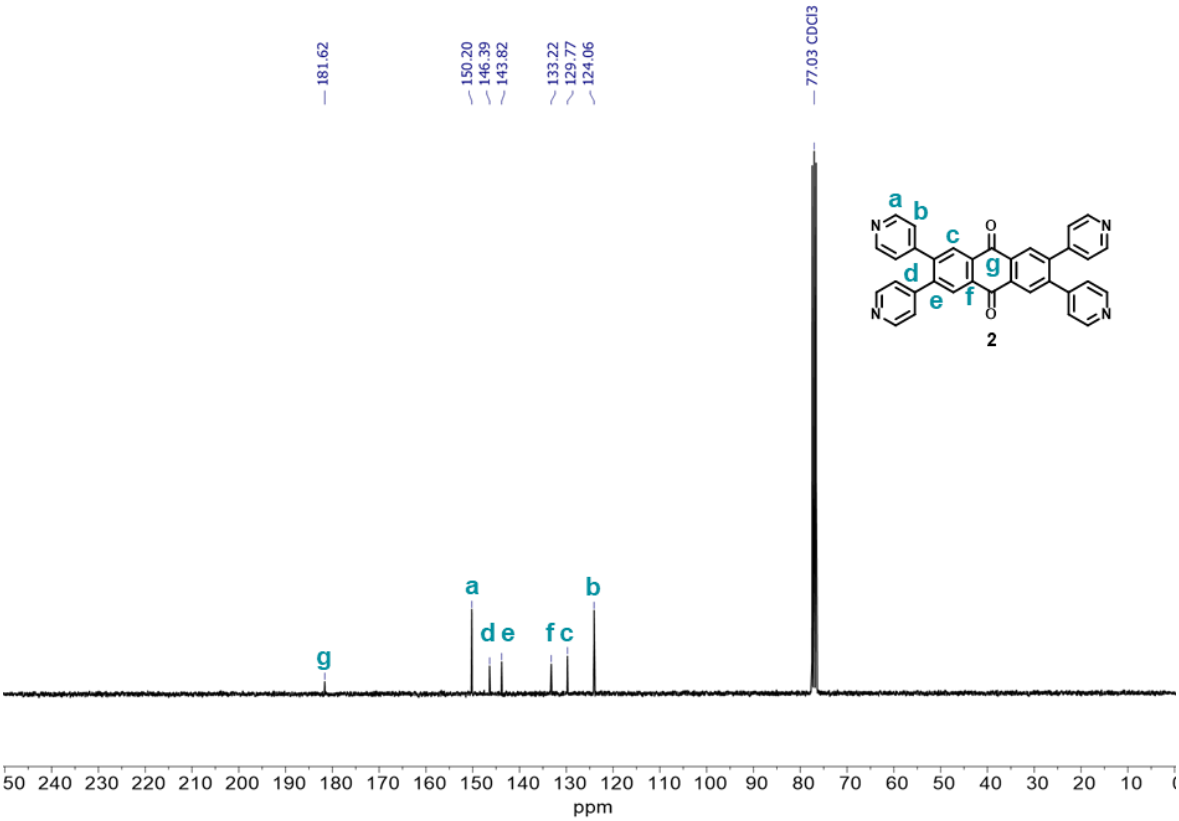


Figure S9. ^{13}C NMR of **2** in $CDCl_3$.

