Mixed Valence Radical Cations and Intermolecular Complexes Derived from Indenofluorene-Extended Tetrathiafulvalenes

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Supporting Information

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Experimental

General Methods. Compounds **4** (S. Merlet, M. Birau and Z. Y. Wang, *Org. Lett.*, 2002, **4**, 2157-2159) and **5** (N. Le Narvor, N. Robertson, E. Wallace, J. D. Kilburn, A. E. Underhill, P. N. Bartlett, and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1996, 823-828) were prepared by literature procedures. The syntheses of the phosphonate esters **7** (previously used without preparative details, J. Rybácek, M. Rybácková, M. Høj, M. Belohradsky, P. Holy, K. Kilså and M. B. Nielsen, *Tetrahedron*, 2007, **63**, 8840-8854) and **9** were performed in analogy to the synthesis of related compounds (A. J. Moore and M. R. Bryce, *Tetrahedron Lett.*, 1992, **33**, 1373-1376). Reactions were performed under an inert atmosphere. Purification of products was carried out by flash chromatography on silica gel. Neutralized silica was prepared by suspending silica in NEt_3:heptane 1:19. After stirring for 2 min, the suspension was added to the column, and then flushed with eluent corresponding to at least 1.5 x the volume of the column. Thin-layer chromatography (TLC) was carried out using aluminum sheets pre-coated with silica gel. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on an instrument with cryoprobe using the residual solvent as the internal standard. All chemical shifts are quoted on the δ scale (ppm), and are referenced to the solvent residual signal ($CDCl_3$: 7.26 and 77.16 for ^{1}H and ^{13}C, respectively). All coupling constants (*J*) are expressed in Hz. IR spectra were measured using the attenuated total reflectance (ATR) method on diamond. The relative peak intensities in IR spectra are designated as vw = very weak, w = weak, m = medium, s = strong, vs = very strong, br = broad, sh = shoulder. Melting points are uncorrected. Elemental analysis was either conducted at Univ. of Copenhagen or at London Metropolitan University.

Cyclic Voltammetry. Electrochemical samples were measured in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 as supporting electrolyte. External reference: Fc/Fc^+ (E = 0.00 V) scanned at 100 mVs^{-1}, measured before and after sample. Fc was also used as a guide to estimate the number of electrons in the reversible redox process. Electrodes: working; glassy carbon disk electrode, counter; platinum. The silver reference electrode was soaked in electrolyte solution.

UV-Vis-NIR Spectroelectrochemistry. Spectroelectrochemical experiments were carried out at room temperature in CH_2Cl_2 solutions with 0.1 M NBu_4PF_6 as electrolyte, using an optically transparent thin-layer electrochemical (OTTLE) cell equipped with a Pt mini grid working electrode (32 wires cm^{-1}) and CaF_2 windows (M. Krejčík, M. Daněk and F. Hartl, *J. Electroanal. Chem.*, 1991, **317**, 179-187). The cell was positioned in the sample compartment so the photon source passed through the working electrode mini grid (The narrow slit width setting was chosen in the instrument settings, to get better resolution. The UV-Vis-NIR (200-3200 nm) spectra were obtained using a Varian Cary 5E spectrophotometer with a scan rate of 1818 nm/min in double beam mode, with normal and reduced slit height and a step size of 1 nm. The controlled-potential electrolysis was carried out using a CH Instruments Model CHI630B potentiostat to manually adjust the potential.

ESR Spectroelectrochemistry. Commercially available CH_2Cl_2 and decamethylferrocene (DmFc) were used without further purification. Bu_4NPF_6 was dried under reduced pressure at 70 °C for 24 h and then stored in a desiccator. Cyclic voltammograms (CV) were recorded using a one-compartment electrochemical cell with platinum wires as working and counter electrodes and a Ag wire as a pseudo-reference electrode. Electrochemical measurements were performed under inert argon atmosphere at rt. *In situ* ESR/UV–Vis–NIR spectroelectrochemical experiments were performed in an optical ESR cavity. Both, the ESR spectrometer and the UV–vis–NIR spectrometer were linked to the potentiostat triggering both spectrometers. For standard *in situ* ESR/Vis-NIR spectroelectrochemical experiments an ESR flat cell was used. A laminated platinum mesh as the working electrode, a silver wire as

the pseudo-reference electrode, and a platinum wire as the counter electrode were used in spectroelectrochemical experiments. To reach the nearly thin layer conditions, the electrolyte volume was reduced by inert foil sheets inserted into the flat cell.

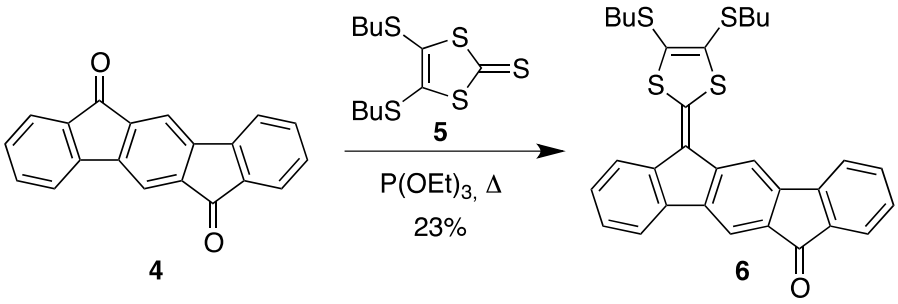
Electrocrystallization. Electrocrystallizations of **10** (typically 6 mg) were carried out in a conventional *H*-type cell with the anode and cathode compartment separated by two glass frits. The anode was a Pt-wire (d = 0.6 mm) that prior to use was cleaned by heating to a red-glowing state in a Bunsen burner. The cathode was a Pt-coil. The solvent was PhCl containing either Bu_4NPF_6 (sat. solution), Bu_4NBF_4 (sat. solution) or Bu_4NTaF_6 (0.02 M) as supporting electrolyte, and the volume of the anode chamber was approximately 25 mL. The current was 1 – 4 μA and maintained at a constant value during the electrolysis. Electrolysis was interrupted after the passage of charge corresponding to 1F; typically the electrolysis time was 7-9 days. A black, conducting deposit appeared after some hours and continued to grow until the electrolysis was stopped. The electrode with the deposit was washed twice with PhCl, then twice with EtOH and finally once with petrol ether (bp 40-65 ^oC) and was then allowed to dry before it was collected from the anode with a spatula.

ESR on Femtomole Samples. The detailed description of our femtomole ESR technique is presented elsewhere (S. E. de Graaf, A. V. Danilov and S. E. Kubatkin, *IEEE Trans. Appl. Supercond.*, 2014, **24**, 1500605; S. E. de Graaf, D. Davidovikj, A. Adamyan, S. E. Kubatkin and A. V. Danilov, *Appl. Phys. Lett.*, 2014, **104**, 052601); here we will briefly describe the set up essentials for the reader's convenience.

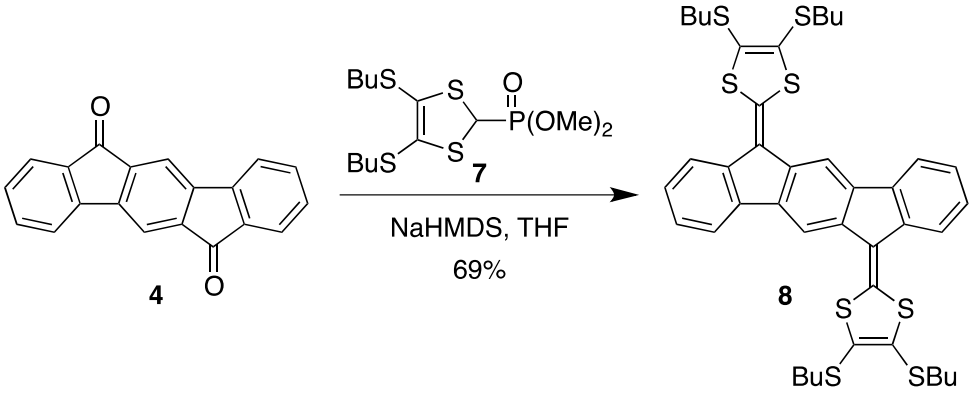
The ESR spectrometer is mounted in a cryogen-free He3 refrigerator, and the central part of the spectrometer is a superconducting thin film resonator (140 nm NbN on Al_2O_3). The design of the resonator is optimized to withstand strong magnetic fields, which otherwise can be detrimental for superconducting cavities, and to have an enhanced magnetic microwave field in a micron-sized volume (S. E. de Graaf, D. Davidovikj, A. Adamyan, S. E. Kubatkin and A. V. Danilov, *Appl. Phys. Lett.* **2014**, *104*, 052601; S. E. de Graaf, A. V. Danilov, A. Adamyan, T. Bauch and S. E. Kubatkin, *J. Appl. Phys*., 2012, **112**, 123905). This enables us to measure the ESR signal in samples of similar size down to T = 300 mK. The resonators used in the experiments had loaded quality factors in the range $1\text{-}3\cdot10^5$. This, together with the reduced mode volume of our 2D cavity, allows us to reach a sensitivity of down to $\sim10^5$ spins/rtHz for microwave frequencies up to the X-band (10 GHz). A cryogenic HEMT amplifier with a noise temperature of 5 K allows us to measure on such small spin ensembles without saturating them and maintaining a good signal-to-noise ratio. Both the frequency and dissipation response of the cavity is monitored in a microwave transmission measurement (V. Ranjan, G. de Lange, R. Schutjens, T. Debelhoir, J. P. Groen, D. Szombati, D. J. Thoen, T. M. Klapwijk, R. Hanson and L. DiCarlo, *Phys. Rev. Lett.*, 2013, **110**, 067004). Spin-parameters were extracted using a model of two coupled oscillators (S. E. de Graaf, A. V. Danilov and S. E. Kubatkin, *IEEE Trans. Appl. Supercond.*, 2014, **24**, 1500605; D. I. Schuster, A. P. Sears, E. Ginossar, L. DiCarlo, L. Frunzio, J. J. L. Morton, H. Wu, G. A. D. Briggs, B. B. Buckley, D. D. Awschalom and R. J. Schoelkopf, *Phys. Rev. Lett.*, 2010, **105**, 140501).

Conductance Measurements. Conductivities of the cation radical salts were measured on compressed powder samples in a shop-made conductivity measurement cell. The cell was constructed so as to allow the compression of powdered samples between two tungsten anvil electrodes (ø 3mm) while having the sample housed in a sleeve of hard PVC, supported in a stainless steel holder. The powder being measured on was compressed by employing a cell design analogous to that used for compression of KBr pellets for IR spectroscopy. This design does not allow for the measurement of the compression force, due to the unknown frictional resistance of the thread employed, but does however allow for a reproducible

degree of compression. The insulation resistance of the conductivity measurement cell was in excess of 20 GΩ when empty with air-spaced electrodes. The Ohmic resistances were measured with a 6.5 digit system multimeter with 100 NPLC integration time (6.5 digit) and automatic offset compensation. The dimension of the samples was given by the diameter of the tungsten anvil electrodes (ø 3mm) and the height of the samples, as measured by a micrometer with 0.01 mm resolution. The errors on the measurements encompass uneven particle size of the powder measured, contact resistance between the conductivity measurement cell and the four wires connecting it to the system multimeter, contact resistance between the sample and the tungsten electrodes and the error on height of the samples as measured by the micrometer. Summing over these uncertainties, the measurements are believed to be within an error of 20%.

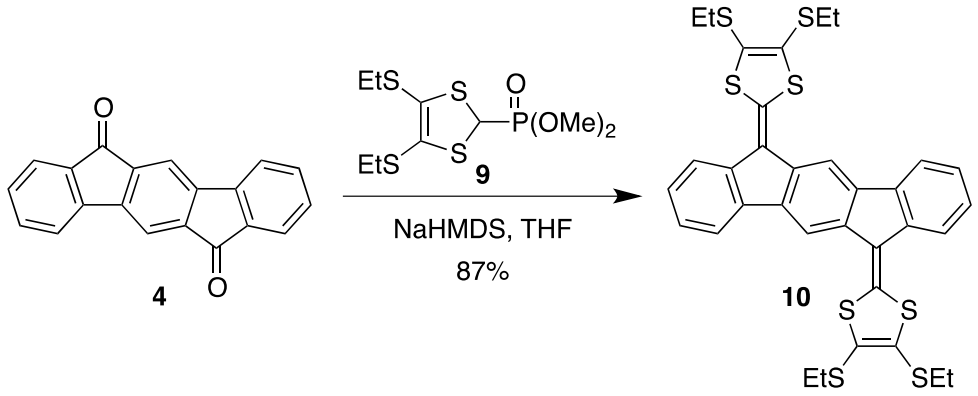


12-[4,5-bis(butylthio)-1,3-dithiol-2-ylidene]indeno[1,2-*b*]fluoren-6(12*H*)-one (6). To a mixture of **4** (100 mg, 0.354 mmol) and **5** (330 mg, 1.06 mmol) was added $P(OEt)_3$ (5 mL) and the mixture was heated to 100 °C for 90 min. The phosphite was then removed under reduced pressure, and the residue subjected to flash column chromatography (neutralized SiO_2, CH_2Cl_2:heptane 1:1), which gave **6** (major red band) as a dark red solid with minor impurities (45 mg, 23%). *Obtaining a spectroscopically pure sample was rather difficult, but achieved by purifying the sample by flash column chromatography (SiO_2, THF:petroleum spirit (40-65 °C) 1:1) followed by concentration to dryness. An attempt of purifying the sample by dissolving it in a minimal amount of CH_2Cl_2 and transferring this solution to stirred MeOH slowly caused an orange precipitate, which, however, deteriorated.* MP: 134 – 136 °C. IR (ART, cm^{-1}): ν = 2952 w, 2923 w, 2868 w, 1702 s (C=O), 1611 m, 1530 s, 1485 m, 1426 s, 1283 m, 1228 m, 1180 m, 1128 m, 945 m, 880 m, 848 m, 759 s, 771 s, 447 s. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.05 (s, 1H), 7.86 - 7.84 (s + d, 2H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.52 (td, *J* = 7.5, 1.1 Hz, 1H), 7.43 (td, *J* = 7.5, 1.1 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.30 (td, *J* = 7.4, 1.0 Hz, 1H), 3.03, 3.02 (2x t, *J* = 7.3 Hz, 4H), 1.81 – 1.64 (m, 4H), 1.58 – 1.46 (m, 4H), 0.97 (q, *J* = 7.6 Hz, 6H). *Chemical shifts are concentration dependent.* ^{13}C NMR (126 MHz, CD_2Cl_2) δ 193.52, 145.32, 144.32, 143.89, 142.47, 138.92, 137.69, 137.45, 135.92, 134.98, 131.81, 131.04, 129.48, 129.33, 127.85, 126.33, 124.28, 123.28, 120.59, 120.57, 120.46, 116.13, 114.98, 37.06, 36.90, 32.44, 32.41, 22.29, 22.27, 13.99, 13.95. MS (MALDI+): *m*/*z* = 544.0 [$M^{\bullet+}$]. EA ($C_{31}H_{28}OS_4$, 544.81): calcd. C 68.34, H 5.18; found C 67.99, H 5.11.

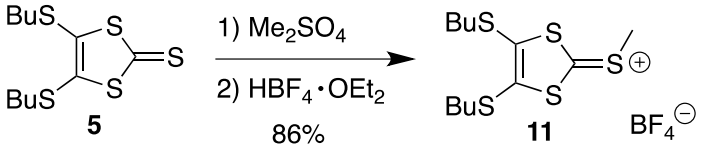


6,12-Bis[4,5-bis(butylthio)-1,3-dithiol-2-ylidene]-6,12-dihydroindeno[1,2-*b*]fluorene (8). The phosphonate ester **7** (485 mg, 1.24 mmol) was dissolved in dry THF (10 mL), and degassed for 15 min. The solution was cooled to –78 °C and NaHMDS (2.00 mL, 0.6 M in toluene, 1.20 mmol) was added. After 1 h of stirring, the mixture was cannulated to a suspension of **4** (88 mg, 0.31 mmol) in THF (10 mL) at –78 °C. The cooling bath was

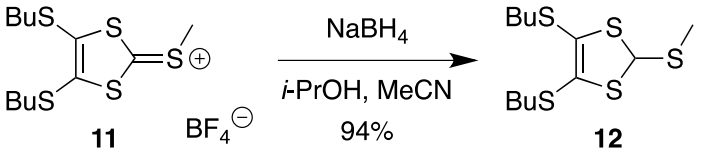
removed, and the mixture was stirred for 2 h, poured into saturated aqueous NH_4Cl (50 mL), and extracted with CH_2Cl_2 (2 x 50 mL). The organic phases were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Flash column chromatography (SiO_2, CS_2) gave **8** (major orange band) as a yellow solid (175 mg, 69%). Crystals suitable for X-ray diffraction studies were grown via vapor diffusion of MeOH into a CH_2Cl_2 solution. MP: 156 – 157 °C. IR (ART, cm^{-1}): ν = 2956 w, 1535 s, 1479 s, 1460 s, 1440 s, 1428 s, 1215 m, 1185 m, 816 m 751 s, 740 m, 699 s, 629 m, 479 s, 458 s. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.94 (d, *J* = 6.7 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.39 – 7.33 (m, 2H), 3.01 (2×t, *J* = 7.4 Hz, 8H), 1.81 – 1.67 (m, 8H), 1.62 – 1.45 (m, 8H), 0.98 (2×t, *J* = 7.4 Hz, 12H). *Chemical shifts are concentration dependent.* ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.52, 137.79, 137.54, 136.78, 135.07, 129.38, 128.44, 126.83, 125.73, 123.09, 121.21, 119.61, 114.38, 36.56, 36.42, 32.04, 31.97, 21.93, 21.89, 13.83, 13.79. MS (MALDI+) *m/z* = 806.6 [$M^{\bullet+}$]. EA ($C_{42}H_{46}S_8$, 807.33): calcd. C 62.48, H 5.74; found C 62.54, H 5.52.



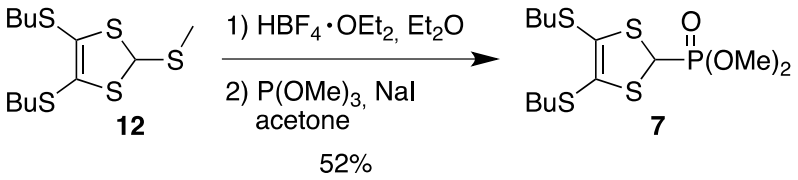
6,12-Bis[4,5-bis(ethylthio)-1,3-dithiol-2-ylidene]-6,12-dihydroindeno[1,2-*b*]fluorene (10). The phosphonate ester **9** (340 mg, 1.02 mmol) was dissolved in dry THF (10 mL), and degassed for 15 min. The solution was cooled to –78 °C and NaHMDS (1.70 mL, 0.6 M in toluene, 1.02 mmol) was added. After 15 min of stirring, the mixture was cannulated to a degassed and sonicated suspension of the dione **4** (72 mg, 0.256 mmol) in THF (10 mL) at –78 °C. The cooling bath was removed, and the mixture was stirred for 2 h, poured into saturated aqueous NH_4Cl (50 mL), and extracted with CS_2 (4 x 40 mL). The organic phases were filtered, and the solvent was removed *in vacuo*. The resulting solid was washed several times with H_2O, MeOH, and pentane before it was dried to give **10** as an orange solid. (154 mg, 87%). Crystals for X-ray crystallography were grown by vapour diffusion of heptanes into a CS_2 solution. MP: 258 – 261 °C. IR (ART, cm^{-1}): ν = 2960 w, 1536 s, 1482 s, 1439 s, 1370 m, 1331 m, 1181 m, 815 m 750 s, 698 s, 630 m, 485 s, 405 s. ^1H NMR (500 MHz, CD_2Cl_2) δ 8.21 (s, 2H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.34 (m, 4H), 3.06 (2×q, *J* = 7.3 Hz, 8H), 1.51 – 1.24 (m, 12H). ^1H NMR (500 MHz, CS_2 with DMSO-d_6 lock tube) δ 7.77 – 7.71 (m, 2H), 7.60 – 7.55 (m, 2H), 7.41 – 7.36 (m, 2H), 7.11 – 7.03 (m, 4H), 2.85 – 2.75 (m, 8H), 1.27 – 1.19 (m, 12H). ^{13}C NMR (126 MHz, CS_2 with DMSO-d_6 lock tube) δ 137.72, 136.99, 136.86, 135.91, 134.40, 129.01, 127.76, 126.06, 125.33, 122.59, 120.96, 118.91, 113.92, 30.82, 30.64, 14.89, 14.83. ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.53, 137.79, 137.60, 136.67, 135.11, 129.59, 128.36, 126.88, 125.81, 123.12, 121.27, 119.68, 114.43, 31.10, 30.95, 15.25, 15.22. MS (MALDI+) *m/z* = 694.1 [$M^{\bullet+}$]. EA ($C_{34}H_{30}S_8$, 695.09): calcd. C 58.75, H 4.35; found C 58.93, H 4.52.



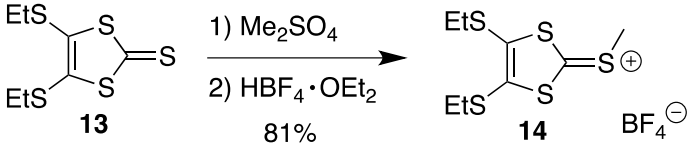
[4,5-Bis(butylthio)-1,3-dithiol-2-ylidene](methyl)sulfonium tetrafluoroborate (11). The thione **5** (918 mg, 2.96 mmol) was suspended in dimethylsulfate (2 mL, 21 mmol) and heated to 80 °C for 1 h. After the mixture was cooled to rt, $HBF_4 \cdot OEt_2$ (1 mL, 7 mmol) was added, and after stirring for 15 min, diethyl ether (25 mL) was added. After 30 min the ether solution was decanted off the semi-crystalline solid. After three successive additions of diethyl ether followed be decantation, the remaining diethyl ether was removed under reduced pressure to give **11** as a yellow-brown solid (1.05 g, 86%). MP: 49-50 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.23 (s, 3H), 3.21 – 3.11 (m, 4H), 1.84 – 1.66 (m, 4H), 1.57 – 1.42 (m, 4H), 0.95 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.00, 147.13, 38.06, 31.35, 23.22, 21.76, 13.61. HRMS (ESP+): *m/z* = 325.0248 $[M\text{-}BF_4]^+$ (calcd for $C_{12}H_{21}S_5^+$: 325.0241).



4,5-Bis(butylthio)-2-(methylthio)-1,3-dithiole (12). A solution of **11** (964 mg, 2.34 mmol) in acetonitrile (5 mL) was slowly added to a suspension of sodium borohydride (107 mg, 2.83 mmol) in dry isopropyl alcohol (0.5 mL), whereupon the color changed from brown to light orange. The mixture was stirred for 30 min and then poured onto water (20 mL). The mixture was extracted with CH_2Cl_2 (2 x 25 mL), washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. Flash column chromatography (SiO_2, CH_2Cl_2:heptane 1:2) gave **12** as a yellow oil. (716 mg, 94%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (s, 1H), 3.03 – 2.87 (m, 2H), 2.78 – 2.64 (m, 2H), 2.25 (s, 3H), 1.74 – 1.57 (m, 4H), 1.52 – 1.33 (m, 4H), 0.93 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 125.21, 57.34, 36.11, 32.07, 21.87, 13.92, 13.83. MS (GCMS) *m/z* = 326.1 $[M^{\bullet+}]$. EA ($C_{12}H_{22}S_5$, 326.63): calcd. C 44.13, H 6.79; found C 44.39, H 6.71.

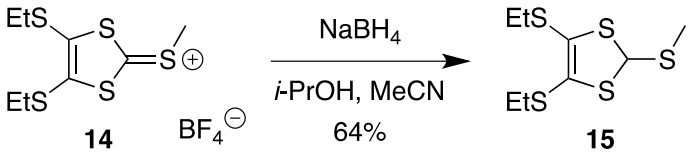


Dimethyl [4,5-bis(butylthio)-1,3-dithiol-2-yl]phosphonate (7). To a solution of **12** (1.56 g, 4.77 mmol) in diethylether (20 mL) was added $HBF_4{\cdot}OEt_2$ (1.3 mL, 9.6 mmol), and the mixture was stirred for 1 h. The mixture was then concentrated *in vacuo*, and the residue redissolved in acetone (20 mL). Trimethylphosphite (1.18 mL, 9.52 mmol) and NaI (1.43 g, 9.52 mmol) were added, and the mixture was stirred for 1 h, and concentrated *in vacuo*. Flash column chromatography (SiO_2, CH_2Cl_2:EtOAc 3:2) gave **7** as a colorless oil (962 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.73 (d, J = 5.4 Hz, 1H), 3.87 (d, J = 10.6 Hz, 6H), 2.96 – 2.68 (m, 4H), 1.74 – 1.57 (m, 4H), 1.51 – 1.35 (m, 4H), 0.92 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 125.58, 54.79 (d, J = 7.2 Hz), 41.41 (d, J = 160.1 Hz), 36.07, 31.90, 21.78, 13.75. MS (GCMS) m/z = 388.1 [$M^{\bullet+}$]. EA ($C_{13}H_{25}O_3PS_8$, 388.57): calcd. C 40.18, H 6.48; found C 39.98, H 6.26.

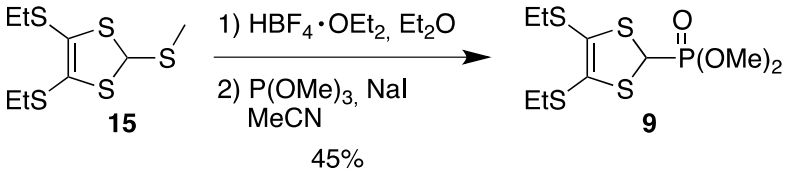


[4,5-Bis(ethylthio)-1,3-dithiol-2-ylidene](methyl)sulfonium tetrafluoroborate (14). Dimethylsulfate (2 mL, 21 mmol) was added to the thione **13**[a)] (1.2 g, 4.72 mmol) and the suspension was heated to 80 °C and stirred for 1 h until the reaction mixture was homogenous. After the mixture had cooled to rt, $HBF_4{\cdot}OEt_2$ (2 mL, 14 mmol) was added, and after 15 min diethylether (50 mL) was added, and an oily precipitate formed. The ether layer was decanted off, and the residue was washed several times with ether. This gave **14** as a brown oil (1.36 g, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.25 – 3.14 (m, 7H), 1.44 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.26, 147.12, 32.63, 23.17, 14.75. HRMS (ESP+): m/z = 268.9641 [M-BF_4]$^+$ (calcd. for $C_8H_{13}S_5^+$: 268.9615).

a) Prepared according to: K. B. Simonsen, N. Svenstrup, J. Lau, O. Simonsen, P. Mørk, G. J. Kristensen and J. Becher, *Synthesis*, 1996, 407-418.



4,5-Bis(ethylthio)-2-methylthio)-1,3-dithiole (15). A solution of the salt **14** (1.34 g, 3.76 mmol) in acetonitrile (10 mL) was slowly added to a suspension of $NaBH_4$ (180 mg, 4.75 mmol) in 2-propanol (1.0 mL) whereupon the color changed from dark red to light orange. The mixture was stirred for 2 h and then poured onto water (30 mL), extracted with CH_2Cl_2 (2 x 40 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Flash column chromatography (SiO_2, heptane:CH_2Cl_2 1:1) gave **15** as an orange solid (650 mg, 64 %). MP: 46.0 – 67.4 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75 (s, 1H), 3.01 – 2.91 (m, 2H), 2.79 – 2.70 (m, 2H), 2.26 (s, 3H), 1.33 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 125.28, 57.30, 30.66, 15.29, 13.99. HRMS (ESP+): *m/z* = 268.9604 $[M-H]^+$ (calcd. for $C_8H_{13}S_5^+$: 268.9615). EA ($C_8H_{14}S_5$, 270.50): calcd. C 35.52, H 5.22; found C 35.54, H 5.09.



Dimethyl [4,5-bis(ethylthio)-1,3-dithiol-2-yl]phosphonate (9). To a solution of **15** (640 mg, 2.37 mmol) in diethyl ether were added acetic anhydride (0.5 mL) and $HBF_4{\cdot}OEt_2$ (0.48 mL, 3.5 mmol) at 0 °C, and a brown precipitate immediately formed. After 1 h, the ether was decanted off, and the residue was washed 3 times with ether and dried under reduced pressure. The salt was dissolved in acetonitrile (20 mL), and then NaI (450 mg, 3.00 mmol) and trimethylphosphite (0.5 mL, 4 mmol) were added, whereupon the mixture turned yellow. After 2 h the mixture was concentrated *in vacuo* and separated between CH_2Cl_2 and water. The organic phase was dried over Na_2SO_4 and the solvent was removed *in vacuo*. Flash column chromatography (SiO_2, EtOAc:CH_2Cl_2 1:1) gave **9** as a colorless oil that solidified over night (354 mg, 45%). MP: 61.5 – 62.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (d, *J* = 5.5 Hz, 1H), 3.88 (d, *J* = 10.6 Hz, 6H), 2.97 – 2.87 (m, 2H), 2.81 – 2.71 (m, 2H), 1.34 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 125.72, 54.81 (d, *J* = 7.3 Hz), 41.29 (d, *J* = 160.8 Hz), 30.66, 15.20. HRMS (ESP+): *m/z* = 332.9875 $[M+H]^+$ (calcd. for $C_9H_{18}O_3PS_4^+$: 332.9871).

NMR Dilution Study of 8

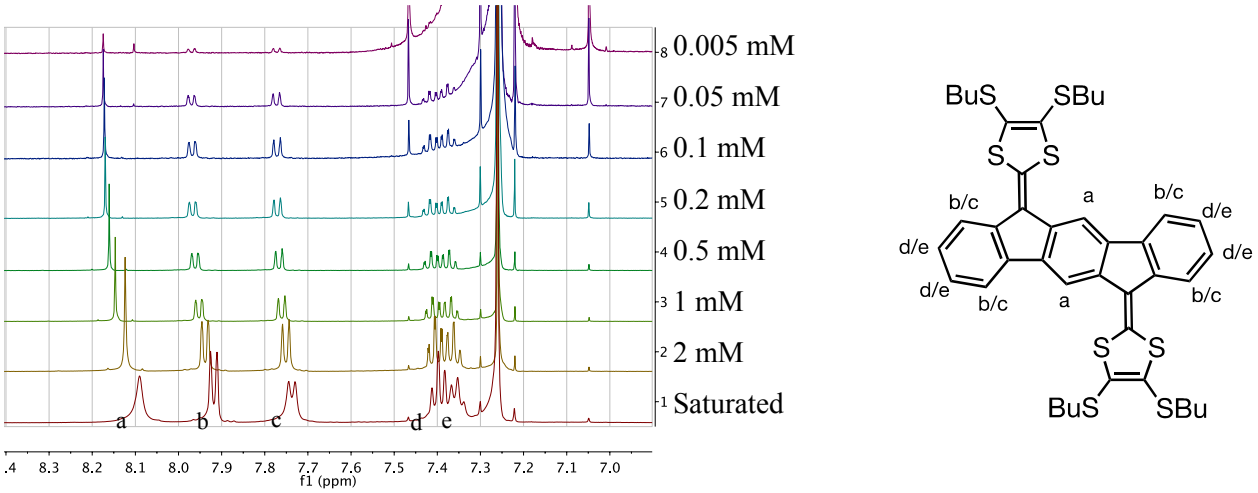


Figure S1. ^{1}H-NMR spectra of **8** at different concentrations ($CDCl_3$, 500 MHz). The signals of the aromatic protons shift by up to 0.08 ppm (signal a) when going from a saturated solution to 0.005 mM. The signals of the aliphatic protons did not change upon dilution. The concentration dependence of the aromatic proton resonances could support the suggested aggregation.

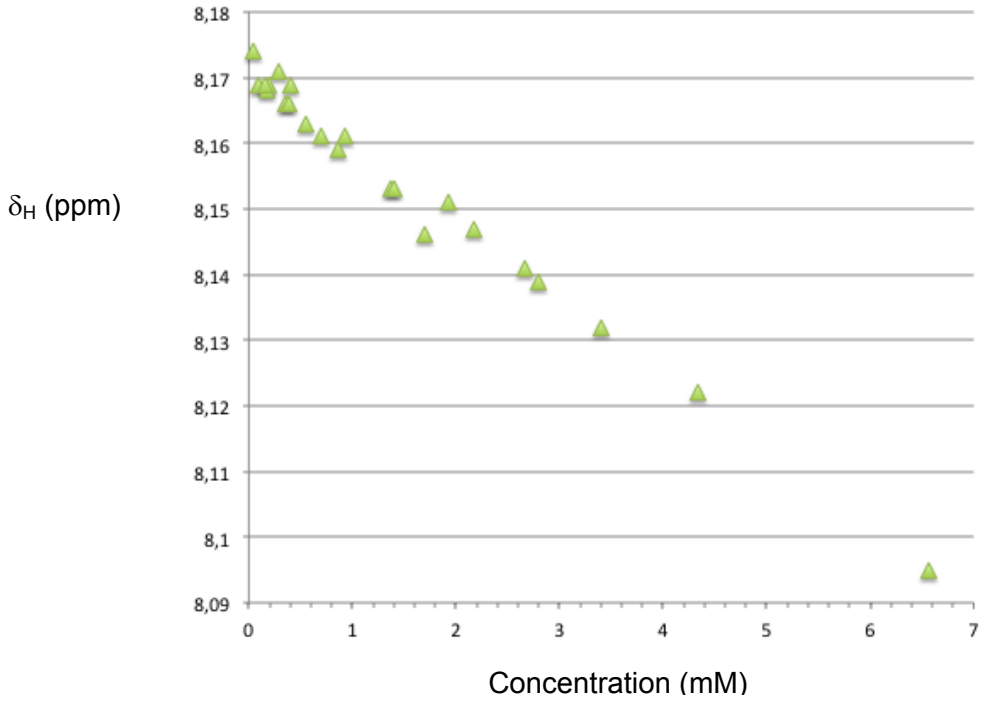
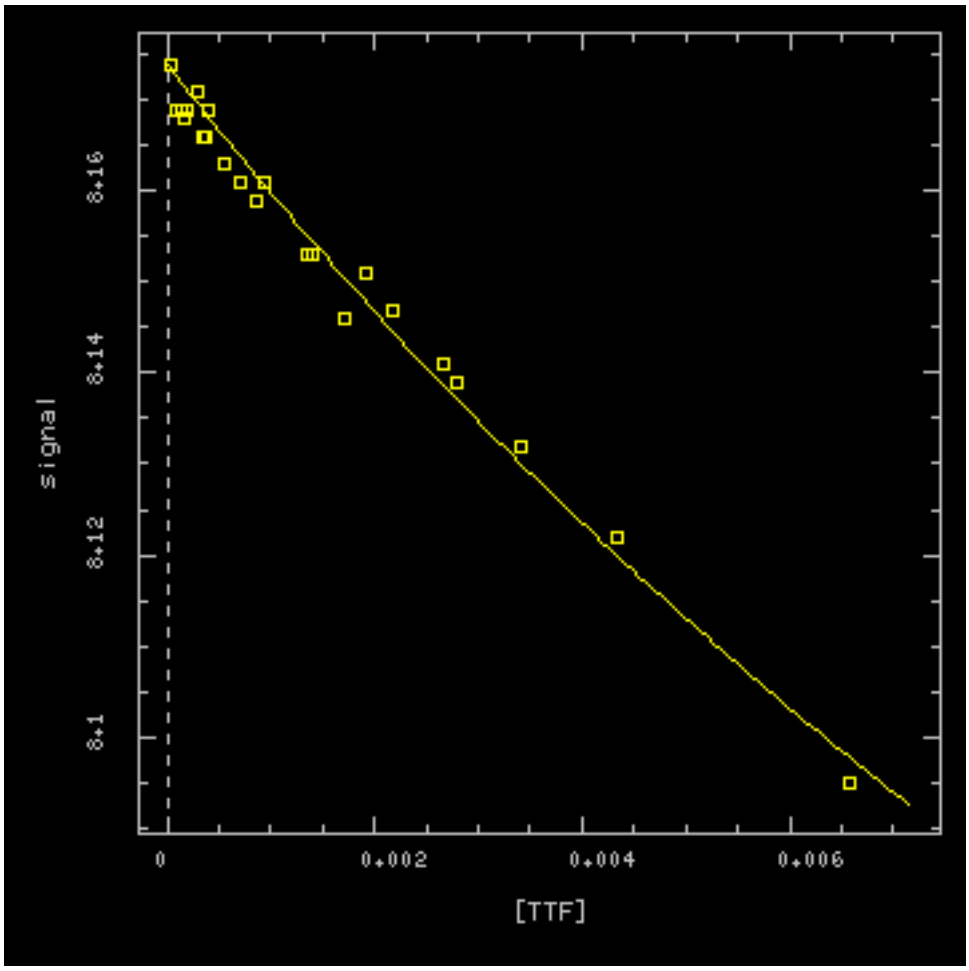


Figure S2. Chemical shift (δ_H) of the central benzene C-H protons (H-a) of **8** as a function of the concentration of **8**.



