Liquid Crystals

DOI: 10.1002/anie.200700305

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] ($CBPQT^{4+}$)/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 $CBPQT^{4+}$ 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 ($TTF^{+\bullet}$) and then to its dication (TTF^{2+}), thus producing Coulombic charge–charge repulsion between the oxidized $TTF^{+\bullet}/TTF^{2+}$ units and the $CBPQT^{4+}$ ring. This repulsion results in the translation[7h] of the $CBPQT^{4+}$ ring to the DNP unit. Reduction of the positive charge(s) on the $TTF^{+\bullet}/TTF^{2+}$ units resets the switch over a period of time which is determined by the activation barrier ($\Delta G^{\neq}$). It has been demonstrated[7c–i] 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 $\Delta G^{\neq}$ value for the resetting step increases when these bistable molecules are switched in progressively more condensed phases. Specifically, the value of $\Delta G^{\neq}$ 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**·4PF_6 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 in the efficient and convergent template-directed synthesis[16] of the LC bistable [2]rotaxane **1**·4PF_6 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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[**] The work at UCLA was supported by the Microelectronics Advanced Research Corporation (MARCO) and its focus center on Functional Engineered Architectonics (FENA), the Defense Advanced Research Project Agency (DARPA), and the Center for Nanoscale Innovation for Defense (CNID). The research at the University of Tokyo was supported by a Grant-in-Aid for Creative Scientific Research of "Invention of Conjugated Electronic Structures and Novel Functions" (no. 16GS0209) and for Scientific Research (B) from the Japan Society for the Promotion of Science (JSPS).

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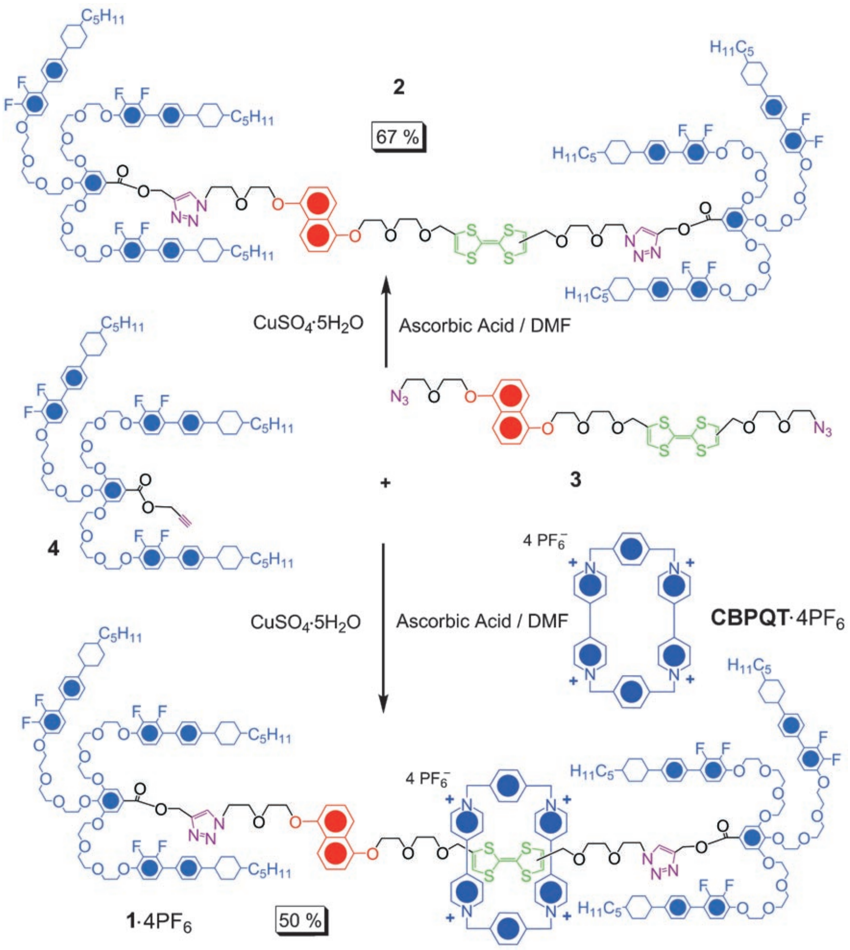

Scheme 1. Synthesis of the LC bistable [2]rotaxane **1**·4 PF_6, and the model dumbbell-shaped compound **2**.