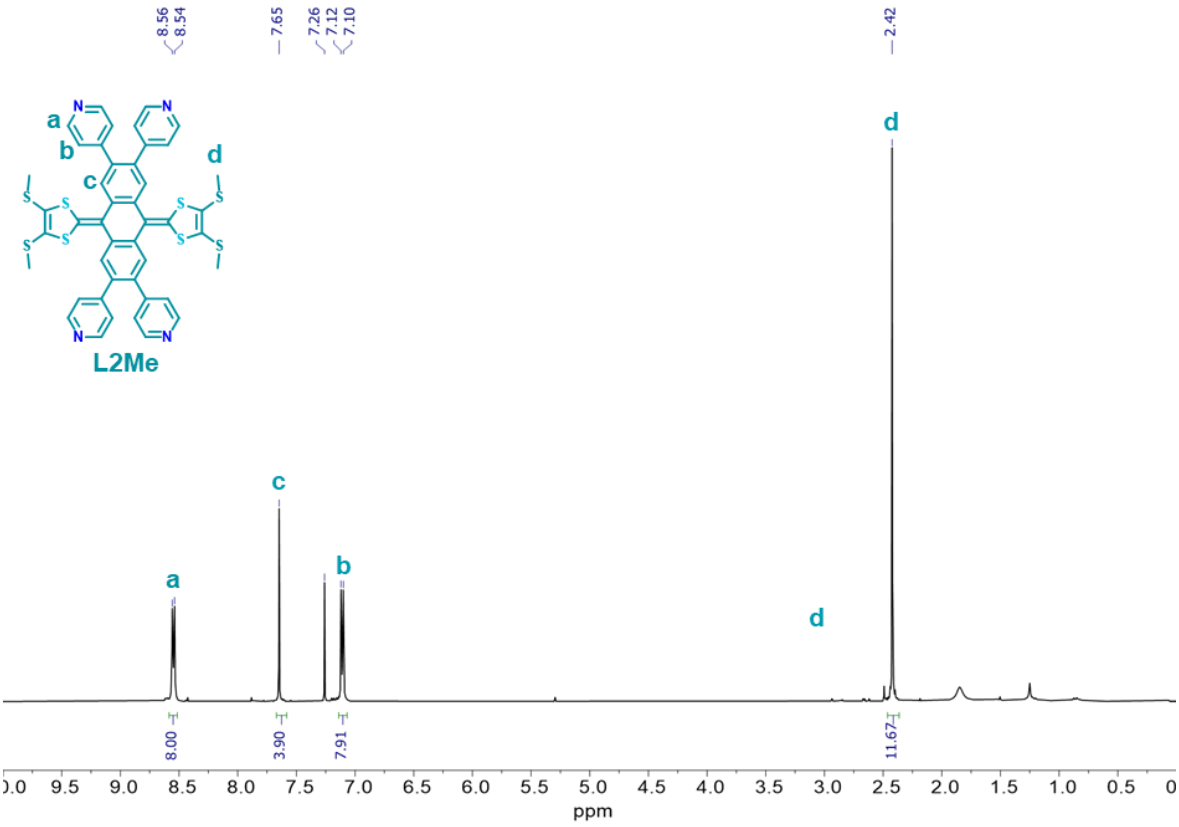


Figure S10. ^{1}H NMR of **L2Me** in $CDCl_3$.

