

Supporting Information

π -Conjugated Multi-Donar/Acceptor Array of Fullerene–Cobaltdithiolene– Tetrathiafulvalene: Synthesis, Structure, and Electronic Interaction in the Array

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X-ray Crystallographic Analysis. Single crystals of **1b** suitable for X-ray analysis were obtained by slow diffusion of ethanol into a solution of **1b** in chlorobenzene. Single crystals suitable of **4**·(PhCl) for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of **4** in chlorobenzene. X-ray crystallographic measurements were performed on RIGAKU R-Axis RAPID II (imaging plate detector) and Saturn 724 (CCD detector), respectively, using MoK α (graphite monochromated, $\lambda = 0.71069$ Å) radiation. The positional and thermal parameters were refined by the full-matrix least-squares method using SHELXL97 program.

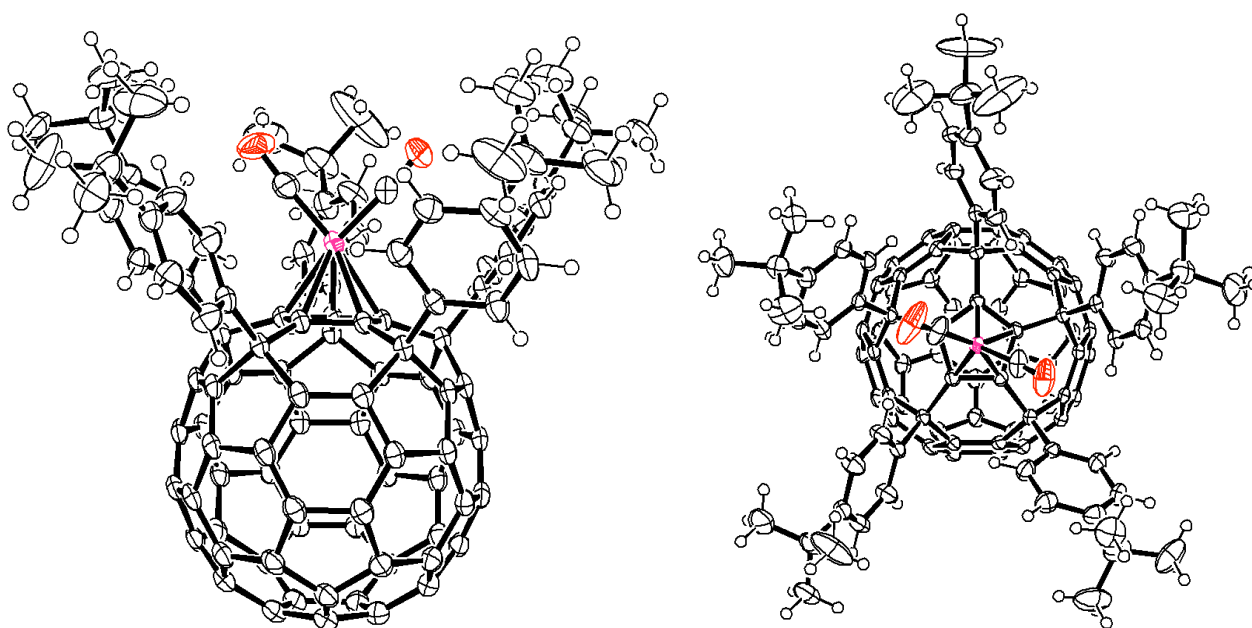


Figure S1. Crystal structure of **1b**·(PhCl)₃. Solvent molecules are omitted for clarity. Left: side view. Right: top view.

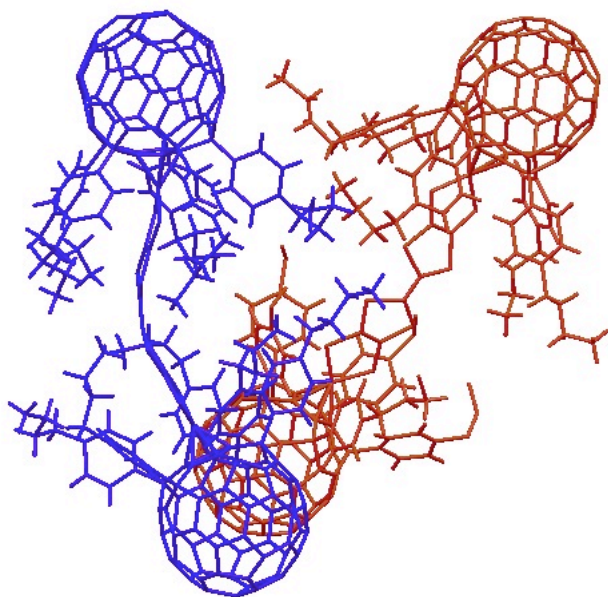


Figure S2. Crystal structure of 4·(PhCl). Solvent molecules are omitted for clarity.