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**·4 PF_6 was achieved by mixing **CBPQT**·4 PF_6 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 [**3**⊂**CBPQT**]·4 PF_6. 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 $CuSO_4$·5 H_2O and ascorbic acid as an in situ reductant. After chromatographic purification, **1**·4 PF_6 was isolated as a green solid in 50% yield. Following the same procedure in the absence of **CBPQT**·4 PF_6 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 ^{1}H NMR spectroscopy. The ESI mass spectrum of **1**·4 PF_6 revealed signals at m/z 1294, 814, and 574, which correspond to the loss of two, three, and four PF_6^- ions. The ^{1}H NMR spectrum of the intensely colored green solution of **1**·4 PF_6 in CD_3COCD_3 shows the presence of primarily (> 95%) a single translational isomer in solution—the one in which the CBPQT^{4+} ring encircles the TTF unit.[8d,11b] The ^{1}H NMR spectrum also shows characteristic resonances that arise from the constitutionally heterotopic methine protons of the CBPQT^{4+}-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 CBPQT^{4+} ring.[19]

The bistable [2]rotaxane **1**·4 PF_6 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) bifringence 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**·4 PF_6 at 40 °C shows (Figure 3) peaks with d spacings of 83.0 (100), 41.5 (200), and 27.3 Å (300). A broad halo centered at 4.6 Å 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**·4 PF_6. 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

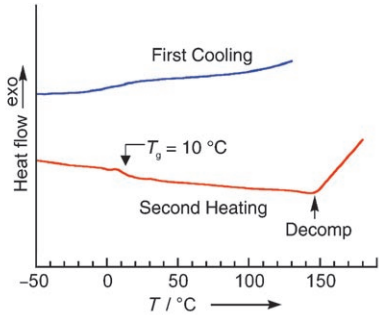

Figure 1. DSC thermogram of the LC bistable [2]rotaxane **1**·4 PF_6 at a scanning rate of 10 °C min^{-1}.

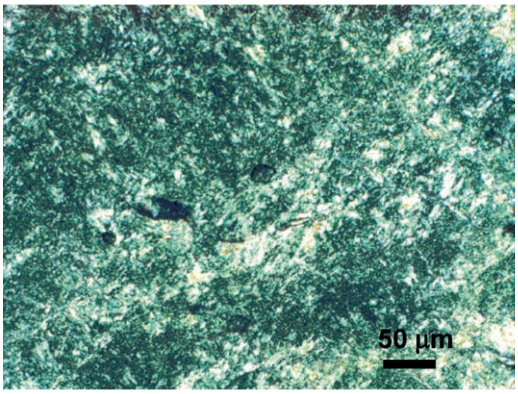

Figure 2. Polarized optical photomicrograph of the LC bistable [2]rotaxane **1**·4 PF_6 at 25 °C.

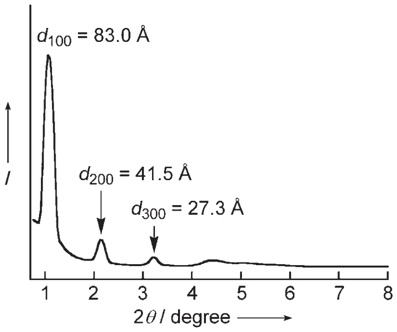

Figure 3. SAXS pattern of the LC bistable [2]rotaxane **1**·4 PF_6 at 40 °C.

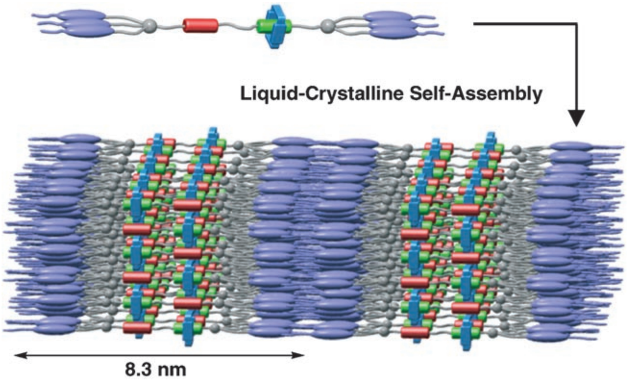

Figure 4. Schematic illustration of the supramolecular organization of the LC bistable [2]rotaxane **1**·4 PF_6 into a smectic A phase.

