

A Liquid-Crystalline Bistable [2]Rotaxane**

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Dedicated to Professor George W. Gray

Liquid crystals are ordered condensed states of molecules that can be used as dynamic functional materials which play significant roles in information transport, sensing, and catalysis, as well as in electrooptical displays.^[1] The ordering of liquid crystals is a cooperative phenomenon that is highly sensitive to small amounts of added dopant molecules. Stimuli-responsive bistable dopants have been exploited both as 1) a means of controlling bulk liquid-crystalline (LC) properties and as 2) a way of amplifying molecular motion into mechanical work.^[2] Despite the potentially useful characteristics of light- and heat-responsive systems, redox-responsive bistable liquid crystals are relatively unexplored materials.^[3] It was for this reason that we decided to try and align electrochemically switchable, bistable [2]rotaxanes^[4] within LC phases.^[5]

Bistable [2]rotaxanes^[4] based on the cyclobis(paraquat-*p*-phenylene)^[6] (CBPQT⁴⁺)/ π -donor motif have emerged as leading candidates for the fabrication of molecular electronic devices.^[7] The bistability in such switchable [2]rotaxanes relies on the ability of the CBPQT⁴⁺ ring to interact much more strongly with a tetrathiafulvalene (TTF) unit than with the less π -electron rich 1,5-dioxynaphthalene (DNP) unit, the two recognition sites commonly incorporated into such

bistable molecules.^[8] Switching is achieved by the reversible oxidation of TTF,^[9] firstly to its radical cation (TTF^{•+}) and then to its dication (TTF²⁺), thus producing Coulombic charge–charge repulsion between the oxidized TTF^{•+}/TTF²⁺ units and the CBPQT⁴⁺ ring. This repulsion results in the translation^[7b] of the CBPQT⁴⁺ ring to the DNP unit. Reduction of the positive charge(s) on the TTF^{•+}/TTF²⁺ units resets the switch over a period of time which is determined by the activation barrier ($\Delta G^\ddagger$). It has been demonstrated^[7c–j] that the switching process is a universal one: it occurs in the solution phase,^[7d] in polymer matrices,^[7f] within self-assembled monolayers^[7g] (SAMs), and in molecular switch tunnel junctions^[7a,c,h] (MSTJs). It transpires that the $\Delta G^\ddagger$ value for the resetting step increases when these bistable molecules are switched in progressively more condensed phases. Specifically, the value of $\Delta G^\ddagger$ increases from 16 to 18 and then finally to 22 kcal mol^{−1} on going from solution, to either polymer matrices or SAMs, and then to MSTJs, while the difference in the ground-state free energies (ΔG) for the two isomeric states of the switch remain essentially unchanged.^[7h]