Optimized Parameters

No.	Par#Set	Initial	Final	Std. Error	CV (%)	Note
#1	K1	5	15.9134	6.21833	39.08	
#2	r(complex1)	8.095	7.23935	0.31426	4.34	

Figure S3. Dimerization of **8** – the NMR data were fitted by allowing the parameters shown in the table to vary (fitting was done based on: P. Kuzmic, *Anal. Biochem.*, 1996, **237**, 260-273.)

Electrochemistry

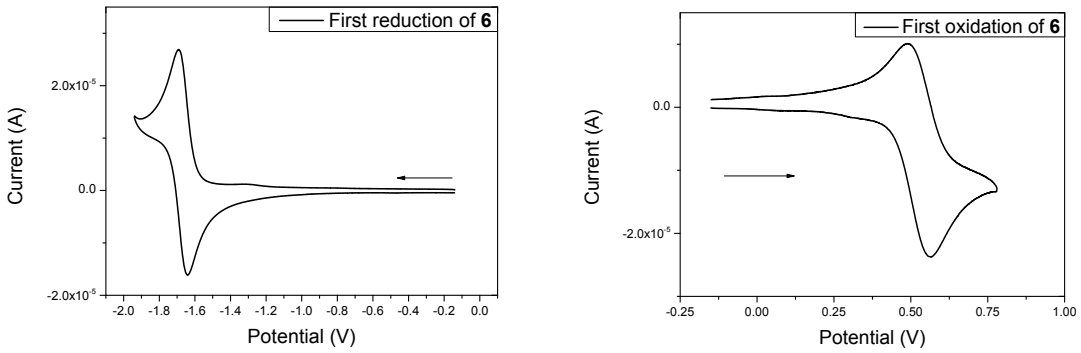


Figure S4. Cyclic voltammograms of the first reversible one-electron reduction (left) and partially reversible (i_a/i_c = 0.9) first one-electron oxidation (right) of **6**.

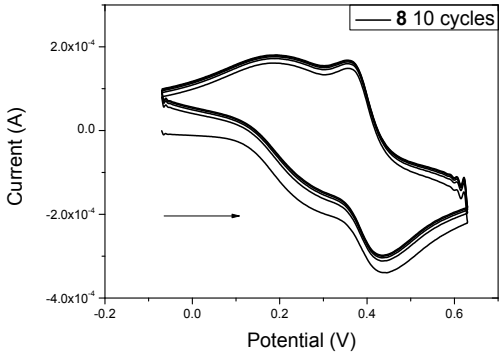


Figure S5. Cyclic voltammograms of compound **8** showing 10 cycles of first two oxidations, showing no sign of degradation.

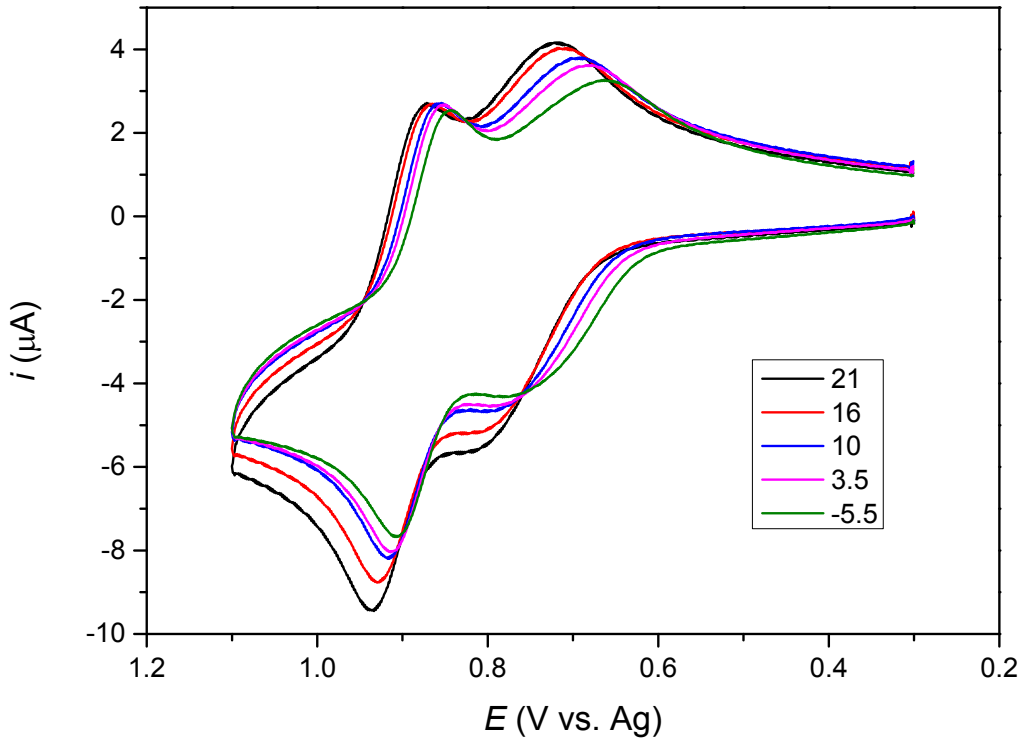


Figure S6. Temperature study (cyclic voltammograms) of **8** ($2.5 \cdot 10^{-4}$ M) in CH_2Cl_2 (Bu_4NPF_6, 0.1M) in a jacketed cell connected to methanol cryostat. The working (glassy carbon) and counter (platinum) electrodes were of the same kind as those used for the room temperature measurements. The reference electrode was a silver wire kept at room temperature and connected to the cell via a thin Teflon tube containing the solvent/supporting electrolyte mixture. The temperatures (°C) are given in text box.

Electrochemical Digital Simulations

Software: DigiSim 3.03

Abbreviations used
n: monomer, neutral
$\mathbf{c}^{\bullet+}$: monomer, radical cation
$\mathbf{d}^{2+}$: monomer, dication
[**n-n**]: dimer, neutral
$[\mathbf{n\text{-}c}]^{\bullet+}$: MV dimer, radical cation
$[\mathbf{c\text{-}c}]^{2+}$: π-dimer, dication

Experimental constants:
Initial concentration of the neutral monomer, $C^{o}(n) = 0.001$ M; temperature, $T = 298.2$ K; voltage sweep rate, $\nu = 0.1$ V s^{-1}.

Assumptions:
All heterogeneous electron transfer processes are assumed to be reversible. Semi-infinite linear diffusion to a planar working electrode is assumed.

First guess
Experimentally determined potentials for $\mathbf{c}^{\bullet+} + e^- \rightleftharpoons \mathbf{n}$ and $\mathbf{d}^{2+} + e^- \rightleftharpoons \mathbf{c}^{\bullet+}$. taken from low concentration experiments at which complexation plays only a minor role.
The E^o values for the dimers were assumed to be lower than those for the corresponding monomers, i.e. $E^o([\mathbf{n\text{-}n}]) < E^o(\mathbf{n})$ and $E^o([\mathbf{n\text{-}c}]^{\bullet+}) < E^o(\mathbf{c}^{\bullet+})$.
Values of the diffusion coefficients, D, were initially taken as 10^{-5} cm^2s^{-1}.
In all equilibria (electron transfer and complexations in solution) the largest second order rate constant was taken as that for a diffussion controlled process, here arbitrarily set as 10^9 $M^{-1}s^{-1}$. The equilibrium constants are in most cases resulting from the values of the formal potentials and are, for that reason, not independent parameters.

The formal potential of the ferrocene/ferrocenium reference system was +0.167 V vs. the Ag-reference electrode used for the experimental data.

The best fit of the theoretical data to the experimental are reproduced in Figure S7 and the resulting values of the most important parameters are summarized in Table S1. However, the value, $6.0 \cdot 10^3$ M^{-1}, of the association constant for two neutral molecules of **8**, Keq.-1 below, may be overestimated by the fitting procedure judged from the fact that we do not have firm spectral evidence for a neutral π-dimer (except for the NMR spectral changes upon dilution). Thus, it was decided to carry out a series of additional fits in which Keq.-1 was fixed at a number of decreasing values in order to investigate whether satisfactory fits might indeed be obtained with lower values of Keq.-1. The results demonstrated that fits of a slightly lower but still acceptable quality could be obtained for lower values of Keq.-1. When using Keq.-1 = 16 M^{-1}, the value obtained by NMR spectroscopy, the resulting fit was still satisfactory, although not of the same quality as that observed for the free running fitting procedure. The corresponding association constants Keq.-2 and Keq.-3 then became 1×10^4 M^{-1} and 4×10^3 M^{-1}, respectively.

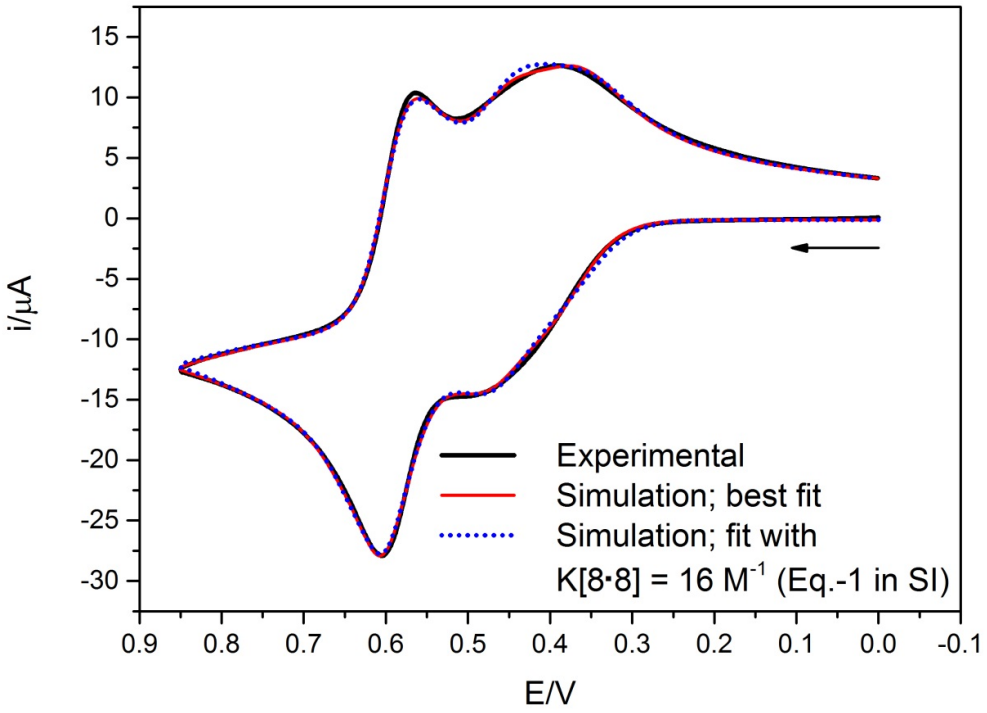


Figure S7. Simulated and experimental CVs of **8** (potentials are uncorrected).

redox-1	$\mathbf{d}^{2+} + e^-$	$\rightleftharpoons$	$\mathbf{c}^{\cdot+}$
redox-2	$\mathbf{c}^{\cdot+} + e^-$	$\rightleftharpoons$	**n**
redox-3	$[\mathbf{c}\text{-}\mathbf{c}]^{2+} + e^-$	$\rightleftharpoons$	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+}$
redox-4	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+} + e^-$	$\rightleftharpoons$	**[n-n]**
Eq.-1	**n + n**	$\rightleftharpoons$	**[n-n]**
Eq.-2	$\mathbf{c}^{\cdot+}$ **+ n**	$\rightleftharpoons$	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+}$
Eq.-3	$\mathbf{c}^{\cdot+} + \mathbf{c}^{\cdot+}$	$\rightleftharpoons$	$[\mathbf{c}\text{-}\mathbf{c}]^{2+}$
Eq.-4	$\mathbf{c}^{\cdot+} + \mathbf{c}^{\cdot+}$	$\rightleftharpoons$	$\mathbf{n} + \mathbf{d}^{2+}$
Eq.-5	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+} + \mathbf{c}^{\cdot+}$	$\rightleftharpoons$	$[\mathbf{c}\text{-}\mathbf{c}]^{2+}$ **+ n**
Eq.-6	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+} + \mathbf{d}^{2+}$	$\rightleftharpoons$	$[\mathbf{c}\text{-}\mathbf{c}]^{2+} + \mathbf{c}^{\cdot+}$
Eq.-7	$\mathbf{c}^{\cdot+}$ **+ [n-n]**	$\rightleftharpoons$	$\mathbf{n} + [\mathbf{n}\text{-}\mathbf{c}]^{\cdot+}$
Eq.-8	$\mathbf{d}^{2+}$ **+ [n-n]**	$\rightleftharpoons$	$\mathbf{c}^{\cdot+} + [\mathbf{n}\text{-}\mathbf{c}]^{\cdot+}$

Scheme S1. Reactions used for the DigiSim simulation.

Table S1. Output data from DigiSim (potentials are uncorrected).

	E^0 [V]	$K_{eq.}$	$k_{forward}/(M^{-1}s^{-1})$	k_{back}
Redox-1	0.547			
Redox-2	0.438			
Redox-3	0.475			
Redox-4	0.372			
Eq.-1		$6.0 \cdot 10^3$ M^{-1}	$1.0 \cdot 10^9$	$1.6 \cdot 10^5$ s^{-1}
Eq.-2		$7.8 \cdot 10^4$ M^{-1}	$1.0 \cdot 10^9$	$1.3 \cdot 10^4$ s^{-1}
Eq.-3		$1.8 \cdot 10^4$ M^{-1}	$1.0 \cdot 10^9$	$5.6 \cdot 10^4$ s^{-1}
Eq.-4		$7.9 \cdot 10^{-7}$ M^{-1}	$7.2 \cdot 10^4$	$9.2 \cdot 10^9$ s^{-1}
Eq.-5		0.23	$2.3 \cdot 10^8$	$9.8 \cdot 10^8$ $M^{-1}s^{-1}$
Eq.-6		16	$1.0 \cdot 10^9$	$6.2 \cdot 10^7$ $M^{-1}s^{-1}$
Eq.-7		13	$1.0 \cdot 10^9$	$7.7 \cdot 10^7$ $M^{-1}s^{-1}$
Eq.-8		$9.1 \cdot 10^2$	$1.0 \cdot 10^9$	$1.1 \cdot 10^6$ $M^{-1}s^{-1}$

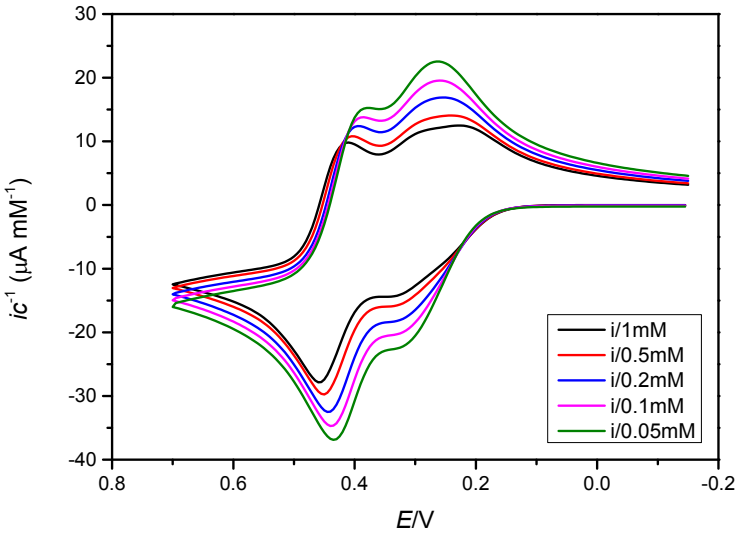


Figure S8. Simulation at varying concentrations, showing similar cyclic voltammograms to the experimental values in Figure 7 (paper).

The deviations observed at low concentrations in comparison with Figure 7 are caused mainly by differences between the real and the simulation diffusion coefficients. The latter are not well determined by the many parameter fit.

Electrochemistry of 10

A saturated solution of **10** was used (ca. 0.2 mM, concentration estimated from UV-Vis absorption spectroscopy).

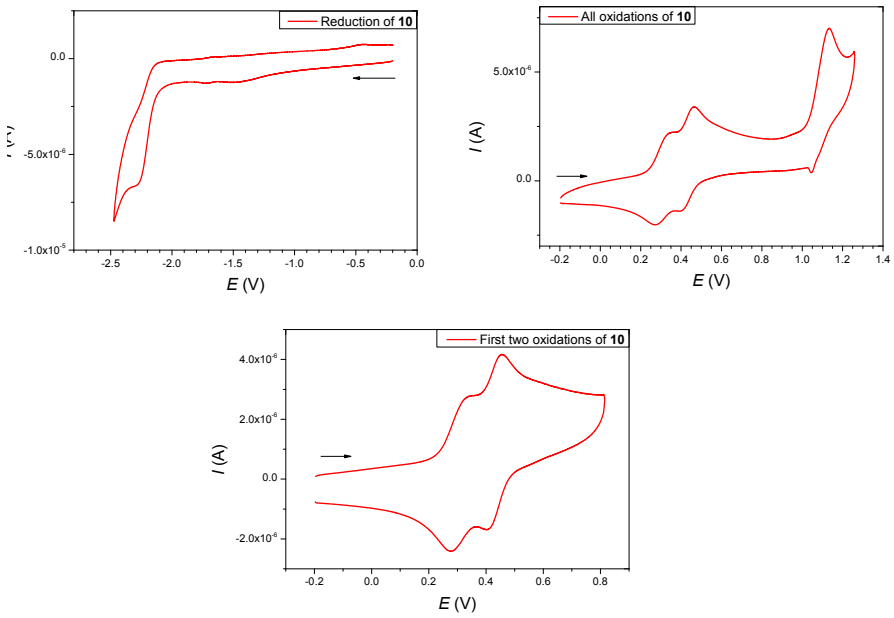


Figure S9. Cyclic voltammograms of compound **10** in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte. Glassy-carbon working electrode, silver reference and platinum counter, scan speed 100 mV/s, potentials *vs* $Fc/Fc^+ = 0$ V.

UV-Vis Absorption Spectra

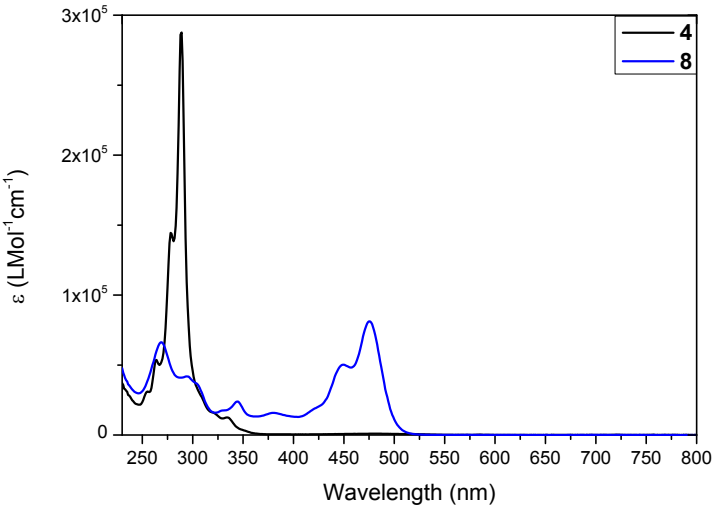


Figure S10. UV-Vis absorption spectra of **4** and **8** in CH_2Cl_2.

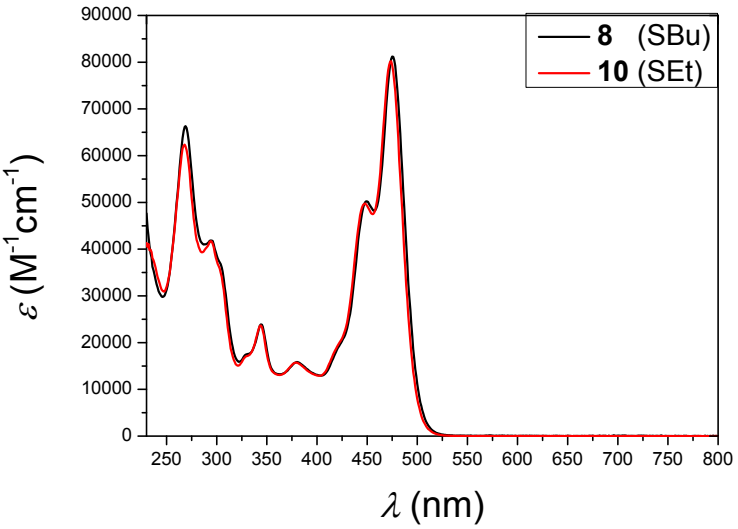


Figure S11. UV-Vis absorption spectra of compounds **8** and **10** in CH_2Cl_2.

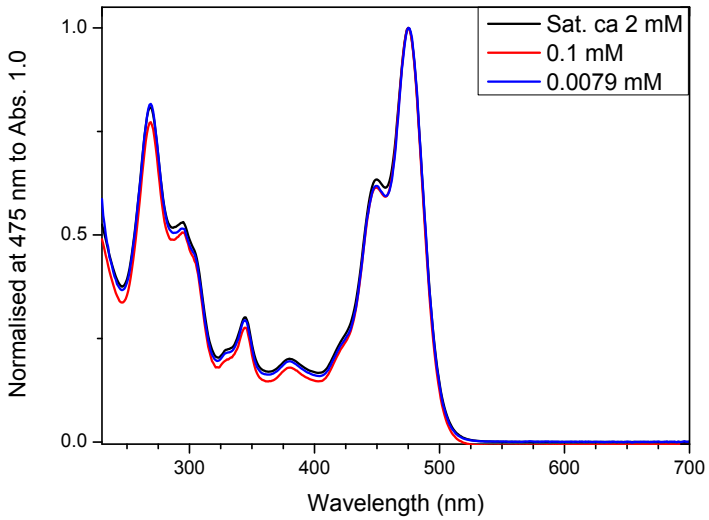


Figure S12. Dilution study of **8**. There is no significant change in the UV-Vis absorption spectra of **8** from the range of saturated (about 2 mM in CH_2Cl_2) to 0.0079 mM in CH_2Cl_2. The λ_{max} at 475 nm has been normalized to absorbance of 1.

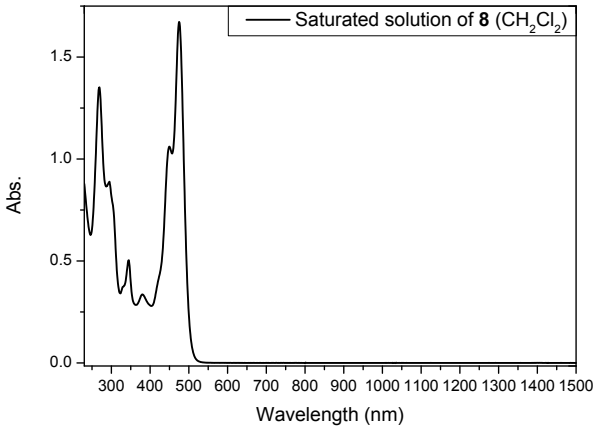


Figure S13. Absorption spectrum of a saturated solution of **8**. There are no bands after the band at λ_{max} (475 nm), that is, from 525 nm to 1500 nm in CH_2Cl_2.

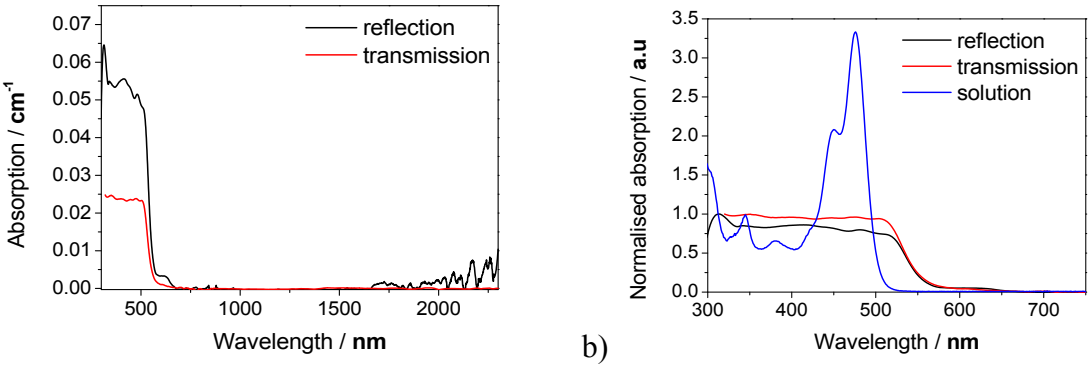


Figure S14. a) Solid-state absorption spectrum recorded on powder form of **8** on a glass coverslip, recorded using a spectrometer fitted with an integrating sphere in reflection and transmission geometry. b) Absorption spectra of **8** in solution and in the solid state.

Studies on Solvatochromism

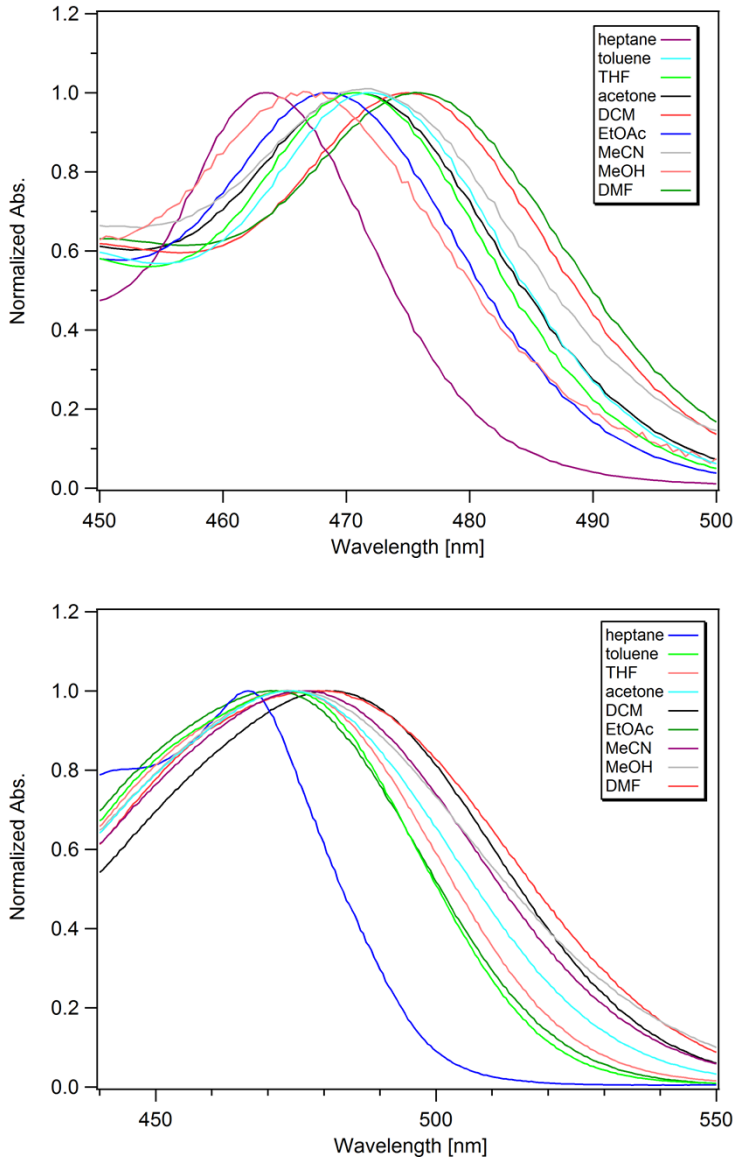


Figure S15. Absorption spectra of **6** (top) and **8** (bottom) in different solvents, showing their solvatochromic behaviour. Spectra were normalized at λ_{max}.

UV-Vis-NIR Spectroelectrochemistry

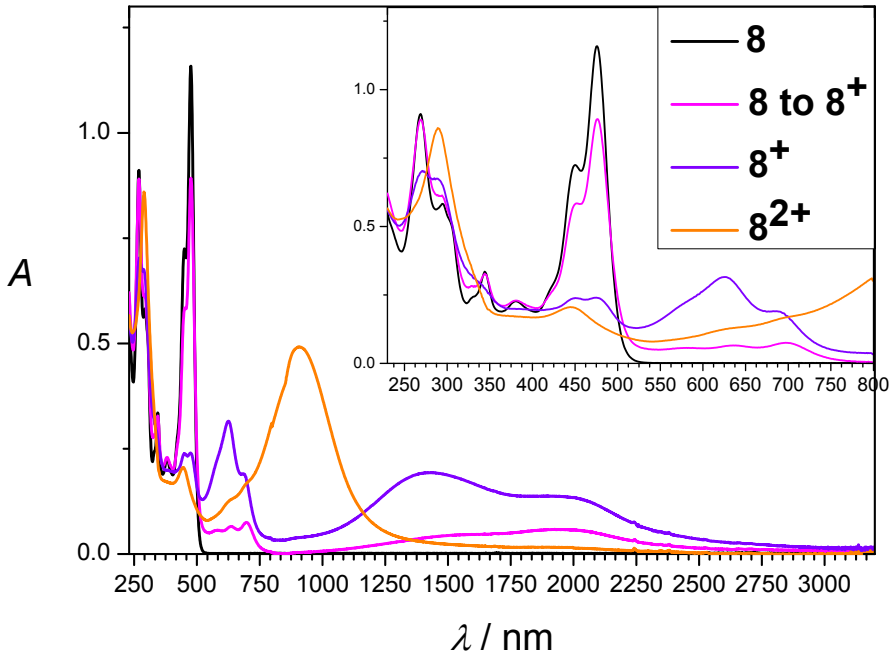
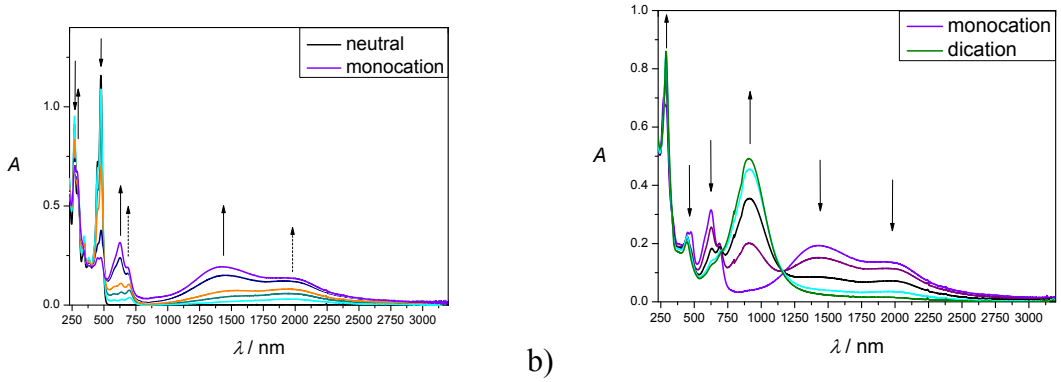


Figure S16. Spectroelectrochemical absorption spectra in the UV-Vis-NIR (230-3200 nm, scan rate 1818.182 nm/min, scanning every 1 nm) of the neutral (black trace), start of oxidation of the neutral (orange trace), monocation (purple) and dication (green). Solution of 0.9 mM of **8** with 0.1 M Bu_4NPF_6 in CH_2Cl_2.



a) b)

Figure S17. Spectroelectrochemical absortion spectra in the UV-Vis-NIR (230-3200 nm) of a 0.9 mM solution of **8** with 0.1 M Bu_4NPF_6 in CH_2Cl_2. (a) oxidation from neutral (black trace) to the monocation (magenta); (b) oxidation of the monocation (magenta) to the dication (blue). Arrows indicate the movement of the bands as the oxidation proceeds, in (a) the arrow with dashed lines indicates the bands that come up first in the monocation.

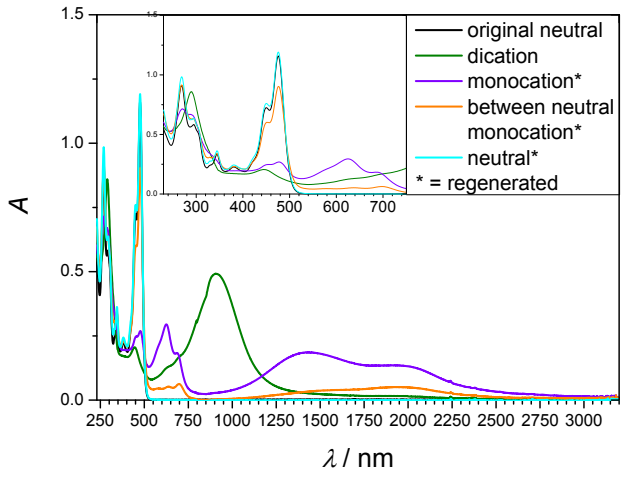


Figure S18. Regeneration of neutral **8** from the dication species of 0.9 mM solution. The regeneration of **8** did not occur as well for the 0.1 mM solution.

