ORGANIC LETTERS

2007
Vol. 9, No. 7
1287−1290

A Clicked Bistable [2]Rotaxane

Ivan Aprahamian,[†] William R. Dichtel,[†,‡] Taichi Ikeda,[†] James R. Heath,*[,‡] and J. Fraser Stoddart*[,†]

California NanoSystems Institute, and Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095, and Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

stoddart@chem.ucla.edu

Received January 8, 2007

ABSTRACT

A universal diazide-terminated polyether, incorporating tetrathiafulvalene (TTF, green) and 1,5-dioxynaphthalene (DNP, red) units, was prepared and subsequently employed in the template-directed synthesis of a switchable donor/acceptor [2]rotaxane. The triazole rings (magenta), which are introduced into the rotaxane during requisite click reactions, do not present themselves as competing recognition sites for the tetracationic cyclophane (blue) as it is induced to switch between the TTF unit, when it becomes dicationic (green adorned with yellow extremities), and the DNP unit.

Switchable donor/acceptor rotaxanes[1] incorporating cyclobis(paraquat-*p*-phenylene)[2] ($CBPQT^{4+}$) as their ring component(s) have found[3,4] applications in the fabrication of Molecular Electronic Devices (MEDs) and as actuating materials in NanoElectroMechanical Systems (NEMS). Until recently, the synthesis of donor/acceptor catenanes and rotaxanes[5] has involved[6] the "clipping" of the π-accepting $CBPQT^{4+}$ ring, using appropriate acyclic precursors around rings and dumbbells containing π-donating units. Since the $CBPQT^{4+}$ ring in these donor/acceptor catenanes and rotaxanes is destroyed by reducing agents, as well as by bases and nucleophiles, the "clipping" reaction is almost always the final step in their synthesis. In practice, these constraints put severe limitations not only on yields, but also on the structural complexity of the mechanically interlocked compounds that can be produced.

Recently, we have described[7] a "threading-followed-by-stoppering" approach that utilizes the high efficiency and

[†] University of California, Los Angeles.
[‡] California Institute of Technology.

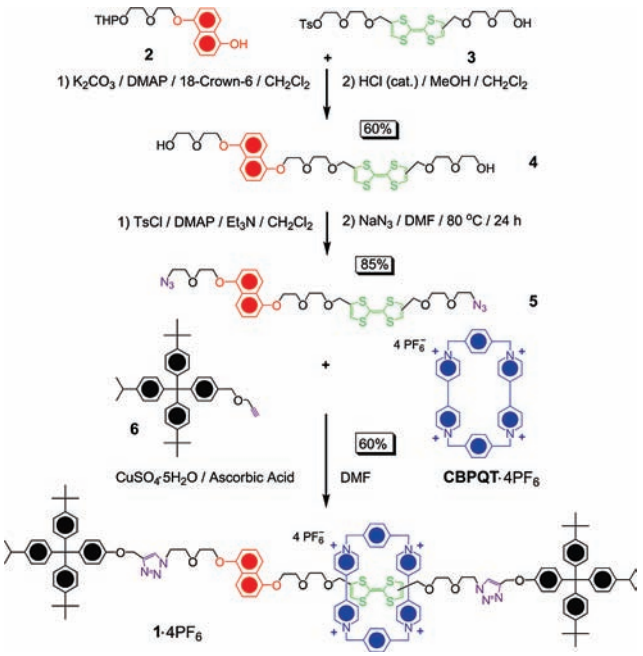
(1) (a) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725−2828. (b) Jäger, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 930−944. (c) Hubin, T. J.; Kolchinski, A. G.; Vance, A. L.; Busch, D. H. *Adv. Supramol. Chem.* **1999**, *5*, 237−357. (d) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A;. Dress, R.; Ishow, E.; Kocian, O.; Preece, J. A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Wenger, S. *Chem. Eur. J.* **2000**, *6*, 3558−3574. (e) Stoddart, J. F.; Tseng, H.-R. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4797−4800. (f) Jeppesen, J. O.; Vignon, S. A.; Stoddart, J. F. *Chem. Eur. J.* **2003**, *9*, 4611−4625. For bistable rotaxanes based on a hydrogen bonding recognition motif, see: (g) Gatti, G.; León, S.; Wong, J. K. Y.; Bottari, G.; Altieri, A.; Morales, M. A. F.; Teat, S. J.; Frochot, C.; Leigh, D. A.; Brouwer, A. M.; Zerbetto, F. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 10−14. (h) Leigh, D. A.; Pérez, E. M. *Chem. Commun.* **2004**, 2262−2263. (i) Marlin, D. S.; Gonzalez, C.; Leigh, D. A.; Slawin, A. M. Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 77−83. (j) Serreli, V.; Lee, C.-F.; Kay, E. R.; Leigh, D. A. *Nature* **2007**, *445*, 523−527.

