

Supporting Information

Synthesis, Electrochemical and Photophysical Studies of Tetrathiafulvalene-annulated Phthalocyanines

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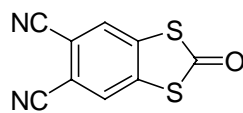
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General Experimental Procedures. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, with TMS as internal reference. Dithranol and DCTB were used as matrices for MALDI mass spectrometry. Luminescence and excitation spectra of **8** in THF were recorded using a right-angle detection geometry. Sample concentrations were kept low enough for optical densities to be below 0.2 at all wavelengths of interest in order to keep effects of reabsorption negligible. All spectra were corrected for the spectral response of the system. Melting points are uncorrected. Electrochemical experiments were carried out using a potentiostat with positive feedback compensation. The equipment consists of a three-electrode cell with a platinum millielectrode of 0.126 cm^2 and a platinum wire counter-electrode; a silver wire served as a quasi-reference electrode and its potential has been checked against the Fc^+/Fc couple before and after each experiment. The electrolytic media involved a mixture of CH_2Cl_2 and CH_3CN (9.5/0.5) and a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF_6). All experiments were performed in a glove box containing dry, oxygen-free argon at room temperature. The number of electrons was determined by thin-layer cyclic voltammetry (TLCV) using 2,3-dichloro-1,4-naphthoquinone as the one-electron standard reference.