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 $CBPQT^{4+}$ 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 PF_6. This observation suggests that the central part of **2** forms coiled structures on account of the absence of the $CBPQT^{4+}$ 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 PF_6 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 $CBPQT^{4+}$ ring in **1**·4 PF_6 encircles preferably the TTF unit in the starting state and moves to the DNP unit as soon as the $TTF^{\bullet+}$ 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 PF_6 has been further investigated in solution by UV/Vis spectroelectrochemistry (SEC; Figure 5). The band centered around 840 nm at the ground state originates from the CT interaction between TTF and $CBPQT^{4+}$ (Figure 5 a). The absorption spectrum starts to change around +0.62 V (versus Ag wire), and the bands corresponding to the $TTF^{\bullet+}$ absorption (λ_{max} = 448 nm and 600 nm) are observed at +0.86 V (Figure 5 b). This process is accompanied by the bleaching of the CT band at 840 nm, an observation which indicates the movement of the $CBPQT^{4+}$ ring away from the TTF radical cation to the DNP unit. The $TTF^{+\bullet}$ band disappears at +0.95 V: the band corresponding to the TTF^{2+} dication absorption, however, which is usually centered around λ_{max} = 380 nm,[8] is not observed (Figure 5 c). 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,

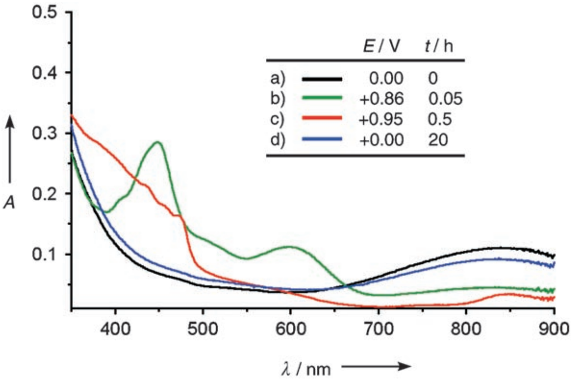

Figure 5. The results of spectroelectrochemistry measurements carried out on **1**·4 PF_6. The UV/Vis spectra were recorded at a) the starting state (E = 0.00 V), b) at +0.86 V, c) at +0.95 V for 30 min, and d) at 0.00 V for 20 h. For more detailed experimental conditions, see the Supporting Information.

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 TTF^{2+} 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 $CBPQT^{4+}$ ring and the π-electron-rich mesogenic stoppers. As far as the bands for the TTF^{2+} 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$\cdot 4PF_6$: The TTF/DNP-containing diazide derivative[11b] **3** (12.0 mg, 0.017 mmol), **CBPQT**$\cdot 4PF_6$ (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 $CuSO_4 \cdot 5H_2O$ in DMF (20 μL, 1.60 μmol, 0.008 M) and ascorbic acid in DMF (20 μL, 3.30 μmol, 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 (SiO_2: Me_2CO followed by a 1% w/v solution of NH_4PF_6 in Me_2CO). After collecting the green band, the Me_2CO 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**$\cdot 4PF_6$ was isolated as a green solid (42 mg, 50% yield); ^1H NMR (600 MHz, CD_3CN): $\delta = 9.38$–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 × s, 4H), 6.02–5.98 (m, 8H), 5.85 (br s, 1H), 5.83 (br s, 1H), 5.78 (br s, 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 (br s, 2H), 4.39 (br s, 2H), 4.21 (br s, 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): $m/z = 2391$ $[M-2PF_6]^{2+}$, 1546 $[M-3PF_6]^{3+}$, 1123 $[M-4PF_6]^{4+}$; HRMS (ESI): m/z calcd for $C_{260}H_{312}F_{36}N_{10}O_{35}P_4S_4$: 1546.0450; found: 1546.0485 $[M-3PF_6]^{3+}$.

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 $CuSO_4 \cdot 5H_2O$ in DMF (20 μL, 0.70 μmol, 0.003 M) and ascorbic acid in DMF (20 μL, 1.40 μmol, 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 (SiO_2: CH_2Cl_2/EtOH 97:3) to give **2** (19 mg, 67%) as a yellow oil; ^1H NMR (600 MHz, CD_2Cl_2): $\delta = 7.88$–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); ^{13}C NMR (150 MHz, CD_2Cl_2): $\delta = 166.1$, 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, 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 $C_{224}H_{280}F_{12}N_6O_{35}S_4$: 3969.9005; found: 3968.5286 $[M-H]^+$.

Received: January 23, 2007

Keywords: bistability · click chemistry · liquid crystals · rotaxanes · template synthesis

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