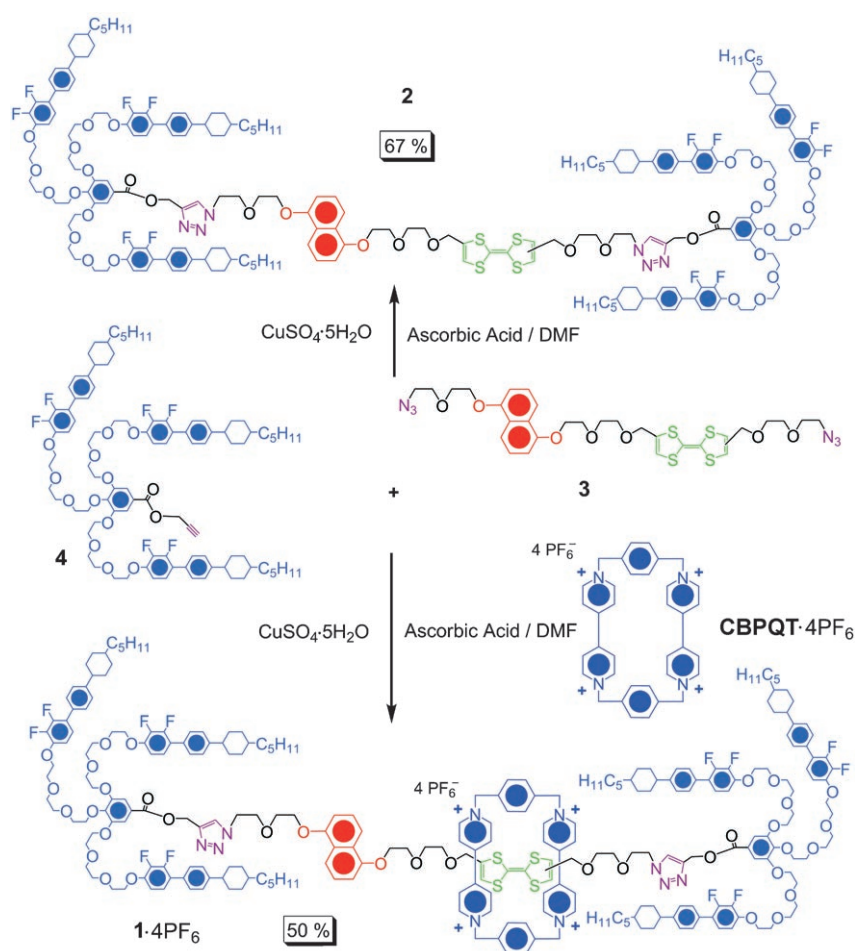
Here, we report the synthesis and characterization of a bistable [2]rotaxane functionalized with dendritic mesogenic stoppers and show that it exhibits a smectic A (S_A) phase over a wide temperature range, including at room temperature. It was expected that the formation of smectic A or C phases would align the bistable rotaxane moieties in layers in their dynamic states. The incorporation of the three rodlike cores with fluoro substituents into both the stoppers of an LC bistable [2]rotaxane **1**·4PF₆ and the control LC dumbbell-shaped compound **2** (Scheme 1) induced and stabilized an S_A LC phase from ambient temperature to over 100 °C. Initially, we faced a major hurdle in our attempts to attach dendritic mesogens in the form of stoppers associated with TTF/DNP-containing dumbbell-shaped compounds.^[10] We anticipated that further synthetic transformations on the mesogen-functionalized template might prove equally challenging. However, we recently developed a convergent threading-followed-by-stoppering approach^[11,12] for the synthesis of mechanically interlocked molecules that takes advantage of the high efficiency and mild conditions developed by Huisgen et al.^[13] for a Cu(I)-catalyzed 1,3-dipolar cycloaddition.^[14] This “click chemistry”^[15] approach has now been applied successfully^[16] of the LC bistable [2]rotaxane **1**·4PF₆ and the dumbbell-shaped compound **2** (Scheme 1). The rodlike cores of the attached LC dendrons, comprised of cyclohexylbiphenyl mesogens, tend to show^[17,18] LC smectic characteristics

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Scheme 1. Synthesis of the LC bistable [2]rotaxane **1·4PF₆**, and the model dumbbell-shaped compound **2**.

with melting points near ambient temperature. Another advantage of the cyclohexylbiphenyl mesogens is that they are electrochemically inactive—unlike most three-ringed mesogens comprised of ester groups which are electrochemically active^[18]—thus rendering them stable to electrochemical switching.

The synthesis (Scheme 1) of **1·4PF₆** was achieved by mixing **CBPQT·4PF₆** with the universal bistable [2]rotaxane precursor^[11b] **3** in DMF at room temperature. This strategy affords a green solution which is indicative of the formation of **[3CBPQT]·4PF₆**. The pseudorotaxane was stirred for 48 h in the presence of 1) two equivalents of the dendritic mesogen **4** functionalized with a propargyl ester, and 2) a catalytic amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and ascorbic acid as an in situ reductant. After chromatographic purification, **1·4PF₆** was isolated as a green solid in 50% yield. Following the same procedure in the absence of **CBPQT·4PF₆** provided (Scheme 1) the model dumbbell-shaped compound **2** as a yellow oil in 67% yield.