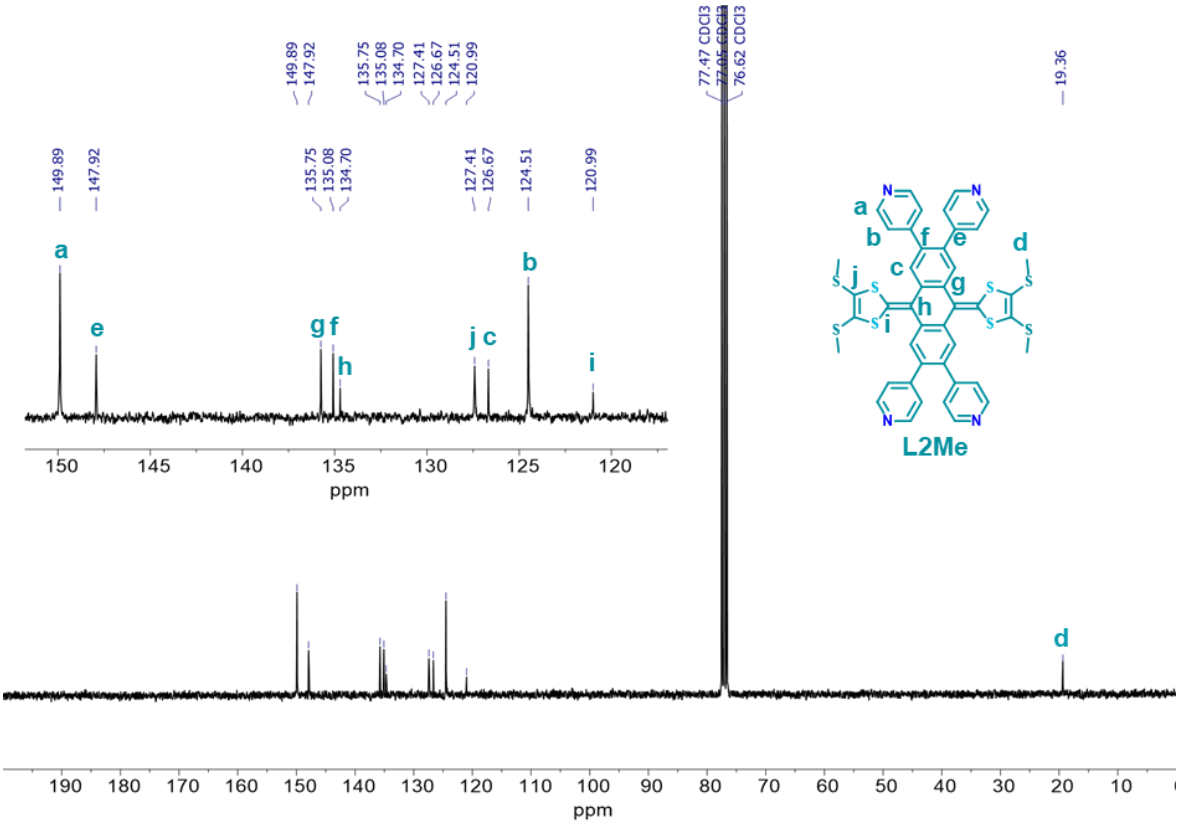


Figure S11. ^{13}C NMR of **L2Me** in $CDCl_3$.