Two nonequivalent molecules are in the crystal, which are colored differently. The colors correspond to those in Figure S3.

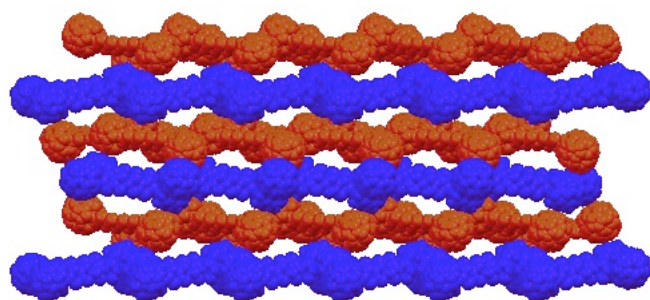
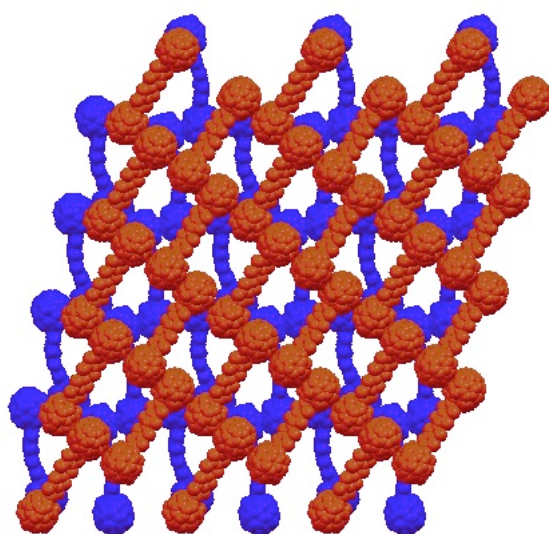
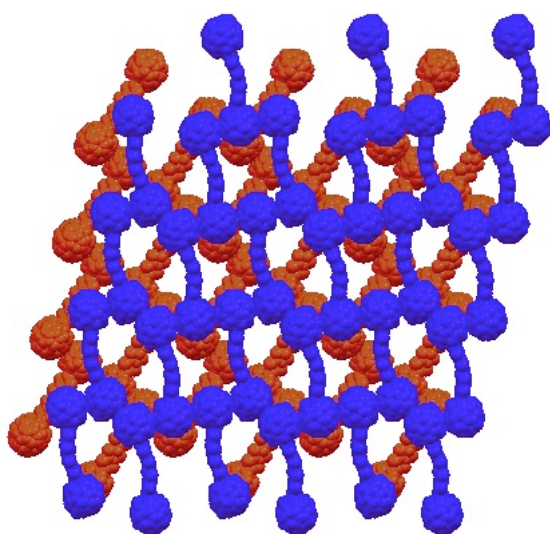


Figure S3. Crystal packing of 4·(PhCl).

Left: view from the c axis. Lower left and right: view from the b axis. Solvent molecules and aryl groups are omitted for clarity. Molecules assemble with fullerene-fullerene interaction to form an alternative layer-by-layer structure.



Spectroscopic Measurements. UV-vis-NIR absorption spectra were recorded on JASCO V-570 spectrophotometer equipped with JASCO Pbs power supply. Measurements were carried out in CH₂Cl₂ solutions under atmospheric conditions at room temperature.