The LC bistable [2]rotaxane was characterized by electrospray ionization mass spectrometry (ESI-MS) and ¹H NMR spectroscopy. The ESI mass spectrum of **1·4PF₆** revealed signals at m/z 1294, 814, and 574, which correspond to the loss of two, three, and four PF_6^- ions. The ¹H NMR spectrum of

the intensely colored green solution of **1·4PF₆** in CD_3COCD_3 shows the presence of primarily (>95%) a single translational isomer in solution—the one in which the **CBPQT⁴⁺** ring encircles the TTF unit.^[8d,11b] The ¹H NMR spectrum also shows characteristic resonances that arise from the constitutionally heterotopic methine protons of the **CBPQT⁴⁺**-encircled TTF units: pairs of signals resonate at $\delta = 6.30, 6.20, 6.14,$ and 6.04 ppm. These resonances originate from the *cis* and *trans* isomers of such a TTF unit encircled by a **CBPQT⁴⁺** ring.^[19]

The bistable [2]rotaxane **1·4PF₆** shows LC behavior, as characterized by differential scanning calorimetry (DSC), polarized optical microscopy, small-angle X-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD) measurements. It exhibits (Figure 1) a glass transition (T_g) at 10°C and a subsequent *S_A* phase up to 150°C on heating, and shows (Figure 2) birefringence in a viscous fluid state at 25°C. This texture was observed between 10 and 150°C. As the temperature rises above 150°C, the sample gradually decomposes and hence the transition to an isotropic phase was not observed. The optical texture does not recover after the thermal decomposition. The SAXS pattern of **1·4PF₆** at 40°C shows (Figure 3) peaks with d spacings of

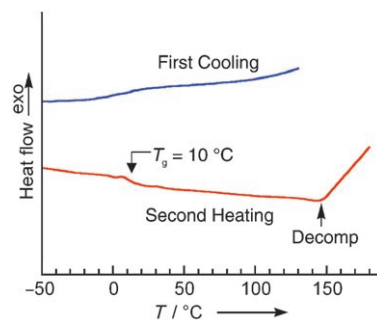


Figure 1. DSC thermogram of the LC bistable [2]rotaxane **1·4PF₆** at a scanning rate of $10^\circ\text{C min}^{-1}$.

83.0 (100), 41.5 (200), and $27.3 \text{ \AA}$ (300). A broad halo centered at $4.6 \text{ \AA}$ is observed in the WAXD pattern (see Figure S1 in the Supporting Information). These results suggest that the bistable [2]rotaxane shows an *S_A* phase. The layer spacing of about 8 nm observed (Figure 4) for the *S_A* phase corresponds to the extended molecular length of **1·4PF₆**. It is noteworthy that this molecule containing forklike mesogens exhibits a thermally stable *S_A* structure in spite of the presence of the tetracationic cyclophane that might disturb the LC molecular packing. The nano-segregation of

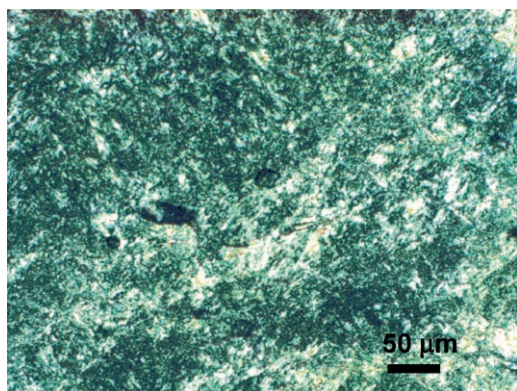


Figure 2. Polarized optical photomicrograph of the LC bistable [2]rotaxane **1-4** PF₆ at 25 °C.

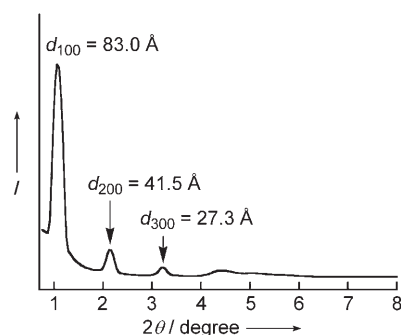


Figure 3. SAXS pattern of the LC bistable [2]rotaxane **1-4** PF₆ at 40 °C.

