Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Reversible Operation of Chiral Molecular Scissors by Redox and UV Light

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1. Measurements

Electronic absorption and circular dichroism (CD) spectra were recorded on a JASCO type V-560 spectrometer and a JASCO type J-720 spectropolarimeter, respectively. Analytical HPLC was performed at 20 ºC using a 4.6 mm-ϕ × 250 mm long silica gel column (Mightysil Si60) on a JASCO Type PU-980 HPLC pump, equipped with a JASCO Type UV-970 variable-wavelength UV-Vis detector. Cyclic voltammetry was carried out on an ALS/CHI619B Electro-chemical Analizer (BAS) using platinum-wire working and counter electrodes and a reference silver-wire electrode RE-5 (BAS). Scan rate was 0.1 V s^{-1}. Sample solutions (0.2 mM in CH_2Cl_2) containing Bu_4NPF_6 (0.1 M) as a supporting electrolyte were degassed by three freeze-to-thaw cycles before measurements.

2. Cyclic Voltammetry of 1

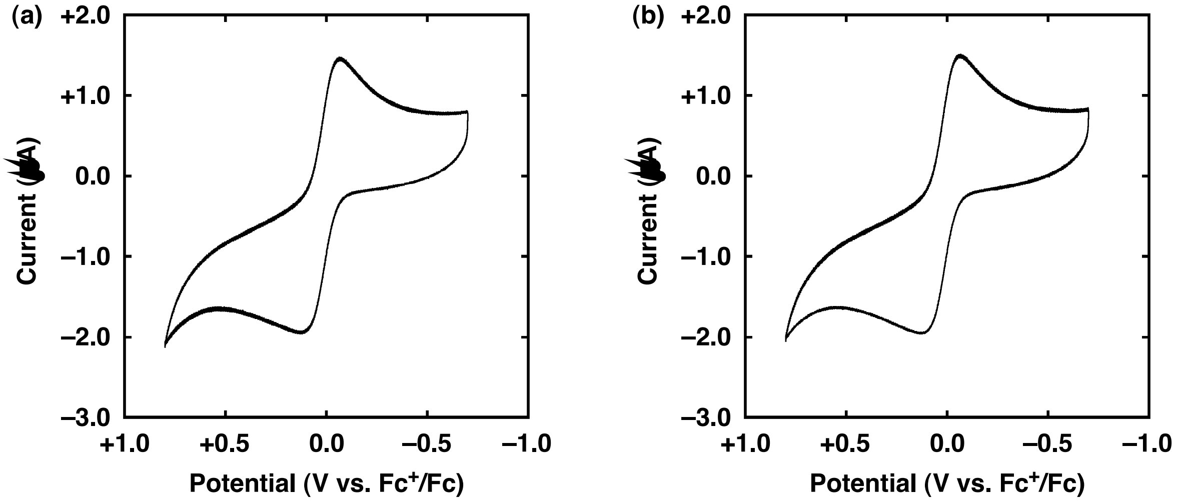
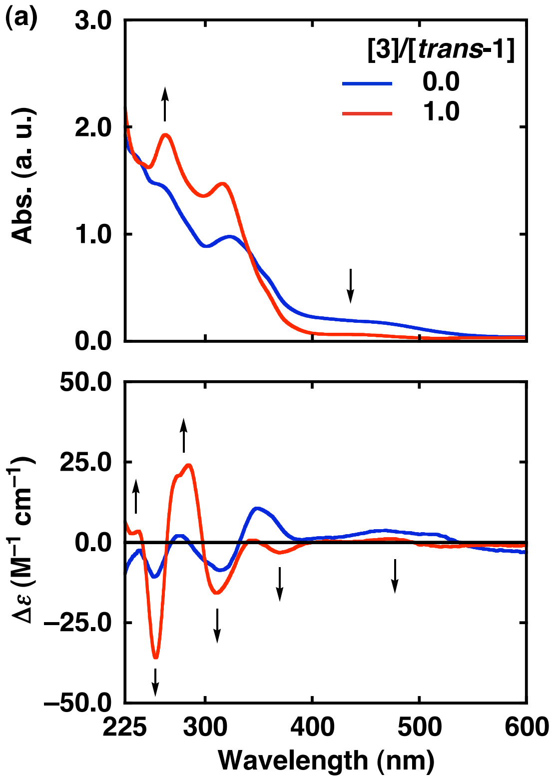
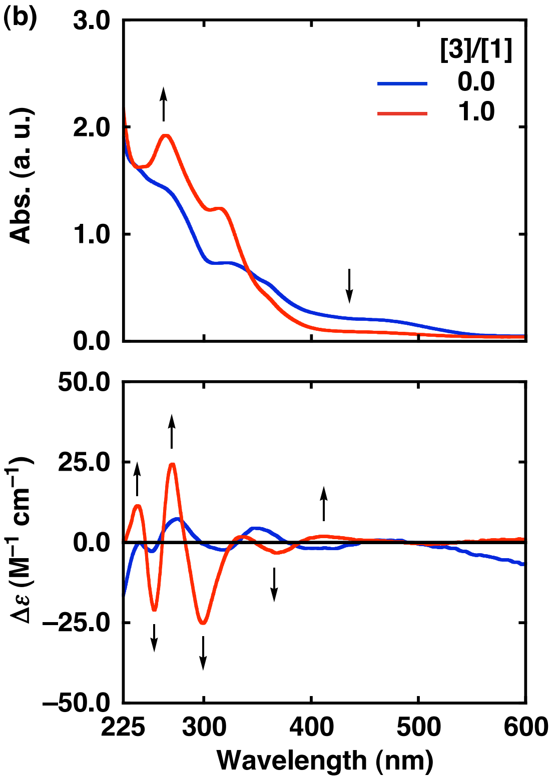


Fig. S1 Cyclic voltammograms of (a) *trans*-**1** and (b) *cis*-**1** (contaminated by 16% with *trans*-**1**) in CH_2Cl_2 (0.2 mM) containing 0.1 M Bu_4NPF_6 at 20 ºC.