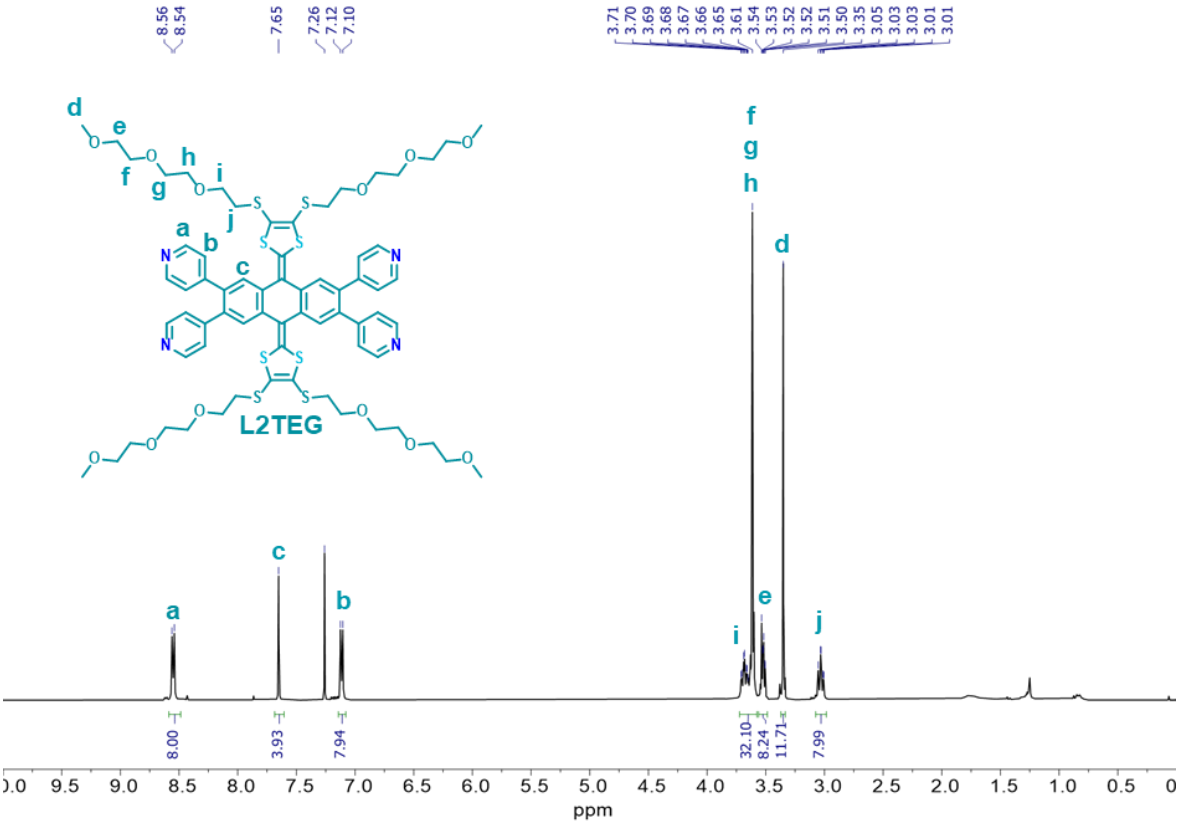


Figure S12. ^{1}H NMR of **L2TEG** in $CDCl_3$.