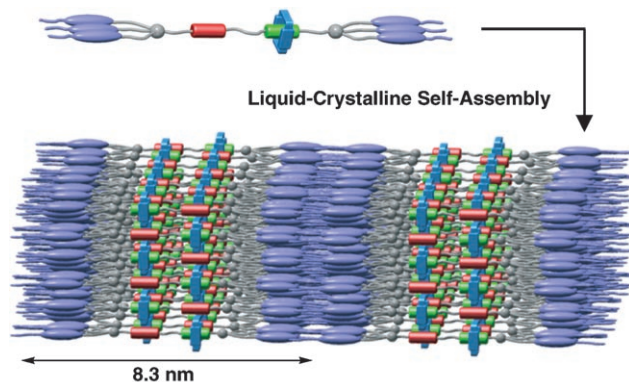


Figure 4. Schematic illustration of the supramolecular organization of the LC bistable [2]rotaxane **1-4** PF₆ into a smectic A phase.

the rotaxane and the mesogenic moieties leads to the formation of a stable layered LC state. The model dumbbell-shaped compound **2** also exhibits (see Figure S2 in the Supporting Information) an S_A phase from 7 to 146 °C. No thermal decomposition is observed at the S_A–isotropic phase transition, presumably because of the absence of the CBPQT⁴⁺ ring. The enthalpy change at the transition is 3.8 kcal mol^{−1}. The layer spacing found (see Figure S3 in the Supporting Information) for **2** is 7.1 nm at 40 °C, a distance which is smaller than that observed for the bistable [2]rotaxane **1-4** PF₆. This observation suggests that the central part of **2**

forms coiled structures on account of the absence of the CBPQT⁴⁺ ring, which increase its flexibility and decreases the volume of the molecule, thereby resulting in the decrease in the thickness of the smectic layer.

The switching of the LC bistable [2]rotaxane **1-4** PF₆ and the electrochemical response of the dendritic mesogen **4** in solution were characterized by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) analysis (see Figures S4 and S5, respectively, in the Supporting Information). Analysis of the measurements (see the Supporting Information) showed that the CBPQT⁴⁺ ring in **1-4** PF₆ encircles preferably the TTF unit in the starting state and moves to the DNP unit as soon as the TTF^{•+} radical cation is formed. The results, which are almost identical with those described for previously investigated^[8] bistable [2]rotaxanes, establish the bistability of the LC [2]rotaxane. The mesogenic dendron **4** showed (see Figure S4b in the Supporting Information) no electrochemical response over the potential range investigated.

The mechanical switching of the bistable [2]rotaxane **1-4** PF₆ has been further investigated in solution by UV/Vis spectroelectrochemistry (SEC; Figure 5). The band centered

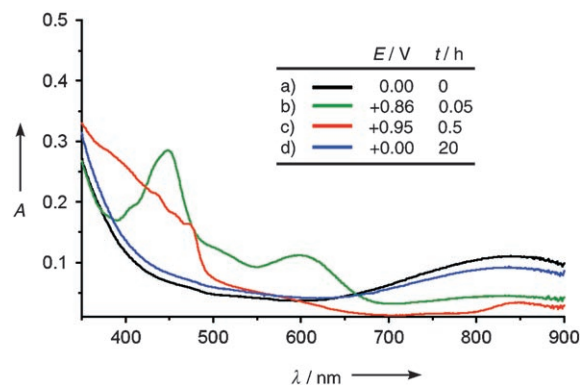


Figure 5. The results of spectroelectrochemistry measurements carried out on **1-4** PF₆. The UV/Vis spectra were recorded at a) the starting state ($E = 0.00$ V), b) at +0.86 V, c) at +0.95 V for 30 min, and d) at 0.00 V for 20 h. For more detailed experimental conditions, see the Supporting Information.