Table S2. UV-vis-NIR spectroelectrochemical data for **8** at 0.9 mM in different oxidation states.

Oxidation state	UV-vis-NIR in nm (Abs.)
Neutral	269 (1.01), 294 sh (0.64), 345 (0.37), 380 (0.25), 450 sh (0.79), 476 (1.26)
From neutral to monocation	269 (0.89), 294 sh (0.61), 343 (0.33), 381 (0.23), 451 (0.58), 476 (0.89), 581 sh (0.06), 635 (0.07), 697 (0.08), ~ 1490 br (0.04), ~ 1925 br (0.06)
Monocation	271 (0.70), 286 (0.68), 450 (0.24), 475 (0.24), 626 (0.32), 683 sh (0.19), ~ 1435 br (0.19), ~ 1945 br (0.14)
Dication	289 (0.86), 445 (0.21), 635 sh (0.129), 701 sh (0.17), 905 (0.49)

br = broad, sh = shoulder.

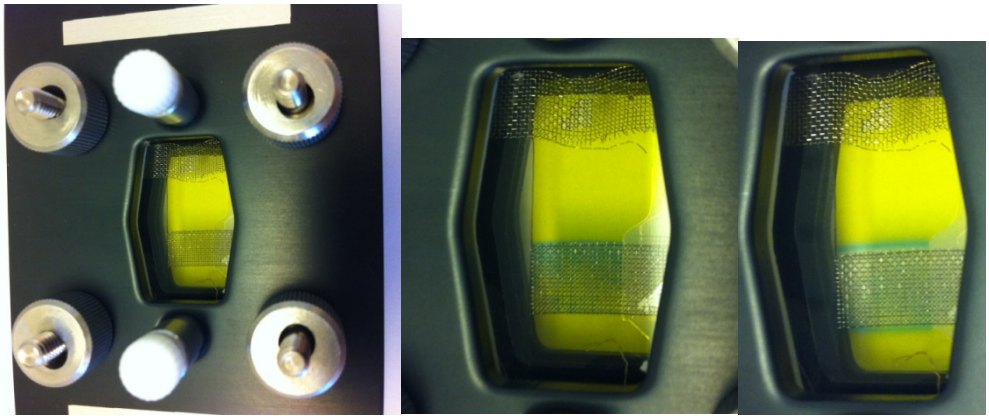
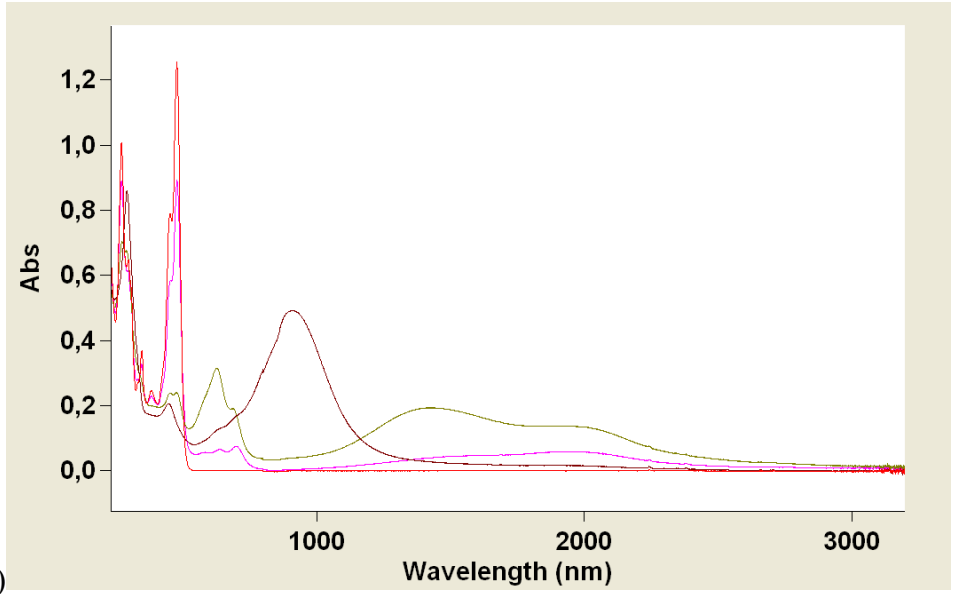


Figure S19. Pictures of OTTLE cell containing a solution of **8** (0.9 mM with 0.1 M Bu_4NPF_6 in CH_2Cl_2) showing the progression of the oxidation (left to right) from the yellow neutral compound to the blue oxidised species.

a)



b)

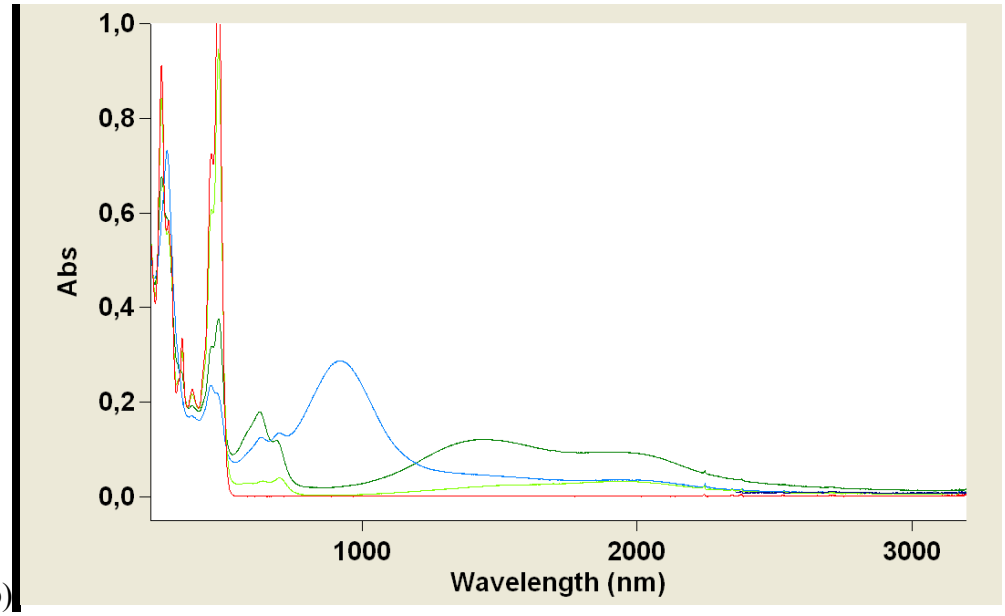


Figure S20. Absorption spectra at different slit widths. This Figure shows how getting the light beam to pass directly through the Pt mini grid and using the narrow slit setting of the spectrometer* to give more defined spectra of compound **8** as it is oxidised. a) narrow slit width setting compared to, b) the usual slit width because the beam is passed directly through the Pt mini grid (see Figure S19).

* If the narrow slit width setting is not available, a mask only allowing light to pass through the mini grid can be used.

Deconvolution of Absorption Spectra (spectroelectrochemistry)

Spectroelectrochemistry of 8

As the electrolysis proceeds, three species are readily recognized. Where the spectra of the dication and the neutral form of **8** are readily assigned, the spectrum of the radical cation appears too complex to be assigned by accounting a single species. As a consequence spectroelectrochemistry was performed at several different concentrations. The spectra are shown below, note that only the 0.5 mM run was performed as a single progression. The runs at 0.1 mM and 0.9 mM were switched back and forth.

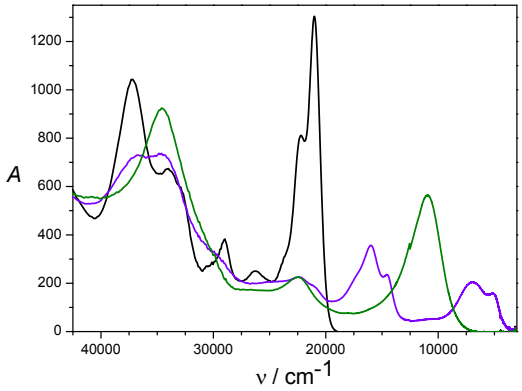


Figure S21. Absorption spectra of the species **8** (black), $\mathbf{8}^{+}$ (purple), and $\mathbf{8}^{2+}$ (green).

Concentration 0.1 mM

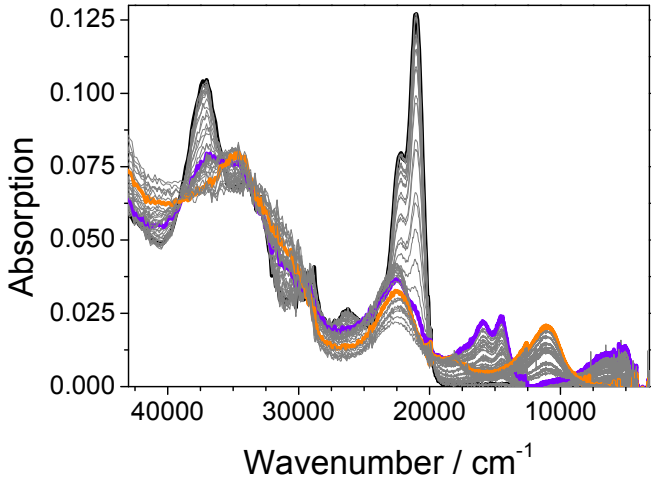


Figure S22. Spectroelectrochemical oxidation of **8** at 0.1 mM.

Concentration 0.5 mM

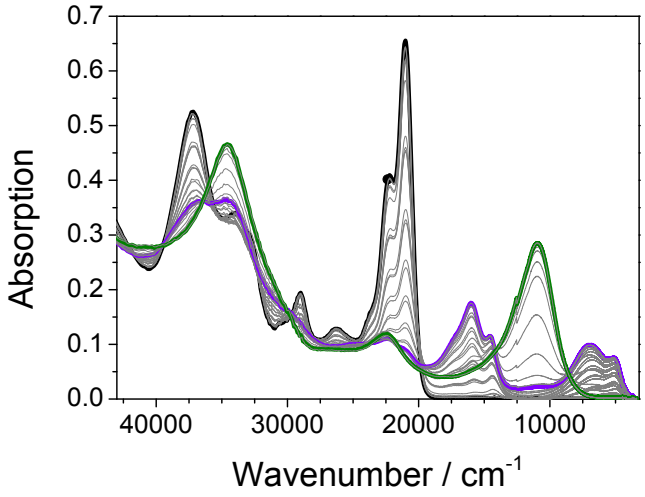


Figure S23. Spectroelectrochemical oxidation of **8** at 0.5 mM.

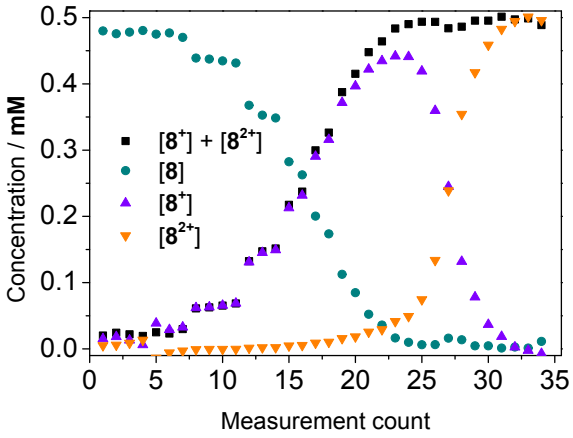


Figure S24. The degree of conversion at different points of measurement, the concentration of the neutral form and the total concentration of the oxidized forms could be calculated using the isosbestic point at ~8700 cm^{-1}, while the concentration of radical cation and the dication could be determined using the peak absorption of the dication.

Concentration 0.9 mM

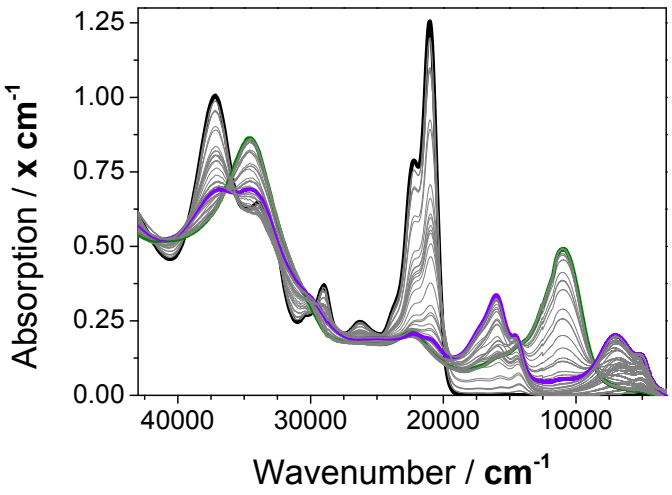


Figure S25. Spectroelectrochemical oxidation of **8** at 0.9 mM.

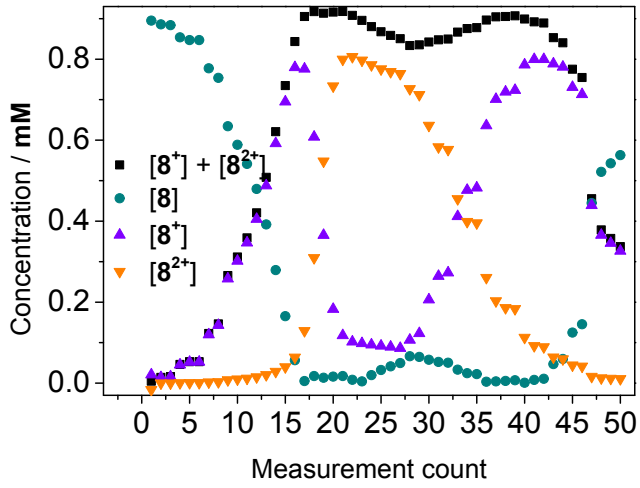


Figure S26. The degree of conversion at different points of measurement, the concentration of the neutral form and the total concentration of the oxidized forms could be calculated using the isosbestic point at ~8700 cm^{-1}, while the concentration of radical cation and the dication could be determined using the peak absorption of the dication.

Resolving the NIR absorptions in the spectroelectrochemistry

Concentration dependence

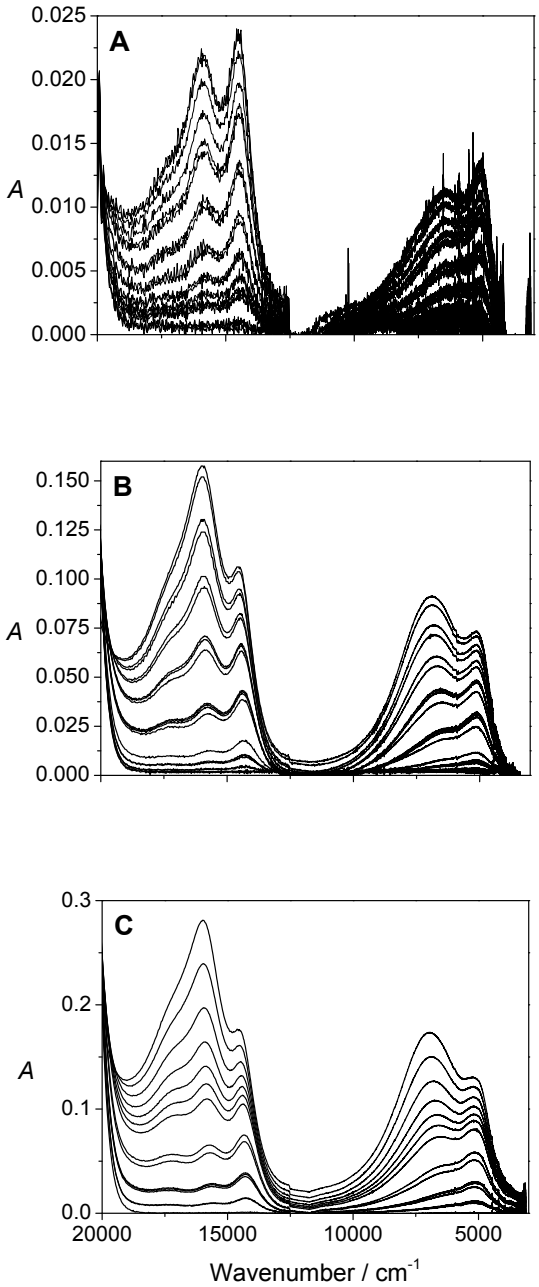


Figure S27. The CT and primary transitions of the radical cation species of **8**, the data from three different concentrations 0.1 mM (A), 0.5 mM (B), and 0.9 mM (C) show that both groups of bands have concentration-dependent behaviour.

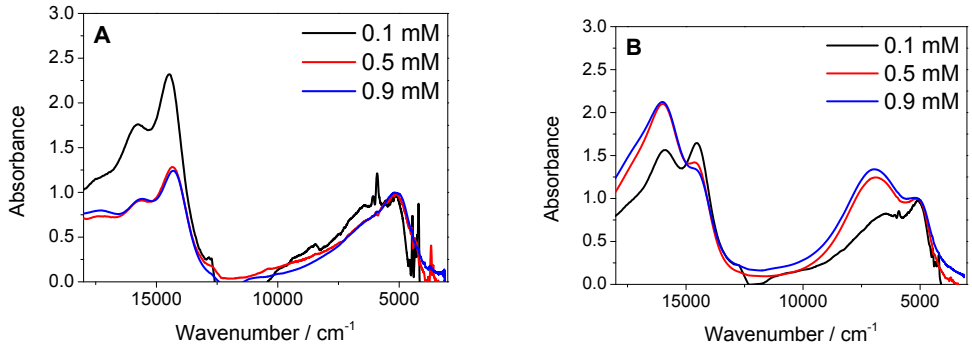


Figure S28. Selected points in the electrolysis of **8** chosen to highlight that the high energy band of both the CT and primary groups of transitions show a high degree of concentration dependence.

Resolving the transitions

The CT bands around 7000 cm^{-1} were fitted to 2 or 3 Gaussian functions using Origin®. The fits were allowed to proceed unrestricted from identical starting conditions. By cursory inspection it can be seen that point 5 through 12 is poorly fitted to only two Gaussian bands, while point 14 through 22 cannot be fitted to the three identical Gaussian bands that fit the initial point of the electrolysis.

While the fit to 2 Gaussians cannot be assumed to be correct for any spectrum, we must conclude that the third band becomes insignificant after measurement points 12-13.

The primary transitions around 15,000 cm^{-1} were fitted to 3 Gaussian functions. The fits were allowed to proceed unrestricted from identical starting conditions. Although good fits were achieved for the red edge of the group of bands, the fit can only be used qualitatively, as a clear vibrational progression is seen in the points of low conversion. These multiple peaks are convoluted in the group of bands, and can be fitted by two narrow Gaussian functions, and a broad, shifting Gaussian function. At higher degrees of conversion, the third band becomes defined and is attributed to the radical cation-dimer.

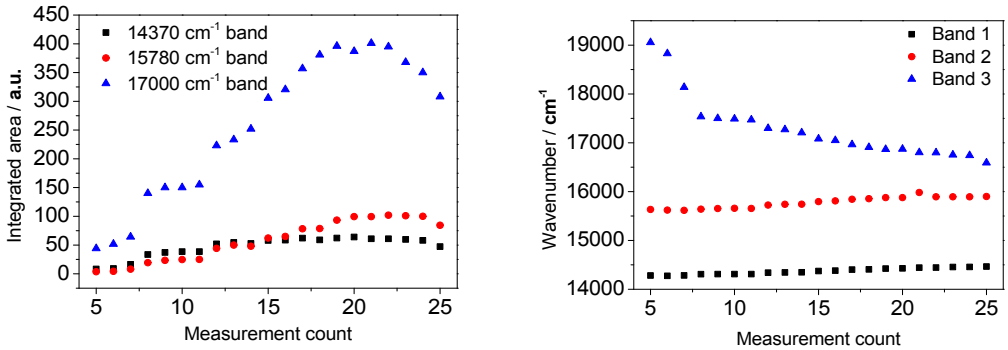


Figure S29. The deconvolution of the primary transitions of the radical cation species. Qualitatively the bands 1-3 can be ascribed to the monomer (band 1), radical cation-neutral dimer (band 2), and radical cation dimer (band 3). The overlapping vibrational progression in the transitions does not allow for quantitative determinations.

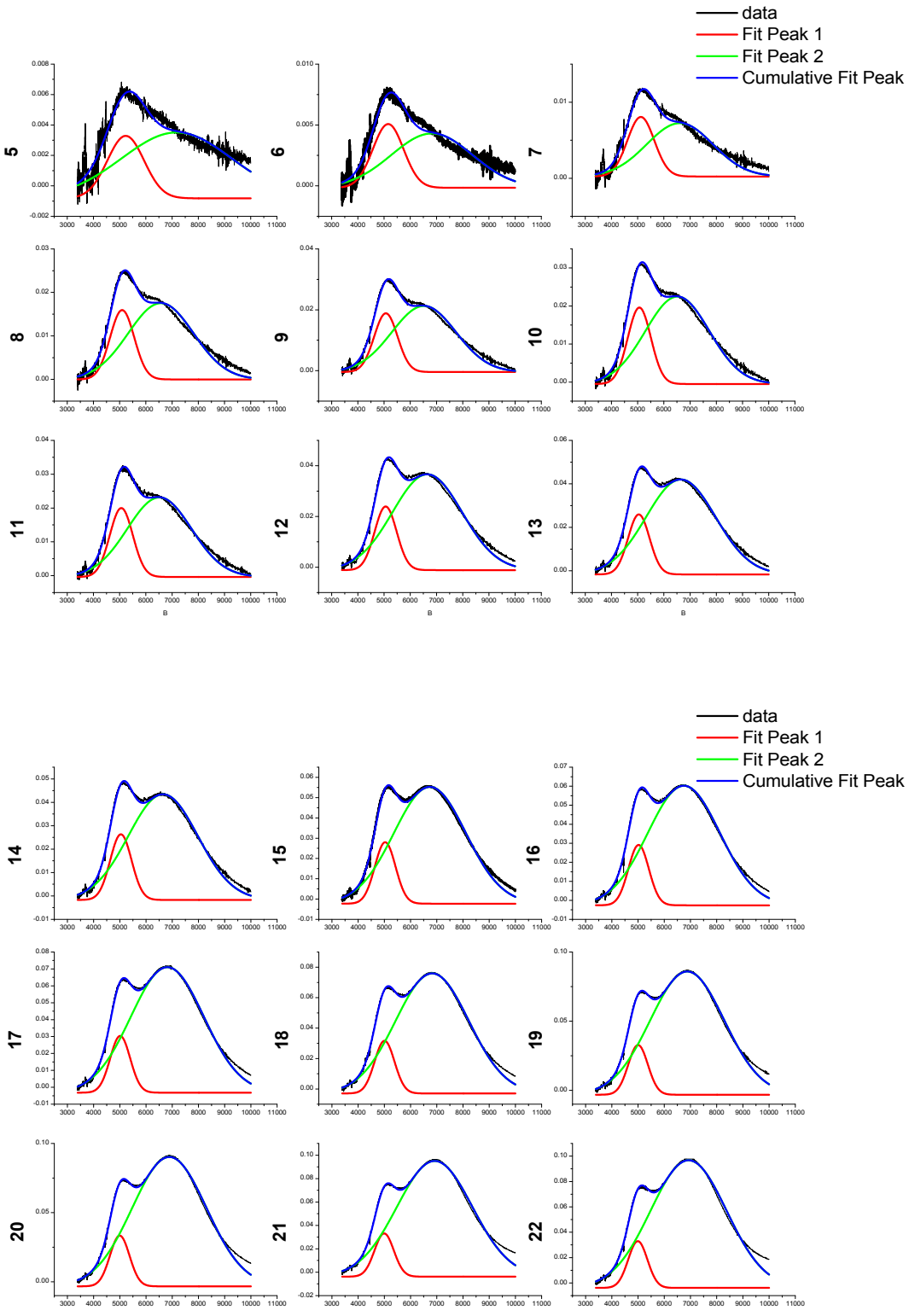


Figure S30. Each point of the 0.5 mM electrolysis (showing CT bands of $\mathbf{8}^{+}$) fitted to two Gaussian functions.

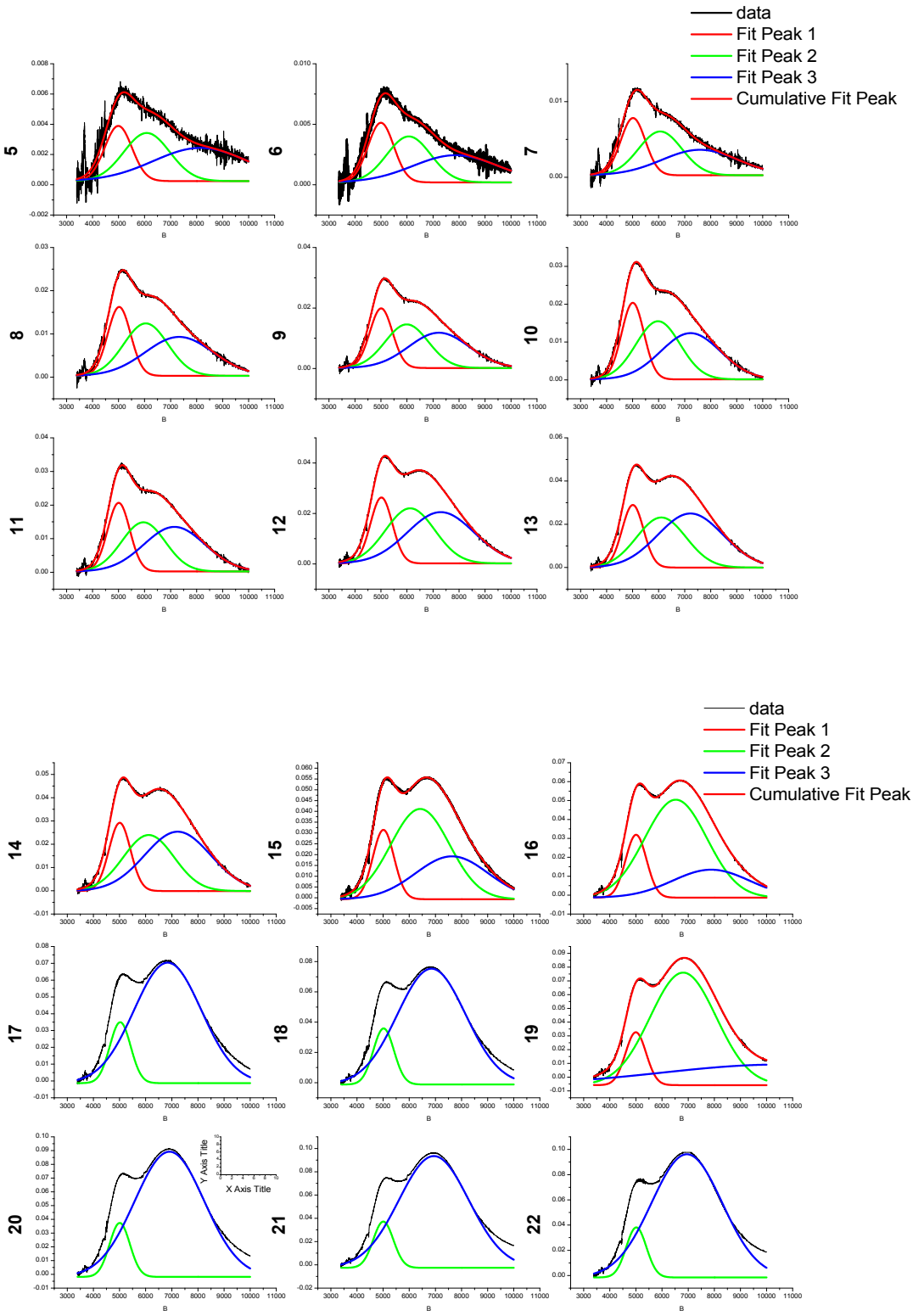


Figure S31. Each point of the 0.5 mM electrolysis (showing CT bands of $\mathbf{8}^{+}$) fitted to three Gaussian functions.

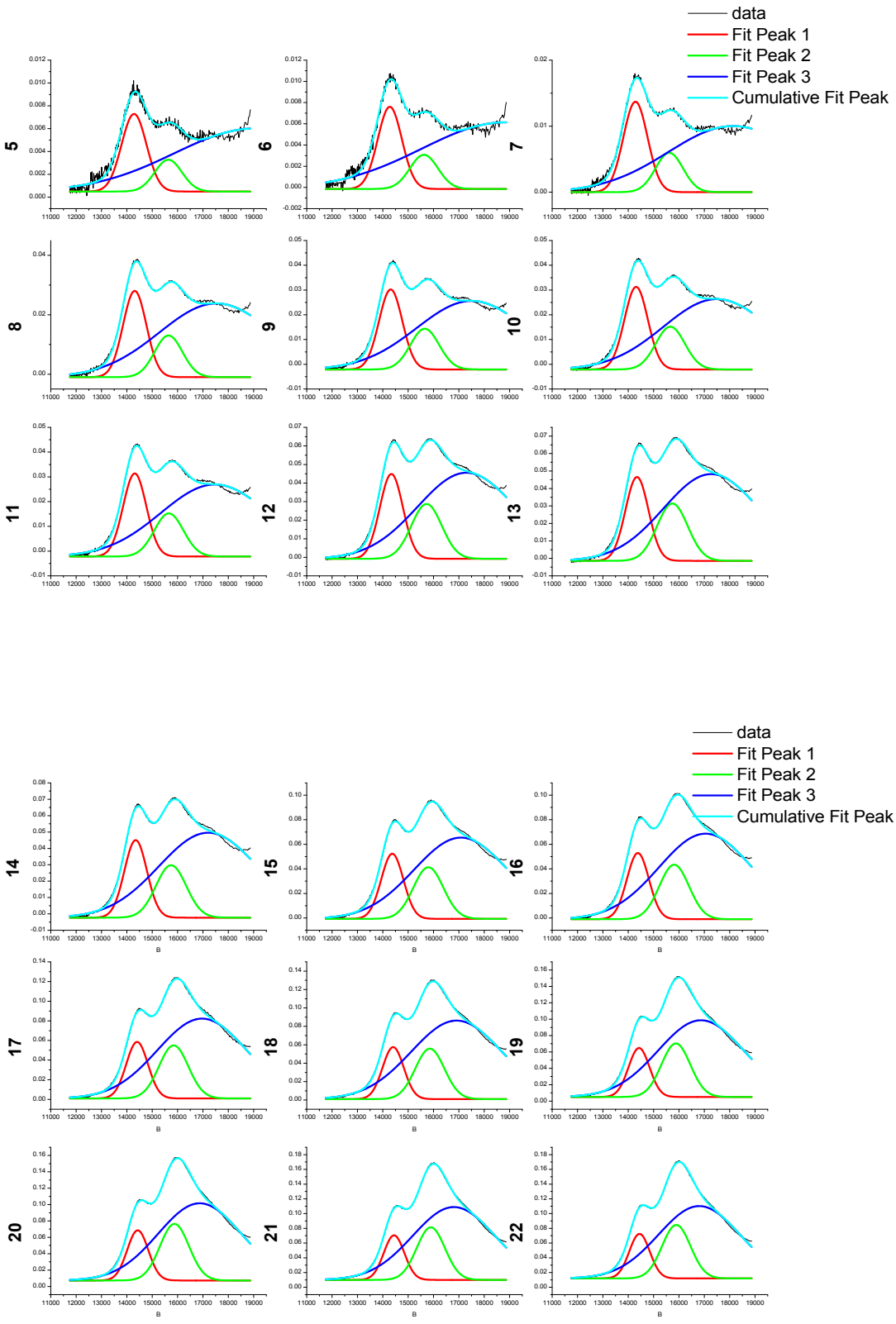


Figure S32. Each point of the 0.5 mM electrolysis (showing primary transitions of $\mathbf{8}^{+}$) fitted to three Gaussian functions.

Assigning the absorptions seen in the spectroelectrochemistry of 8

Assigning the species is done based on the order of appearance of each species. This can be done by following single points in the spectra or by monitoring the actual concentrations. The assignment shown in Table S3 is done based on the data shown in Figure S28. The species formed by association of **8** and $\mathbf{8}^+$ disappears first, then $\mathbf{8}^+$ is removed closely followed by the dimer of $\mathbf{8}^+$. The latter is readily identified as it is formed to a much lower extend at lower concentrations.

The λ_{max} values are assigned in the fits where all three bands can be resolved. As peak 2 and 3 are highly overlapping the values will change depending on the contribution from each transition to observed fit. See tables below for details.

Table S3. The photophysical parameters and assignment of each band appearing in the absorption spectrum from the electrolysis of **8**. The bands attributed to the radical cation species are taken from the resolved spectra shown above.

Species	**Neutral**	**Radical cation CT**			**Radical cation S1**			**Dication**
Abs max		1	2	3	1	2	3	
cm^{-1}	20971	5012	6040	7230	14370	15780	16850	10950
nm	477	1995	1656	1384	696	634	593	913
Assignment		$\mathbf{8}^+$ monomer	[**8**:$\mathbf{8}^+$] dimer	[$\mathbf{8}^+$:$\mathbf{8}^+$] dimer	$\mathbf{8}^+$ monomer	[**8**:$\mathbf{8}^+$] and [$\mathbf{8}^+$:$\mathbf{8}^+$] dimers		

Table S4. Peak values for the three transitions (cm^{-1}).

	Only 2 peaks fitted			All 3 peaks fitted		
Point	Peak 1	Peak 2	Point	Peak 1	Peak 2	Peak 3
14	5040	6600	5	5010	6070	8025[a]
15	5030	6670	6	5000	6060	7880[a]
16	5020	6730	7	5030	6060	7550[a]
17	5020	6800	8	5040	6070	7330
18	5010	6850	9	5000	5990	7180
19	4990	6890	10	5000	5990	7180
20	4990	6930	11	5020	5940	7160

21	4990	6920	12	5000	6090	7280
22	5000	6890	13	5030	6090	7220
Average	5010	6810		5014	6040	7230
Error	18	100		15	50	60
Combined average	5012	6975				
Combined error	17	225				

[a] Ignored as very little of the band is present in the spectrum.

Table S5. Peak values for the three transitions (nm).

	Only 2 peaks fitted			All 3 peaks fitted		
Point	Peak 1	Peak 2	Point	Peak 1	Peak 2	Peak 3
14	1984	1515	5	1996	1647	1246[a]
15	1988	1499	6	2000	1650	1269[a]
16	1992	1486	7	1988	1650	1325[a]
17	1992	1471	8	1984	1647	1364
18	1996	1460	9	2000	1669	1393
19	2004	1451	10	2000	1669	1393
20	2004	1443	11	1992	1683	1397
21	2004	1445	12	2000	1642	1373
22	2000	1451	13	1988	1642	1385
Average	1996	1469		1994	1656	1384
Error	7	24		6	14	12
Combined average	1995	1435				
Combined error	7	50				

[a] Ignored as very little of the band is present in the spectrum.