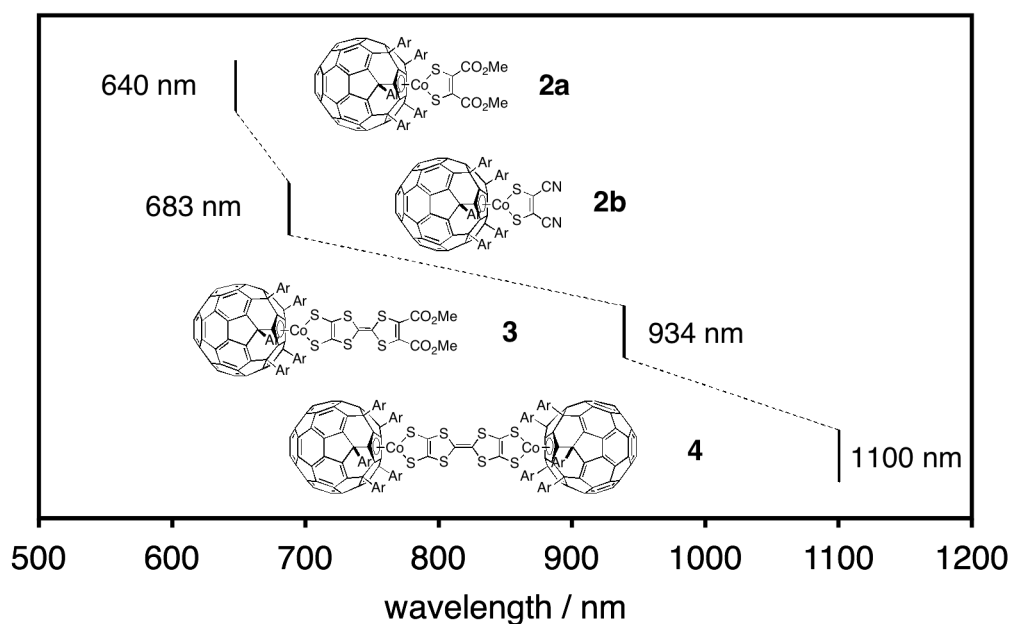


Figure S4. Visible-near infrared absorption maxima of cobaltadithiolene fullerene complexes in CH₂Cl₂.

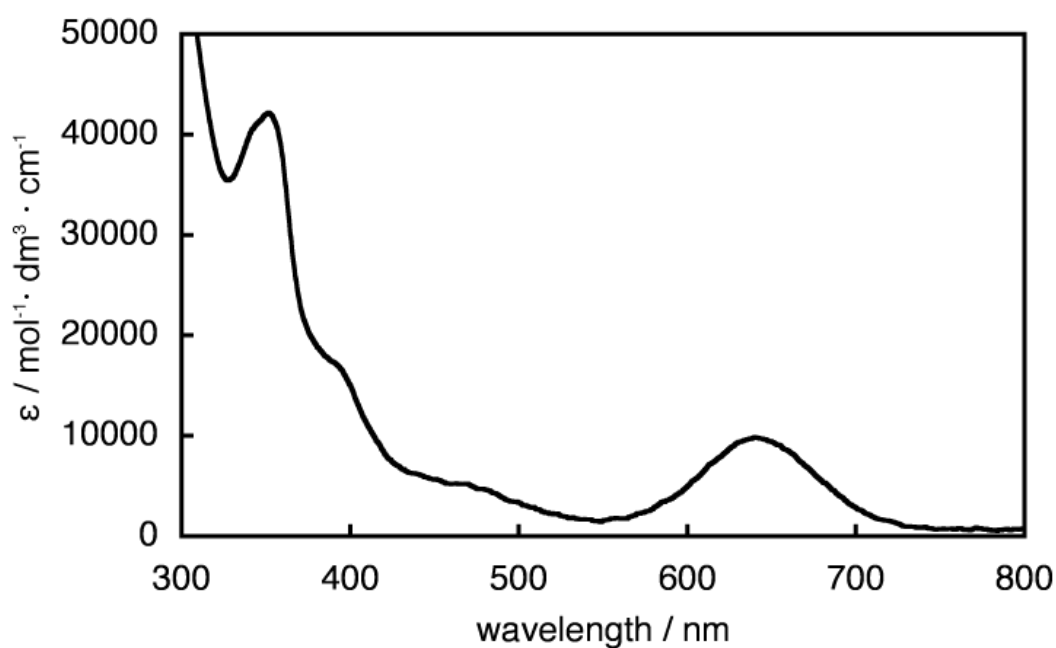


Figure S5. UV-vis-NIR absorption spectrum of **2a** in CH₂Cl₂ (λ_{max} = 640 nm, ε = 0.98×10⁴ mol⁻¹·dm³·cm⁻¹).