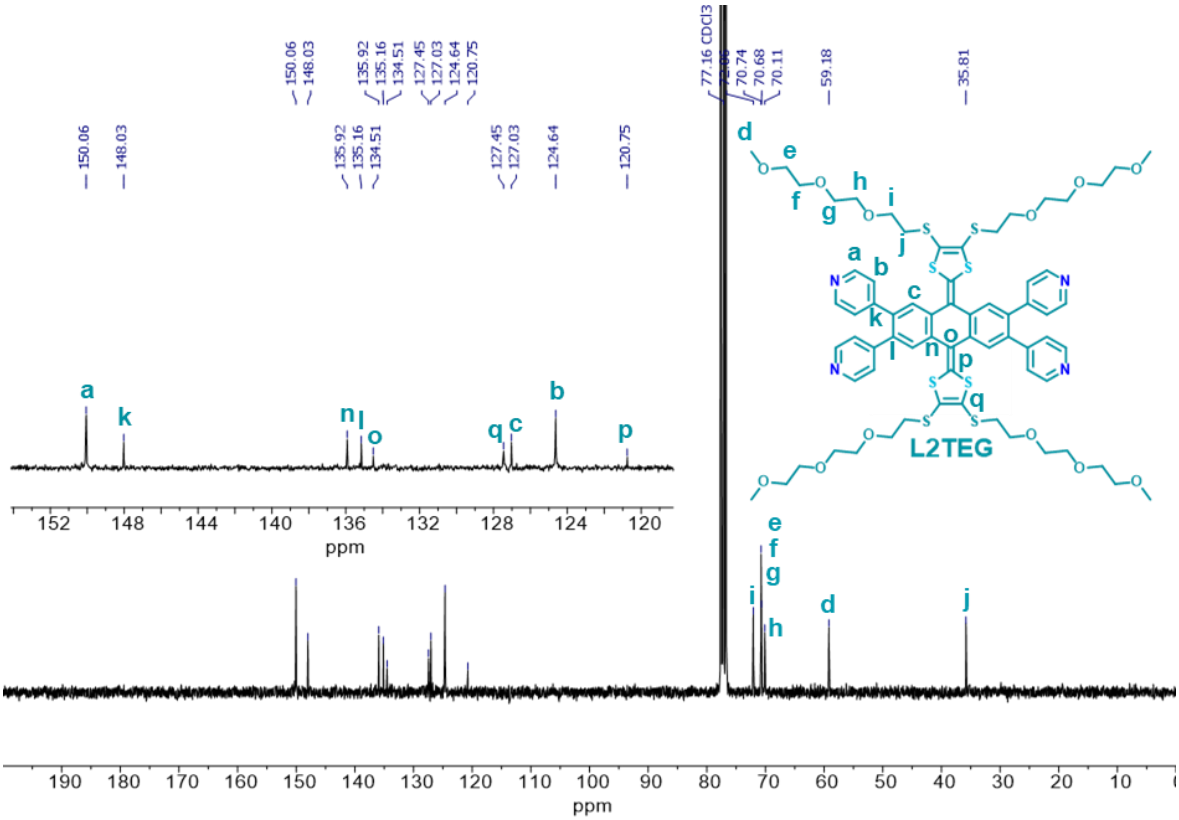


Figure S13. ^{13}C NMR of **L2TEG** in $CDCl_3$.

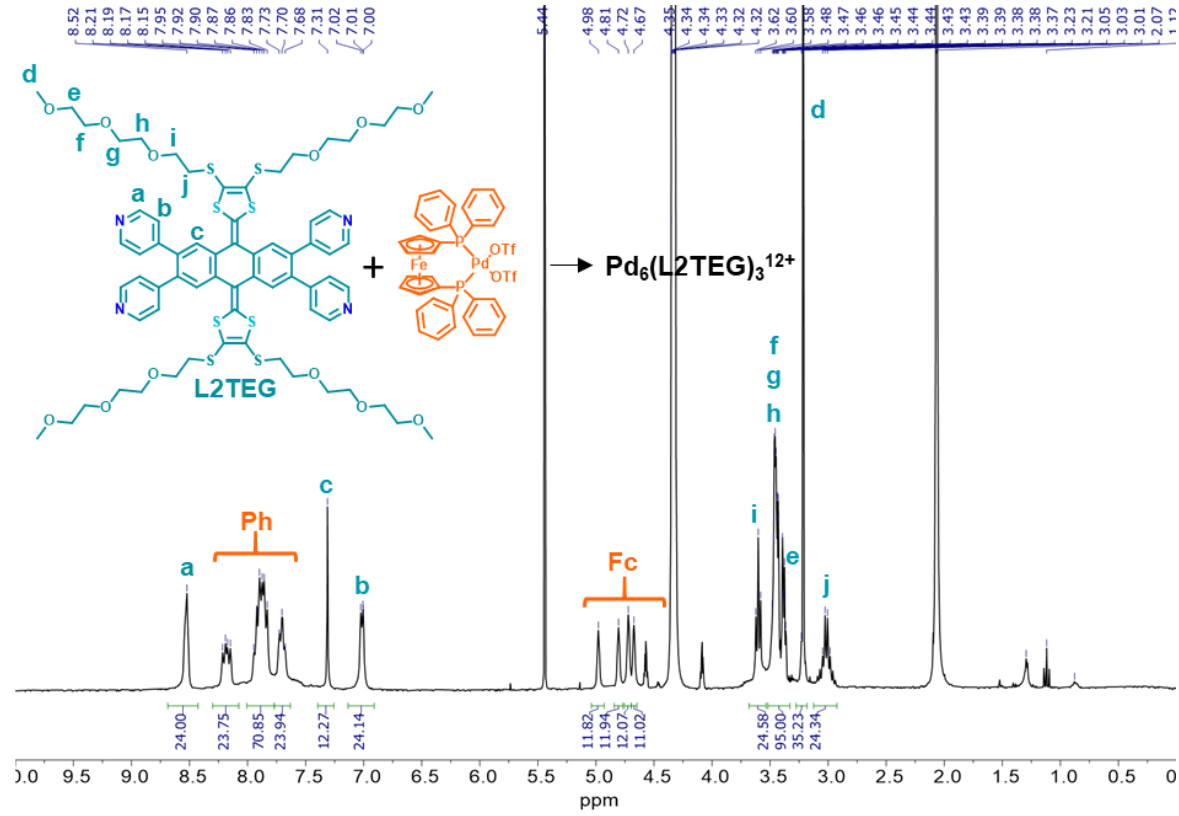


Figure S14. ^{1}H NMR of **$Pd_6(L2TEG)_3^{12+}$** in CD_3NO_2 at C = 2×10^{-3} M.