around 840 nm at the ground state originates from the CT interaction between TTF and CBPQT⁴⁺ (Figure 5a). The absorption spectrum starts to change around +0.62 V (versus Ag wire), and the bands corresponding to the TTF^{•+} absorption ($\lambda_{\text{max}} = 448$ nm and 600 nm) are observed at +0.86 V (Figure 5b). This process is accompanied by the bleaching of the CT band at 840 nm, an observation which indicates the movement of the CBPQT⁴⁺ ring away from the TTF radical cation to the DNP unit. The TTF^{•+} band disappears at +0.95 V: the band corresponding to the TTF²⁺ dication absorption, however, which is usually centered around $\lambda_{\text{max}} = 380$ nm,^[8] is not observed (Figure 5c). In addition, extra bands around 420–480 nm and 840 nm are observed. To shed light on these observations SEC measurements were also performed on the model dumbbell compound **2** and the mesogenic dendron **4** (see Figures S6 and S7,

respectively, in the Supporting Information). The latter shows no activity in the SEC measurements and so it is presumed that it cannot, by itself, account for the observed phenomena. Neither the TTF²⁺ dication absorption bands nor the extra bands around 420–480 nm and 840 nm could be observed for **2**. Recently, we have demonstrated^[11b] that the triazole unit does not exhibit any activity in the SEC measurements and therefore these two bands may arise from the CT interaction between the electron-deficient CBPQT⁴⁺ ring and the π -electron-rich mesogenic stoppers. As far as the bands for the TTF²⁺ dication are concerned, it seems that this species is not long-lasting in THF and so its bands cannot be detected clearly. The spectrum recorded at +0.95 V (Figure 5c) returns gradually to its original shape when the sample is left at room temperature at zero bias (Figure 5d), thus indicating that the electrochemical reaction is fully reversible.

Where conventional approaches to the synthesis of LC bistable [2]rotaxanes with large mesogenic stoppers have failed, click chemistry has once again come to the rescue. The attachment of LC dendrons to functional molecules such as fullerene,^[3a–e] ferrocene,^[3b,e] and silsesquioxane^[1g] has been reported. However, it should be noted that the current bistable [2]rotaxane is much larger and forms a more complex superstructure. It should also be noted that the LC rotaxane shows a stable smectic A phase over a wide temperature range—from ambient temperature to 150 °C. The next step in this program of research will be to effect redox switching of LC bistable [2]rotaxanes in devices and then monitoring what effect this mechanical switching has on the LC properties of the system as a whole.

Experimental Section

1-4PF₆: The TTF/DNP-containing diazide derivative^[11b] **3** (12.0 mg, 0.017 mmol), **CBPQT-4PF₆** (19.2 mg, 0.017 mmol), and the alkyne-functionalized mesogen **4** (56.8 mg, 0.035 mmol) were dissolved in DMF (0.4 mL) at room temperature to form a deep green solution. Stock solutions of CuSO₄·5H₂O in DMF (20 μ L, 1.60 μ mol, 0.008 M) and ascorbic acid in DMF (20 μ L, 3.30 μ mol, 0.016 M) were added. The solution was stirred at room temperature for 48 h. The crude product, obtained after the removal of the solvent, was purified by column chromatography (SiO₂: Me₂CO followed by a 1% w/v solution of NH₄PF₆ in Me₂CO). After collecting the green band, the Me₂CO was evaporated to a minimum volume, and the product was precipitated from this solution through the addition of an excess of cold water. The liquid-crystalline bistable [2]rotaxane **1-4PF₆** was isolated as a green solid (42 mg, 50% yield); ¹H NMR (600 MHz, CD₃CN): δ = 9.38–9.03 (m, 16H), 8.28–7.64 (m, 36H), 7.46–7.35 (m, 26H), 7.30–7.25 (m, 34H), 7.24–7.20 (m, 2H), 7.17–7.12 (m, 14H), 6.98–6.94 (m, 12H), 6.87–6.90 (m, 2H), 6.57–6.55 (m, 2H), 6.30, 6.20, 6.14, 6.04 (4 $\times$ s, 4H), 6.02–5.98 (m, 8H), 5.85 (brs, 1H), 5.83 (brs, 1H), 5.78 (brs, 1H), 5.71 (d, J = 12.9 Hz, 1H), 5.43 (s, 4H), 5.35 (s, 2H), 5.31 (s, 2H), 5.75–4.66 (m, 8H), 4.44 (brs, 2H), 4.39 (brs, 2H), 4.21 (brs, 40H), 4.08–4.02 (m, 36H), 3.09–3.77 (m, 60H), 3.68–3.65 (m, 52H), 2.51 (t, J = 12.50 Hz, 12H), 1.88–1.86 (m, 48H), 1.49 (dd, J = 12.5 Hz, 24H), 1.34–1.22 (m, 108H), 1.07 (dd, J = 12.5 Hz, 24H), 0.88 ppm (t, J = 6.8 Hz, 36H); MS (ESI): m/z = 2391 [M -2PF₆]²⁺, 1546 [M -3PF₆]³⁺, 1123 [M -4PF₆]⁴⁺; HRMS (ESI): m/z calcd for C₂₆₀H₃₁₂F₃₆N₁₀O₃₅P₄S₄: 1546.0450; found: 1546.0485 [M -3PF₆]³⁺.