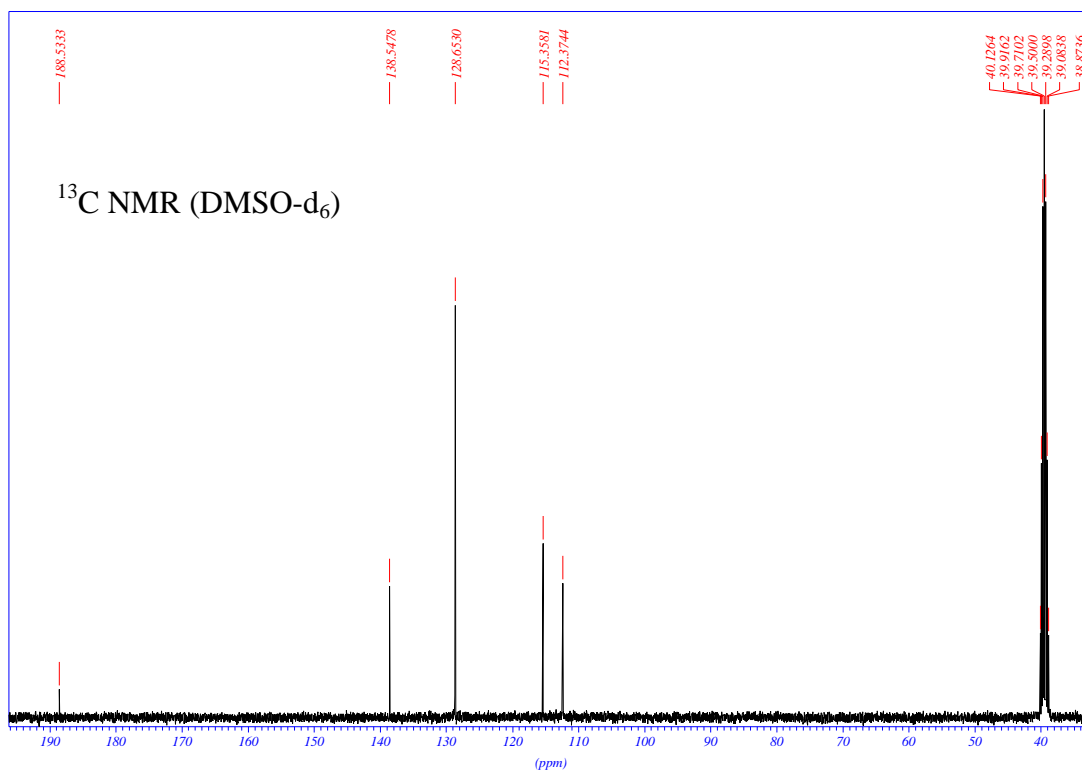
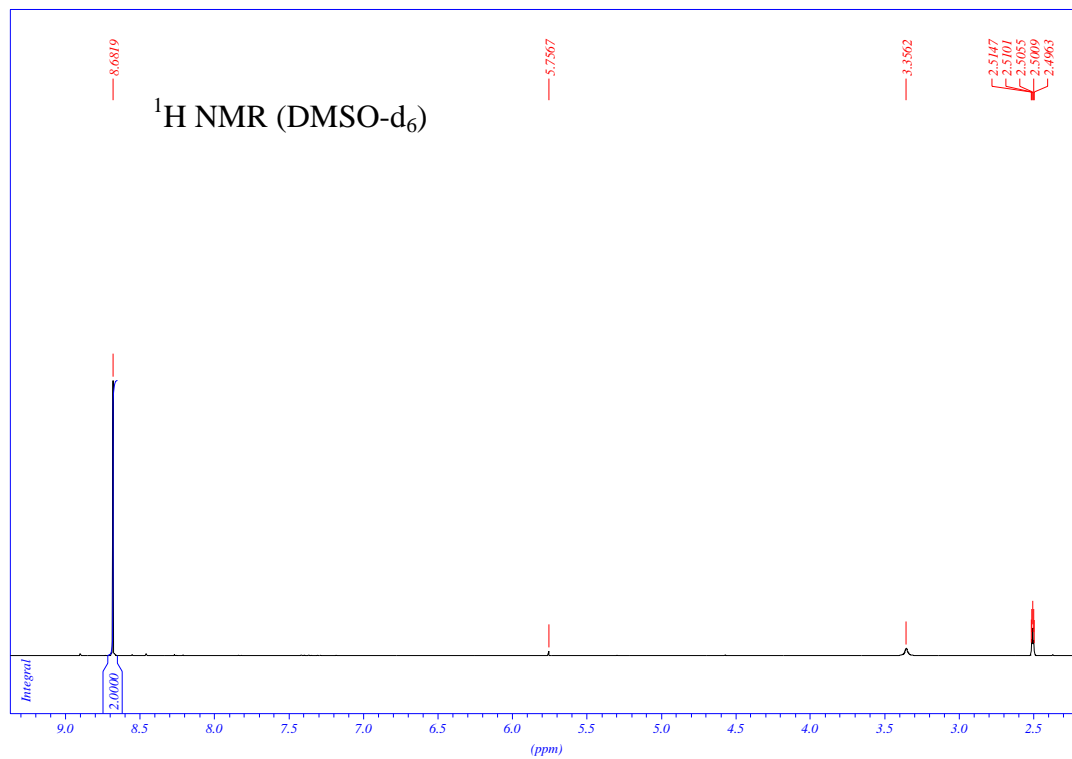
Procedure for Preparation of compound **1**: To a suspension of NaH (0.6 g, 25 mmol) in anhydrous DMF (10 ml) under Ar at room temperature, benzyl mercaptan (3 ml, 25 mmol) was added in one portion. After completion of reaction the milky suspension became a transparent solution. Then 4,5-dichlorophthalonitrile (2.5 g, 12.5 mmol) was added in one portion and the mixture was kept stirring for 12h. The resulting yellow solution was cooled (-20°C) for some time (at least 1 day) until a yellow solid was formed which was collected by filtration and washed with DMF. The crude product was dissolved in dichloromethane (40 ml). After filtration, methanol (100 ml) was added until precipitation. Compound **1** was collected as a white solid (2.6 g, 55 %). mp: 190-191°C ; ¹H NMR (CD₂Cl₂): δ 7.47 (s, 2H), 7.34 (m, 10H), 4.24 (s, 4H); EI-MS *m/z* (relative intensity, %) 372 (M⁺, 14).

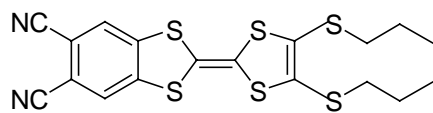
Procedure for Preparation of compound **3**: To a solution of di(tetraethylammonium) bis(1,3-dithiol-2-thione-4,5-dithiolate)zincate (5.00 g, 7.0 mmol) in acetonitrile was added 3-bromopropane (2.5 mL, 2.8 mmol) and the mixture was refluxed for 1 h. The resulting solution was cooled to r.t. and the precipitated salt was filtered off. The yellow-orange filtrate was concentrated in vacuo, the crude product was redissolved in CH₂Cl₂ (80 mL) and washed with water (4 x 60 mL), dried (Na₂SO₄) and the solvent was removed under reduced pressure. Purification by means of column chromatography (silica, CH₂Cl₂/hexane 1/1) afforded compound **3** as a red oil (3.2 g, 80%). ¹H NMR (CDCl₃): δ 2.87 (t, 4H, *J* = 7.14 Hz), 1.75 (m, 4H, *J* = 7.14 Hz, *J* = 7.35 Hz), 1.05 (t, 6H, *J* = 7.35 Hz); EI-MS *m/z* (relative intensity, %) 282 (M⁺, 52).