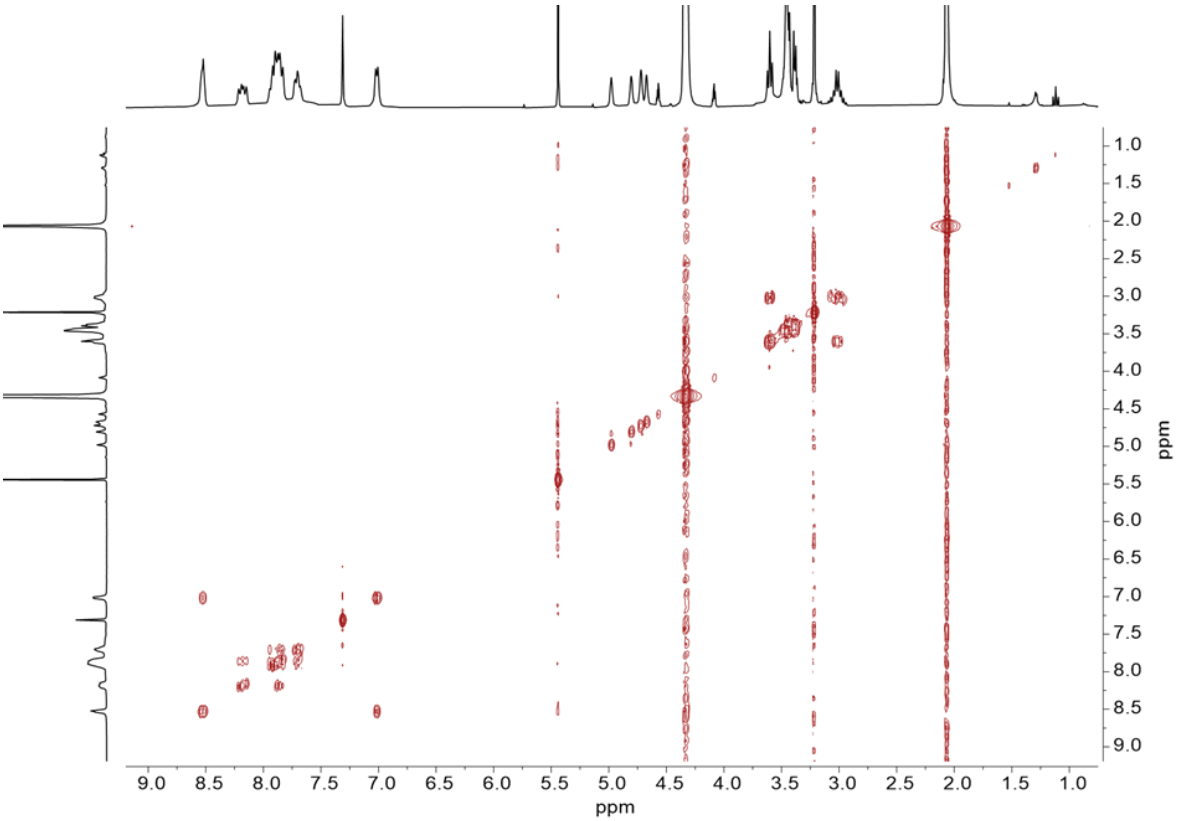


Figure S15. ^{1}H COSY NMR of **$Pd_6(L2TEG)_3^{12+}$** in CD_3NO_2 at C = 2 × 10^{-3} M.