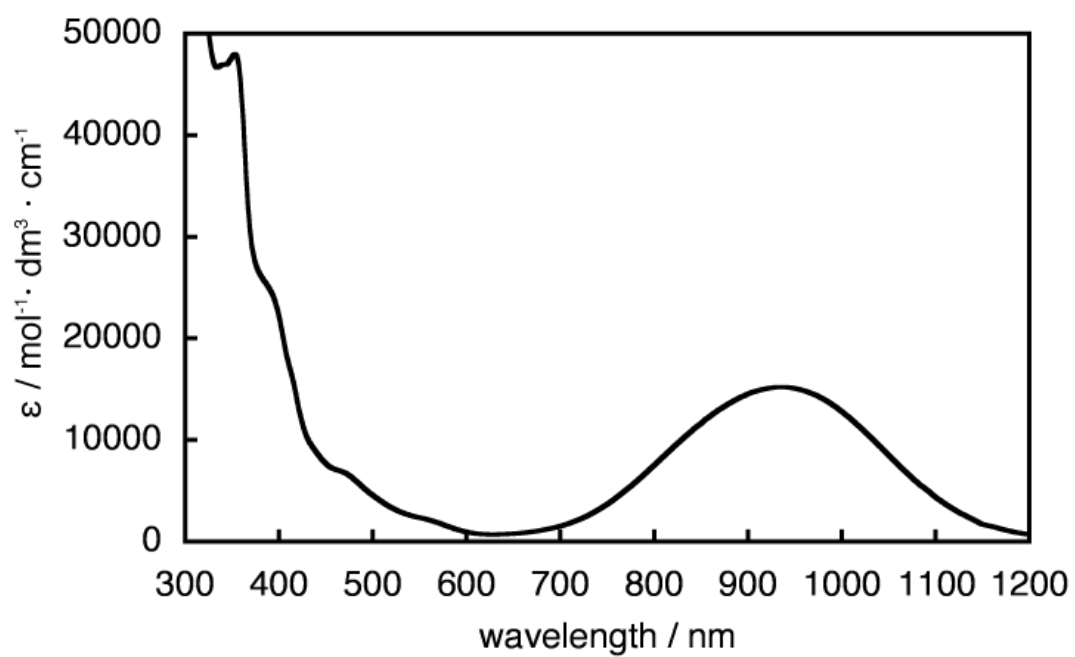


Figure S6. UV-vis-NIR absorption spectrum of **3** in CH_2Cl_2 ($\lambda_{\text{max}} = 934 \text{ nm}$, $\epsilon = 1.5 \times 10^4 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$).

Electrochemical Measurements. Electrochemical measurements were performed using a Hokuto DenkoHZ-5000 voltammetric analyzer. A glassy carbon electrode, a platinum coil and an Ag/Ag⁺ electrode were used as the working electrode, the counter electrode, and the reference electrode, respectively. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV·s⁻¹. The potential was corrected against Fc/Fc⁺.

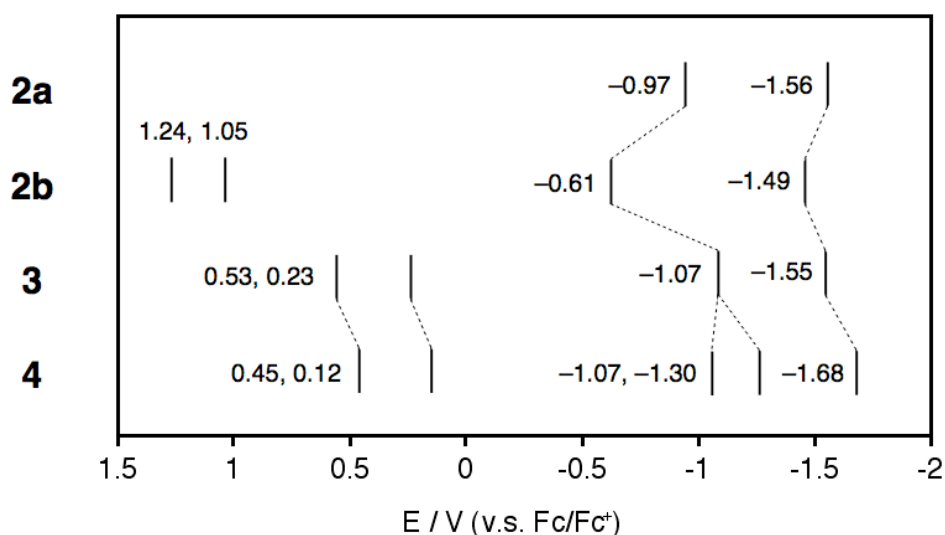


Figure S7. Oxidation and reduction potentials of cobaltadithiolene fullerene complexes in CH₂Cl₂.