Table S6. FWHM of fitted peaks values for the three transitions (cm^{-1}), *not defined fits are in red*.

	All 3 peaks fitted				Only 2 peaks fitted	
Point	Peak 1	Peak 2	Peak 3		Peak 1	Peak 2
5	1230	2080	4260		1650	4950
6	1180	1990	3860		1380	3640
7	1120	1960	3450		1210	2960
8	1040	2000	3070		1090	2930
9	1020	1950	2730		1050	2870
10	1010	1990	2710		1040	2870
11	1010	1980	2770		1040	2880
12	990	2230	3010		990	3110
13	980	2240	2950		960	3110
14	970	2280	2970		960	3120
15	960	2650	3280		930	3230
16	940	2810	3470		920	3230
17					900	3270
18					890	3280
19					880	3310
20					880	3330
21					870	3370
22					860	3400
Mean	970±60	2000±140	3100±210			

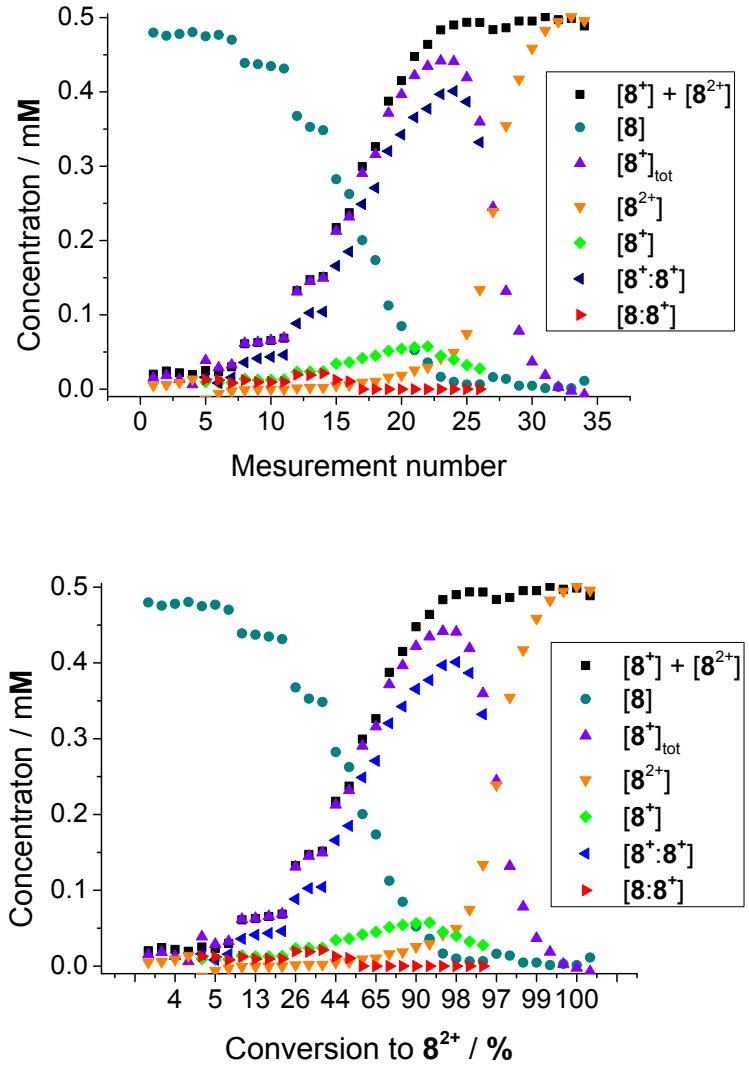


Figure S33. The concentration profile of all involved species as a function of the progression (number top, percentage bottom) of the electrolysis.

ESR Spectroelectrochemistry

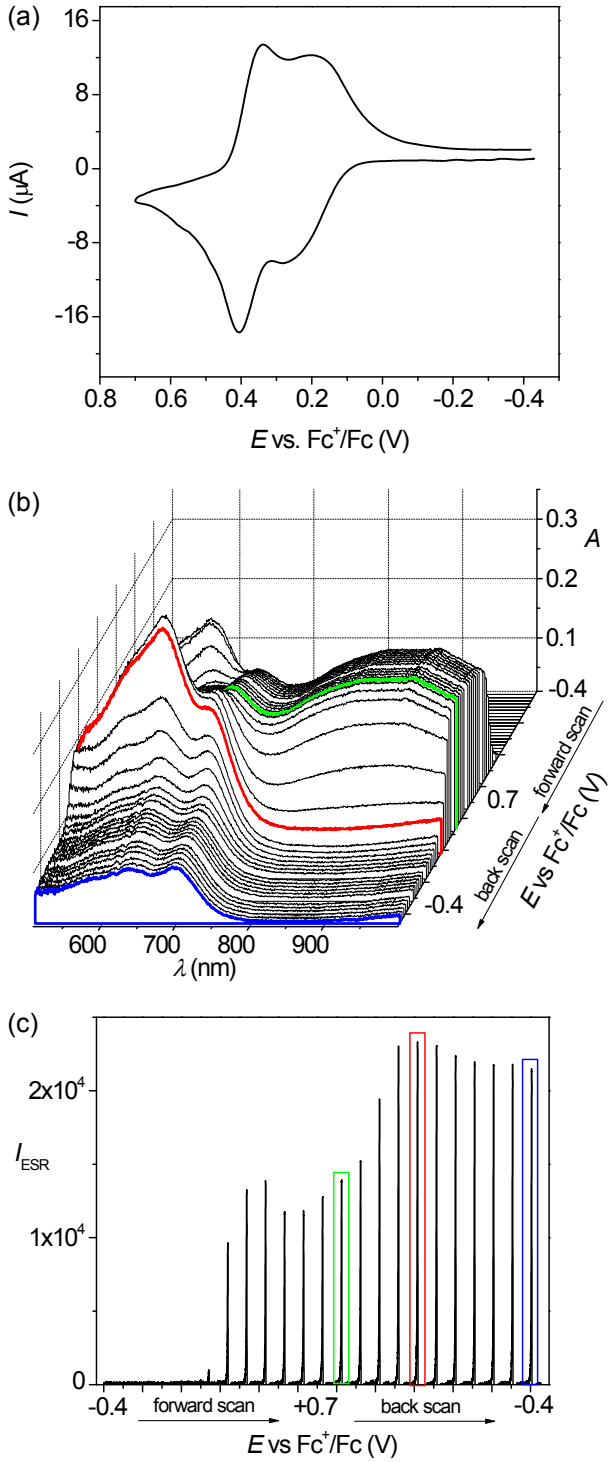


Figure S34. *In situ* ESR/UV−vis−NIR spectroelectrochemistry for 1 mM sample **8** in 0.2 M Bu_4NPF_6 in CH_2Cl_2 (scan rate 5 mV s^{-1}). (a) *In situ* cyclic voltammogram with the simultaneously taken (b) UV-vis-NIR spectra. (c) Corresponding potential dependence of ESR spectra (positive part is shown for clarity) observed upon oxidation of **8** during the *in situ* voltammetric scan.

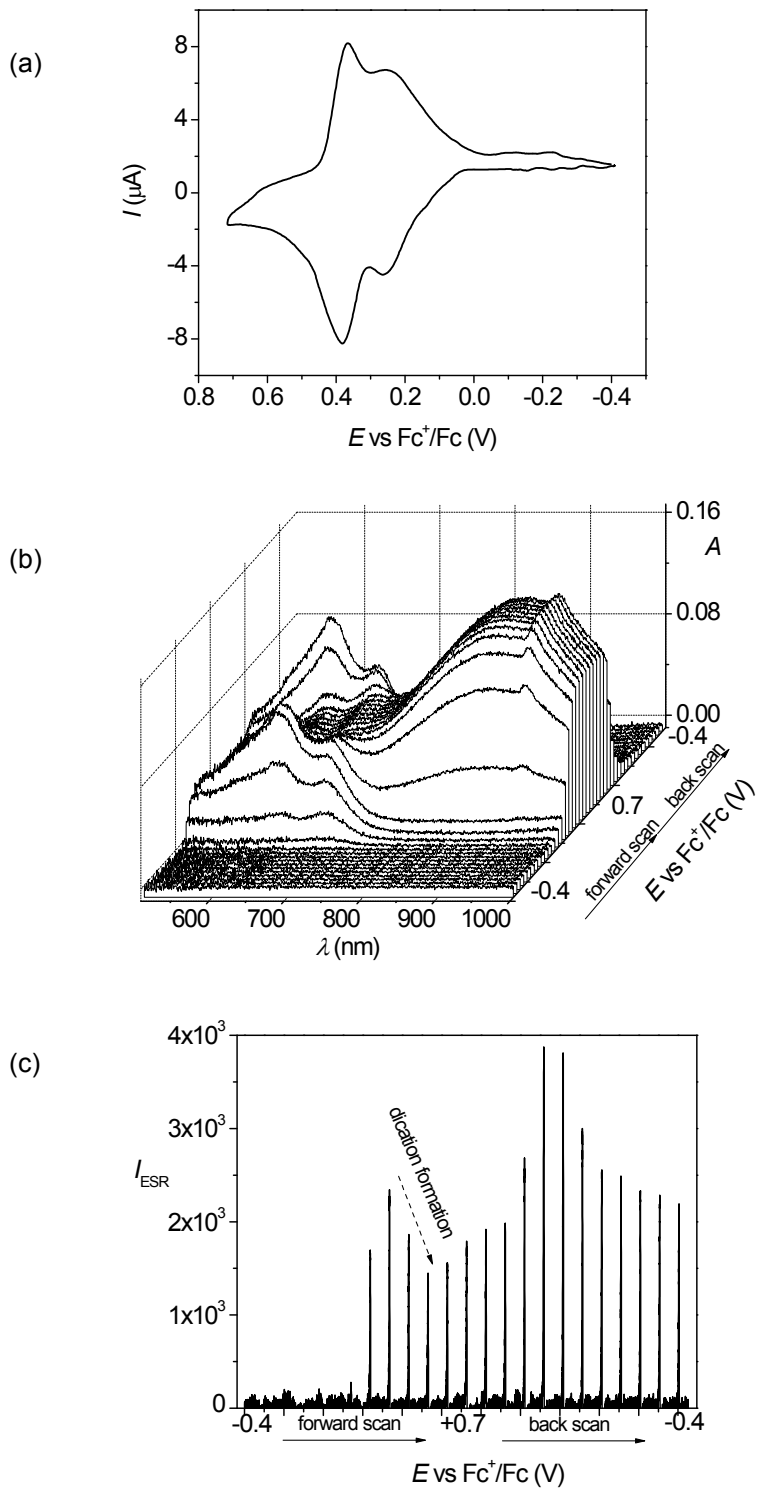


Figure S35. *In situ* ESR/UV−vis−NIR spectroelectrochemistry for 0.5 mM sample **8** in 0.2 M Bu_4NPF_6 in CH_2Cl_2 (scan rate 5 mV s^{-1}). (a) *In situ* cyclic voltammogram with the simultaneously taken (b) UV-vis-NIR spectra. (c) Corresponding potential dependence of ESR spectra (positive part is shown for clarity) observed upon oxidation of **8** during the *in situ* voltammetric scan.

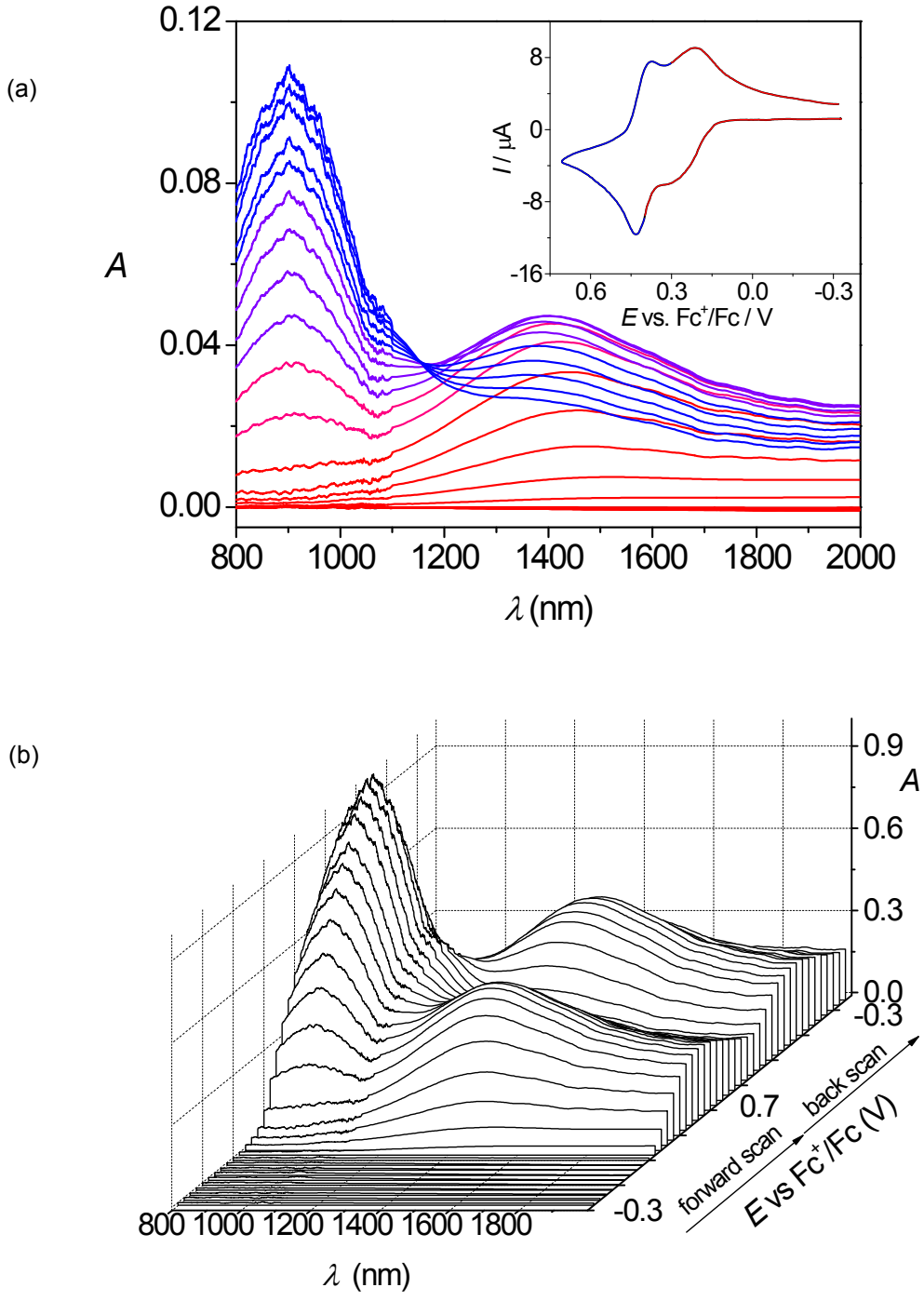


Figure S36. *In situ* NIR - cyclic voltammetry for 0.5 mM sample **8** in 0.2 M Bu_4NPF_6 in CH_2Cl_2 (scan rate 5 mV s^{-1}). (a) *In situ* cyclic voltammogram (inset) with the simultaneously taken NIR spectra in forward scan (in 2D plot) and (b) the corresponding potential dependence of NIR spectra (in 3D plot) observed upon oxidation of **8** during the *in situ* voltammetric scan.

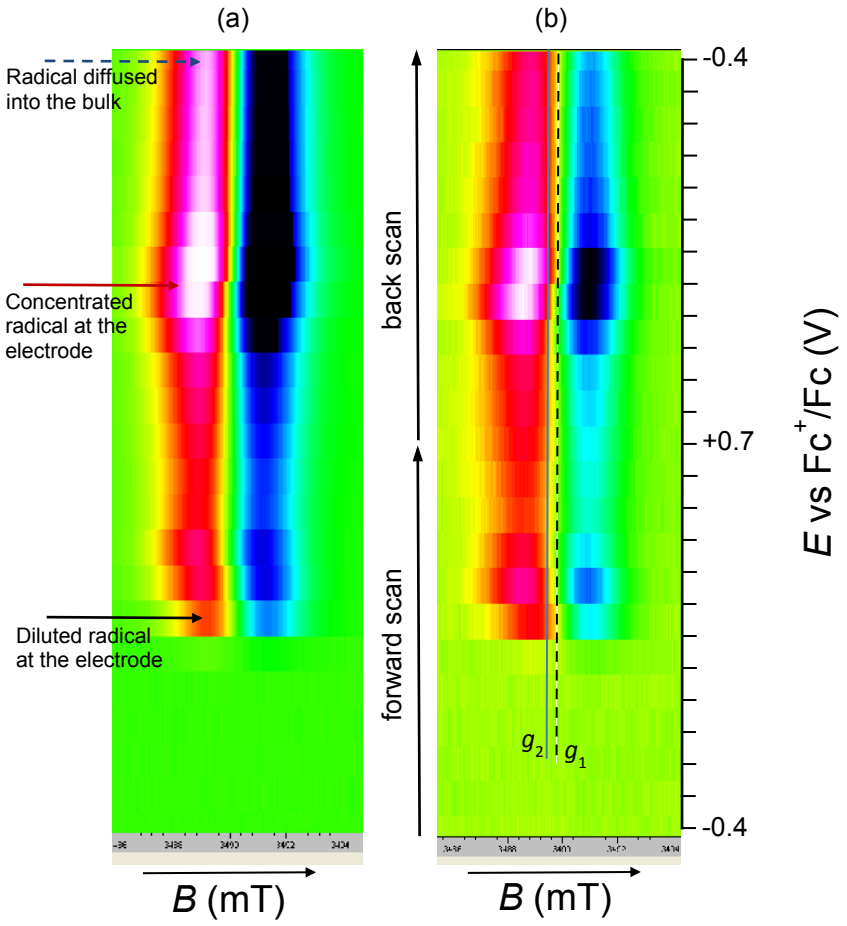


Figure S37. 2D ESR density plot showing the shift of *g*-value of ESR signal (g_1, g_2) observed during the *in situ* ESR/spectroelectrochemistry for (a) 1 mM sample **8** and (a) 0.5 mM sample **8** in 0.2 M Bu_4NPF_6 in CH_2Cl_2 (scan rate 5 mV s^{-1}).

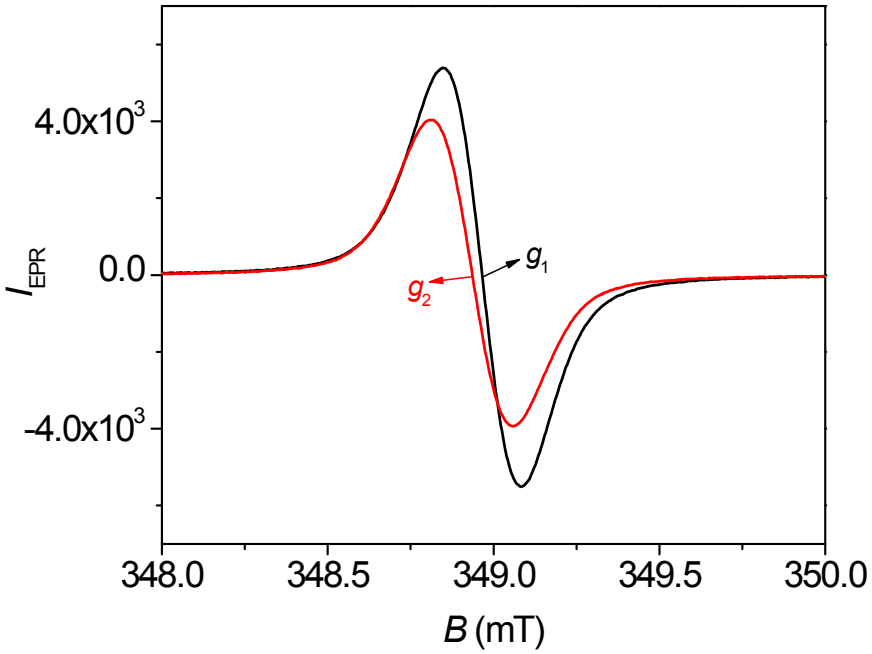


Figure S38. Two different ESR spectra of radical in diluted (black line) and concentrated (red line) form observed upon oxidation of 0.5 mM **8** in 0.2 M Bu_4NPF_6 in CH_2Cl_2 using large Pt mesh and chronopotentiometric conditions.

Electrocrystallization – Photos

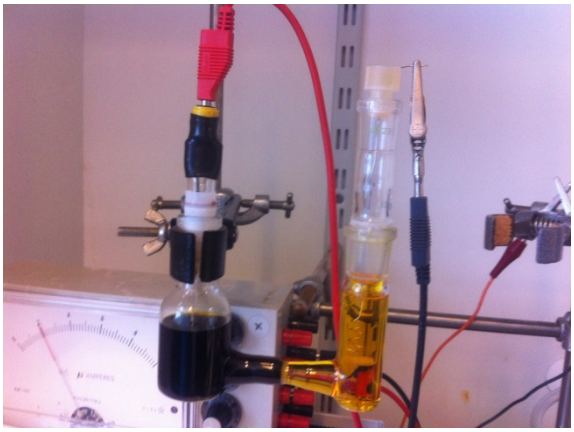


Figure S39. Electrocrystallization of **8** (SBu) in CH_2Cl_2 with Bu_4NPF_6 as electrolyte. No crystals formed at electrode.

Figure S40. Electrocrystallization of **10** (SEt) in PhCl with Bu_4NPF_6 as electrolyte (the salt obtained with Bu_4NBF_4 as electrolyte looked similar).

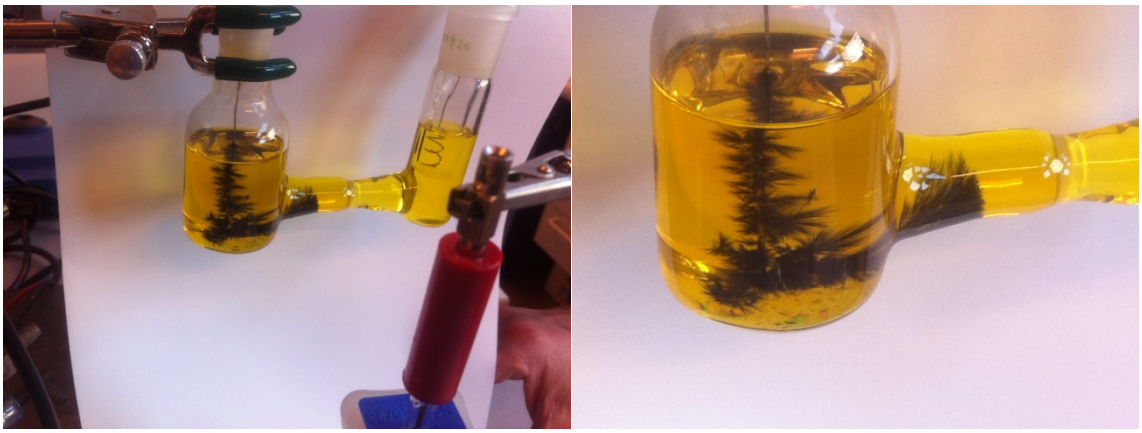


Figure S41. Electrocrystallization of **10** (SEt) in PhCl with Bu_4NTaF_6 as electrolyte.

Elemental Analysis Results of Salts Obtained by Electrocrystallization of 10

Crystals grown from CH_2Cl_2, Bu_4NPF_6 – Composition: (**10**•PF_6)$_2$•Bu_4NPF_6

Calculated: C, 48.80; H, 4.68; N, 0.68; found (Copenhagen): C, 48.48; H, 4.36, N, 0.66

Crystals grown from PhCl, Bu_4NPF_6 – Composition: **10**•PF_6

- *First batch:*

Calculated: C, 48.61; H, 3.60; found (London): C, 48.61 / 48.92; average = 48.77; H, 3.43 / 3.35; average = 3.39

- *Second batch:*

Calculated: C, 48.61; H, 3.60; found (London): C; 48.38 / 48.45; average = 48.42; H, 3.77 / 3.71; average = 3.74

Crystals grown from PhCl, Bu_4NBF_4 – Composition: **10**•$(BF_4)_{1.5}$

Calculated: C, 49.48; H, 3.66; found (London): C, 48.91 / 48.99; average = 48.95; H, 4.09 / 4.07; average = 4.08

X-Ray Crystal Data

A crystal of **8** suitable for X-ray crystallography was mounted and intensity data was collected at 123(2) K on an Enraf-Nonius KappaCCD area detector using ω and θ scans. The program EVALCCD (A. J. M. Duisenberg, L. M. J. Kroon-Batenburg ans A. M. Schreurs, *J. Appl. Crystallogr.*, 2003, **36**, 220) was used for data reduction and the data was corrected for absorption by integration (P. Coppens, *Crystallographic Computing*, in: F. R. Ahmed (Ed.), Munksgaard, Copenhagen, 1970, p. 255). The structure was solved with direct methods utilizing SHELXS (G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467) and refined by least-squares methods using SHELXL97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112).

The other four X-ray diffraction studies were performed using a Bruker D8 Venture diffractometer using ω and θ scans with the raidiation monochromated by a doubly curved silicon crystal (Mo Kα). The datasets were collected and processed using Brukers Apex2, with the SAINT (Bruker (2007). *Apex2, SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA) and SADABS (Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.) programs and refined using Olex2 (O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann *J. Appl. Cryst.* 2009, **42**, 339-341.
All non-hydrogen atoms were refined using anisotropic displacement parameter. All hydrogen atoms were included and refined with isotropical factor of $1.2U_{eq}$ of the parent carbon atom except for methyl hydrogens, which were refined with $1.5U_{eq}$ of the parent carbon atom. Crystallographic data is given in Table S7.

Table S7. Crystallographic data for **8** (CCDC: 962757), **10** (CCDC: 1010187), **10**•PF_6 (CCDC: 1010186), **10**•$(BF_4)_{1.5}$ (CCDC: 1010185) and **10**•TaF_6 (CCDC: 1010188).

Compound	**8**	**10**	**10•PF_6**	**10•$(BF_4)_{1.5}$**	**10•TaF_6**
Formula	$C_{42}H_{46}S_8$	$C_{34}H_{30}S_8$	$C_{34}H_{30}S_8PF_6$	$C_{34}H_{30}B_{1.5}F_6S_8$	$C_{34}H_{30}F_6S_8Ta$
M (g mole^{-1})	807.35	695.14	840.11	825.37	990.08
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	$P2_1/n$	C2/c	P-1	P-1
a (Å)	8.4030(6)	5.2379(16)	24.306(3)	7.3803(8)	9.4413(5)
b (Å)	9.035(1)	15.5022(8)	24.770(3)	15.8329(15)	13.8707(7)
c (Å)	14.003(1)	19.0966(11)	6.7903(6)	16.5567(15)	15.4171(7)
α (°)	103.543(9)	90	90	115.025(3)	106.242(2)
β (°)	106.211(12)	97.145(2)	104.828(6)	92.031(4)	98.995(2)
γ (°)	94.229(10)	90	90	96.727(4)	107.963(2)
U (Å^3)	981.83(17)	1538.6(6)	3952.1(7)	1733.2(3)	1777.67(16)
Z	1	2	4	2	2
D_x (g cm^{-3})	1.365	1.500	1.168	1.581	1.850
T (K)	123(2)	122(2)	122(2)	122(2)	122(2)
μ	0.486	0.607	0.742	0.575	3.620
Measured/unique refl.	30687/5715	24414/3158	15137/2661	16846/6108	25042/6270
Parameters refined	205	191	193	501	445
Final $R1$ [$I > 2\sigma(I)$]	0.0300	0.0317	0.0793	0.0804	0.0482
wR_2 [$I > 2\sigma(I)$]	0.0749	0.0686	0.2442	0.1980	0.1098
$R1$ (all data)	0.0404	0.0462	0.1286	0.1418	0.0673
wR_2 (all data)	0.0819	0.0743	0.2860	0.2365	0.1187
S (GoF)	1.034	1.042	1.026	1.057	1.035

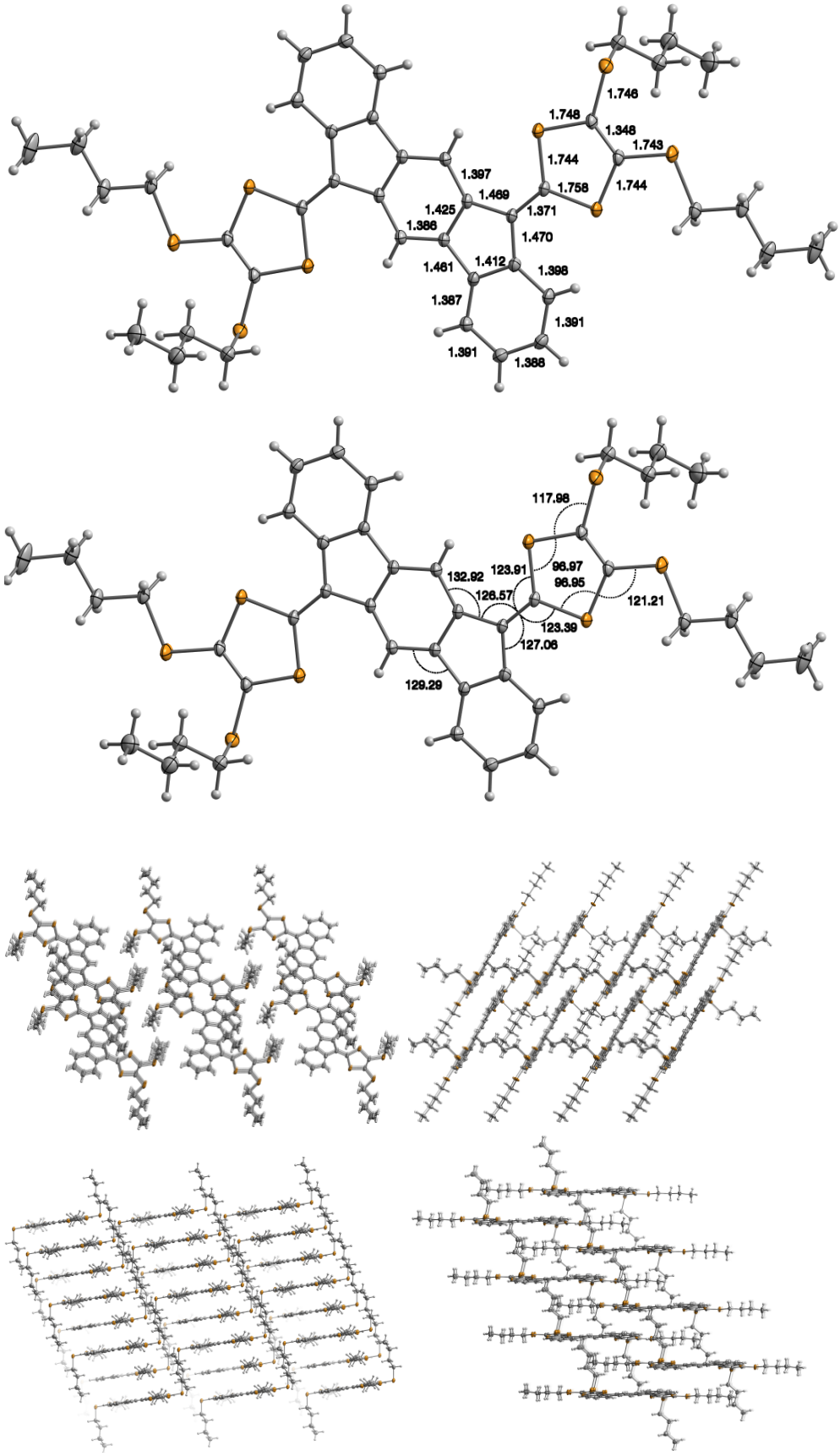


Figure S42. Bond distances and angles for **8** along with perspective views of the packing of the molecules.

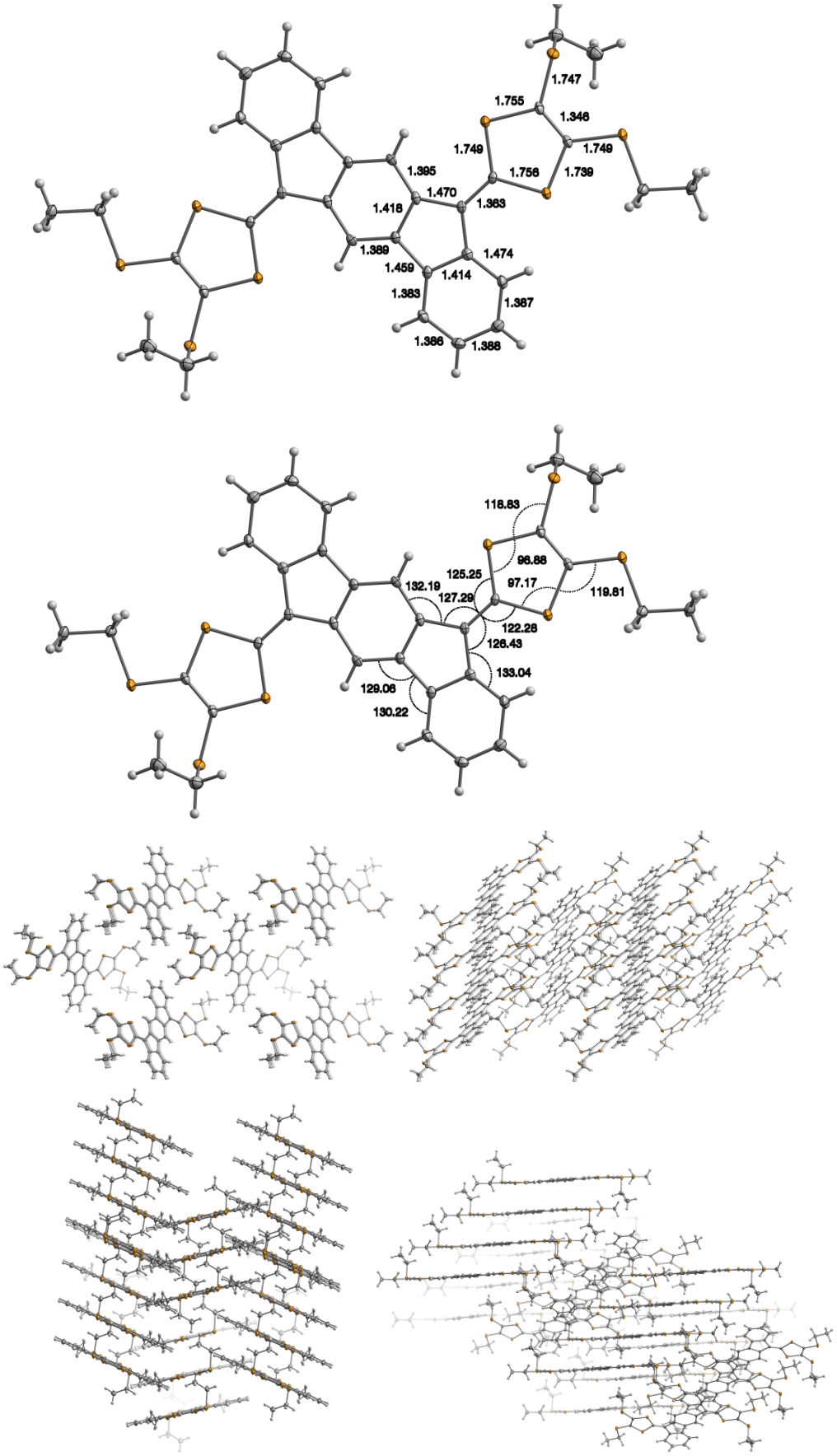


Figure S43. Bond distances and angles for **10** along with perspective views of the packing of the molecules.