(2) (a) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1547−1550. (b) Anelli, P.-L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193−218. (c) Asakawa, M.; Dehaen, W.; L'abbé, G.; Menzer, S.; Nouwen, J.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *J. Org. Chem.* **1996**, *61*, 9591−9595. (d) Doddi, G.; Ercolani, G.; Mencarelli, P.; Piermattei, A. *J. Org. Chem.* **2005**, *70*, 3761−3764.

10.1021/ol070052u CCC: $37.00
Published on Web 02/28/2007

functional group tolerance, together with the mild reaction conditions associated with "click" chemistry,[8] to overcome these limitations, and results in the efficient and convergent preparation of [2]-, [3]-, and [4]rotaxanes, as well as of [2]-catenanes. This synthetic strategy relies upon the formation of pseudorotaxanes, wherein the π-electron-deficient $CBPQT^{4+}$ ring threads linear molecules containing π-electron-rich recognition units and terminated by azide and/or alkyne functions which can undergo Cu(I)-catalyzed Huisgen[9] 1,3-dipolar cycloadditions,[10] forming rotaxanes and catenanes incorporating 1,2,3-triazole units. Herein, we report the template-directed synthesis[11] (Scheme 1) of a redox-switchable

Scheme 1. Synthesis of the Bistable [2]Rotaxane **1**·$4PF_6$



[2]rotaxane **1**·$4PF_6$, comprised of a $CBPQT^{4+}$ ring, which can be electrochemically induced to move between tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) recognition units[12] located along its dumbbell component. This bistable compound was characterized by (i) electrospray ionization mass spectrometry (ESI-MS) and (ii) ^{1}H NMR spectroscopy, and its switching behavior was demonstrated by using (iii) cyclic voltammetry (CV), (iv) differential pulse voltammetry (DPV), and (v) UV−vis spectroelectrochemistry (SEC).

The acyclic polyether **4**, incorporating both TTF and DNP units, was prepared in 60% yield by the alkylation (K_2CO_3/DMAP/18C6/CH_2Cl_2) of the known[13] THP-protected DNP

(3) (a) Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172−1175. (b) Collier, C. P.; Jeppesen, J. O.; Luo, Y.; Perkins, J.; Wong, E. W.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 12632−12641. (c) Luo, Y.; Collier, C. P.; Jeppesen, J. O.; Nielsen, K. A.; DeIonno, E.; Ho, G.; Perkins, J.; Tseng, H.-R.; Yamamoto, T.; Stoddart, J. F.; Heath, J. R. *ChemPhysChem* **2002**, *3*, 519−525. (d) Flood, A. H.; Peters, A. J.; Vignon, S. A.; Steuerman, D. W.; Tseng, H.-R.; Kang, S.; Heath, J. R.; Stoddart, J. F. *Chem. Eur. J.* **2004**, *10*, 6558−6564. (e) Diehl, M. R.; Steuerman, D. W.; Tseng, H.-R.; Vignon, S. A.; Star, A.; Celestre, P. C.; Stoddart, J. F.; Heath, J. R. *ChemPhysChem* **2003**, *4*, 1335−1339. (f) Steuerman, D. W.; Tseng, H.-R.; Peters, A. J.; Flood, A. H.; Jeppesen, J. O.; Nielsen, K. A.; Stoddart, J. F.; Heath, J. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6486−6491. (g) Choi, J. W.; Flood, A. H.; Steuerman, D.; Nygaard, S.; Braunschweig, A. B.; Moonen, N. N. P.; Laursen, B. W.; Luo, Y.; DeIonno, E.; Peters, A. J.; Jeppesen, J. O.; Xu, K.; Stoddart, J. F.; Heath, J. R. *Chem. Eur. J.* **2006**, *12*, 261−279. (h) DeIonno, E.; Tseng, H.-R.; Harvey, D. D.; Stoddart, J. F.; Heath, J. R. *J. Phys. Chem. B* **2006**, *110*, 7609−7612. (i) Saha, S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 77−92. (j) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72−191.

