Electronic Supplementary Information (ESI):

A redox-switchable [2]rotaxane in a liquid-crystalline state

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Experimental details for electrochemical and spectroscopic measurements.

The liquid-crystalline (LC) films of the bistable [2]rotaxane **1** were prepared by casting or spin-coating it onto indium-tin-oxide (ITO) glass electrodes from a THF solution (1–2 g L^{-1}). Cyclic voltammetry was performed on an ALS CHI 600B electrochemical analyzer using a three-electrode electrochemical cell equipped with a [2]rotaxane **1**-coated ITO working, and platinum counter and Ag^+/Ag reference electrodes in Bu_4NPF_6/MeCN (0.10 M) electrolyte. The potentials were calibrated with a Fc^+/Fc couple using ferrocene as an internal reference. Spectroelectrochemical measurements were conducted on a JASCO V-670 spectrometer, together with a potentiostat. The polymer electrolyte used for the electrochromic cells was prepared from a solution in MeCN (50 wt-%) containing polymethylmethacrylate (PMMA purchased from Aldrich, 7 wt-%, M_w = 120000 and 350000), propylene carbonate (PC, 40 wt-%), and $LiPF_6$ (3 wt-%). The resulting transparent viscous solution was spread over an ITO counter electrode, which was stored for 1 day at room temperature for self-supporting film formation. For the fabrication of a two-electrode electrochromic cell (Figure S1), the ITO counter electrode with the polymer electrolyte was set on the LC film-coated side of the ITO working electrode.

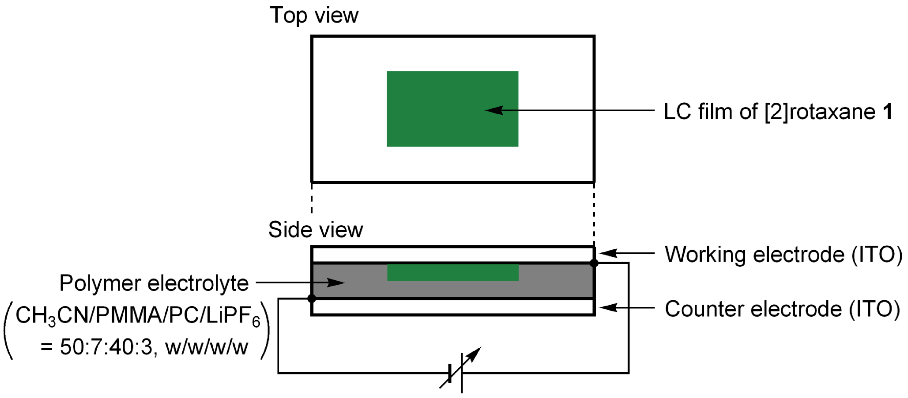

Fig. S1 Schematic illustration of a two-electrode electrochromic cell based on an LC film of the bistable [2]rotaxane **1**.

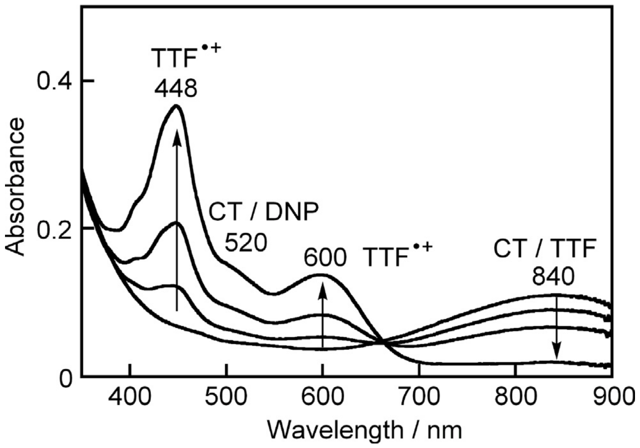

Fig. S2 UV–vis spectra of **1** (0.5 mM) recorded during the stepwise electrochemical oxidation in a Bu_4NPF_6/THF (0.10 M) electrolyte solution. Arrows indicate the direction of spectral changes. The absorption bands at 448 and 600 nm are ascribed to the formation of the TTF radical cation as the monomeric species.

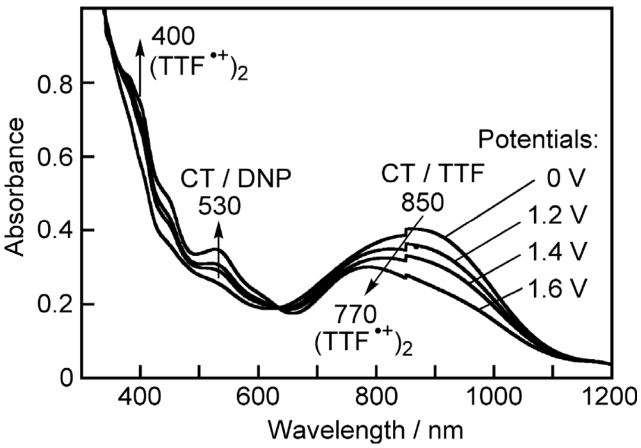

Fig. S3 Changes in absorption of the LC film of **1** in the electrochromic cell during the stepwise oxidation. Arrows indicate the direction of spectral changes.