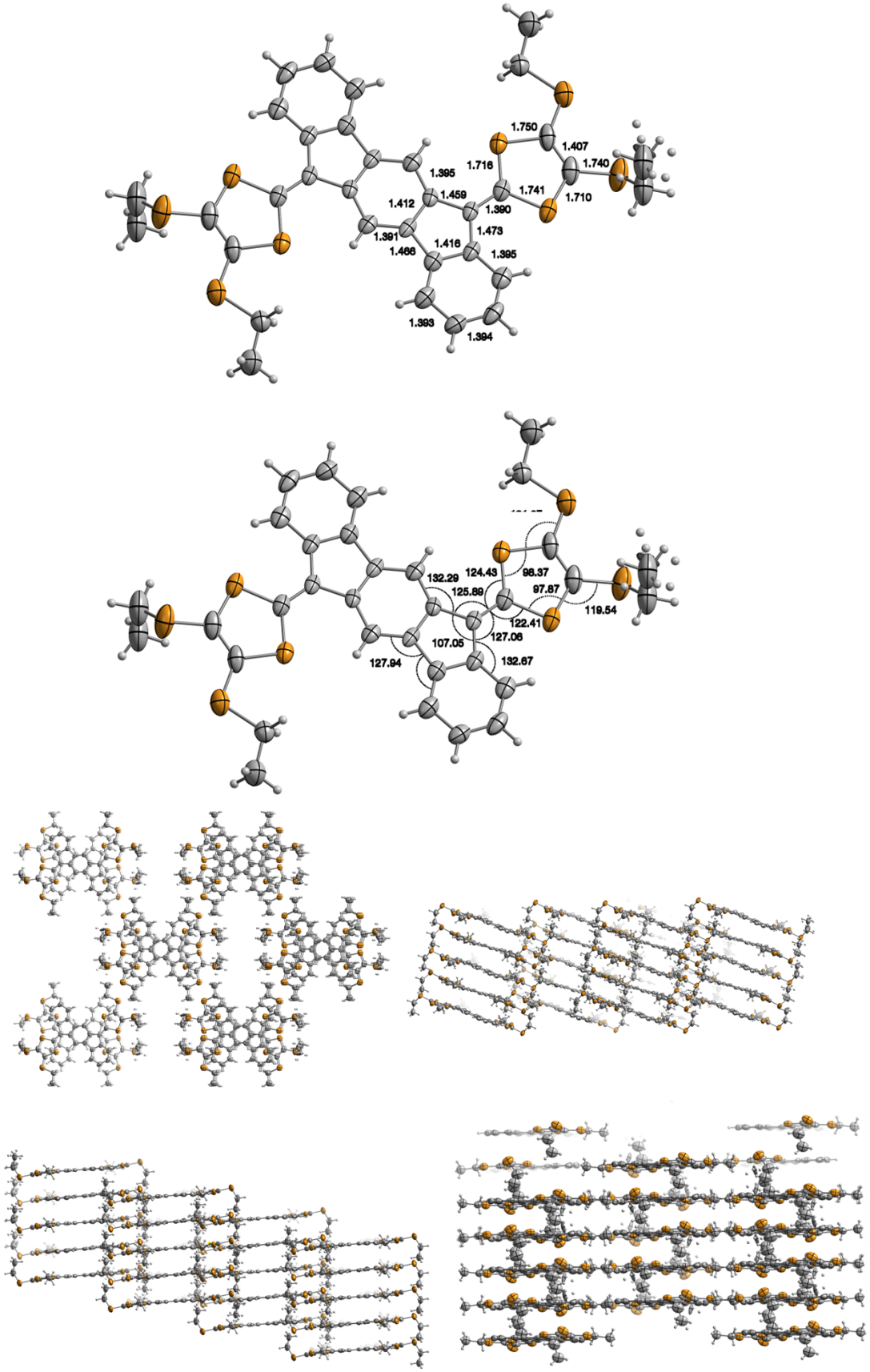


Figure S44. Bond distances and angles for **10**•PF_6 along with perspective views of the packing of the molecules. The stoichiometry (number of PF_6^- per organic molecule) could not be determined from this structure (see paper for details).

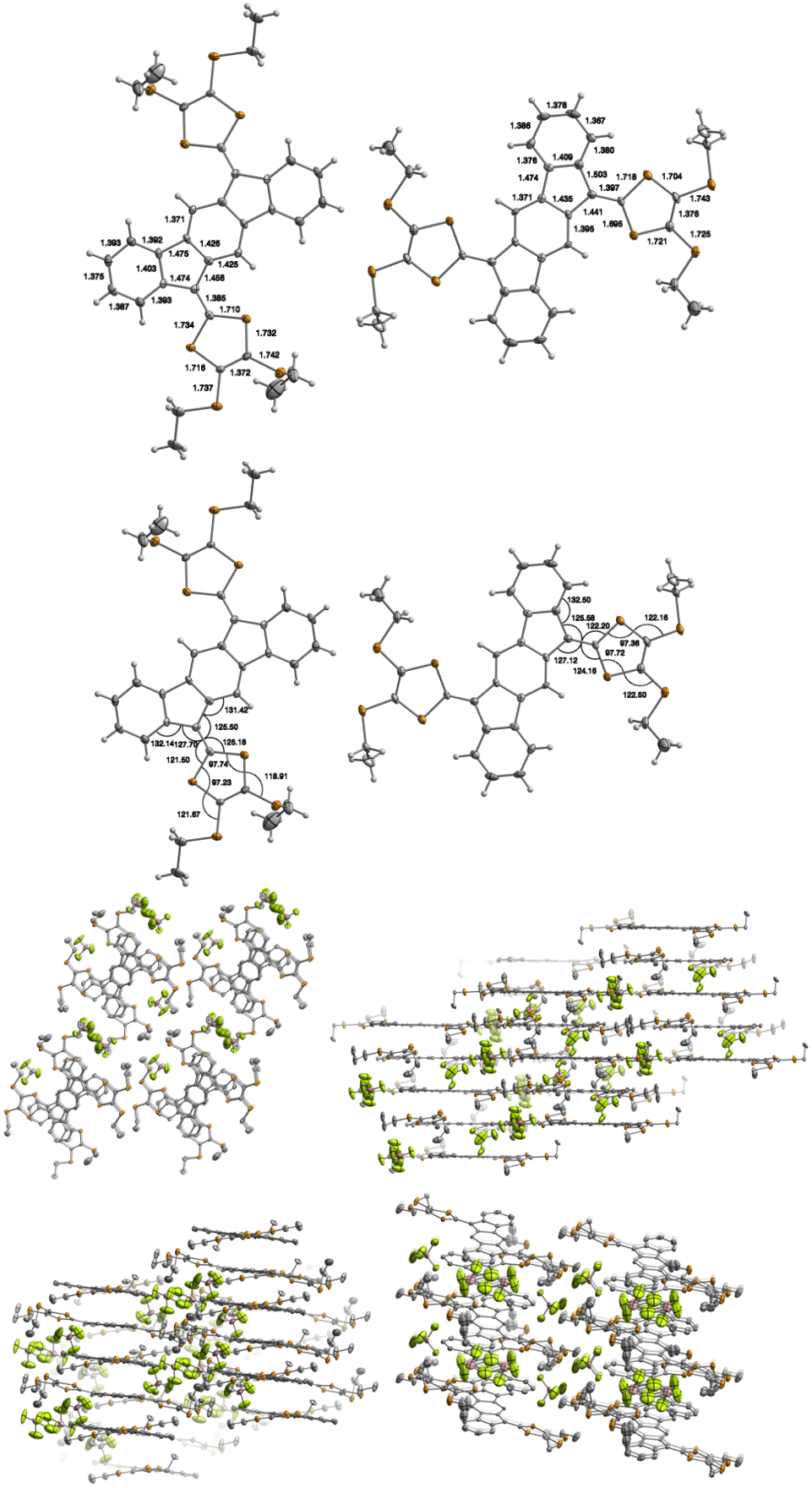


Figure S45. Bond distances and angles for **10**•$(BF_4)_{1.5}$ along with perspective views of the packing of the molecules.

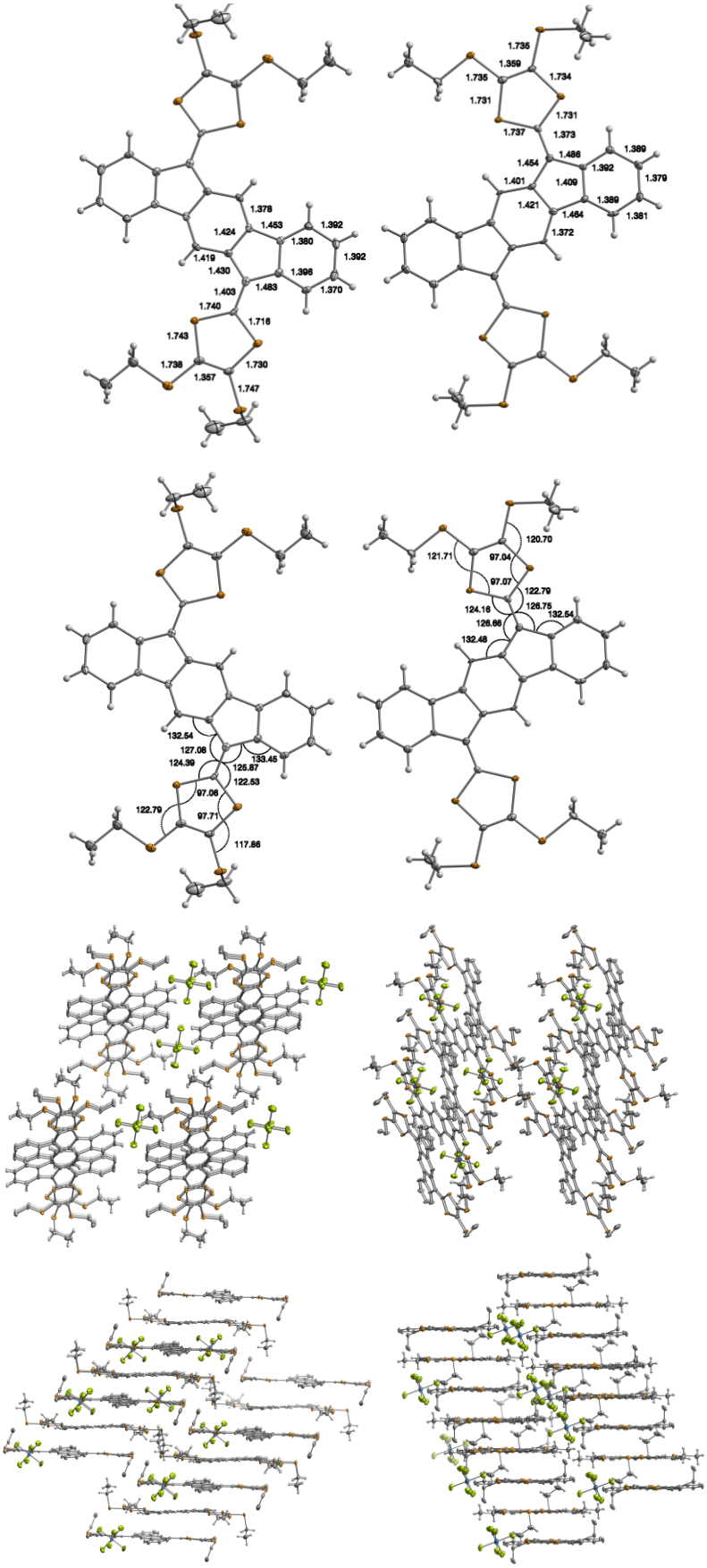


Figure S46. Bond distances and angles for **10**•TaF_6 along with perspective views of the packing of the molecules.

Calculations

Density Functional Theory calculations (geometry optimizations and energies, Tables S8-S10) were performed using *Gaussian 09*:

Gaussian 09, EM64L-G09RevB.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

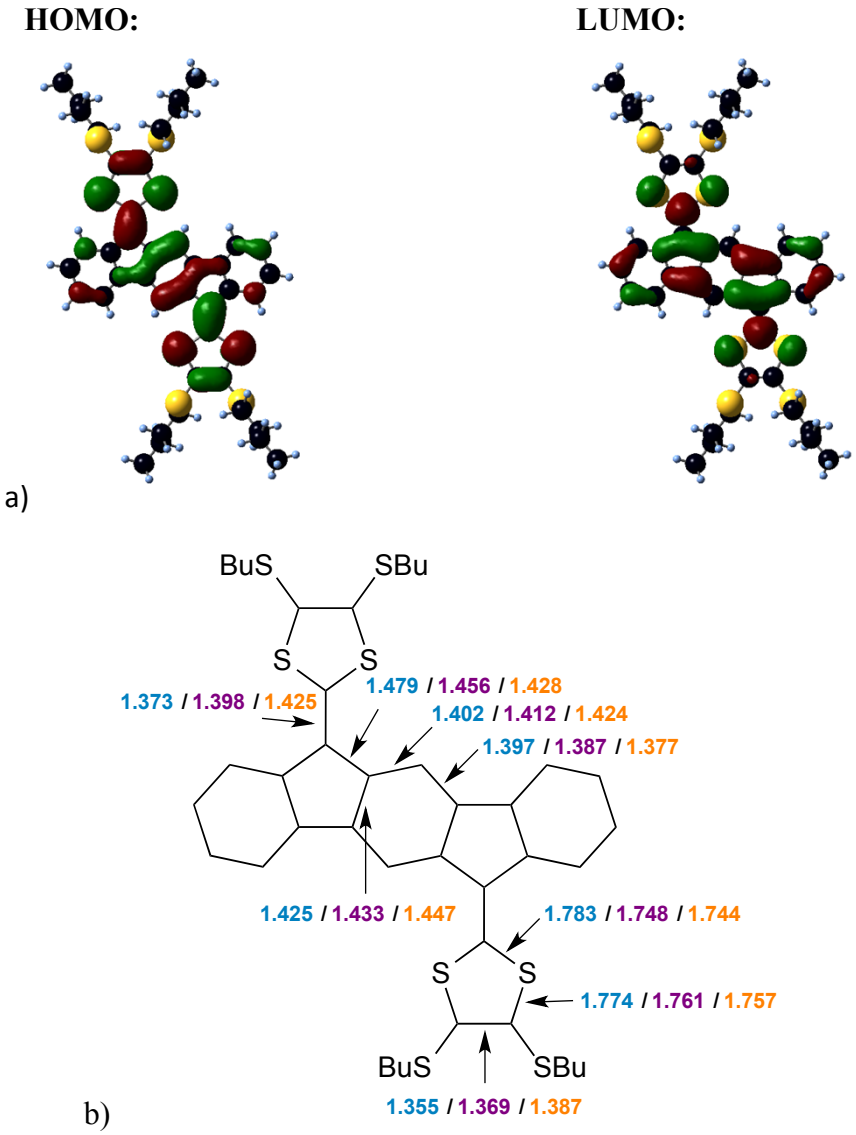
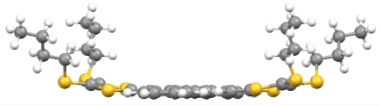
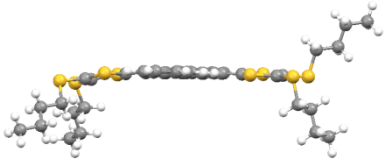
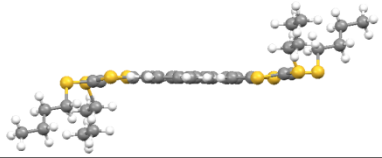
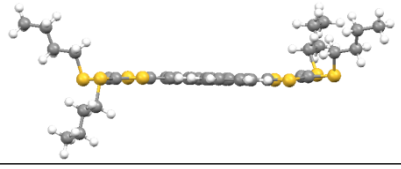
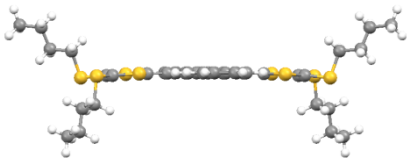
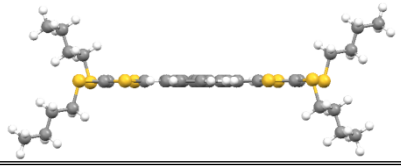


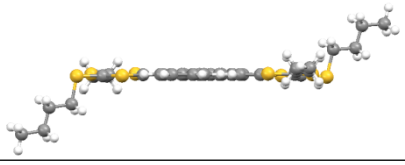
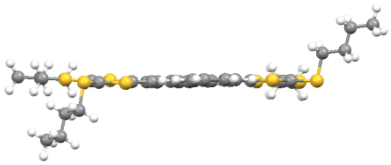
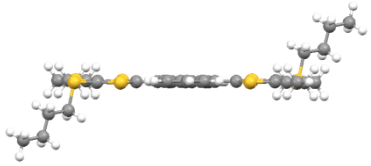
Figure S47. a) Frontier Orbitals (HOMO/LUMO) resulting from B3LYP/cc-pVDZ calculations. b) Bond distances (in Å) for **8**, $\mathbf{8}^{+}$ and $\mathbf{8}^{2+}$ resulting from B3LYP/cc-pVDZ calculations.

Table S8. Conformers of the neutral **8** (SBu).[a]

Charge	Conformations (structures and abbreviations)		Φ[b]	Energy (a.u.)	G_{298} (a.u.)	Boltzmann distribution (%)[c]
0		*Syn-syn-syn*	4°	-4813.9203858	-4813.257142	3.0
0		*Syn-syn-anti*	1°	-4813.9210487	-4813.258937	20.3
0		*Syn-anti-syn*	0°	-4813.9204210	-4813.258918	19.9
0		*Syn-anti-anti*	1°	-4813.9211021	-4813.258284	10.2
0		*Anti-syn-anti*	2°	-4813.9218149	-4813.257666	5.3
0		*Anti-anti-anti*	0°	-4813.9218046	-4813.259609	41.4

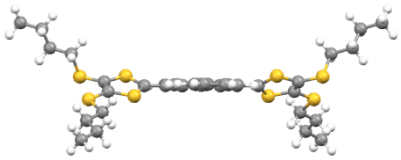
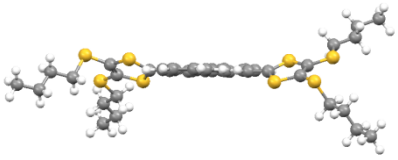
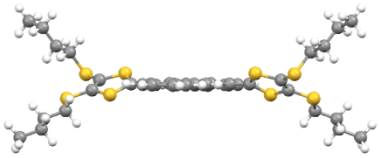
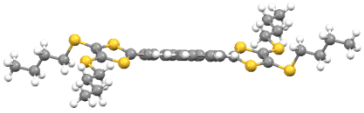
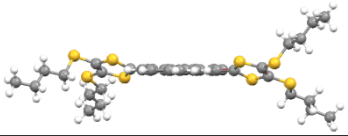
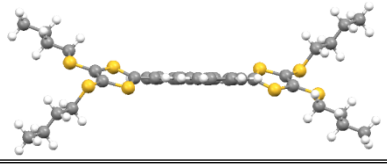
[a]Results from Gaussian 09 DFT RB3LYP/cc-pVDZ calculations (opt=tight). [b]Angle between the planes defined by the two DT-units. [c]At 298K calculated from G_{298}.

Table S9. Conformers of the radical cation of **8** (SBu).[a]

Charge	Conformations (structures and abbreviations)		Φ[b]	Energy (a.u.)	G_{298} (a.u.)	Boltzmann distribution (%)[c]
+1		*1,1'-Syn*	1°	-4813.7091994	-4813.045201	3.0
+1		*1,2'-Syn*	0°	-4813.7096273	-4813.045817	5.7
+1		*2,2'-Syn*	11°	-4813.71018628	-4813.047557	36.4
+1		*1,1'-Anti*	4°	-4813.7091833	-4813.046497	11.8
+1		*1,2'-Anti*	5°	-4813.7096621	-4813.046336	10.0
+1		*2,2'-Anti*	0°	-4813.71021290	-4813.047468	33.1

[a]Results from Gaussian 09 DFT RB3LYP/cc-pVDZ calculations (opt=tight). [b]Angle between the planes defined by the two DT-units. [c]At 298K calculated from G_{298}.

Table S10. Conformers of the dication of **8** (SBu).[a]

Charge	Conformations (structures and abbreviations)		Φ[b]	Energy (au)	G_{298} (a.u.)	Boltzmann distribution (%)[c]
+2		*1,1'-Syn*	52°	-4813.4004805	-4812.733913	0.08
+2		*1,2'-Syn*	55°	-4813.4015958	-4812.736610	1.4
+2		*2,2'-Syn*	55°	-4813.40336304	-4812.736236	0.9
+2		*1,1'-Anti*	0°	-4813.3998482	-4812.735127	0.3
+2		*1,2'-Anti*	0°	-4813.4014782	-4812.734632	0.2
+2		*2,2'-Anti*	0°	-4813.40302314	-4812.740603	97.1

[a]Results from Gaussian 09 DFT RB3LYP/cc-pVDZ calculations (opt=tight). [b]Angle between the planes defined by the two DT-units. [c]At 298K calculated from G_{298}.

8 (SBu): Inner reorganization energy (neutral to radical cation):

c and n represent the geometry of radical cation and the neutral compound in the relaxed state. The signs 0 and + represent the charge. Thus, c0 is the neutral with the geometry of the radical cation and so forth.

The energies of the two relaxed states, n0 and c+, are taken from the tables above as the values for the lowest energy conformers. The energies of the c0 and n+ states are the results of single point Gaussian 09 DTF RB3LYP/cc-pVDZ calculations.

λ_i = [*E*(c0) - *E*(n0)] + [*E*(n+) - *E*(c+)]

= [-4813.9157613 - (-4813.9218149)] + [-4813.7053367 - (-4813.71021290)]

= 0.0060536 + 0.0048762 = 0.0109298

= 0.30 eV

= 28.6 kJ mol^{-1}

This is essentially the same value as obtained for the parent TTF (6.8 kcal mol^{-1} = 28.5 kJ mol^{-1}) (S. V. Rosokha and J. K. Kochi, *J. Am. Chem. Soc.*, 2007, **129**, 828-838).

8 (SBu): Inner reorganization energy (radical cation to dication):

d and c represent the geometry of dication and radical cation in the relaxed state. The signs + and 2+ represent the charge. Thus, d+ is the radical cation with the geometry of the dication and so forth.

The energies of the two relaxed states, c+ and d2+, are taken from the tables above as the values for the lowest energy conformers. The energies of the d+ and c2+ states are the results of single point Gaussian 09 DTF RB3LYP/cc-pVDZ calculations.

λ_i = [*E*(d+) - *E*(c+)] + [*E*(c2+) - *E*(d2+)]

= [-4813.7027296 - (-4813.71021290)] + [-4813.3977611 - (-4813.40336304)]

= 0.0074833 + 0.00560194 = 0.01308425

= 0.36 eV

= 34.3 kJ mol^{-1}

Dication of 8 – Calculation of exchange couplings

For evaluation of the exchange couplings, the broken-symmetry (BS) approach of Noodleman (L. Noodleman, *J. Chem. Phys.*, 1981, **74**, 5737-5743) as implemented in the ORCA ver. 2.8 suite of programs ((a) F. Neese, ORCA Version 2.8, revision 2131, 2010, Institut für Physikalische und Theoretische Chemie, Universitaet Bonn, Germany. (b) F. Neese, *Coord. Chem. Rev.*, 2009, **253**, 526–563. (c) S. Sinnecker, F. Neese and W. Lubitz, *J. Biol. Inorg. Chem*., 2005, **10**, 231-238) was employed. The formalism of Yamaguchi, which employs calculated expectation values $\langle S^2 \rangle$ for both high-spin and broken-symmetry states was used ((a) K. Yamaguchi, Y. Takahara and T. Fueno, in *Applied Quantum Chemistry* (Ed. Vh. H. Smith, (Reidel, Dordrecht, 1986, p. 155). (b) T. Soda; Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka and K. Yamaguchi, *Chem. Phys. Lett*., 2000, **319**, 223-230). Calculations related to magnetic interactions have been performed using the PBE0 functional. The def2-TZVP basis function set from Ahlrichs was used (F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297-3305). Spin densities were visualized using the UCSF Chimera program ver. 1.5.3.

Calculated exchange coupling: J = -688 cm^{-1} (antiferromagnetic) following the convention $H_{HDvV} = -2JS_1S_2$.

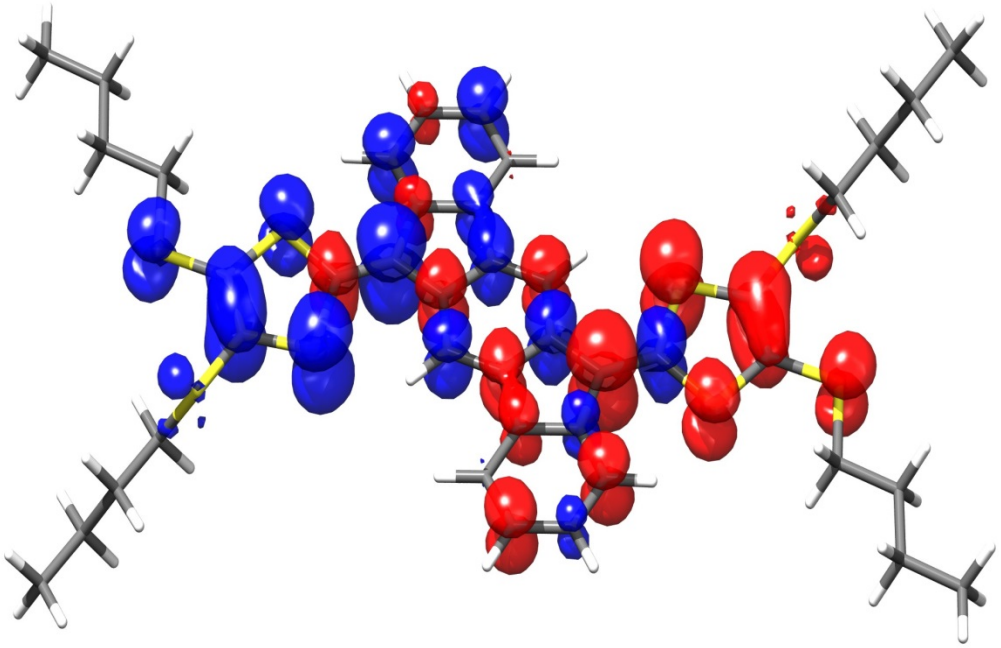
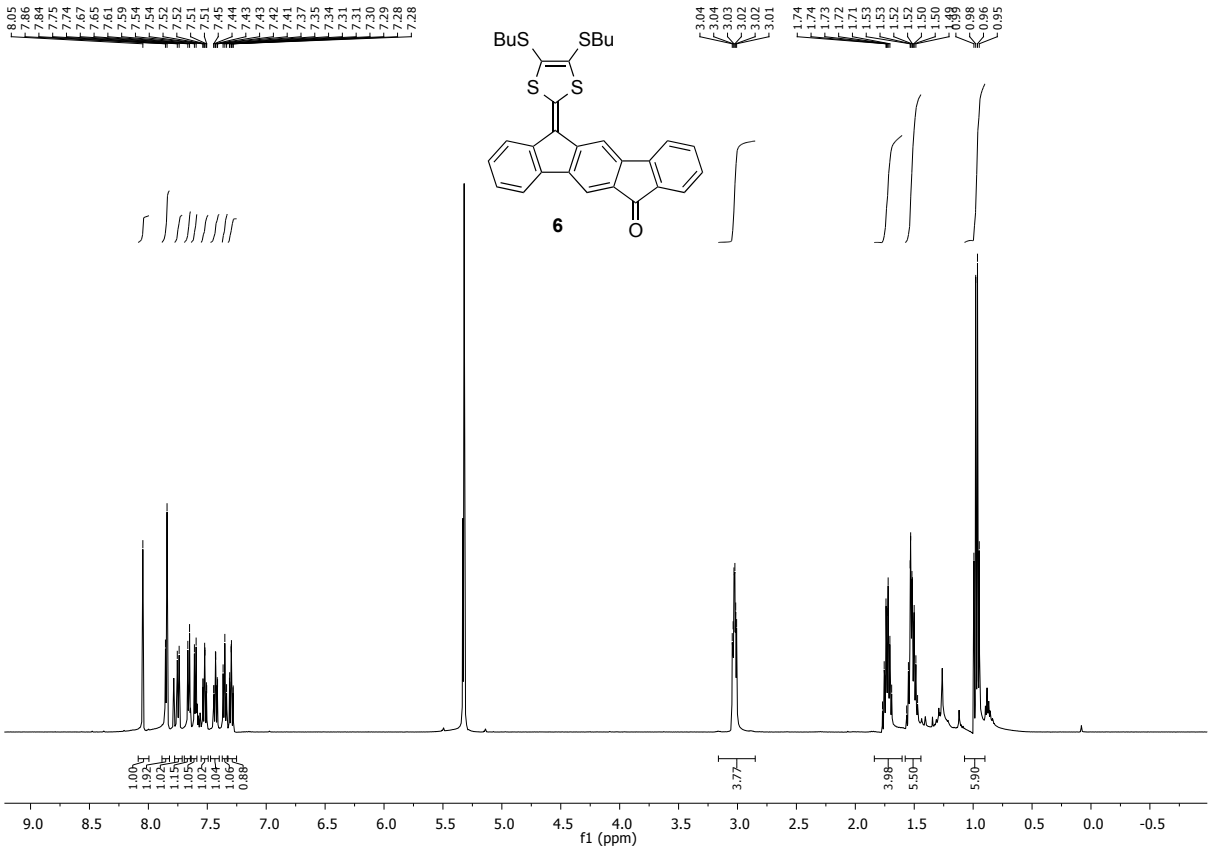


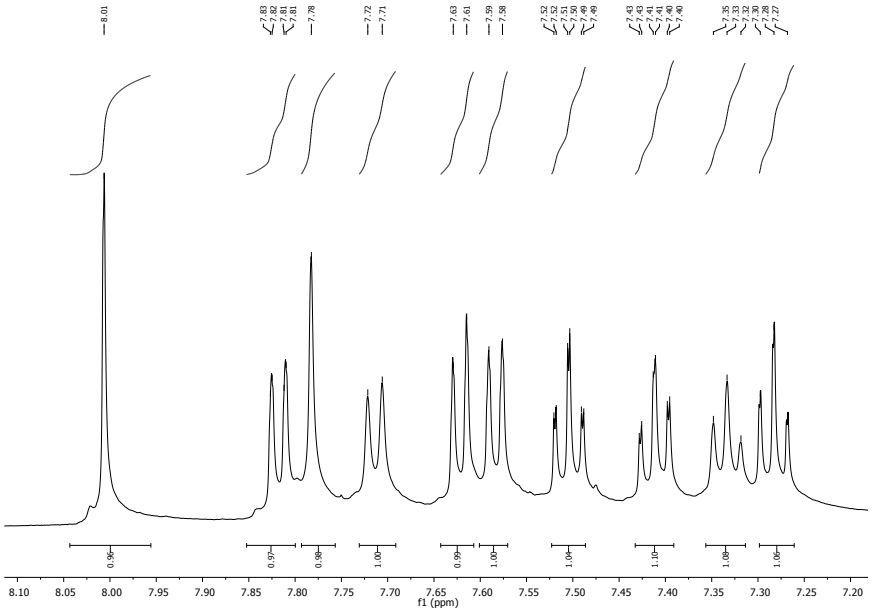
Figure S48. Spin density distribution of **8**$^{2+}$.