(4) (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391. (b) Ballardini, R.; Balzani, V.; Dehaen, W.; Dell'Erba, A. E.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. *Eur. J. Org. Chem.* **2000**, 591−602. (c) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines−A Journey into the Nano World*; Wiley-VCH: Weinheim, Germany, 2003. (d) Badjić, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845−1849. (e) Tseng, H.-R.; Wu, D. M.; Fang, N. X. L.; Zhang, X.; Stoddart, J. F. *ChemPhysChem* **2004**, *5*, 111−116. (f) Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *Top. Curr. Chem.* **2005**, *262*, 29−62. (g) Moonen, N. N. P.; Flood, A. H.; Fernandez, J. M.; Stoddart, J. F. *Top. Curr. Chem.* **2005**, *262*, 99−132. (h) Braunschweig, A. B.; Northrop, B. H.; Stoddart, J. F. *J. Mater. Chem.* **2006**, *16*, 32−44. (i) Green, J. E.; Choi, J. W.; Boukai, A.; Bunimovich, Y.; Johnston-Halperin, E.; DeIonno, E.; Luo, Y.; Sheriff, B. A.; Xu, K.; Shin, Y. S.; Tseng, H.-R.; Stoddart, J. F.; Heath, J. R. *Nature* **2007**, *445*, 414−417. (j) Ball, P. *Nature* **2007**, *445*, 362−363.

(5) (a) Schill, G. *Catenanes, Rotaxanes and Knots*; Academic Press: New York, 1971. (b) *Molecular Catenanes, Rotaxanes and Knots*; Sauvage, J.-P., Dietrich-Buchecker, C. O., Eds; Wiley-VCH: Weinheim, Germany, 1999.

(6) (a) Ashton, P. R.; Goodnow, T. T.; Kaifer, A. E.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1396−1399. (b) Anelli, P.-L.; Spencer, N.; Stoddart, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 5131−5133.

(7) (a) Dichtel, W. R.; Miljanić, O. Š.; Spruell, J. M.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10388−10390. (b) Miljanić, O. Š.; Dichtel, W. R.; Mortezaei, S.; Stoddart, J. F. *Org. Lett.* **2006**, *8*, 4835−4838.

(8) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021.

(9) (a) Huisgen, R. *Pure. Appl. Chem.* **1989**, *61*, 613−628. (b) Huisgen, R.; Szeimies, G.; Möbius, L. *Chem. Ber.* **1967**, *100*, 2494−2507. (c) Bastide, J.; Hamelin, J.; Texier, F.; Ven, V. Q. *Bull. Chim. Soc. Fr.* **1973**, 2555−2579. (d) Bastide, J.; Hamelin, J.; Texier, F.; Ven, V. Q. *Bull. Chim. Soc. Fr.* **1973**, 2871−2887.

(10) (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596−2599. (b) Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057−3064.

(11) (a) Busch, D. H.; Stephenson, N. A. *Coord. Chem. Rev.* **1990**, *100*, 119−154. (b) Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *Acc. Chem. Res.* **1993**, *26*, 469−475. (c) Breault, G. A.; Hunter, C. A.; Mayers, P. C. *Tetrahedron* **1999**, *55*, 5265−5293. (d) *Templated Organic Synthesis*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 2000. (e) Hubin, T. J.; Busch, D. H. *Coord. Chem. Rev.* **2000**, *200*, 5−52. (f) Blanco, M.-J.; Chambron, J.-C.; Jiménez, M. C.; Sauvage, J.-P. *Top. Stereochem.* **2003**, *23*, 125−173. (g) Busch, D. H. *Top. Curr. Chem.* **2005**, *249*, 1−65.