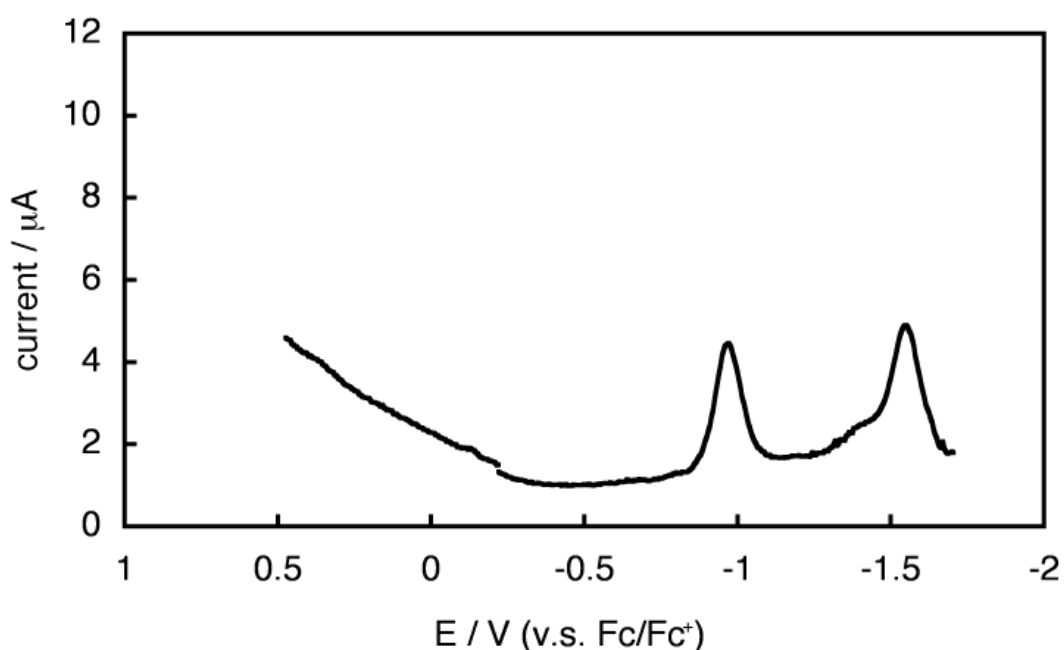


Figure S8. Differential pulse voltammogram of **2a** (50 μM) in CH₂Cl₂ containing 0.1 M TBAP as supporting electrolyte. $E_1^{\text{red}} = -0.97$ V, $E_2^{\text{red}} = -1.56$ V (v.s. Fc/Fc⁺).