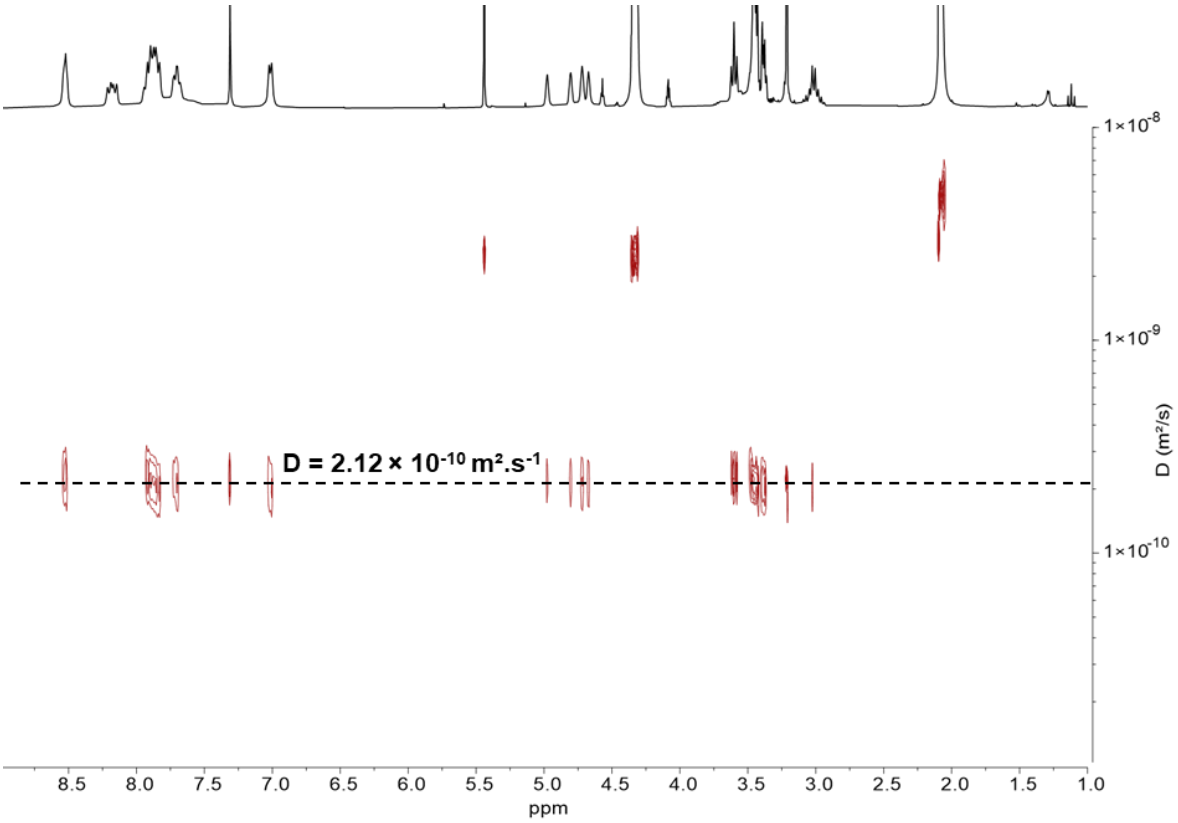


Figure S16. ^{1}H DOSY NMR of **$Pd_6(L2TEG)_3^{12+}$** in CD_3NO_2 at C = 2 × 10^{-3} M.