NMR Spectra

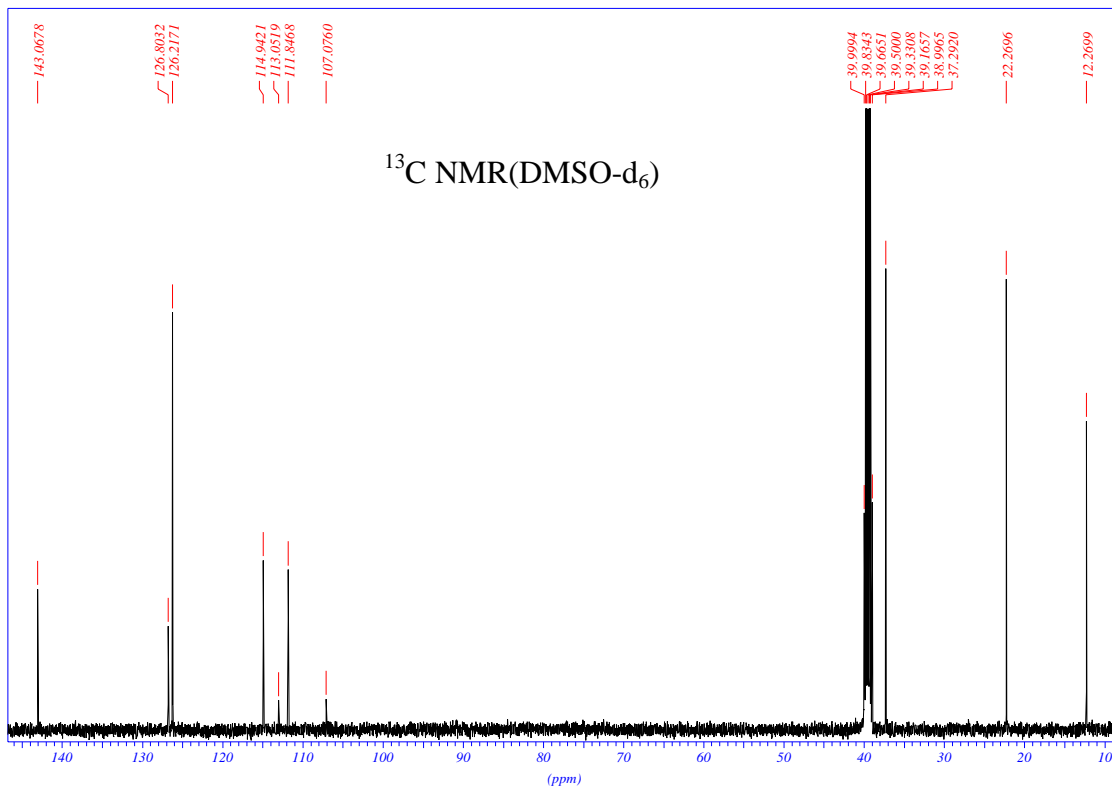
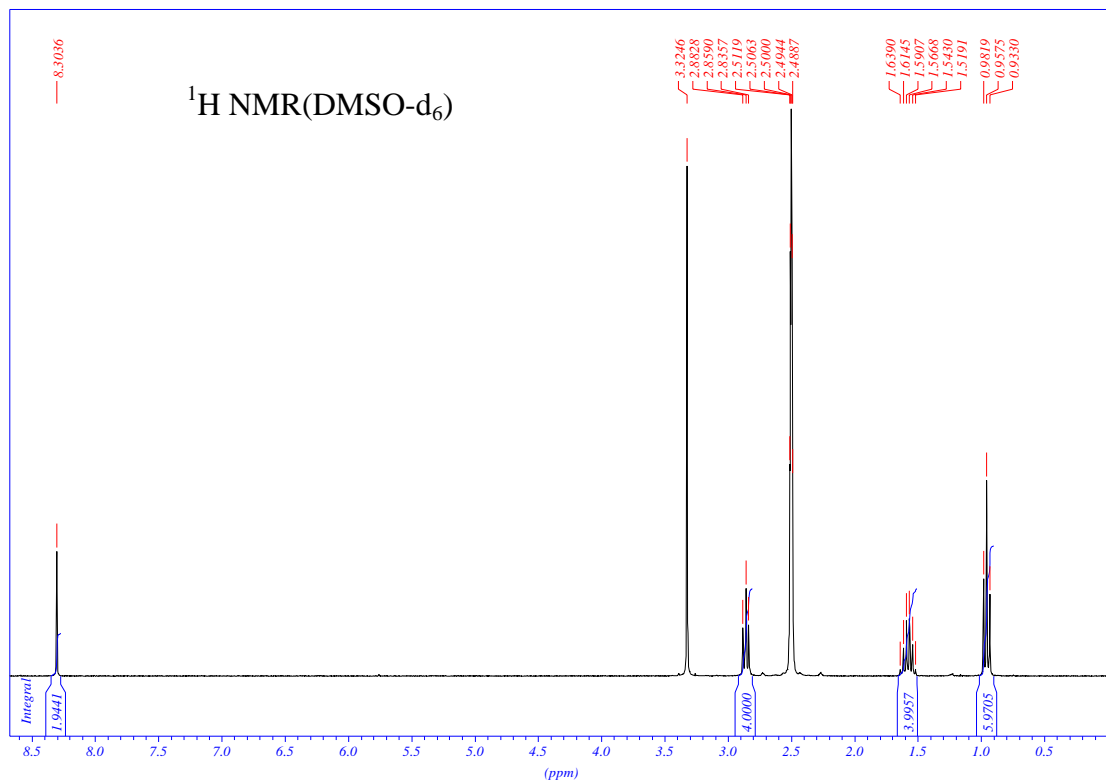