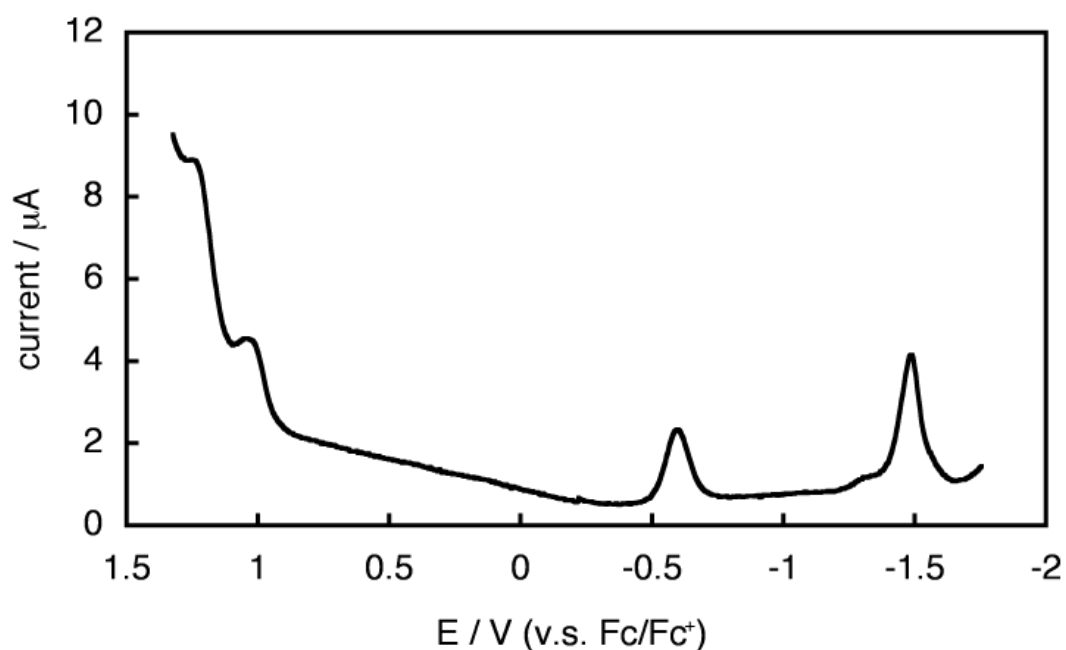


Figure S9. Differential pulse voltammogram of **2b** (50 μM) in CH_2Cl_2 containing 0.1 M TBAP as supporting electrolyte. $E_1^{\text{red}} = -0.61$ V, $E_2^{\text{red}} = -1.49$ V, $E_1^{\text{ox}} = 1.05$ V, $E_2^{\text{ox}} = 1.24$ V (v.s. Fc/Fc^+).

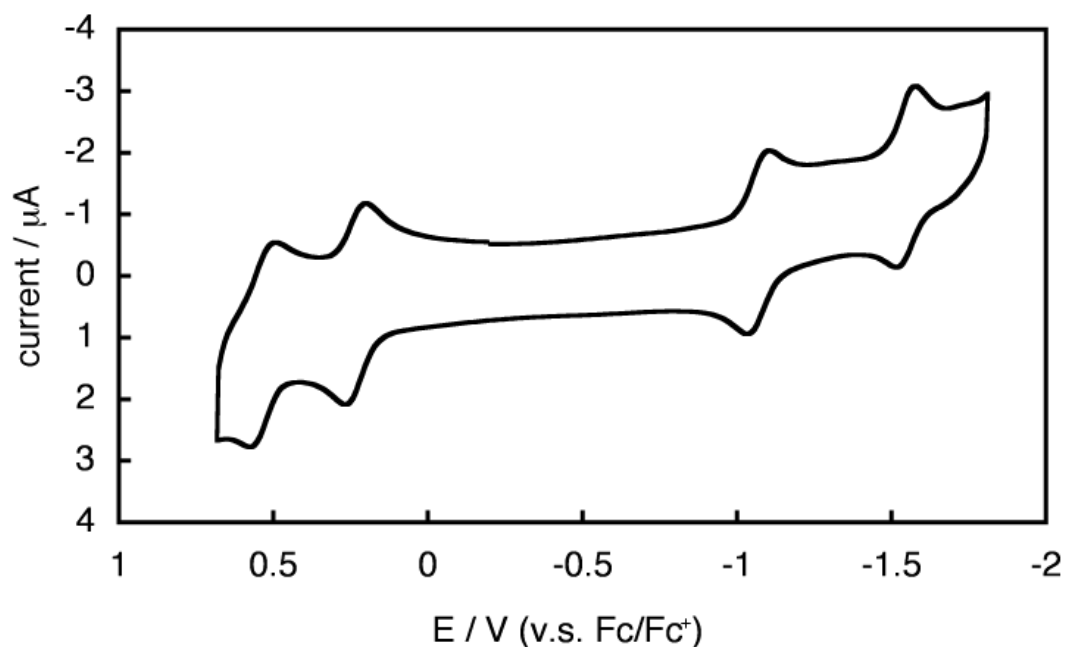


Figure S10. Cyclic voltammogram of **3** (50 μM) in CH_2Cl_2 containing 0.1 M TBAP as supporting electrolyte. $E_1^{\text{red}} = -1.07$ V, $E_2^{\text{red}} = -1.55$ V, $E_1^{\text{ox}} = 0.23$ V, $E_2^{\text{ox}} = 0.53$ V (v.s. Fc/Fc^+).

Nanosecond Flash Photolysis Experiments.