2: The TTF/DNP-containing diazide derivative^[11b] **3** (5.0 mg, 0.007 mmol) and the alkyne-functionalized mesogen **4** (23.7 mg, 0.015 mmol) were dissolved in DMF (1.0 mL) at room temperature.

Stock solutions of CuSO₄·5H₂O in DMF (20 μ L, 0.70 μ mol, 0.003 M) and ascorbic acid in DMF (20 μ L, 1.40 μ mol, 0.006 M) were added. The resulting reaction mixture was stirred at room temperature for 48 h. The crude product, obtained after the removal of the solvent, was purified by column chromatography (SiO₂: CH₂Cl₂/EtOH 97:3) to give **2** (19 mg, 67%) as a yellow oil; ¹H NMR (600 MHz, CD₂Cl₂): δ = 7.88–7.86 (m, 3H), 7.82 (d, J = 8.4 Hz, 1H), 7.44–7.37 (m, 13H), 7.33–7.28 (m, 17H), 7.12–7.10 (m, 6H), 6.89–6.84 (m, 8H), 6.23 (s, 1H), 6.22 (s, 1H), 5.43 (s, 2H), 5.33 (s, 2H), 4.59 (t, J = 4.8 Hz, 2H), 4.55 (d, J = 4.8 Hz, 2H), 4.55 (d, J = 5.6 Hz, 2H), 4.23–4.14 (m, 20H), 4.03 (t, J = 4.9 Hz, 4H), 3.99–3.94 (m, 4H), 3.89–3.84 (m, 20H), 3.822–3.77 (m, 6H), 3.74–3.71 (m, 22H), 3.67–3.65 (m, 4H), 3.61–3.58 (m, 2H), 3.57–3.55 (m, 2H), 2.54 (t, J = 12.3 Hz, 6H), 1.95–1.88 (m, 24H), 1.54–1.48 (dd, J = 12.3 Hz, 12H), 1.35–1.29 (m, 54H), 1.13–1.07 (dd, J = 12.3 Hz, 12H), 0.95–0.93 ppm (t, J = 7.2 Hz, 18H); ¹³C NMR (150 MHz, CD₂Cl₂): δ = 166.1, 166.1, 154.8, 154.6, 152.7, 152.7, 148.5, 148.2, 148.1, 147.7, 147.7, 147.6, 147.6, 143.0, 142.9, 142.8, 141.3, 141.2, 135.8, 135.4, 135.0, 134.9, 134.8, 132.5, 129.0, 128.9, 127.4, 127.1, 127.0, 125.7, 125.5, 125.4, 125.3, 125.1, 124.1, 124.0, 123.9, 123.7, 123.6, 116.9, 116.6, 116.6, 114.9, 114.6, 110.6, 110.2, 109.1, 109.1, 106.1, 106.05, 72.7, 72.8, 71.3, 71.2, 71.1, 71.1, 70.7, 70.8, 70.2, 70.1, 70.0, 69.9, 69.8, 69.8, 69.74, 69.7, 69.6, 69.3, 69.2, 68.6, 68.5, 68.5 (2X), 68.4, 68.1, 58.6, 58.5, 50.8, 50.7, 44.7, 37.8, 37.7, 34.7, 34.0, 32.6, 27.0, 23.1, 14.3 ppm; MS (MALDI-TOF): m/z calcd for C₂₂₄H₂₈₀F₁₂N₆O₃₅S₄: 3969.9005; found: 3968.5286 [M -H]⁺.

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