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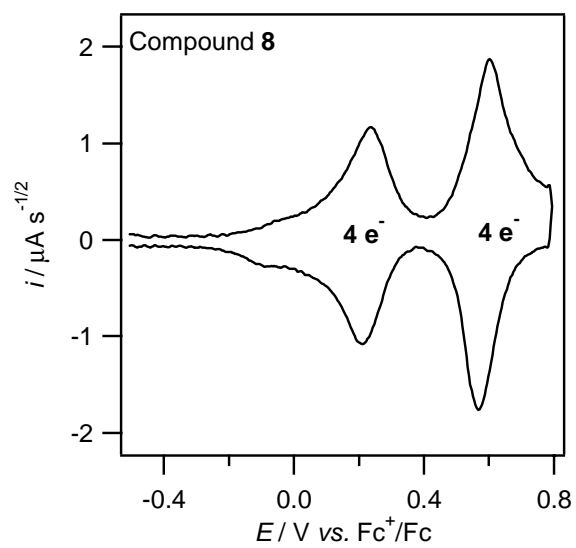
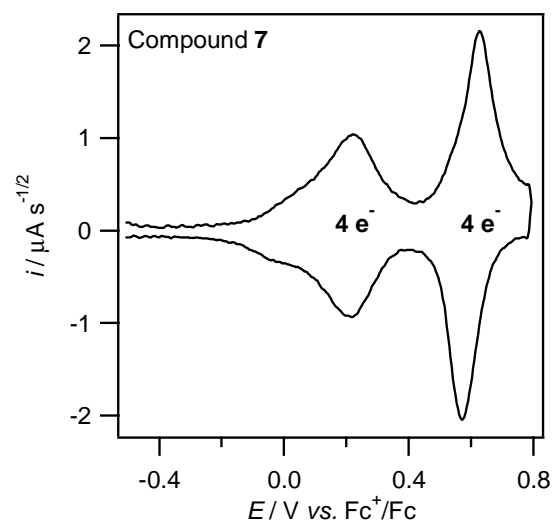
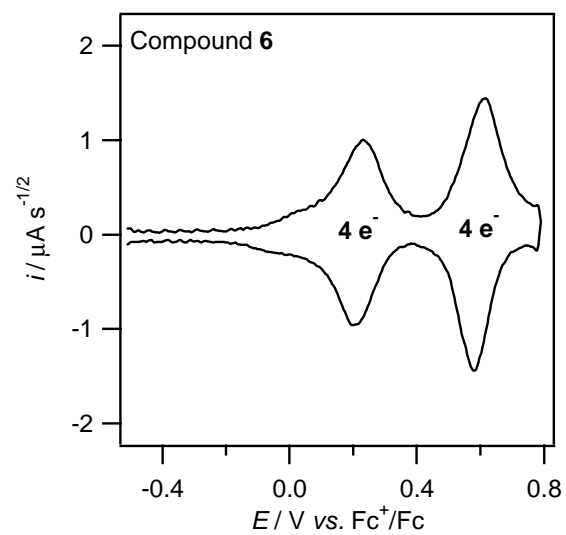




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Thin Layer Cyclic Voltammogram



UV-Vis spectra of compounds 5 (d), 6 (b), 7(c) and 8 (a) in pyridine