(12) (a) Jeppesen, J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Org. Lett.* **2000**, *2*, 3547−3550. (b) Jeppesen, J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1216−1221. (c) Yamamoto, T.; Tseng, H.-R.; Stoddart, J. F.; Balzani, V.; Credi, A.; Marchioni, F.; Venturi, M. *Collect. Czech. Chem. Commun.* **2003**, *68*, 1488−1514. (d) Tseng, H.-R.; Vignon, S. A.; Celestre, P. C.; Perkins, J.; Jeppesen, J. O.; Di Fabio, A.; Ballardini, R.; Gandolfi, M. T.; Venturi, M.; Balzani, V.; Stoddart, J. F. *Chem. Eur. J.* **2004**, *10*, 155−172. (e) Tseng, H.-R.; Vignon, S. A.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1491−1495. (f) Tseng, H.-R.; Vignon, S. A.; Celestre, P. C.; Perkins, J.; Jeppesen, J. O.; Di Fabio, A.; Ballardini, R.; Gandolfi, M. T.; Venturi, M.; Balzani, V.; Stoddart, J. F. *Chem. Eur. J.* **2004**, *10*, 155−172. (g) Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H.-R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C.-M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9745−9759. (h) Jeppesen, J. O.; Nygaard, S.; Vignon, S. A.; Stoddart, J. F. *Eur. J. Org. Chem.* **2005**, 196−220. (i) Nygaard, S.; Leung, K. C.-F.; Aprahamian, I.; Ikeda, T.; Saha, S.; Laursen, B. W.; Kim, S.-Y.; Hansen, S. W.; Stein, P. C.; Flood, A. H.; Stoddart, J. F.; Jeppesen, J. O. *J. Am. Chem. Soc.* **2006**, *128*, 960−970.

(13) Yamamoto, T.; Tseng, H.-R.; Stoddart, J. F.; Balzani, V.; Credi, A.; Marchioni, F.; Venturi, M. *Collect. Czech. Chem. Commun.* **2003**, *68*, 1488−1514.

derivative **2** with the TTF-containing monotosylate[12d] **3**, followed by deprotection (HCl/MeOH/CH_2Cl_2). Tosylation (TsCl/DMAP/NEt_3/CH_2Cl_2) of **4** afforded a ditosylate, which, on reaction with NaN_3 in DMF at 80 °C for 1 day, gave **5** in 85% yield. When the diazide **5** was mixed with 1.1 equiv of **CBPQT**·$4PF_6$ in DMF, an intense green solution was obtained immediately, indicating the formation of [**5** ⊂ **CBPQT**]·$4PF_6$. This pseudorotaxane was stirred for 2 days in the presence of (i) 2.0 equivs of the propargyl ether functionalized stopper[7a] **6** and (ii) a catalytic amount of $CuSO_4$·$5H_2O$ and ascorbic acid as an in situ reductant. Chromatographic purification (SiO_2: 1% w/v NH_4PF_6/Me_2CO) of the crude product from the reaction mixture afforded **1**·$4PF_6$ as a green solid in 60% yield. The ESI-MS of this solid revealed peaks at *m*/*z* 1294, 814, and 574, corresponding to the loss of two, three, and four PF_6^- anions, respectively, from the bistable [2]rotaxane, described by the structural formula **1**·$4PF_6$ in Scheme 1.

The ^{1}H NMR spectrum of **1**·$4PF_6$ in CD_3COCD_3 indicated the presence of predominantly (>95%) a single translational isomer in solution—namely, the one in which the $CBPQT^{4+}$ ring encircles the TTF unit.[10e] This assignment follows from the observation that (i) the signals for the DNP protons are all to be found at low field and (ii) the fact that no correlations are observed in the COSY spectrum involving high-field DNP proton resonances—a characteristic spectroscopic signature[12] when the DNP unit is encircled by the $CBPQT^{4+}$ ring. This observation indicates that the presence of triazole rings in **1**·$4PF_6$ does not influence the isomeric distribution between the only two translational isomers that are populated to any extent. The NOESY spectrum shows no correlations between the triazole ring proton and the $CBPQT^{4+}$ ring protons, indicating that the 1,2,3-triazole rings do not act as recognition units toward the $CBPQT^{4+}$ ring.[14]

The electrochemical behavior of **1**·$4PF_6$, as indicated (Figure 1) by CV measurements, is similar to those previously reported[12d,g] for TTF/DNP two-station [2]rotaxanes, suggesting that the presence of the two triazole rings does not affect either the thermodynamics or the kinetics of the switching process. The first oxidation peak for the TTF unit, which is observed[15] around +0.50 V for "free" TTF, was hardly detectable (Figure 1) in the anodic scan. DPV analysis revealed (Figure 2a) a small peak at +0.44 V. These observations show that the existence of "free" TTF is associated with a very small amount of the minor translational isomer of **1**·$4PF_6$ at equilibrium, supporting the conclusions reached by NMR spectroscopy. The first substantial TTF oxidation peak is shifted to higher potential and overlaps (Figure 1) with the second oxidation peak. In the DPV analysis, the peak maxima for the first and second