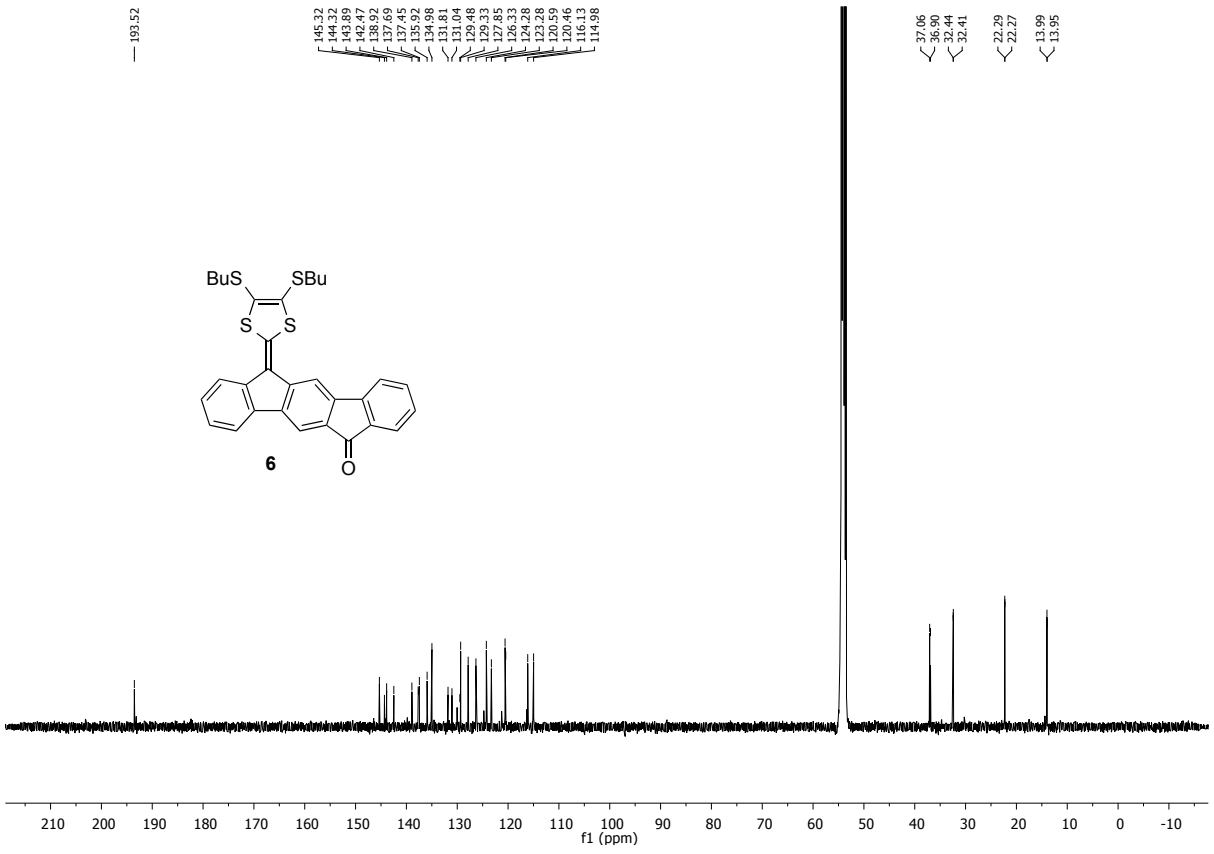
NMR spectra

NMR spectra of **6** in CD_2Cl_2

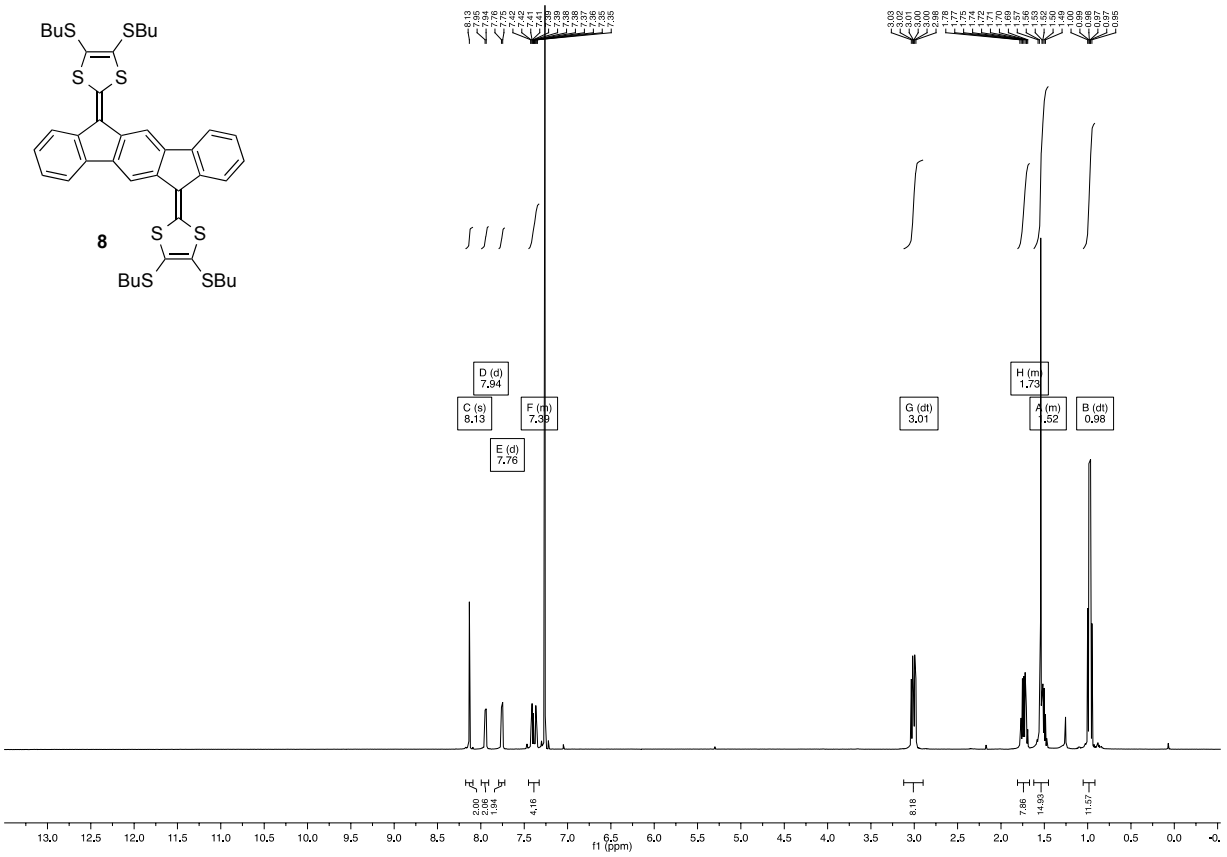


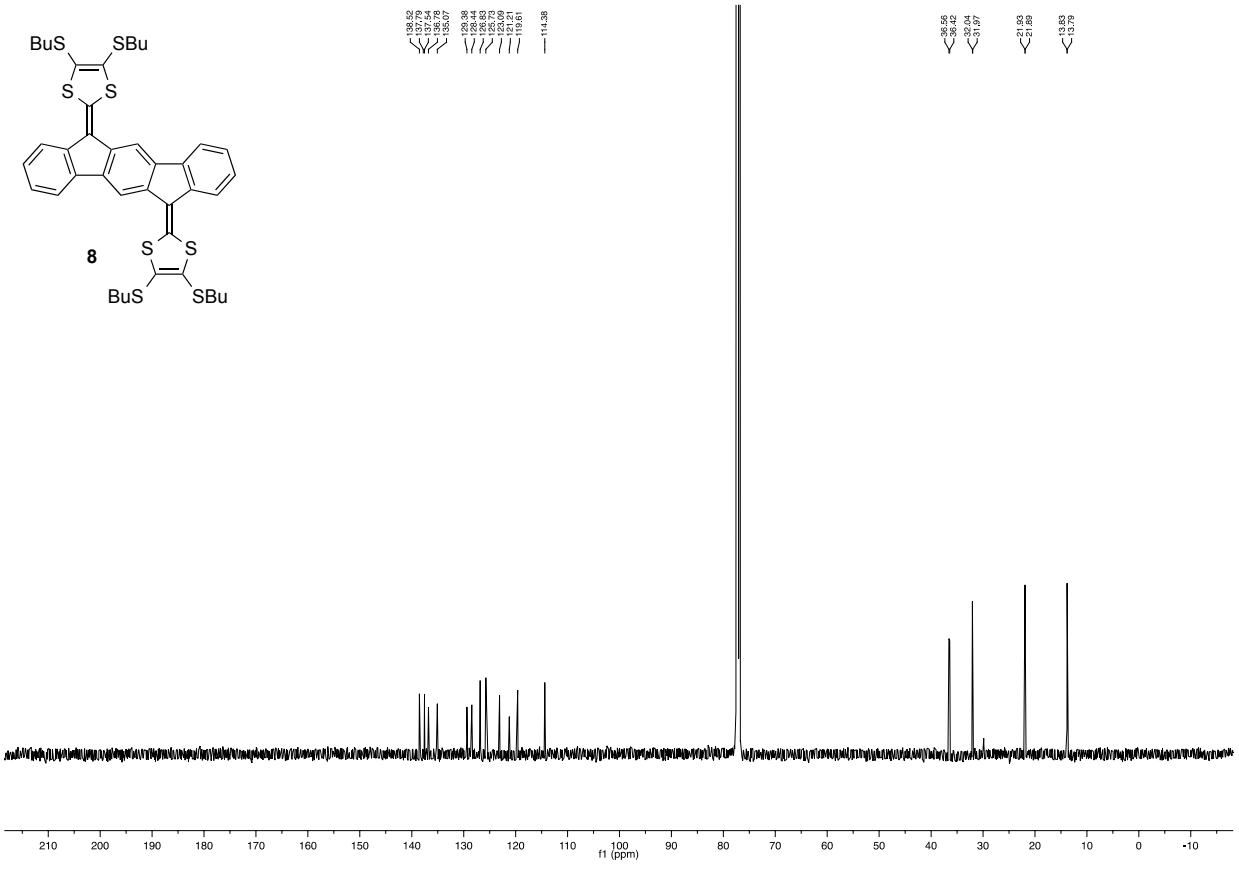
Zoom of aromatic region of **6** at a different concentration in CD_2Cl_2:



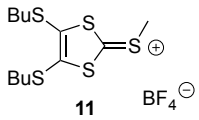

193.52
145.32
144.32
143.89
142.47
138.92
137.69
137.45
135.92
134.98
131.81
131.04
129.48
129.33
127.85
126.33
124.28
123.28
120.59
120.46
116.13
114.98
37.06
36.90
32.44
32.41
22.29
22.27
13.99
13.95
BuS
SBu
S
S
O
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

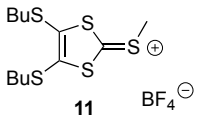
NMR spectra of **8** in $CDCl_3$



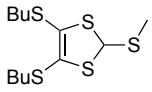


NMR spectra of **11** in $CDCl_3$

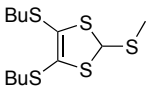




NMR spectra of **12** in $CDCl_3$

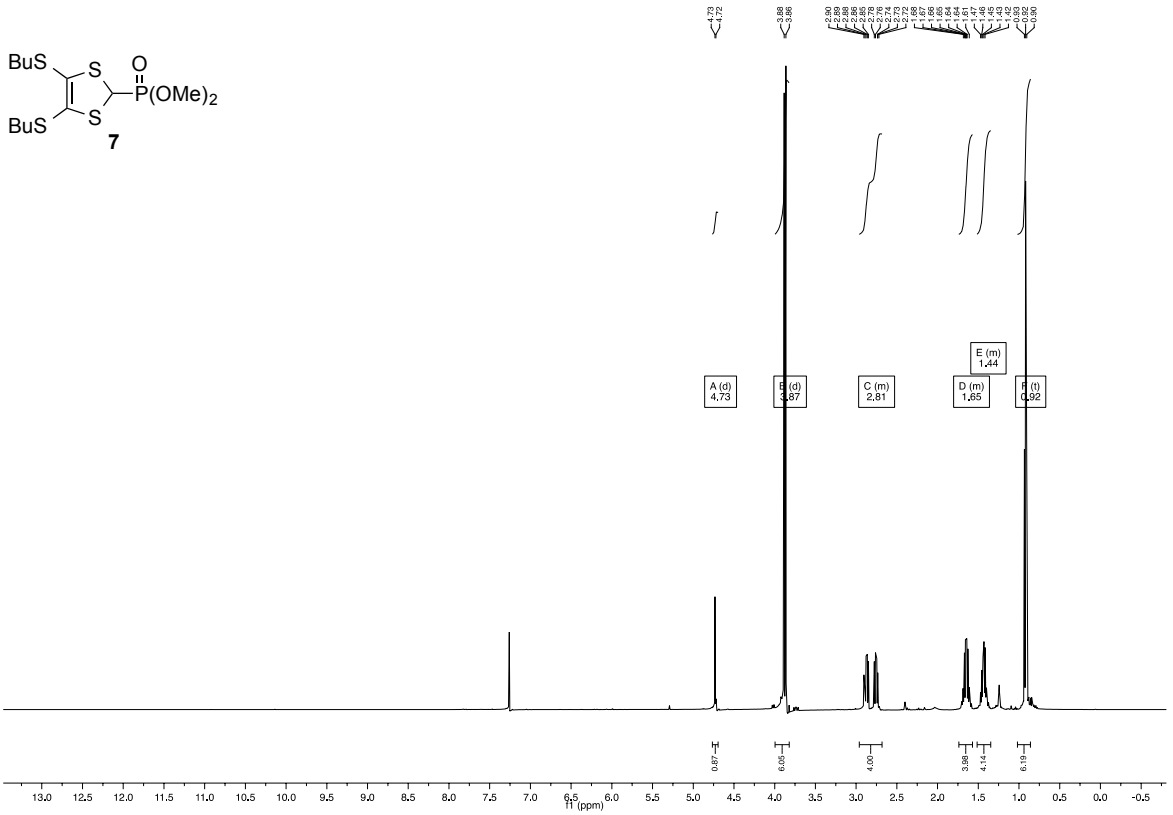


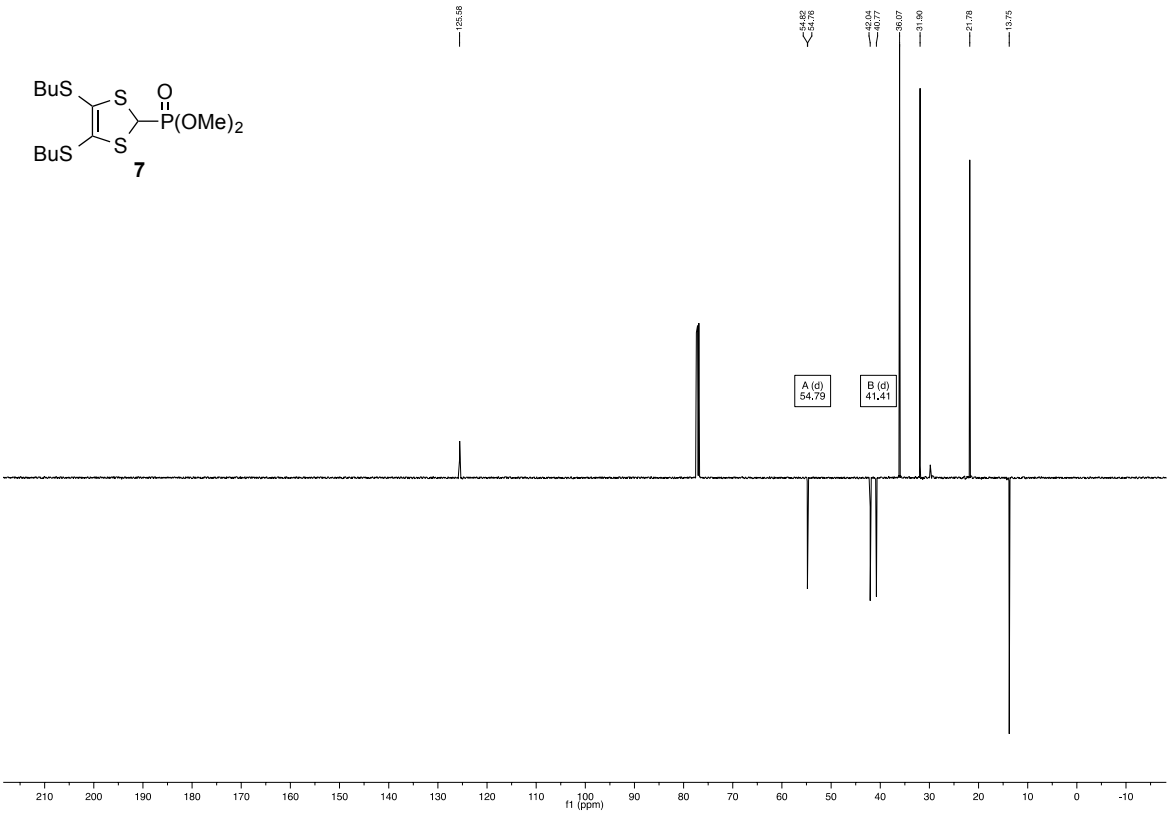
12



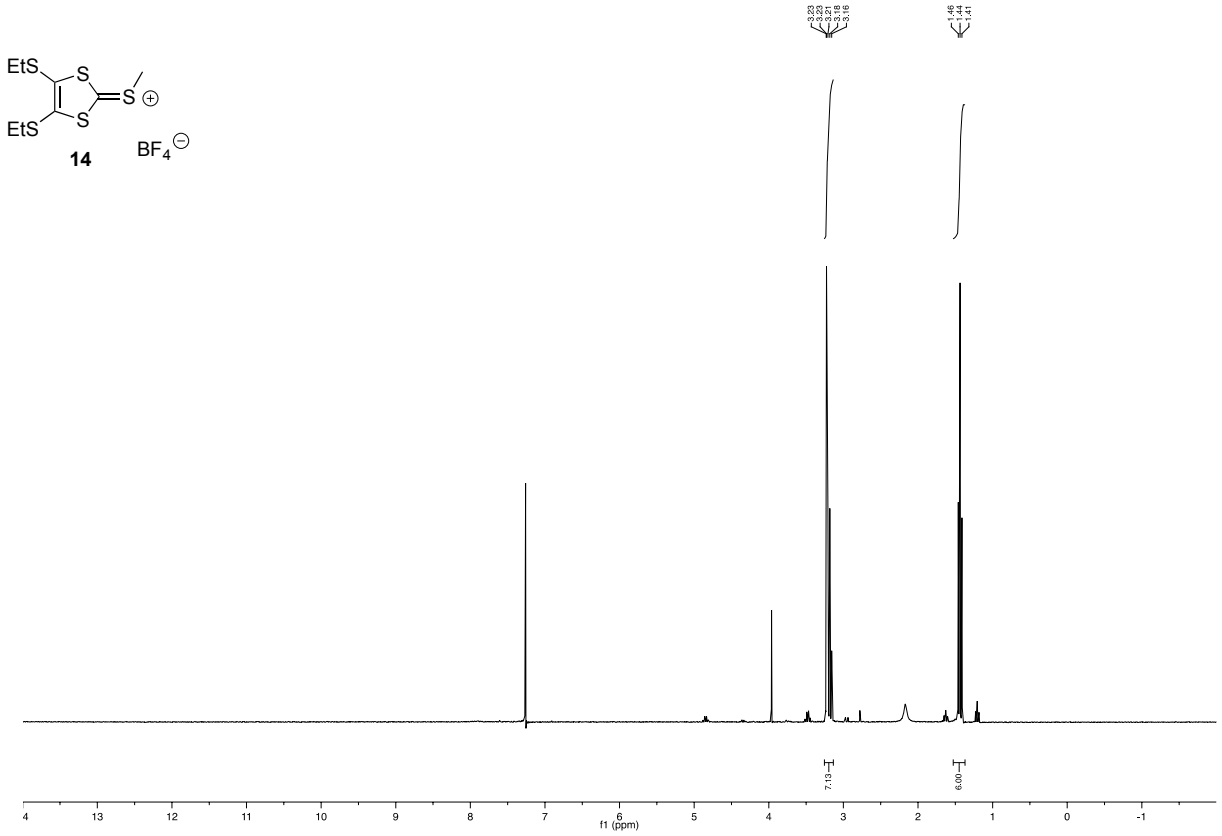
12

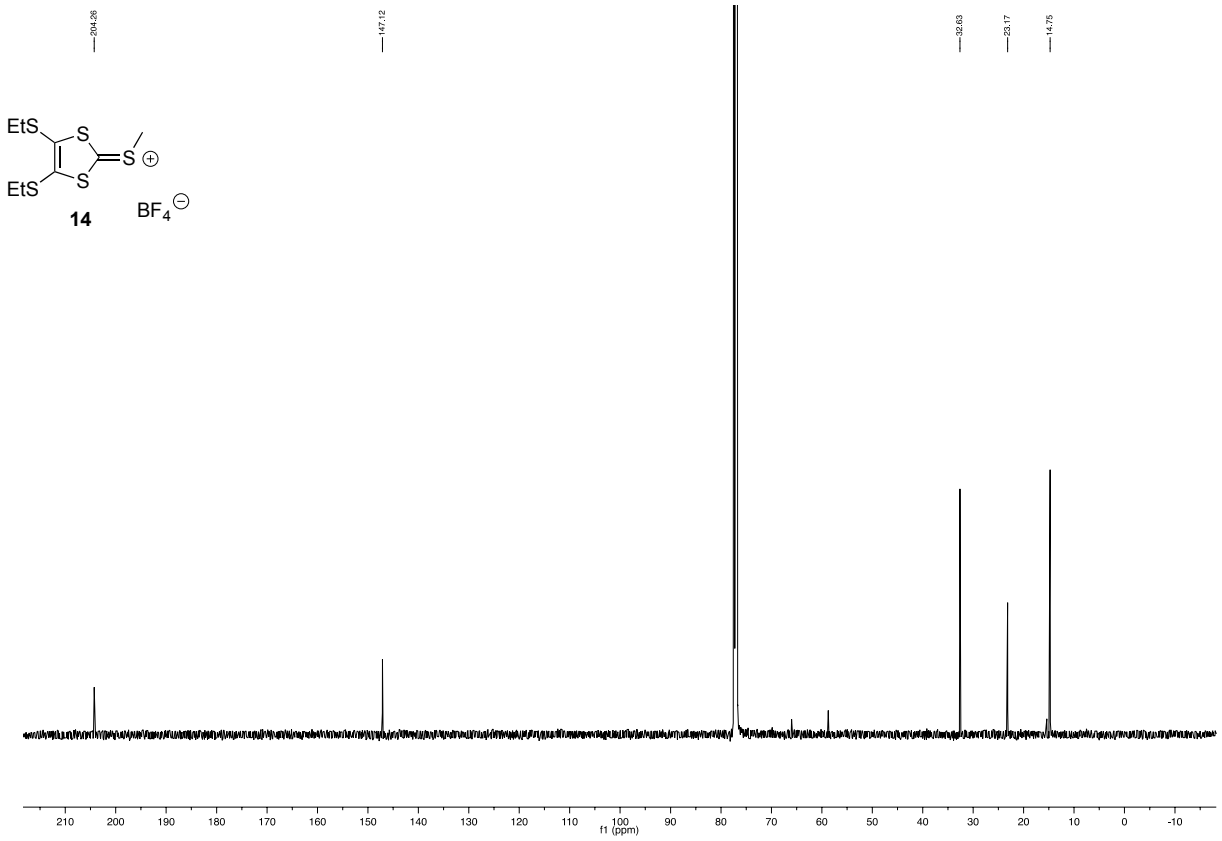
NMR spectra of **7** in $CDCl_3$



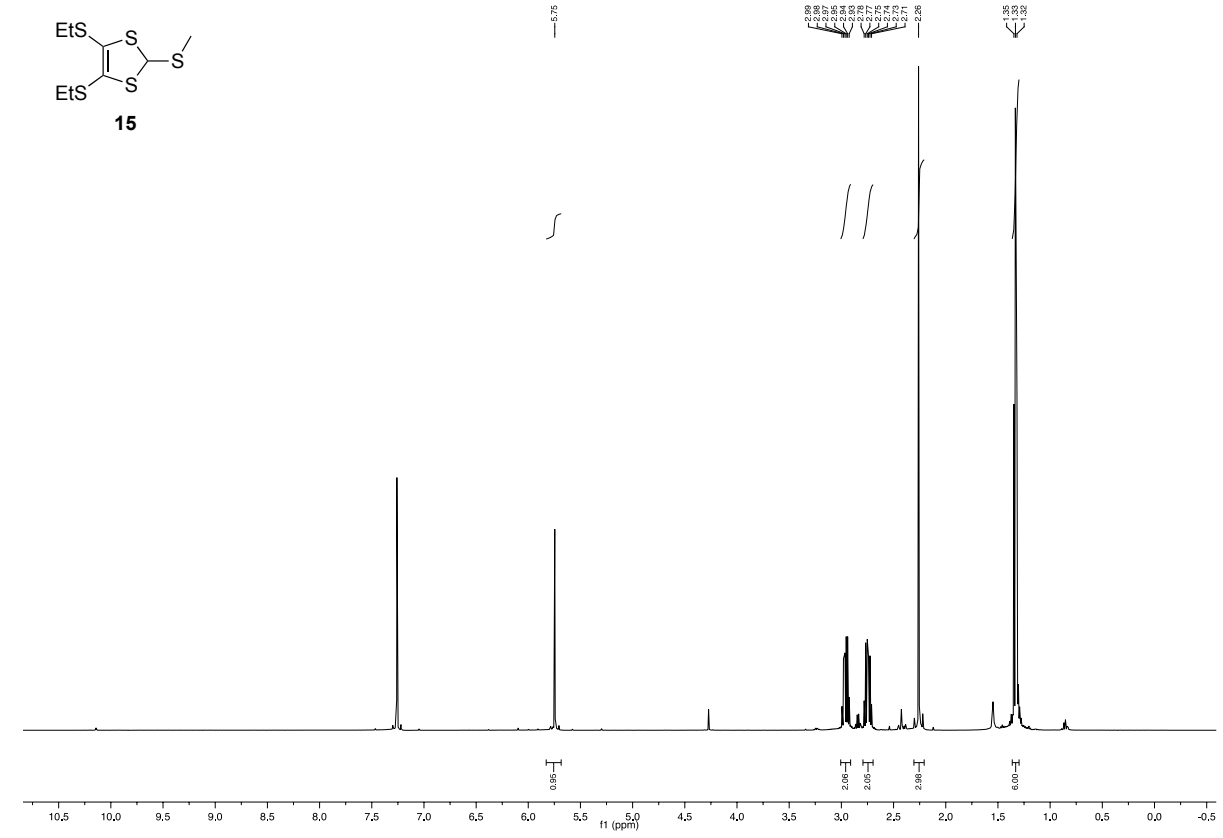


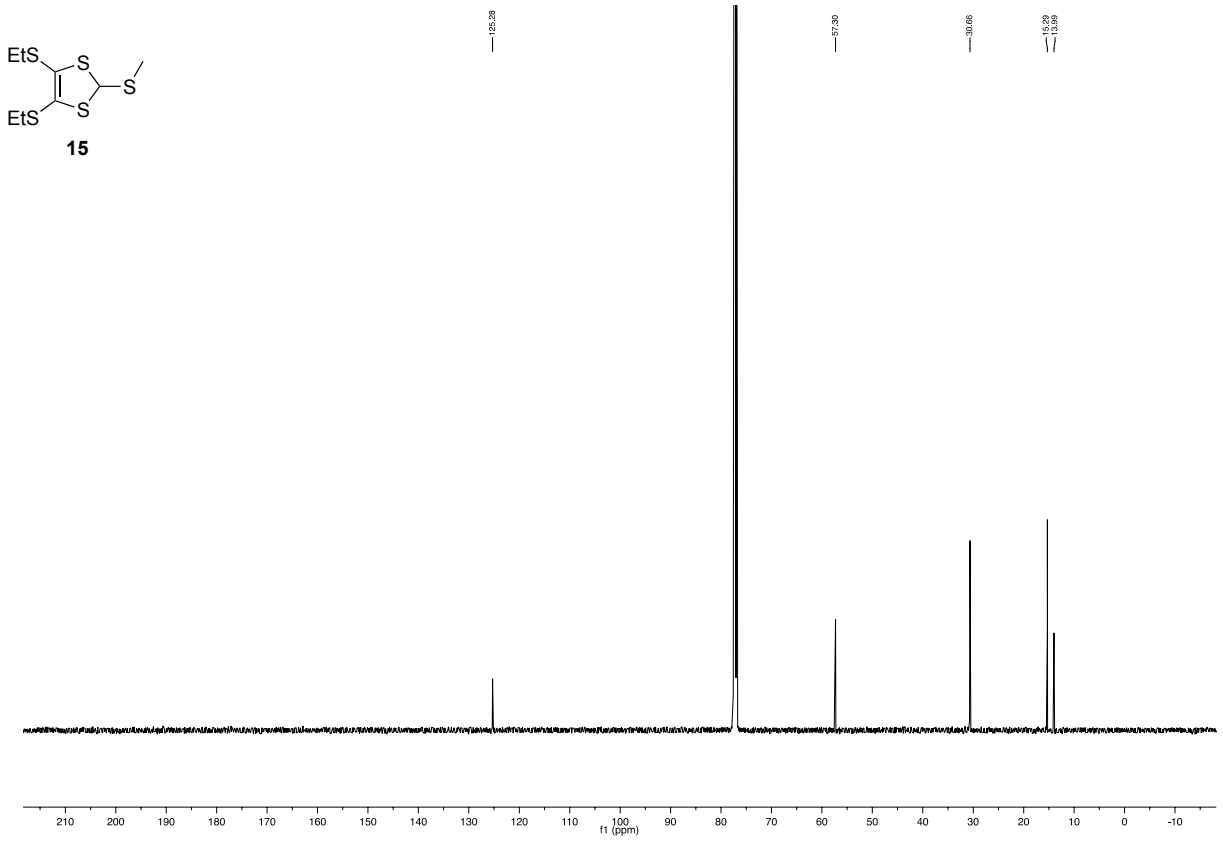
NMR spectra of **14** in $CDCl_3$



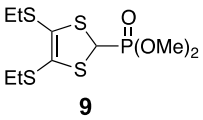


NMR spectra of **15** in $CDCl_3$

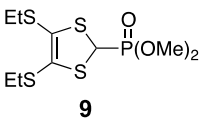




NMR spectra of **9** in $CDCl_3$

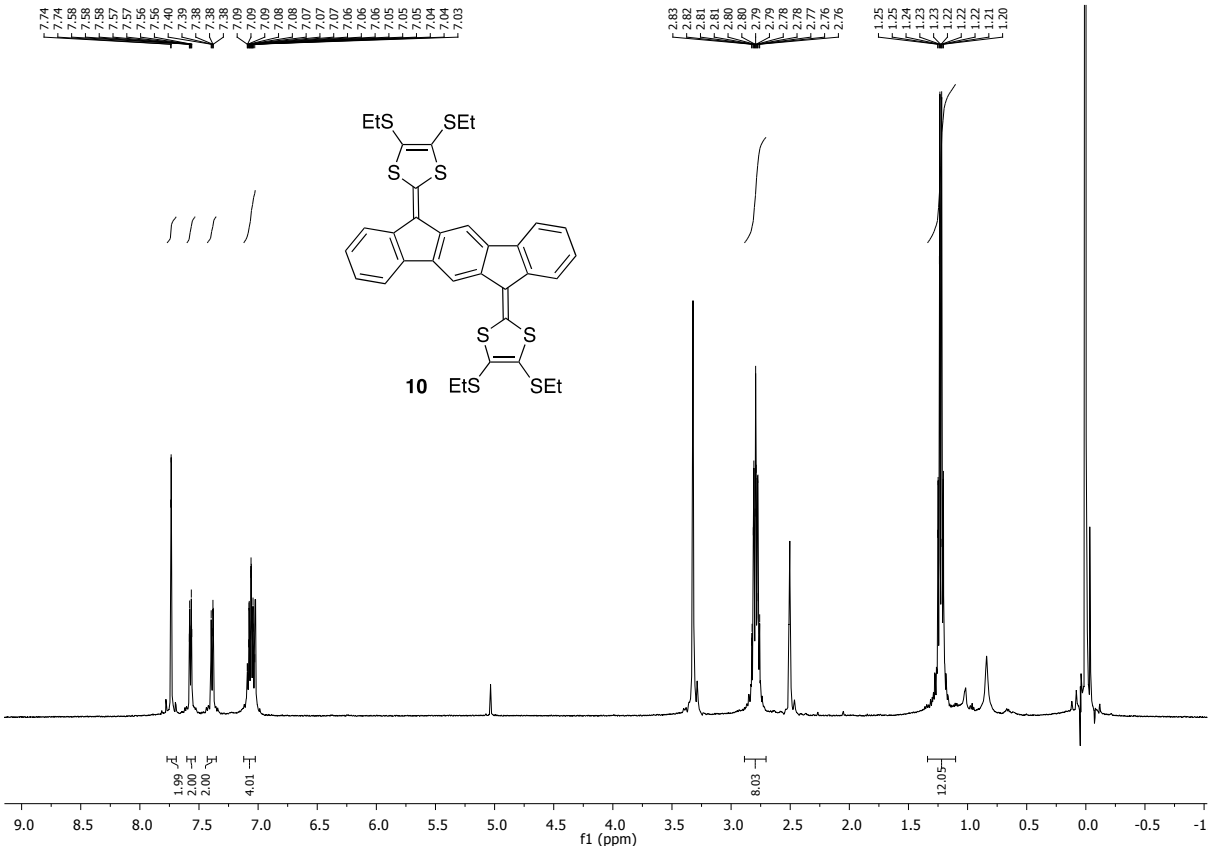


9

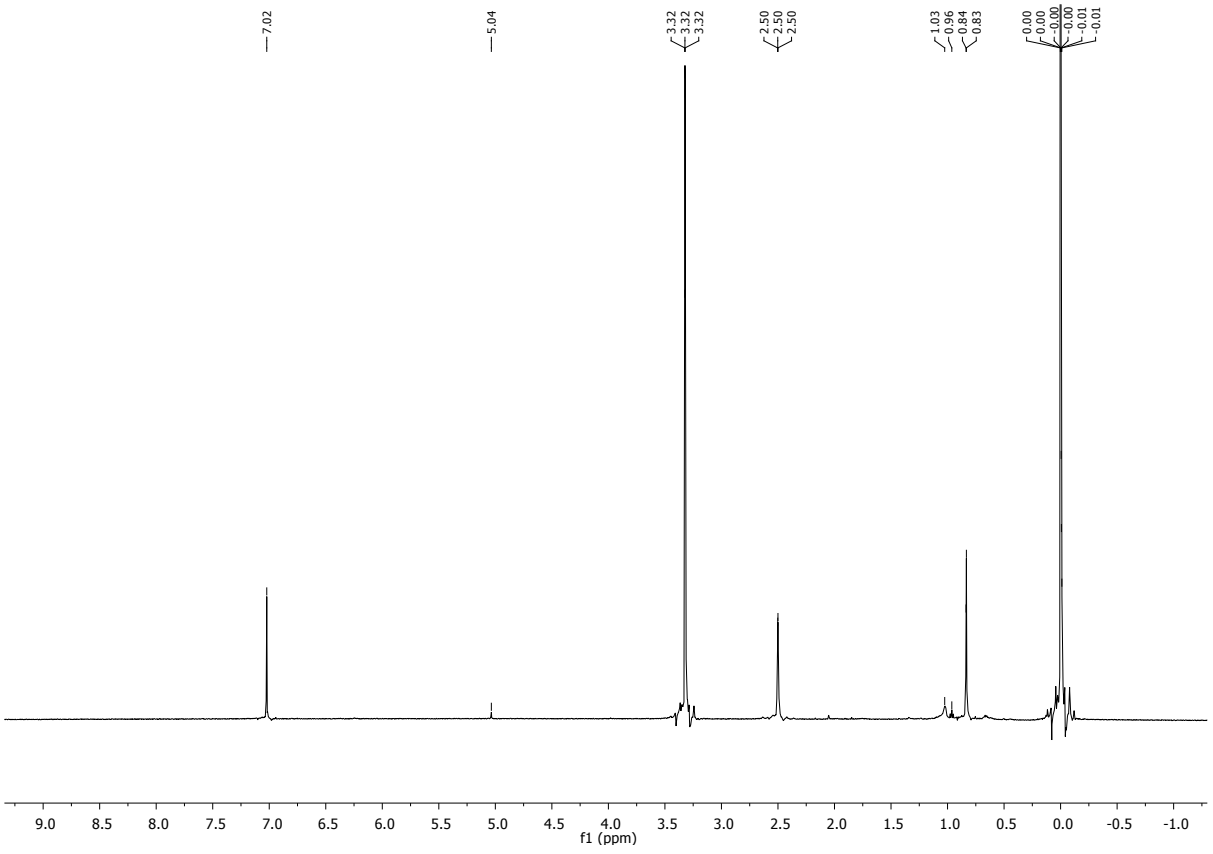


9

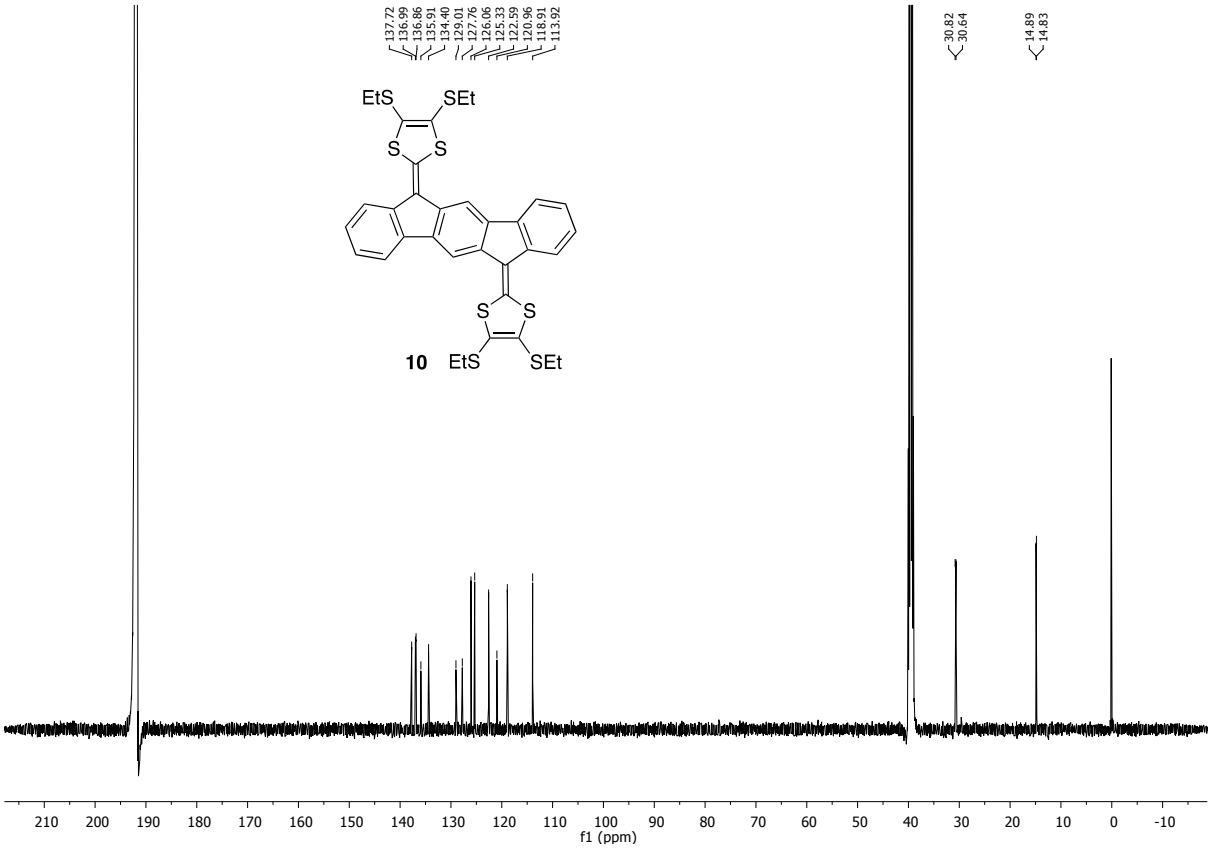
^{1}H-NMR spectrum of **10** in CS_2 with a DMSO-d_6 lock tube:



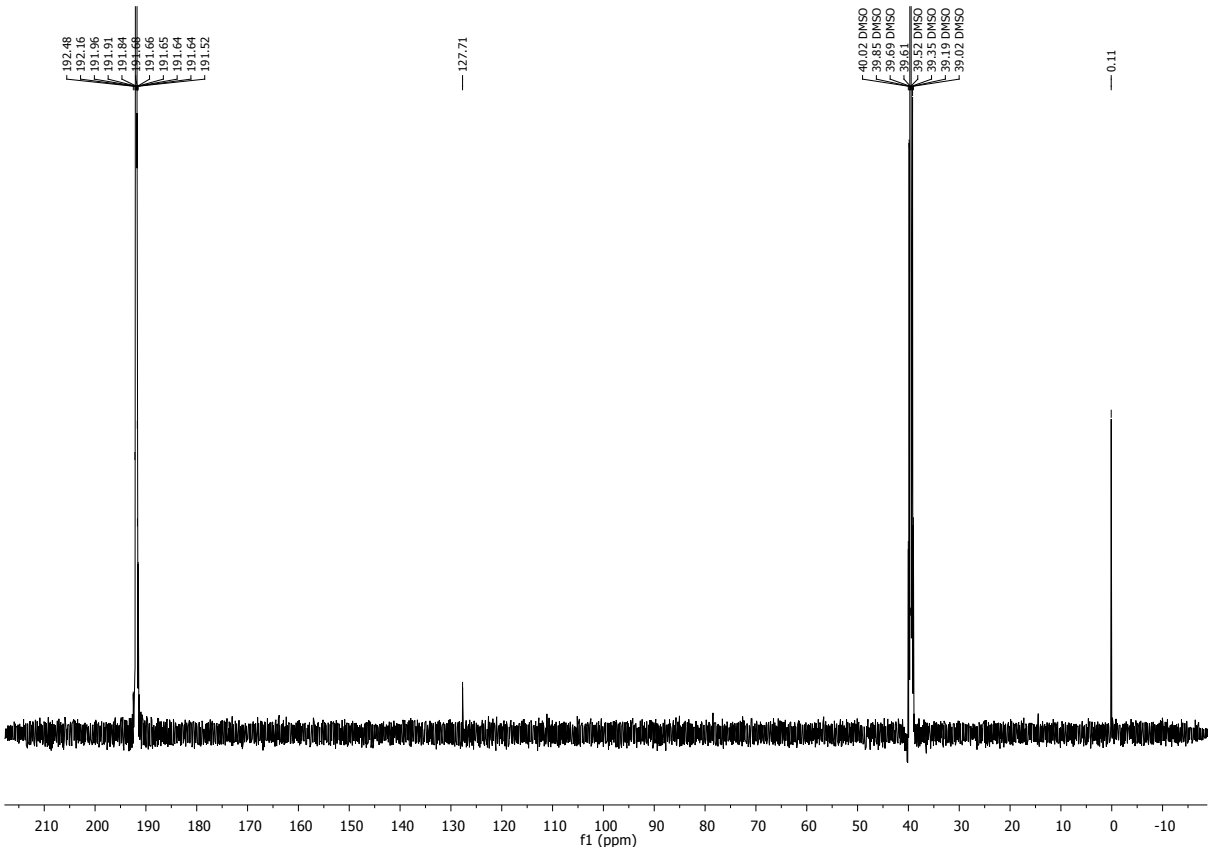
^{1}H-NMR blank spectrum of CS_2 with a DMSO-d_6 lock tube:



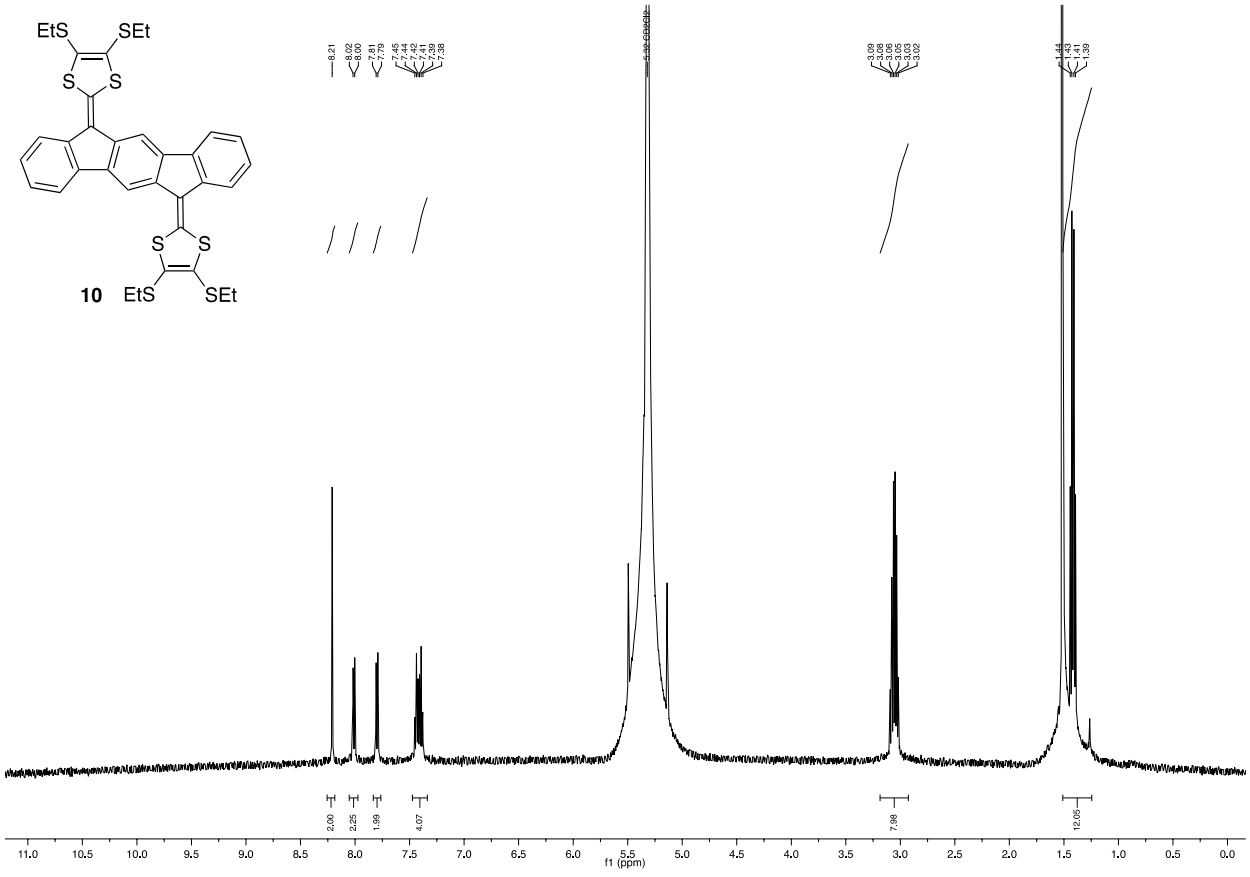
^{13}C-NMR spectrum of **10** in CS_2 with a DMSO-d_6 lock tube:



^{13}C-NMR blank spectrum of CS_2 with a DMSO-d_6 lock tube:



^{1}H NMR spectrum of **10** in CD_2Cl_2:



Summary of Computational Results

Summary of computational results for 8 (see also Table S9)

8 (anti-anti-anti)


```
\\# opt=tight freq=noraman rb3lyp/cc-pvdz\\DDTIF SBu anti-anti-anti (f
 rom syn-anti-syn )\\0,1\C,1.9742891394,-2.7678455841,0.5288580839\C,0.
 5799658948,-2.7521066387,0.2435811265\C,-0.1509546783,-3.9379806543,0.
 1505120636\C,0.5022334039,-5.1591666515,0.3422784229\C,1.873436993,-5.
 185874184,0.6244817378\C,2.6136745858,-4.000946689,0.7193070646\C,2.46
 30683948,-1.3704026779,0.5597072246\C,1.2853832877,-0.5208763978,0.281
 4871909\C,0.1520141694,-1.3637681103,0.0907547912\H,-1.2208500055,-3.9
 138873247,-0.0690988363\H,-0.0580213503,-6.0941955806,0.2726392734\H,2
 .3781701109,-6.1428334109,0.7743725669\H,3.6772078635,-4.0704429568,0.
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 8681290815,0.1838385051\H,1.9487417915,1.5626972875,0.3202482268\C,-0.
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8 (syn-anti-anti)

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8 (syn-syn-anti)

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3137699\S,6.6682021291,1.9032788277,1.3298895277\S,7.8486134455,-1.380

6735566,1.3861467254\C,8.6882629367,-1.0202647168,-0.2304763982\H,8.61
79106578,0.063964773,-0.4040139934\H,8.1344664383,-1.5469657378,-1.022
655391\C,6.6536764288,1.9365586068,3.186758729\H,5.6042309401,1.897316
6213,3.5163307509\H,7.1731504623,1.0321780524,3.5377925891\S,-4.431395
2089,-1.1044281732,-1.0784967675\S,-5.4093677243,1.6623880708,-1.22783
51495\C,-6.1981574636,-0.8893297381,-1.0846437645\C,-6.6500160638,0.38
86214549,-1.1555568886\S,-7.1929818654,-2.3560766535,-1.1171249277\S,-
8.3443626094,0.881581902,-1.3164559372\C,-6.8691819733,-3.0447531981,0
.5778478942\H,-5.7806734894,-3.1201924788,0.722155483\H,-7.2695241808,
-2.3301964053,1.3136820162\C,-8.5667016887,1.9483631353,0.1876204559\H
,-8.3604693673,1.3297568811,1.0746683883\H,-7.8316416385,2.7668644132,
0.1552081014\C,-9.9939379835,2.4945671109,0.2108930906\H,-10.711113114
6,1.6541019786,0.2081092559\H,-10.182468109,3.0688771178,-0.7139578105
\C,-10.2546751084,3.38742832,1.4314515116\H,-9.5307736436,4.2225825535
,1.4329060065\H,-10.0579122824,2.8108135745,2.3536012436\C,-11.6802048
125,3.9430525406,1.4673181097\H,-11.8398994293,4.5801297263,2.35173699
46\H,-11.8948914181,4.5522669873,0.5730816694\H,-12.4258361663,3.13075
10025,1.5010940339\C,-7.5384993062,-4.4119113276,0.7120803977\H,-8.620
8341629,-4.3158277107,0.5107204118\H,-7.1369233058,-5.0943696108,-0.05
82270123\C,-7.3295742092,-5.025166648,2.1030955449\H,-6.2461017441,-5.
1099206151,2.3040863752\H,-7.7293967124,-4.3359693555,2.8690986927\C,-
7.9887339634,-6.3981606289,2.2535241194\H,-7.5848588028,-7.1181312571,
1.5218212185\H,-7.821396766,-6.8148935534,3.2594679189\H,-9.0785839987
,-6.3391179692,2.0929444562\C,7.345150562,3.2050517567,3.6837993731\H,
6.8239883059,4.0919150405,3.2809109214\H,8.3767279569,3.2416001493,3.2
892765987\C,7.3814806663,3.2825592493,5.2162444559\H,7.8963007453,2.38
91224078,5.6138110489\H,6.3487098097,3.2401464502,5.6074747721\C,8.074
5303263,4.5464324817,5.7305753146\H,8.0864962533,4.5767394023,6.831710
6082\H,9.120202771,4.5988706804,5.3831416909\H,7.5617492179,5.45669871
92,5.3764889026\C,10.1440947916,-1.4801206898,-0.1701947268\H,10.18231
04113,-2.5621173991,0.0497752846\H,10.6567722802,-0.9716476698,0.66627
28889\C,10.8938515438,-1.1949804887,-1.4785000526\H,10.3751772075,-1.7
011812502,-2.3128733676\H,10.8435426745,-0.113081825,-1.6983990143\C,1
2.3566328982,-1.6429083627,-1.4357378187\H,12.43855955,-2.7276797072,-
1.2525755616\H,12.8700695512,-1.4251862216,-2.385779104\H,12.909448502
4,-1.1285744311,-0.631414178\\Version=EM64L-G09RevB.01\State=1-A\HF=-4
813.9210487\RMSD=1.139e-09\RMSF=4.585e-07\Dipole=0.3293456,0.2807676,1
.4278882\Quadrupole=34.9201658,-8.7683419,-26.1518239,2.6927165,-9.968
3259,4.5810895\PG=C01 [X(C42H46S8)]\\@

8 (syn-anti-syn)

\\# opt=tight freq=noraman rb3lyp/cc-pvdz\\DFTIF SBu trans (with 'SMe'
as input)\\0,1\C,2.309313634,-2.5529274817,0.121831231\C,0.9007235566
,-2.6810657234,-0.0362963991\C,0.2994511246,-3.9349262458,-0.160172848
7\C,1.0986162522,-5.0815452749,-0.1252199794\C,2.4850142663,-4.9669360
159,0.0340793932\C,3.095597109,-3.7129801623,0.159602009\C,2.641992338
5,-1.1126512246,0.2154528436\C,1.3546006487,-0.390766967,0.1240597328\
C,0.3086276316,-1.3455566345,-0.035033678\H,-0.782666416,-4.0207707712
,-0.283190459\H,0.6409460358,-6.068712268,-0.2203699099\H,3.1038303839
,-5.8664834784,0.0642886115\H,4.1759544554,-3.6713798119,0.2867201472\
C,-1.0303924568,-0.9694295378,-0.1614210254\C,1.0287406731,0.972263501
9,0.1607580723\H,1.7834098084,1.7467017357,0.2850261343\C,-0.310279138
2,1.3483902827,0.0343667007\C,-1.3562535305,0.3935997804,-0.1247082755
\H,-1.7850588038,-1.743867011,-0.2857088545\C,-2.6436469507,1.11548242
58,-0.2160796743\C,-0.9023729674,2.6839002127,0.0356037212\C,-2.310963
677,2.5557606153,-0.1225121452\C,-0.3010977571,3.9377627967,0.15944488

11\H,0.7810205083,4.0236087981,0.2824555826\C,-3.0972451896,3.7158130958,-0.1603150902\H,-4.1776021234,3.6742104607,-0.2874350309\C,-1.1002610512,5.0843824948,0.1244631767\C,-2.4866597127,4.9697715003,-0.0348301422\H,-0.6425885513,6.0715514598,0.2195834198\H,-3.1054737718,5.8693195397,-0.0650661128\C,3.8918956585,-0.5597857441,0.3428931327\C,-3.893558616,0.5626137997,-0.3434181186\S,5.3988688823,-1.5002185704,0.4686659716\S,4.2087189111,1.1863278842,0.4800859972\C,6.5335322369,-0.1328408389,0.3701315382\C,5.9836215652,1.1082672434,0.3748852247\S,6.8702697494,2.6421009955,0.4184957219\S,8.2668885264,-0.498033903,0.4103366466\C,8.4730295681,-1.4974656514,-1.1415298601\H,8.1566575669,-0.8728937123,-1.9911139547\H,7.8121396074,-2.376018759,-1.0896391424\C,6.3711240009,3.4011338877,-1.2020419292\H,6.7435295267,2.7508351295,-2.0086794817\H,5.2720778298,3.4275513299,-1.2546781378\S,-4.2103951338,-1.1835086993,-0.480476805\S,-5.4005397321,1.5030377511,-0.4691530937\C,-5.9852866937,-1.1054394865,-0.3750910349\C,-6.5351955902,0.1356692595,-0.3703837068\S,-6.8719405813,-2.6392767898,-0.4184568498\S,-8.2685539699,0.5008687282,-0.4104303325\C,-6.3724871559,-3.3982114012,1.2020323603\H,-5.2734311564,-3.4246641348,1.2544430644\H,-6.7447007035,-2.7478384804,2.0086988929\C,-8.4745395733,1.5003179578,1.1414459934\H,-8.15813444,0.8757345962,1.9910096247\H,-7.8136105033,2.3788382579,1.0895007152\C,-9.9369710395,1.9231017336,1.2777545255\H,-10.5801535162,1.025135789,1.3010887998\H,-10.2377281604,2.4997966908,0.384570907\C,-10.1836964249,2.7640756455,2.5375608949\H,-9.5355539614,3.6588233367,2.51040637\H,-9.8721271977,2.1876295503,3.4276142421\C,-11.6450704638,3.1926548234,2.6887994916\H,-11.7939340927,3.7946606286,3.5992675389\H,-11.9751778623,3.7995169307,1.8287701585\H,-12.3141544639,2.3179402329,2.7528996508\C,-6.9633813365,-4.8037995738,1.3042744471\H,-8.0620426783,-4.7509450136,1.1978415458\H,-6.5974280115,-5.4171643423,0.4614372254\C,-6.6111763636,-5.4907013699,2.6306023813\H,-5.5120260321,-5.5333134999,2.7381680048\H,-6.9767782669,-4.8718209093,3.4701719065\C,-7.1931868002,-6.9017424473,2.741582124\H,-6.8175960108,-7.5542571607,1.9353252906\H,-6.9264209235,-7.3704530384,3.7021348682\H,-8.2939605048,-6.8877161495,2.6703428813\C,6.9619939316,4.8067487651,-1.3040514577\H,8.0606319466,4.7539209814,-1.1973644978\H,6.5958245225,5.4200427211,-0.4612567441\C,6.6100817076,5.4937343654,-2.6304139099\H,5.510955831,5.5363135502,-2.7382421162\H,6.9759102757,4.8749304451,-3.4699409769\C,7.1920645422,6.9048061938,-2.7411474887\H,6.9255177651,7.373575563,-3.7017322642\H,6.8162482118,7.5572471162,-1.9349360695\H,8.2928210812,6.8908176875,-2.6696360555\C,9.9354905486,-1.920181151,-1.2777327531\H,10.2362124855,-2.4968553988,-0.384523829\H,10.5786320917,-1.0221852935,-1.3010288921\C,10.1823430491,-2.7611540689,-2.5375149431\H,9.5342401832,-3.6559315018,-2.5103982483\H,9.8708093541,-2.1847297002,-3.4275947317\C,11.6437477197,-3.1896661968,-2.6886475745\H,11.9738223955,-3.7965084453,-1.8285916377\H,11.7927041786,-3.7916697327,-3.5991019595\H,12.3127953509,-2.3149206284,-2.7527045838\\Version=EM64L-G09RevB.01\State=1-A\HF=-4813.9204209\RMSD=2.189e-09\RMSF=3.610e-07\Dipole=0.0002135,0.0000305,0.0001164\Quadrupole=24.2708884,0.3349306,-24.605819,0.2101639,-32.6403148,-4.5961596\PG=C01 [X(C42H46S8)]\\@

8 (syn-syn-syn)

\\# opt=tight freq=noraman rb3lyp/cc-pvdz\\DFTIF SBu cis (with 'SMe' as input)\\0,1\C,2.3135647335,2.5557203132,-0.2808859144\C,0.8963723475,2.6852702983,-0.2806095804\C,0.2863727305,3.9410245155,-0.2848403214\C,1.0856115035,5.0881000749,-0.2892912522\C,2.4809774971,4.9719795915,-0.2909332902\C,3.1003610877,3.7160473406,-0.2887590821\C,2.6532241484,1.1139574853,-0.2740713229\C,1.3627178567,0.3918324703,-0.2774785411\C,0.3066339832,1.3488037747,-0.278203331\H,-0.8026355701,4.0277580644,

-0.286853485\H,0.6211748763,6.076680447,-0.2944448647\H,3.1003633541,5
.871616251,-0.2974744247\H,4.1880909605,3.6734546527,-0.2948461592\C,-
1.038674438,0.9738975459,-0.2803062458\C,1.0409996564,-0.9726976973,-0
.2790863639\H,1.8035003983,-1.7494960518,-0.2827628544\C,-0.3043087985
,-1.347601251,-0.276527853\C,-1.3603929255,-0.390629629,-0.2770027884\
H,-1.8011749385,1.7506908971,-0.2849558322\C,-2.6508995969,-1.11274989
73,-0.2727076946\C,-0.894047309,-2.6840700323,-0.2772755147\C,-2.31124
00104,-2.5545204325,-0.277724844\C,-0.2840477061,-3.9398287142,-0.2799
380344\H,0.8049606474,-4.026564871,-0.2818341363\C,-3.0980363084,-3.71
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.083286599,-5.0869088196,-0.2829676561\C,-2.4786525662,-4.9707904442,-
0.2847657288\H,-0.6188500547,-6.0754948351,-0.2868867855\H,-3.09803831
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4\C,-3.907519507,-0.560633525,-0.2627103573\S,5.4216028739,1.502638021
6,-0.2915752138\S,4.2382116896,-1.187935016,-0.3038892053\C,6.54714236
63,0.1424054476,-0.0741263014\C,6.0009279285,-1.1000533187,-0.08122697
14\S,6.8904198063,-2.6320661158,-0.020488963\S,8.2765445761,0.52408488
54,0.0063614819\C,8.3766233676,1.4200376197,1.6305694093\H,8.101773004
6,0.7095515271,2.4256580847\H,7.6423703335,2.2399798176,1.6262790294\C
,6.3005312552,-3.3379032208,1.5934387422\H,6.6199353777,-2.6566881854,
2.3973311645\H,5.2005047658,-3.3738386158,1.5829898779\S,-5.4192785189
,-1.5014514696,-0.289750729\S,-4.2358865841,1.1891040471,-0.305401366\
C,-6.5448191145,-0.1409493618,-0.0740008961\C,-5.9986044149,1.10149950
32,-0.0826424783\S,-8.2742216844,-0.5225289154,0.0069506927\S,-6.88809
69487,2.6335864176,-0.0238159663\C,-8.3743106991,-1.41645535,1.6322741
536\H,-7.6400566191,-2.2364013245,1.6290111128\H,-8.0994663787,-0.7049
778311,2.4264778846\C,-6.298212636,3.3414352838,1.589231922\H,-6.61761
6417,2.6612217884,2.3939721092\H,-5.1981862351,3.3773603841,1.57874021
06\C,-6.8945310449,4.7364413734,1.7729249792\H,-7.9969304278,4.6744280
767,1.7280583622\H,-6.5840093953,5.3815398604,0.9315338721\C,-6.472823
6892,5.3832085811,3.0993057714\H,-5.3699090294,5.4392975788,3.14327819
83\H,-6.7795842267,4.7308169054,3.9371134793\C,-7.0663570208,6.7804873
854,3.2927230736\H,-8.1691019871,6.7510882108,3.2870295441\H,-6.748466
7722,7.221573225,4.250768054\H,-6.7493714507,7.4647901309,2.4877013511
\C,-9.7932972122,-1.9480550189,1.8306662774\H,-10.0461815275,-2.635200
3191,1.0034965572\H,-10.5127442198,-1.1112703488,1.7721200422\C,-9.961
9421479,-2.6735135047,3.1723063214\H,-9.23453913,-3.5035563633,3.23170
88851\H,-9.704759886,-1.9822436718,3.9954543693\C,-11.3778877563,-3.21
57555899,3.3803836779\H,-11.6503114119,-3.9364819148,2.5909656025\H,-1
1.4713185943,-3.7307816419,4.3496964972\H,-12.1245715396,-2.403954248,
3.3594403527\C,9.7956092105,1.9518827113,1.8283076882\H,10.5150556749,
1.115024946,1.7708092084\H,10.0484995102,2.6379960523,1.0002835919\C,9
.9642464002,2.6790130075,3.1690433579\H,9.2368436561,3.5091298309,3.22
74066826\H,9.707058534,1.9887700311,3.9930508973\C,11.3801911525,3.221
5129668,3.3764533196\H,11.4736164912,3.73774666,4.3451240465\H,12.1268
744624,2.4096856114,3.3565263319\H,11.6526201187,3.941254643,2.5861392
256\C,6.8968459988,-4.7326807516,1.7788709904\H,7.9992455931,-4.670726
0621,1.7339287269\H,6.5863240234,-5.3788265364,0.9382840088\C,6.475135
2212,-5.3777935361,3.1060561503\H,5.3722203739,-5.4338250969,3.1500968
989\H,6.7818961276,-4.7243590414,3.9430506473\C,7.0686649712,-6.774831
6408,3.3012154045\H,6.7507724377,-7.2147224668,4.2598089142\H,6.751678
8086,-7.4601363356,2.4970466862\H,8.1714100093,-6.7454422029,3.2954866
654\\Version=EM64L-G09RevB.01\State=1-A\HF=-4813.9203858\RMSD=1.483e-0
9\RMSF=3.662e-08\Dipole=-0.0000041,0.0015496,2.4815921\Quadrupole=21.7
907211,2.110311,-23.9010321,-0.9734153,0.0007833,-0.016204\PG=C01 [X(C
42H46S8)]\\@

Summary of computational results for $8^{\bullet+}$ (see also Table S10)

$8^{\bullet+}$ (1,1'-anti)


```
\\# opt=tight freq=noraman ub3lyp/cc-pvdz\\DDTIF SBu c+ 1,1'-anti
 \\1,2\C,-2.3795434627,-2.4329739119,-0.4414383087\C,-0.9716428719,-2.
 6294527154,-0.454821868\C,-0.4211283813,-3.9084987944,-0.4894585003\C,
 -1.2762862185,-5.0168631066,-0.5097904088\C,-2.6628416786,-4.835859821
 8,-0.4919437304\C,-3.2224933891,-3.5519799382,-0.4569946355\C,-2.64394
 51911,-0.9738946439,-0.4024231576\C,-1.3463002446,-0.3141237576,-0.387
 8528643\C,-0.3239826846,-1.3187228712,-0.4224853425\H,0.6616728896,-4.
 0499535664,-0.4995995269\H,-0.8602017264,-6.0256667861,-0.5373616728\H
 ,-3.3237707669,-5.7043040676,-0.5037756189\H,-4.3069494767,-3.46522219
 03,-0.4378158638\C,1.0255039384,-0.9989112265,-0.4252821966\C,-0.96505
 45255,1.0450432257,-0.3597000897\H,-1.6937155899,1.85293843,-0.3397085
 865\C,0.384425811,1.3648196773,-0.3617102596\C,1.4067800349,0.36016711
 5,-0.3925165549\H,1.7541444725,-1.806462178,-0.4569025244\C,2.70427613
 99,1.0203707281,-0.3937767575\C,1.0318710038,2.6758301708,-0.340216554
 2\C,2.4397187013,2.4796117377,-0.3604388925\C,0.4812059121,3.954789274
 4,-0.3042322571\H,-0.6015701672,4.0959551619,-0.2887076613\C,3.2824988
 282,3.5986829815,-0.341124927\H,4.3670465123,3.5117535041,-0.351094753
 1\C,1.3361571613,5.0633455281,-0.2873472436\C,2.7227304335,4.882471454
 1,-0.3050586381\H,0.9199591102,6.0720993441,-0.2596551033\H,3.38357999
 24,5.7509446861,-0.2908176383\C,-3.9015174538,-0.3647042053,-0.3917253
 074\C,3.9618556582,0.4119222802,-0.4246065143\S,-5.415767664,-1.234230
 1771,-0.467156856\S,-4.1421983156,1.3826958646,-0.2922818049\C,-6.5007
 599179,0.1522127908,-0.4293328894\C,-5.9051210685,1.3814348177,-0.3398
 354509\S,-6.834390151,2.8762457095,-0.2574940853\S,-8.246710496,-0.142
 8793724,-0.4413170552\C,-8.604639115,-0.1041150668,-2.2708880026\H,-8.
 0267809536,-0.9107178471,-2.7472617583\H,-8.255355253,0.8647649852,-2.
 6578923337\C,-5.5357867946,4.1933747073,-0.298625054\H,-4.8830373227,4
 .0716140032,0.5804555644\H,-4.9364199724,4.0692142279,-1.2144608366\S,
 5.4744929779,1.2847257037,-0.4888536743\S,4.2037446279,-1.3382664974,-
 0.4170754496\C,6.561465126,-0.100887102,-0.4966675489\C,5.9665919395,-
 1.3335694821,-0.4726282361\S,8.3024885424,0.1953359217,-0.6188724612\S
 ,6.8951851378,-2.8306034664,-0.5089967416\C,8.7791214889,0.3300561849,
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6S8)]\\@

8$^{\bullet+}$ (1,1'-syn)

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1 [X(C42H46S8)]\\@

8$^{\bullet+}$ (1,2'-anti)

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,-4.6031232015,3.6784316285\H,8.8054614288,-3.6842253191,3.5456615848\
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\C,11.7810911168,4.2642967363,-0.717415368\H,11.935671229,5.3542142827
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8)]\\@

8$^{\bullet+}$ (1,2'-syn)

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9666911,0.5948109444\H,-6.9492667283,5.6836324063,-1.1721431624\C,-5.2
251989649,6.7517358737,-0.3982752366\H,-4.5072030897,6.6539069059,0.43
64332051\H,-4.6331877814,6.6650200145,-1.3276222016\C,-5.8957044096,8.
1261067946,-0.341236351\H,-6.4684367181,8.2536411875,0.5922868324\H,-5
.1493948918,8.9340892953,-0.3884784932\H,-6.5942459165,8.2662474555,-1
.1827847518\C,-10.1849871105,-0.4200112608,-2.3302950719\H,-10.7346591
934,0.4029330491,-1.8400213116\H,-10.4747366075,-1.3484266814,-1.80681
06644\C,-10.6022202102,-0.5104870884,-3.8052531076\H,-10.3016286536,0.
4165855733,-4.3262644717\H,-10.0447306331,-1.3314837811,-4.2915482748\
C,-12.1059023894,-0.7351777569,-3.9798957065\H,-12.3770478542,-0.79811
83043,-5.0452016934\H,-12.4298574555,-1.6717978262,-3.4962173514\H,-12
.6885683662,0.08830045,-3.5343626389\C,7.859841555,-4.4450272197,-2.50
54066248\H,8.8163403051,-4.3851330051,-1.9565272916\H,7.2911259759,-5.
2788966635,-2.0566147081\C,8.1345688287,-4.7485750579,-3.9852832211\H,
8.6943878625,-3.9068870159,-4.4317774898\H,7.1748083865,-4.8033385373,
-4.530577644\C,8.9155641414,-6.0494367095,-4.1851173416\H,8.3656078365
,-6.9139762174,-3.7772606862\H,9.0979333087,-6.243254509,-5.2535503265
\H,9.8951173473,-6.0098291799,-3.6802544821\C,10.0149119966,2.28520935
89,-0.4805736316\H,10.4719539915,1.8625831334,0.4313818367\H,10.502115
4761,1.7892424297,-1.3383079217\C,10.2811236498,3.7958249115,-0.538617
8239\H,9.7847447082,4.2861275373,0.3184107576\H,9.8114928698,4.2134863
807,-1.4477627201\C,11.7740214833,4.1315973337,-0.5301459358\H,11.9357
489581,5.2196343808,-0.5747780505\H,12.2639279567,3.7578802609,0.38429
94936\H,12.2908324974,3.680740013,-1.3936143362\\Version=EM64L-G09RevB
.01\State=2-A\HF=-4813.7096273\S2=0.757942\S2-1=0.\S2A=0.750034\RMSD=2
.374e-09\RMSF=8.642e-07\Dipole=0.4214939,1.0684124,-0.9129579\Quadrupo
le=96.9237618,-17.7895089,-79.1342529,-6.7406622,3.2287441,10.4833623\
PG=C01 [X(C42H46S8)]\\@

8$^{\bullet+}$ (2,2'-anti)