3. Absorption and CD Spectral Changes of (1*S*,1'*S*)-1^{III} upon Reduction





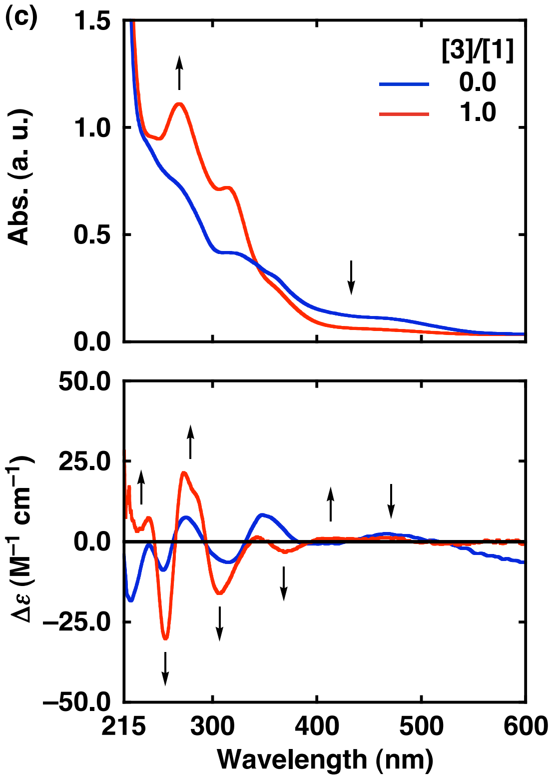


Fig. S2 (a) Absorption (upper) and CD (lower) spectral changes at 20 ºC of a CH_2Cl_2 solution of (1*S*,1'*S*)-*trans*-$\mathbf{1}^{III}$ (generated by oxidation of (1*S*,1'*S*)-*trans*-$\mathbf{1}^{II}$ (1.8×10^{-4} M) with a stoichiometric amount of **2**) upon addition of a stoichiometric amount of reductant **3**. (b) Absorption (upper) and CD (lower) spectral changes at 20 ºC of a CH_2Cl_2 solution of (1*S*,1'*S*)-$\mathbf{1}^{III}$ (generated by oxidation of (1*S*,1'*S*)-$\mathbf{1}^{II}$ (2.1×10^{-4} M; *trans*/*cis* = 16/84) with a stoichiometric amount of **2**) upon addition of a stoichiometric amount of reductant **3**. (c) Absorption (upper) and CD (lower) spectral changes at 20 ºC of a CH_2Cl_2 solution of (1*S*,1'*S*)-$\mathbf{1}^{III}$ (generated by oxidation of (1*S*,1'*S*)-$\mathbf{1}^{II}$ (1.1×10^{-4} M; *trans*/*cis* = 16/84) with a stoichiometric amount of **2**, followed by UV ($\lambda = 350 \pm 10$ nm) irradiation for 60 s) upon addition of a stoichiometric amount of reductant **3**. Arrows indicate directions of the spectral changes.

4. HPLC Analysis of (1*S*,1'*S*)-1

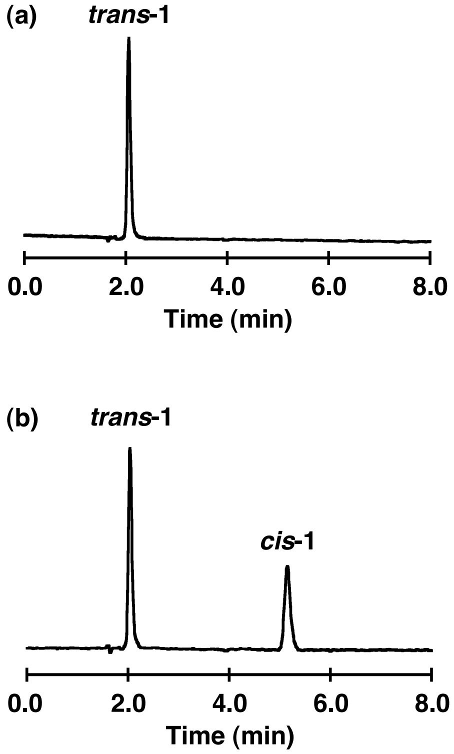


Fig. S3 HPLC chromatograms of (a) (1*S*,1'*S*)-*trans*-$\mathbf{1}^{\mathrm{II}}$ as a reference and (b) an isomer mixture of (1*S*,1'*S*)-$\mathbf{1}^{\mathrm{II}}$, generated from (1*S*,1'*S*)-$\mathbf{1}^{\mathrm{III}}$ (*trans*/*cis* = 16/84) by UV irradiation for 60 s, followed by addition of a stoichiometric amount of reductant **3**. HPLC was performed at 20 °C with a Mightysil Si60 column using CH_2Cl_2/hexane (40/60) as an eluent at a flow rate of 2.0 mL min^{-1}, and the chromatograms were obtained by monitoring the absorbance at 369.0 nm, an isosbestic point for the photoisomerization of $\mathbf{1}^{\mathrm{II}}$ in CH_2Cl_2/hexane (40/60).