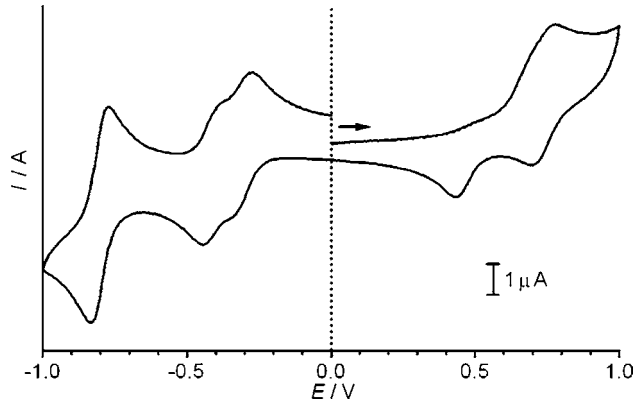


Figure 1. Cyclic voltammetry of the bistable [2]rotaxane **1**·$4PF_6$. The cyclic voltammogram was recorded at 200 mV s^{-1} in argon-purged MeCN. The concentrations of the **1**·$4PF_6$ sample and the supporting electrolyte **TBA**·PF_6 were 0.5 mM and 0.1 M, respectively.

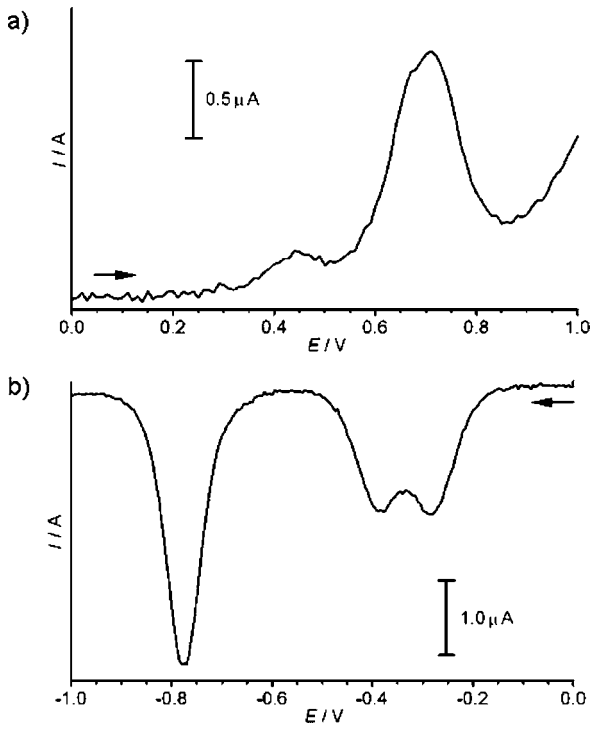


Figure 2. DPV results of the bistable [2]rotaxane **1**·$4PF_6$: (a) oxidation region (E > 0 V) and (b) reduction region (E < 0 V). All the data were recorded in argon-purged MeCN at 298 K.

(14) The ^{1}H NMR spectrum shows characteristic resonances that arise from the constitutionally heterotopic methine protons of the $CBPQT^{4+}$-encircled TTF units: pairs of signals resonate at δ 6.14, 6.03 (2H) and 5.87 ppm. These resonances originate from the *cis* and *trans* isomers of such a TTF unit encircled by a $CBPQT^{4+}$ ring. See: (a) Kreitsberga, Y. N.; Liepin'sh, É.; Mazheika, I. B.; Neilands, O. Y. *Zh. Org. Khim.* **1986**, *22*, 416−420. (b) Souizi, A.; Robert, A.; Batail, P.; Ouahab, L. *J. Org. Chem.* **1987**, *52*, 1610−1611. (c) Ballardini, R.; Balzani, V.; Becher, J.; Di Fabio, A.; Gandolfi, M. T.; Mattersteig, G.; Nielsen, M. B.; Raymo, F. M.; Rowan, S. J.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2000**, *65*, 4120−4126. (d) Liu, Y.; Flood, A. H.; Moskowitz, R. M.; Stoddart, J. F. *Chem. Eur. J.* **2004**, *11*, 369−385.