\\# opt=tight freq=noraman ub3lyp/cc-pvdz\\DFTIF SBu trans c+ (w
ith 'SMe' as input)\\1,2\C,2.3810364297,2.4814524717,0.1316979469\C,0.
9714446496,2.6576718757,0.1973016951\C,0.4059588873,3.9239277699,0.327
3201983\C,1.2475428167,5.0409991765,0.393957519\C,2.6352946174,4.88071
11625,0.3314399255\C,3.2095302897,3.6094530508,0.2013060859\C,2.661182
1337,1.0307166374,0.005073708\C,1.3710883791,0.355342197,-0.0084237757
\C,0.3386225175,1.3421814691,0.1081149807\H,-0.6776258261,4.0490574926
,0.3786076243\H,0.8192939396,6.039811135,0.4960709429\H,3.28532752,5.7
558406983,0.3850425746\H,4.294566608,3.5386421618,0.1600260696\C,-1.00
66310476,1.0047483141,0.1216520071\C,1.0079239078,-1.0045204484,-0.116
7228361\H,1.7460534479,-1.7981233445,-0.2139138931\C,-0.3373296574,-1.
3419535173,-0.1031864285\C,-1.3697954271,-0.3551142767,0.0133525847\H,
-1.7447605948,1.7983510607,0.2188448052\C,-2.6598889805,-1.0304888892,
-0.0001415702\C,-0.9701519126,-2.6574437971,-0.1923736884\C,-2.3797435

463,-2.4812243634,-0.1267686332\C,-0.4046665556,-3.9236994863,-0.32239
52635\H,0.6789180344,-4.0488293782,-0.3736837509\C,-3.2082378934,-3.60
92243072,-0.1963806242\H,-4.2932743007,-3.5384127593,-0.1551026804\C,-
1.2462508148,-5.0407705016,-0.3890352817\C,-2.634002622,-4.8804822801,
-0.3265179262\H,-0.8180021924,-6.0395822898,-0.4911514917\H,-3.2840357
839,-5.7556114507,-0.3801239992\C,3.9168652668,0.4232551489,-0.0797599
258\C,-3.9155718515,-0.423028001,0.0847001257\S,5.4251889493,1.3393101
655,-0.1215667133\S,4.1924643358,-1.3021663358,-0.1608137533\C,6.53137
83083,-0.0288492891,-0.2338017793\C,5.9520177317,-1.269071766,-0.24437
63938\S,6.8128221407,-2.8089623503,-0.3930949304\S,8.2752339149,0.2007
472083,-0.340949583\C,8.4791152804,2.0310432738,-0.1589889875\H,8.0369
418994,2.3409191715,0.8010041561\H,7.9410824943,2.5277145912,-0.982009
2328\C,7.1739782241,-3.1920654812,1.3957065842\H,7.7551397542,-2.35289
4514,1.8062422396\H,6.2130457644,-3.2576145797,1.9282816189\S,-4.19117
1677,1.302393951,0.1657444985\S,-5.4238942349,-1.3390841121,0.12653288
87\C,-5.9507238854,1.2692981857,0.2493336908\C,-6.5300834847,0.0290748
76,0.238776228\S,-6.8115270757,2.8091893043,0.3980567157\S,-8.27393719
74,-0.2005219778,0.3459540725\C,-7.1727115956,3.1922820858,-1.39074119
3\H,-6.2117875514,3.2578300918,-1.9233315839\H,-7.7538780332,2.3531078
883,-1.8012631912\C,-8.4778205817,-2.0308201881,0.1640181002\H,-8.0356
72497,-2.3407058109,-0.7959836243\H,-7.9397653667,-2.5274821961,0.9870
293507\C,-7.9497945797,4.5051657074,-1.4771573796\H,-8.881886521,4.421
6923788,-0.8907509109\H,-7.3588663415,5.3163066581,-1.015706044\C,-8.2
878081857,4.8763597849,-2.9283812153\H,-8.8731927462,4.0583178693,-3.3
858288499\H,-7.3527049091,4.94949495,-3.5127868159\C,-9.0668974421,6.1
892272206,-3.0355164389\H,-9.2976165533,6.430060341,-4.0848555456\H,-1
0.02199371,6.1337833331,-2.4870665801\H,-8.4915149708,7.0320541073,-2.
6173934597\C,-9.9715539169,-2.3620279297,0.2119978883\H,-10.3970164934
,-2.0036403127,1.1657198249\H,-10.4947357451,-1.8167287749,-0.59303044
3\C,-10.2293642429,-3.8682769089,0.0659752415\H,-9.6966679416,-4.40862
97585,0.8694209568\H,-9.7928414476,-4.221556516,-0.8858783475\C,-11.71
86985334,-4.2170626632,0.1105874145\H,-12.2718495101,-3.7164493542,-0.
7014226308\H,-11.8752247995,-5.3013917631,0.0024415102\H,-12.174470773
4,-3.9067762288,1.0654401861\C,9.9728501874,2.3622502844,-0.2069250538
\H,10.4960090001,1.81694662,0.5981151713\H,10.398339511,2.0038674011,-
1.1606368454\C,10.2306568506,3.8684983726,-0.060887393\H,9.6979868763,
4.4088552356,-0.8643478478\H,9.7941033634,4.2217739776,0.8909536597\C,
11.7199926733,4.2172838778,-0.1054493676\H,12.1757962303,3.9070021837,
-1.0602887191\H,11.87651561,5.3016124109,0.0027070339\H,12.273117052,3
.7166664991,0.7065763015\C,7.9510574404,-4.5049510337,1.4821280611\H,7
.3601346758,-5.3160885303,1.0206637206\H,8.8831585554,-4.4214766655,0.
8957362278\C,8.2890485055,-4.8761527541,2.9333552704\H,7.3539363958,-4
.9492889513,3.5177466221\H,8.8744278033,-4.0581140913,3.3908154622\C,9
.0681337204,-6.1890221605,3.0404958141\H,10.0232382834,-6.1335773791,2
.4920605091\H,9.2988366834,-6.4298607445,4.0898371908\H,8.4927559103,-
7.031845886,2.6223601681\\Version=EM64L-G09RevB.01\State=2-A\HF=-4813.
7102129\S2=0.757973\S2-1=0.\S2A=0.750036\RMSD=4.638e-09\RMSF=9.286e-07
\Dipole=-0.0000097,-0.0000031,0.0000147\Quadrupole=113.9788368,-28.043
8654,-85.9349714,15.5793969,20.6138157,-10.4913977\PG=C01 [X(C42H46S8)
]\\@

8$^{\bullet+}$ (2,2'-syn)

\\# opt=tight freq=noraman ub3lyp/cc-pvdz\\DFTIF SBu cis c+ (wit
h 'SMe' as input)\\1,2\C,-2.3811974212,-2.4833415045,-0.119606477\C,-0
.9708161208,-2.6646606207,-0.114746727\C,-0.4054366103,-3.9376245045,-
0.1218056221\C,-1.2480631976,-5.0558542455,-0.1314908681\C,-2.63668564

28,-4.8904840514,-0.1282782712\C,-3.2108158969,-3.6125787831,-0.120854
6548\C,-2.6611638711,-1.0275131238,-0.1035417538\C,-1.3705839123,-0.35
32114302,-0.0878667208\C,-0.3375354865,-1.3464168742,-0.0965338222\H,0
.6788403648,-4.0672542136,-0.1190988553\H,-0.8198929649,-6.0598817184,
-0.1389514845\H,-3.2872587032,-5.766877219,-0.1305656934\H,-4.29635732
9,-3.5368034169,-0.1092054214\C,1.0082862156,-1.0110598076,-0.09606239
01\C,-1.0081309695,1.0111580817,-0.0961232713\H,-1.7477273538,1.809232
2354,-0.11314117\C,0.3376906824,1.3465152226,-0.0966048056\C,1.3707391
208,0.3533101974,-0.0878776142\H,1.7478827814,-1.8091349072,-0.1130327
436\C,2.6613192675,1.0276110929,-0.1035829154\C,0.9709714726,2.6647580
362,-0.114886889\C,2.38135292,2.4834386373,-0.1197290055\C,0.405592158
6,3.9377216158,-0.1220198142\H,-0.6786848105,4.0673515881,-0.119326606
4\C,3.2109715473,3.6126758409,-0.1210345964\H,4.2965130281,3.536901018
2,-0.1093748698\C,1.2482188984,5.0559507688,-0.1317622718\C,2.63684134
89,4.8905807557,-0.1285321997\H,0.8200487625,6.0599778557,-0.139281326
7\H,3.2874144466,5.7669738201,-0.1308641921\C,-3.9174791759,-0.4154271
364,-0.1099454856\C,3.9176347532,0.4155247814,-0.1099483471\S,-5.42469
59816,-1.3195806212,-0.2755181738\S,-4.193969364,1.305535059,0.0340400
043\C,-6.5308462748,0.0520452887,-0.2206738198\C,-5.9525727691,1.28358
3519,-0.0691797939\S,-6.8131852772,2.8302070911,-0.0290086406\S,-8.273
6676102,-0.1600802679,-0.3704202585\C,-8.4799736962,-1.9976244157,-0.4
463077862\H,-8.0527849788,-2.4388014404,0.4680729587\H,-7.9296981889,-
2.3768422627,-1.3220359912\C,-7.2074728238,2.9767528658,1.7877445885\H
,-7.7955136282,2.0922263746,2.0745834817\H,-6.2566014843,2.9708718831,
2.3420128693\S,5.424851978,1.3196690105,-0.2755687133\S,4.1941248107,-
1.3054292926,0.0341364506\C,6.5310014084,-0.0519548318,-0.2206558582\C
,5.9527276781,-1.2834845797,-0.0690926769\S,8.2738221614,0.1601605404,
-0.3704235325\S,6.8133377143,-2.8301076057,-0.0288421225\C,8.480130040
1,1.9977000281,-0.4464165384\H,7.9298496742,2.3768686833,-1.3221630706
\H,8.0529473301,2.4389295228,0.4679417732\C,7.207686464,-2.9765290786,
1.7879079997\H,7.7957326114,-2.0919804991,2.0746678459\H,6.25683374,-2
.9706159822,2.342207817\C,-7.9872174751,4.2684689002,2.0291551527\H,-8
.9084359925,4.2623529583,1.4199810027\H,-7.3888849709,5.131423152,1.68
64726111\C,-8.3518693593,4.4506853419,3.5096122666\H,-8.9440419356,3.5
812231339,3.8480393085\H,-7.4276117347,4.4478109437,4.1155485729\C,-9.
1347796654,5.7395032089,3.7701513127\H,-10.0801763767,5.7553400178,3.2
02573501\H,-9.3840243143,5.8442190686,4.8375132203\H,-8.5536343483,6.6
285630713,3.4733777065\C,-9.9730392037,-2.3140302334,-0.5623950429\H,-
10.383121027,-1.8232379605,-1.4624373707\H,-10.5077690582,-1.885519503
6,0.3034254717\C,-10.2356429921,-3.824912789,-0.6339669134\H,-9.690027
964,-4.2489453578,-1.496362274\H,-9.8163945042,-4.3105687006,0.2659303
435\C,-11.7245340827,-4.1576110832,-0.7521738623\H,-11.8849344752,-5.2
457058061,-0.7995226494\H,-12.2906349162,-3.7730446293,0.1124575617\H,
-12.1630425912,-3.7147308537,-1.6617791381\C,7.987446795,-4.2682245577
,2.0293783457\H,7.3891045153,-5.1312059859,1.686781237\H,8.9086405909,
-4.2621473071,1.420166359\C,8.352160132,-4.4503342179,3.5098334875\H,7
.427927497,-4.44742181,4.1158077392\H,8.9443421475,-3.5808449275,3.848
1745655\C,9.1350883808,-5.7391293422,3.7704313945\H,10.0804615741,-5.7
550008448,3.2028153767\H,9.3843779994,-5.843768082,4.8377903742\H,8.55
39358139,-6.6282135374,3.473744947\C,9.9731951471,2.3140983724,-0.5625
305298\H,10.5079294701,1.8856391557,0.3033127205\H,10.3832722865,1.823
2526927,-1.4625458884\C,10.2357981782,3.8249766675,-0.6341936831\H,9.8
165525704,4.3106862053,0.2656759968\H,9.6901798475,4.2489572717,-1.496
6125268\C,11.7246887585,4.1576685232,-0.752425844\H,11.885088526,5.245
7604478,-0.7998413699\H,12.2907926995,3.7731548767,0.1122270537\H,12.1
631944816,3.7147331301,-1.6620056328\\Version=EM64L-G09RevB.01\State=2
-A\HF=-4813.7101863\S2=0.758011\S2-1=0.\S2A=0.750036\RMSD=2.603e-09\RM
SF=6.285e-07\Dipole=0.000013,0.0000258,0.7694538\Quadrupole=114.934689

9,-31.6346538,-83.300036,18.0411232,-0.0004169,-0.0013423\PG=C01 [X(C4
2H46S8)]\\@

Summary of computational results for 8^{2+} (see also Table S11)

8^{2+} (1,1'-anti)

\\# opt=tight freq=noraman rb3lyp/cc-pvdz\\DDTIF SBu dication 1,1'
-anti\\2,1\C,-2.4484314115,2.1308105556,-1.1491892902\C,-1.0483870117,
2.3426282097,-1.2716345934\C,-0.5510806277,3.4769869249,-1.9031171734\
C,-1.4561251007,4.4157133742,-2.4243420064\C,-2.834220314,4.2055365518
,-2.3231522791\C,-3.3417359567,3.0604391171,-1.6934019843\C,-2.6561355
475,0.8334603648,-0.4715570346\C,-1.3745872677,0.2790488666,-0.1834598
154\C,-0.36275393,1.1990690305,-0.662881527\H,0.5237025499,3.640485417
5,-2.003230247\H,-1.0805440905,5.3114059017,-2.9218388936\H,-3.5266003
315,4.9355904911,-2.7448914667\H,-4.4214110312,2.9167501175,-1.6586125
177\C,0.9793775517,0.9378134638,-0.5095200056\C,-0.9806606003,-0.91441
10967,0.4871179764\H,-1.7159632717,-1.6143043711,0.8835211657\C,0.3614
708915,-1.1756666192,0.6404798709\C,1.3733040961,-0.2556470234,0.16105
67895\H,1.7146804927,1.6377064312,-0.9059232417\C,2.6548520028,-0.8100
607999,0.449149135\C,1.0471044697,-2.319226319,1.2492318362\C,2.447148
6376,-2.1074103048,1.1267818818\C,0.5497995356,-3.4535840839,1.8807170
39\H,-0.5249833484,-3.6170818625,1.9808341233\C,3.3404546261,-3.037038
5645,1.6709922936\H,4.4201294713,-2.8933492768,1.6361988038\C,1.454845
3389,-4.3923106149,2.4019396853\C,2.8329403468,-4.1821350314,2.3007452
966\H,1.0792653236,-5.2880022966,2.8994387354\H,3.525321019,-4.9121890
389,2.7224830852\C,-3.9257301735,0.2653284888,-0.1547254938\C,3.924446
6117,-0.2419330954,0.132308804\S,-5.3454552869,1.2028902399,0.10388637
55\S,-4.203994209,-1.449204531,0.0074355855\C,-6.4555361393,-0.0970128
395,0.4526575709\C,-5.9107978232,-1.37074756,0.424824281\S,-6.86436950
38,-2.7928803273,0.7773678341\S,-8.1179682392,0.3024067993,0.905422712
8\C,-9.0032526287,0.1654945539,-0.7396007429\H,-8.8222744965,-0.845357
9301,-1.1333112453\H,-8.5607508265,0.9088231867,-1.4194456363\C,-5.686
0969245,-4.1906145978,0.479625899\H,-5.3323717037,-4.1293613564,-0.562
2928144\H,-4.830834079,-4.0723130532,1.1650691624\S,4.2027179802,1.472
599504,-0.0298388785\S,5.344161419,-1.1795010676,-0.1263326003\C,5.909
5158976,1.3941364758,-0.447250128\C,6.454245705,0.1203986274,-0.475104
6295\S,6.8630915088,2.8162675241,-0.7997887043\S,8.1166669519,-0.27902
55106,-0.9279045995\C,5.6848281016,4.2140043655,-0.5020226363\H,4.8295
572168,4.0957117431,-1.1874573491\H,5.3311139634,4.152744552,0.5398994
059\C,9.0019776916,-0.1421894957,0.7171105951\H,8.8210354868,0.8686561
062,1.1108549431\H,8.5594647217,-0.8855258403,1.3969396455\C,-10.49186
89651,0.4247874152,-0.5110146931\H,-10.8874729705,-0.3077594814,0.2139
447719\H,-10.6301003653,1.4239957047,-0.0622103018\C,-11.2878744622,0.
3339968371,-1.8227725222\H,-11.1360404843,-0.6639377197,-2.2721369705\
H,-10.8830119476,1.0648018315,-2.5459236759\C,-12.7833958374,0.5857103
139,-1.6164102908\H,-13.328903722,0.5160227185,-2.5697233273\H,-13.222
4765242,-0.1517561562,-0.924536059\H,-12.9672488618,1.5888336383,-1.19
78383229\C,-6.4213185919,-5.5089723399,0.7379715882\H,-6.7981573749,-5
.5222691015,1.7753035279\H,-7.3029948315,-5.5722516901,0.0769667354\C,
-5.5114220343,-6.7233576483,0.50142787\H,-5.131912269,-6.6974544968,-0
.5361420795\H,-4.6259019479,-6.6484625089,1.158925045\C,-6.2312077165,
-8.0499642062,0.7547394306\H,-5.5577158922,-8.9024426945,0.5798042504\
H,-6.5946282395,-8.1172446773,1.7932013347\H,-7.1000561214,-8.16796400
72,0.0868497184\C,10.4905828852,-0.4015191379,0.4884936266\H,10.886195
7498,0.3310341493,-0.2364545576\H,10.628778015,-1.4007202235,0.0396622
809\C,11.2866138686,-0.3107831953,1.8002398469\H,11.1348174318,0.68714

50505,2.2496306846\H,10.881742449,-1.0415934295,2.5233806845\C,12.7821
239723,-0.5625363888,1.5938446678\H,13.2212148494,0.1749355907,0.90198
28351\H,13.3276508171,-0.4928915679,2.5471499229\H,12.9659386766,-1.56
56537956,1.1752417584\C,6.420051982,5.5323612974,-0.7603661037\H,6.796
8805712,5.545664146,-1.7977016342\H,7.3017348843,5.5956328561,-0.09936
94886\C,5.5101618748,6.7467480305,-0.5238048585\H,5.1306622766,6.72083
89426,0.5137686318\H,4.6246350493,6.6718603665,-1.1812937814\C,6.22994
94297,8.0733539421,-0.7771143568\H,6.5933601202,8.1406402741,-1.815579
3081\H,5.5564620771,8.9258334241,-0.60216687\H,7.0988046649,8.19134641
11,-0.1092322784\\Version=EM64L-G09RevB.01\State=1-A\HF=-4813.3998482\
RMSD=5.752e-09\RMSF=1.016e-06\Dipole=-0.0000086,-0.000001,0.000008\Qua
drupole=161.0391713,-36.2500198,-124.7891516,42.9692112,21.7182251,-27
.0349066\PG=C01 [X(C42H46S8)]\\@

8^{2+} (1,1'-syn)

\\# opt=tight freq=noraman rb3lyp/cc-pvdz\\DDTIF SBu dication 1,1'
syn 52o angle between the two DT planes\\2,1\C,-1.9959211758,2.8699438
808,-0.8404698576\C,-0.5750372778,2.8354709558,-0.8291914435\C,0.16885
56876,3.9772686877,-1.1051765344\C,-0.5059682268,5.1722776397,-1.40191
06637\C,-1.9027034799,5.2085061971,-1.4369364342\C,-2.6583373268,4.059
4973807,-1.1647482528\C,-2.4876775633,1.5082990145,-0.5373479807\C,-1.
3521320814,0.6660041599,-0.3442388295\C,-0.1571358428,1.4648731711,-0.
5211530946\H,1.2603529029,3.9540259545,-1.0964327684\H,0.0645018023,6.
0775911511,-1.6160680796\H,-2.4153491148,6.1391279893,-1.6846773698\H,
-3.744326805,4.1211294618,-1.2287447198\C,1.0999344209,0.9211242996,-0
.3848228965\C,-1.234492439,-0.6964930817,0.0522850758\H,-2.1124542723,
-1.3057081809,0.2670767038\C,0.0225902379,-1.2395287014,0.1913181172\C
,1.2172577263,-0.4599642162,-0.0587889471\H,1.9783166579,1.5550851797,
-0.5057908549\C,2.353003858,-1.2904454437,0.1791083787\C,0.4409244337,
-2.5846882911,0.5958046258\C,1.8617361002,-2.6233809118,0.5910827023\C
,-0.3027297071,-3.712432788,0.9250722093\H,-1.3941639426,-3.6854875838
,0.9303658974\C,2.5240390029,-3.8195960342,0.8901018181\H,3.6095869713
,-3.9071745834,0.855722524\C,0.3722235572,-4.8998371092,1.2506388068\C
,1.7686926244,-4.9517151931,1.2263273339\H,-0.1980184517,-5.791749687,
1.5156063264\H,2.2813000363,-5.8846012554,1.4654819417\C,-3.8576329674
,1.1304946921,-0.4392451784\C,3.7228938668,-0.9164301611,0.0666356361\
S,-5.122947161,2.2353683521,-0.0597628409\S,-4.4346861141,-0.494193612
8,-0.7094669303\C,-6.471788215,1.1349081545,-0.1660878648\C,-6.1477416
748,-0.1778476122,-0.4743100467\S,-7.3693763462,-1.410785829,-0.677101
6327\S,-8.0963590432,1.8062805002,0.0125274617\C,-8.592376787,1.218367
6944,1.7198031998\H,-7.8680240434,1.6378751317,2.4334882098\H,-8.53128
40832,0.1205947325,1.7373293232\C,-6.4026136046,-2.9161338954,-1.15549
81651\H,-5.8307072548,-2.6793938774,-2.0672191392\H,-5.7056137453,-3.1
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37857242,-1.6932292964,0.9310358613\C,6.0097275541,0.1993760273,-0.628
3127724\C,6.3392496375,-0.7913293666,0.2845140365\S,7.2268884813,1.169
2268356,-1.4230198445\S,7.9667412468,-1.2908716259,0.7573790282\C,6.25
28233465,2.2449606946,-2.573480508\H,5.6738199716,1.5906330257,-3.2450
21976\H,5.5621896392,2.8591084646,-1.9728602721\C,8.4757513938,0.06146
99097,1.9484064912\H,8.4123806615,1.0252261905,1.4227613888\H,7.758335
982,0.0501095683,2.7821963021\C,-10.012943679,1.7088697889,1.998560598
1\H,-10.0481788478,2.8092105788,1.9147790434\H,-10.6995217026,1.308737
3286,1.2321930308\C,-10.4938912398,1.2834140427,3.394940101\H,-9.79729
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185\C,-11.914772091,1.7669690238,3.6945460074\H,-12.2341943281,1.44978
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.7793913741,-2.1975587296\C,-6.6517710735,-5.3567071891,-1.8036540404\
H,-6.0475654622,-5.1659812342,-2.7090945648\H,-5.9390916612,-5.6342128
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7591,-7.4270133572,-2.3491797337\H,-8.2094139644,-6.7523903618,-1.1628
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9366507026,-1.2294984044,2.8903884795\C,10.3913810465,0.8268333745,3.4
217192474\H,10.3455079708,1.8245750415,2.9490694149\H,9.7020630184,0.8
600324104,4.2846118815\C,11.8157888523,0.5507977608,3.9089130292\H,12.
5323171842,0.5448543512,3.0711429242\H,12.1429170434,1.3213030547,4.62
33898899\H,11.8839491929,-0.4260496199,4.4152489021\C,7.2283052182,3.1
218733971,-3.3640022694\H,7.9315298614,2.4782632993,-3.9198592424\H,7.
831478567,3.7257297508,-2.6640593038\C,6.4911434202,4.0478574929,-4.34
30425221\H,5.7845683789,4.6843890946,-3.7797897904\H,5.8797901576,3.43
67278882,-5.0315416095\C,7.4508440126,4.9277513277,-5.1475403938\H,8.1
484049031,4.3172859621,-5.743859698\H,6.899058337,5.5788927402,-5.8421
281573\H,8.0510169726,5.5745938337,-4.4869832875\\Version=EM64L-G09Rev
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884492,24.3578251,-7.6227298,-14.6736849\PG=C01 [X(C42H46S8)]\\@

8^{2+} (1,2'-anti)

\\# opt=tight freq=noraman rb3lyp/cc-pvdz\\DDTIF SBu dication 1,2'
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2.5679429216,-1.3135422426\C,-0.4951343857,3.7013042414,-1.9254097458\
C,-1.377888596,4.6644996657,-2.4400601014\C,-2.7605402089,4.4794056801
,-2.352674166\C,-3.2946024642,3.3359964337,-1.7421968713\C,-2.66177446
66,1.0804628555,-0.5458846737\C,-1.3914410479,0.4971122329,-0.25673250
05\C,-0.3591998526,1.4013339674,-0.7185333006\H,0.583291468,3.84527729
81,-2.01593929\H,-0.9812273772,5.55915713,-2.9228661488\H,-3.435137206
6,5.2277044375,-2.7713368059\H,-4.3769455314,3.2106191416,-1.719835689
5\C,0.9770253191,1.1055090966,-0.5695407707\C,-1.0273791283,-0.7140804
17,0.396577571\H,-1.778237858,-1.4037347458,0.7813353745\C,0.308182739
,-1.0101514225,0.5447737585\C,1.3418901515,-0.1082127581,0.0802280445\
H,1.7285720395,1.7939765838,-0.9554719381\C,2.6100215367,-0.6999630291
,0.3607746884\C,0.9634475805,-2.1805344198,1.1349145645\C,2.3685470127
,-2.0019706245,1.0178376069\C,0.4350707052,-3.3130477065,1.744144802\H
,-0.6437007769,-3.4523045689,1.8376930631\C,3.236389884,-2.9636505242,
1.5481963376\H,4.3194105797,-2.8473391863,1.5186385363\C,1.3148481883,
-4.2836746094,2.2501997724\C,2.6981317586,-4.1061876433,2.156485675\H,
0.9148956648,-5.178619683,2.7296943495\H,3.3706535811,-4.8609438317,2.
5667685598\C,-3.9357410083,0.515600837,-0.2491103858\C,3.8933150625,-0
.1600884166,0.0537116774\S,-5.3618161664,1.4896710278,-0.004706226\S,-
4.2468940564,-1.1723926708,-0.1060078547\C,-6.4760871587,0.1849565503,
0.3736073577\C,-5.9361693091,-1.0916228599,0.3265940839\S,-6.752505174
9,-2.6051827425,0.7297734227\S,-8.1386571223,0.4750529908,0.8275201377
\C,-8.3097193869,2.3174400838,0.7275931442\H,-8.0850787875,2.630065791
7,-0.3049711225\H,-7.5759404084,2.7663769413,1.4164335798\C,-7.8412577
921,-2.88870888,-0.7679699059\H,-8.4999649799,-2.0160461676,-0.8835724
359\H,-7.1785937003,-2.9666436454,-1.6424416426\S,4.2133561928,1.54843
25057,-0.1010322075\S,5.2912542621,-1.1305587428,-0.2045082277\C,5.926
2366596,1.4319117846,-0.4848219021\C,6.4399556258,0.145622825,-0.51613
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68081,-0.9417830508\C,5.771603955,4.2569573307,-0.5114612379\H,4.94817

42386,4.1824602475,-1.2405642229\H,5.3652823606,4.1802731303,0.5101224
213\C,8.9080505517,-0.3979151846,0.7448713339\H,8.7535219429,0.5643031
076,1.2546796366\H,8.398382612,-1.1959011307,1.3055160121\C,-9.7403035
205,2.6950213979,1.1221898598\H,-10.4533138874,2.1928661758,0.44561271
96\H,-9.949877715,2.3252342404,2.1407329909\C,-9.9591754334,4.21473266
26,1.0686179778\H,-9.7413554662,4.5782475224,0.0480952015\H,-9.2329327
88,4.7106900236,1.7377001967\C,-11.3825801937,4.6120440579,1.466394244
\H,-11.5126982165,5.7037222061,1.4210019011\H,-12.1284778882,4.1576610
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488998\H,-9.2519355375,-4.0728958982,0.3696057798\C,-9.5485224642,-4.4
885649793,-1.7420832518\H,-10.2352559951,-3.6398647165,-1.9119074058\H
,-8.9312449609,-4.5754224647,-2.6543723677\C,-10.3550377832,-5.7733575
73,-1.5396722035\H,-10.9967771344,-5.9756488772,-2.4105431319\H,-9.693
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6530273731\C,10.3927045375,-0.7051006709,0.5528119179\H,10.857719097,0
.0875116511,-0.0589988939\H,10.5064417273,-1.6489329155,-0.0086707423\
C,11.1253873422,-0.8137101314,1.8993519872\H,10.9997233864,0.130544546
6,2.4592910116\H,10.6501990968,-1.6022561213,2.5104579798\C,12.6155461
624,-1.1192077927,1.7303069761\H,13.1232823966,-0.3307075939,1.1508285
378\H,13.1154644583,-1.1898128515,2.7082364332\H,12.7722843878,-2.0753
513454,1.2044299475\C,6.5553741773,5.5596261541,-0.6974504178\H,7.0042
488265,5.5785041122,-1.7057015528\H,7.3894813484,5.5912783768,0.024437
5599\C,5.6602835449,6.7933090913,-0.5074980207\H,5.1999810737,6.758261
4519,0.4966383173\H,4.8279825569,6.7534623221,-1.2337226043\C,6.431344
053,8.1044891592,-0.6766092336\H,6.8758129897,8.1812623576,-1.68236671
21\H,5.7688265719,8.9718602358,-0.5362611301\H,7.2486246342,8.18530782
38,0.0584807573\\Version=EM64L-G09RevB.01\State=1-A\HF=-4813.4014782\R
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rupole=181.3018101,-51.3232574,-129.9785527,12.1203475,13.7536154,-16.
1403252\PG=C01 [X(C42H46S8)]\\@

8^{2+} (1,2'-syn)

\\# opt=tight freq=noraman rb3lyp/cc-pvdz\\DDTIF SBu dication 1,2'
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2.5542303916,-0.9003326488\C,-0.0061307993,3.7715368028,-1.1062602685\
C,-0.7850321968,4.923026576,-1.3039128405\C,-2.1806633682,4.8501370752
,-1.275720784\C,-2.8314210224,3.6267538523,-1.0635963254\C,-2.43540653
89,1.0627690592,-0.6306462014\C,-1.2310108918,0.3124229671,-0.48074298
98\C,-0.1094341953,1.2139656287,-0.643173898\H,1.0833609709,3.84144100
15,-1.1133899341\H,-0.2967792672,5.8845218292,-1.4712561263\H,-2.77357
4454,5.7555200934,-1.4136826545\H,-3.9203065705,3.6123052739,-1.018960
1923\C,1.1901316635,0.7674697771,-0.56469967\C,-0.995860864,-1.0817661
896,-0.3101146902\H,-1.817101516,-1.7967147302,-0.2607236325\C,0.30317
31309,-1.5288026059,-0.2348436531\C,1.4252620726,-0.61679552,-0.323126
9153\H,2.0129068201,1.4675575016,-0.7104109904\C,2.6279355026,-1.37929
85548,-0.2408009835\C,0.8372586371,-2.8860696158,-0.0902162382\C,2.256
1279421,-2.8017534648,-0.096289941\C,0.1956104362,-4.1105580649,0.0576
079005\H,-0.8939085292,-4.1798985551,0.0638156427\C,3.0218152363,-3.96
04184758,0.0780200216\H,4.1104720637,-3.9350034257,0.1221096855\C,0.97
37463466,-5.2704718915,0.2046139891\C,2.3693946767,-5.1929760257,0.219
851616\H,0.4840627102,-6.239197226,0.3169693643\H,2.9613631744,-6.1001
100974,0.3499337396\C,-3.7621942128,0.5478483026,-0.5609104285\C,3.961
8007648,-0.8801067346,-0.313508576\S,-5.1060249592,1.2960596697,-1.382
5442811\S,-4.2204719965,-0.8466299953,0.3397889102\C,-6.3413245894,0.1
366478605,-0.9162900857\C,-5.9109468461,-0.8930127405,-0.092825376\S,-

6.8719350063,-2.2575372692,0.486701463\S,-7.9898584599,0.2453562367,-1
.4863053007\C,-7.9940664884,1.7759768566,-2.531180905\H,-7.2628675761,
1.635768336,-3.3436766855\H,-7.6852927285,2.6255704146,-1.900821359\C,
-7.8979213879,-1.4751787783,1.8444167995\H,-7.198345527,-1.0907694978,
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,0.7317021499,0.1777381744\S,5.2936204696,-1.8068195058,-0.8859826002\
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-0.7006574001\S,7.2339409707,1.9546976361,0.0202264189\S,8.184916347,-
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5.3682523599,3.5150273375,0.1326715912\H,5.7634115411,2.8329263239,1.7
50165457\C,8.9523412815,-1.6535635188,0.3365873316\H,8.8754049267,-0.8
677519979,1.1022335291\H,8.365953251,-2.5300739961,0.6505572625\C,-9.4
054652113,1.9837532362,-3.0874366803\H,-9.706808916,1.0941048418,-3.66
70249819\H,-10.1198660513,2.0792302172,-2.2515498497\C,-9.4819235593,3
.2322218425,-3.9794514043\H,-8.758104363,3.131577006,-4.8082709784\H,-
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56688766\H,-10.2752451341,-1.1227596753,3.1912866008\C,-10.6279685097,
-3.0318998984,4.158650673\H,-11.2299972565,-2.6047522927,4.9749216808\
H,-11.3240889761,-3.4225243439,3.3982954234\H,-10.0656877246,-3.886742
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8^{2+} (2,2'-anti)

\\# opt=tight freq=noraman rb3lyp/cc-pvdz\\DTFIF SBu trans dicatio
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286,-0.5817158124\C,-1.2710641236,5.0127221923,-0.7638258818\C,-2.6566
990983,4.8282849481,-0.7681058049\C,-3.2123270764,3.5550997591,-0.5804
569177\C,-2.6206166721,1.0221035965,-0.186679661\C,-1.3602920228,0.357
9467441,-0.0858237112\C,-0.3134929007,1.3504679053,-0.2041533799\H,0.6
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44423131\H,-3.3165227159,5.6824740215,-0.9271400927\H,-4.2957943908,3.
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,0.0851114523,0.825552403\C,-8.2761536574,1.8610139641,1.334454906\H,-
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537261939,-1.9208405819\H,11.4545318336,-4.8973854496,-3.0316414212\H,
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1.9711017046\H,8.0999360298,4.6894677092,2.0511279158\H,9.362924435,3.
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8^{2+} (2,2'-syn)

\\# opt=tight freq=noraman rb3lyp/cc-pvdz\\DTFIF SBu cis dication
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2289898,-4.8961871465,-0.0740509092\C,-3.2011636367,-3.6110002413,-0.0

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