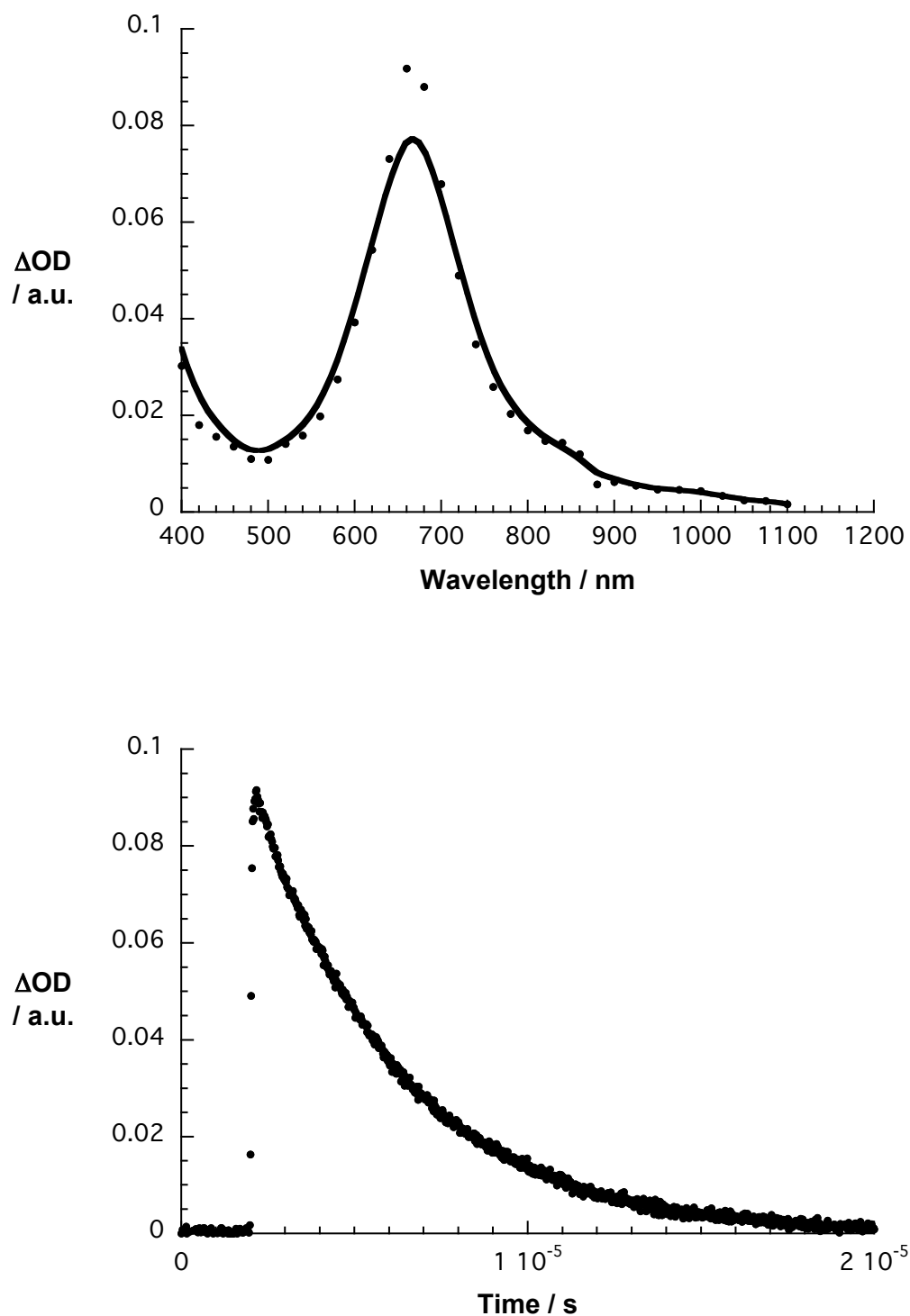


Figure S11. Time-resolved photophysical data for the array **4**. Upper part – differential absorption spectra (visible and near infrared) obtained upon nanosecond flash photolysis (355 nm) of **4** (10^{-6} M) in toluene with a time delay of 100 ns at room temperature. Lower part – time-absorption profiles of the spectra at 660 nm.

Spectroelectrochemical Measurements. The spectroelectrochemical measurements were done on a Varian Cary 5000 UV-Vis-NIR spectrophotometer connected to a Princeton PGstat 263A using a three electrode configuration system. A platinum mesh, a platinum plate and a silver wire were employed as the working, counter and reference electrodes respectively in an analyte solution of *o*-dichlorobenzene containing 0.2 M tetrabutylammonium perchlorate supporting electrolyte. The absorbances of the analysed compounds were fixed between 0.1 – 0.15. The desired potential was applied and the system output was measured for around 30 cycles. The difference between the spectrum with and without an applied potential was plotted as ΔOD .