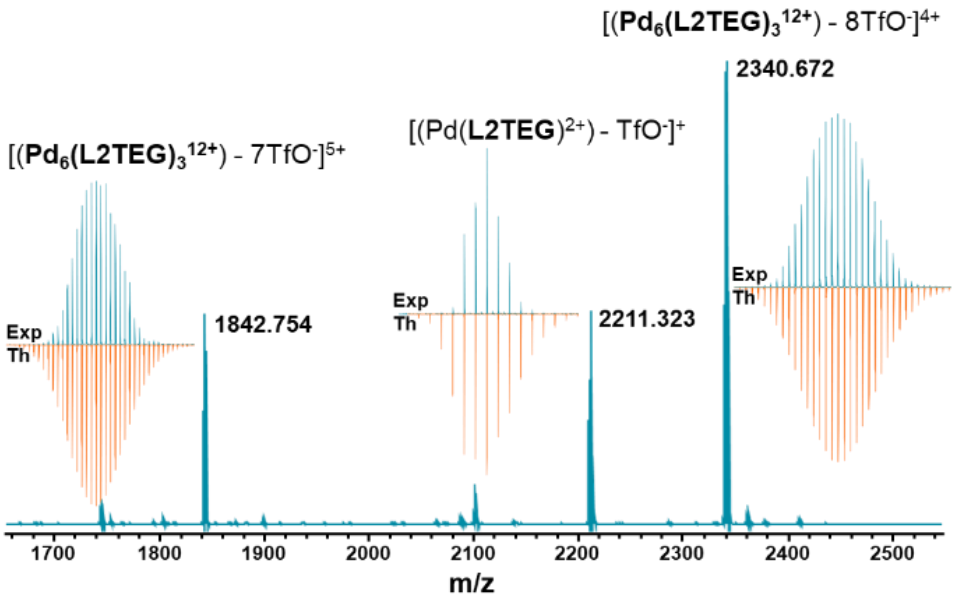


Figure S17. ESI-FTICR-HRMS of self-assembly **$Pd_6(L2TEG)_3^{12+}$** recorded at C = 10^{-3} M in CH_3NO_2.

X-Ray diffraction

X-ray single-crystal diffraction data for **L2Me** was collected at 150 K on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector and micro-focus Cu-Kα radiation (λ = 1.54184 Å). The structure was solved by direct methods, expanded and refined on F^2 by full matrix least-squares techniques using SHELX programs (G. M. Sheldrick, SHELXS 2013/1 and SHELXL 2016/4). All non-hydrogen atoms were refined anisotropically and the H atoms were included in the calculation without refinement. Multiscan empirical absorption was corrected using CrysAlisPro program (CrysAlisPro, Rigaku O.D., V1.171.38.46, 2015).

Crystallographic data for **L2Me**: $C_{44}H_{32}N_4S_8$, M = 873.21, orange prism, 0.371 x 0.223 x 0.201 mm^3, monoclinic, space group $P2_1/c$, a = 13.6654(2) Å, b = 14.8503(2) Å, c = 20.1186(3) Å, β = 92.850(1)°, V = 4077.7(1) $Å^3$, Z = 4, ρcalc = 1.422 g/cm^3, μ = 4.358 mm^{-1}, F(000) = 1808, θmin = 3.238°, θmax = 76.421°, 17395 reflections collected, 8328 unique (R_{int} = 0.0236), parameters / restraints = 509 / 0, R1 = 0.0490 and wR2 = 0.1314 using 7702 reflections with I>2σ(I), R1 = 0.0538 and wR2 = 0.1359 using all data, GOF = 1.035, -0.702< Δρ < 0.789 e.$Å^{-3}$. CCDC 2109395.

Molecular Modeling

Molecular modeling was performed by using the molecular mechanics force field MM+ method from the HyperChem Professional 8.0.3 program (Hypercube, Inc., Waterloo, ON, Canada,) configured *in vacuo*, with an RMS of 10^{-5} kcal/mole, a number of maximum cycles of 32500, and a Polak-Ribiere algorithm. Counter anions were omitted to simplify the calculation.

1. C. Wang, A. S. Batsanov, M. R. Bryce and J. A. K. Howard, *Synthesis*, 1998, **11**, 1615.
2. A. K. Bar, R. Chakrabarty, K. W. Chi, S. R. Batten and P. S. Mukherjee, *Dalton Trans.*, 2009, 3222.
3. D. Bailey and V. E. Williams, *Tetrahedron Letters*, 2004, **45**, 2511.
4. G. J. Marshallsay and M. R. Bryce, *J. Org. Chem.*, 1994, **59**, 6847.