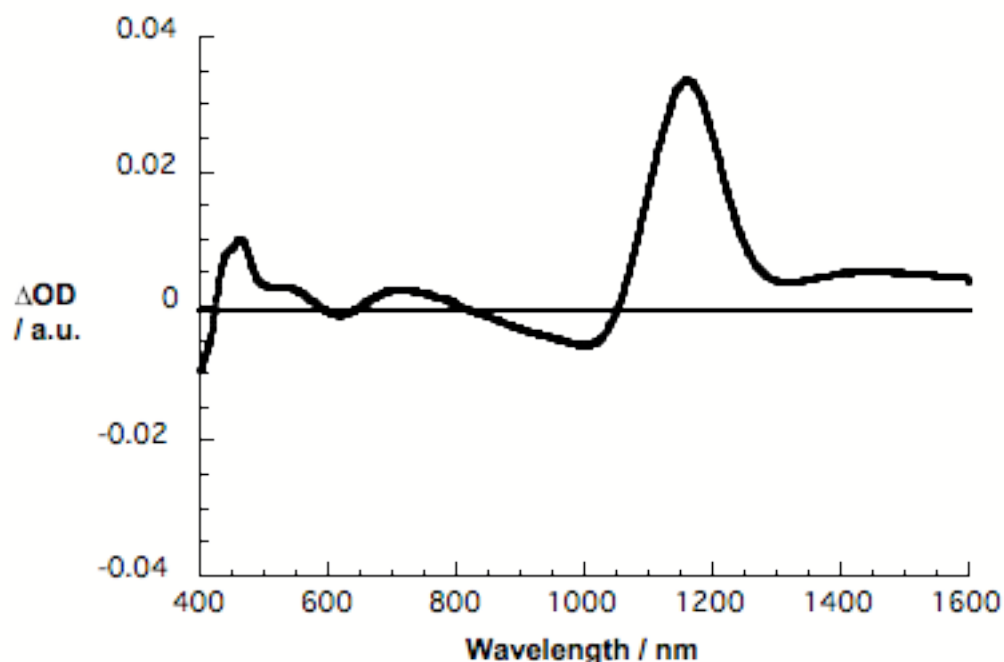


Figure S12. Differential absorption spectrum of **4** upon electrochemical oxidation with applied bias 0.1 V in *o*-dichlorobenzene at room temperature.

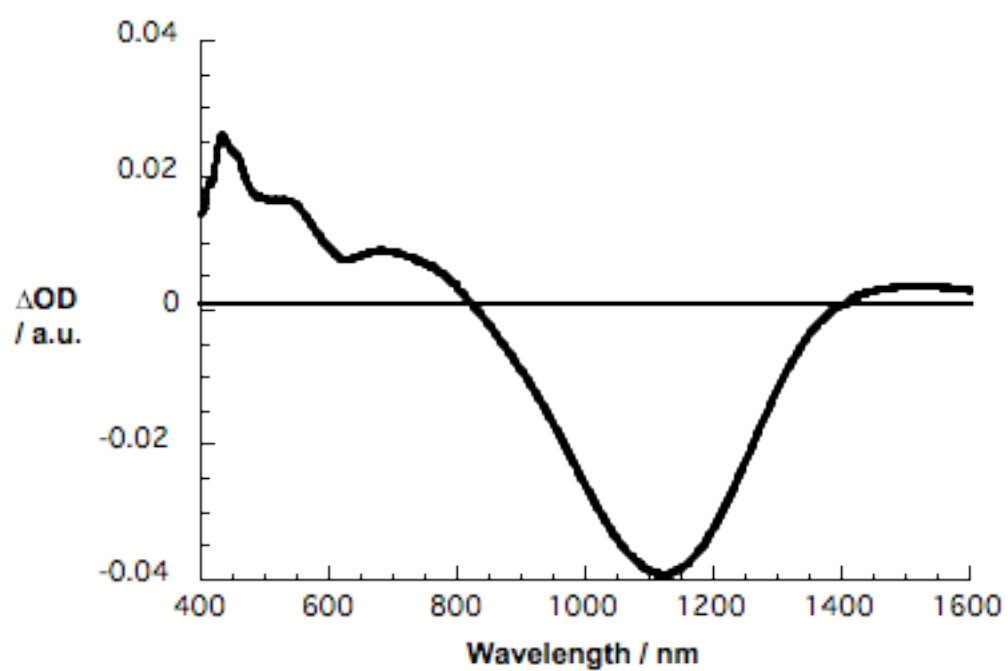


Figure S13. Differential absorption spectrum of **4** upon electrochemical reduction with applied bias -1.12 V in *o*-dichlorobenzene at room temperature.