(15) (a) Balzani, V.; Credi, A.; Mattersteig, G.; Matthews, O. A.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2000**, *65*, 1924−1936. (b) Ballardini, R.; Balzani, V.; Di Fabio, A.; Gandolfi, M. T.; Becher, J.; Lau, J.; Nielsen, M. B.; Stoddart, J. F. *New J. Chem.* **2001**, *25*, 293−298. (c) Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Mattersteig, G.; Matthews, O. A.; Montalti, M.; Spencer, N.; Stoddart, J. F.; Venturi, M. *Chem. Eur. J.* **1997**, *3*, 1992−1996.

oxidations were to be found (Figure 2a) at +0.66 and +0.73 V, respectively. The first oxidation potential of the $CBPQT^{4+}$-encircled TTF unit is shifted to higher potential because of the lowering[16] of the HOMO energy level caused by the encapsulation by the $CBPQT^{4+}$ ring. The second oxidation potential (DPV peak maximum observed[15] at +0.73 V) of the TTF unit in **1**·$4PF_6$ is not influenced by the $CBPQT^{4+}$ ring, indicating that it has already moved to the DNP unit. In the cathodic scan, two well-separated CV peaks are observed, corresponding to the reduction of the oxidized $TTF^{\bullet+}$ radical cation and the TTF^{2+} dication. The positions of these peaks are consistent with those for "free" TTF units, an observation which means that the $CBPQT^{4+}$ ring remains on the DNP unit during the process.

In the reduction region phase of the CV, a typical[12e,2b,17] splitting of the first two-electron reduction peak and no splitting of the second two-electron reduction peak of the $CBPQT^{4+}$ ring are observed (Figure 1). DPV analysis reveals (Figure 2b) three clear peaks at −0.28, −0.39, and −0.78 V (vs SCE).

The splitting of the first reduction peak can be attributed to (i) the electronic mixing from the charge transfer (CT) interaction[16,17] between TTF and $CBPQT^{4+}$ and/or (ii) the generation of asymmetry by the back-folding[2b,12g,15a] of the aromatic rings in the stoppers. The absence of any splitting in the second peak indicates that the CT interaction between TTF and $CBPQT^{2+/\bullet+}$ is much weaker.

The mechanical switching in $\mathbf{1}^{4+}$ has also been investigated (Figure 3) by SEC. The band centered around 840 nm in the ground state ($E = 0$ V) originates[2b,12e,15a,18] from the CT interaction between TTF and $CBPQT^{4+}$. The absorption spectrum starts to change around +0.50 V (vs Ag wire), and the peaks ($\lambda_{max} = 445$ and 595 nm) corresponding to the $TTF^{\bullet+}$ absorption increase until the applied potential reaches +0.80 V. This process is accompanied by the bleaching of the CT band around 840 nm, an observation which indicates that the $CBPQT^{4+}$ ring has moved away from the $TTF^{\bullet+}$ radical cation to the DNP unit. When the applied potential is increased above +0.80 V, the absorption band of the $TTF^{\bullet+}$ radical cation starts to bleach and a new peak ($\lambda_{max} = 380$ nm), assignable to the TTF^{2+} dication, emerges (Figure 3).

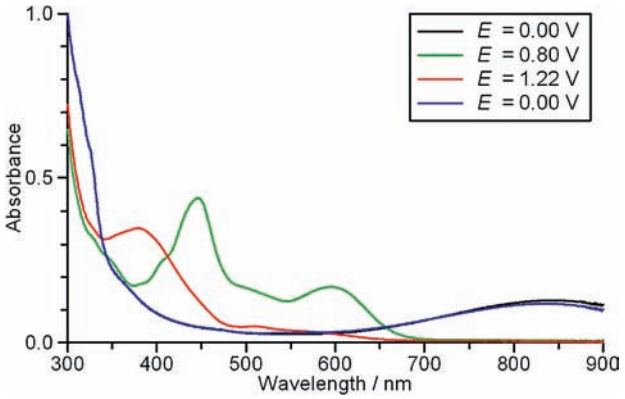


Figure 3. The change in UV−vis spectra during the SEC measurements. The applied potential changes from $E = 0$ to 1.22 V and then back to $E = 0$ V. All the data were recorded at 0.25 mV s^{-1} in argon-purged MeCN. The concentrations of the sample and supporting electrolyte were 0.5 mM and 0.1 M, respectively.

At $E = 1.22$ V, a small absorption peak at around 530 nm associated with the CT band between DNP and $CBPQT^{4+}$ can be detected. When the applied potential is switched off ($E = 0$ V), the spectrum gradually changes back to its original form, verifying the full reversibility of the electrochemical reaction.

It is now clear that a "threading-followed-by-stoppering" synthetic strategy for the making of redox switchable donor/acceptor [2]rotaxanes by click chemistry is a viable one, and promises to gain in popularity during the furtherance of a much wider range of applications for these mechanically operated molecular switches.

Acknowledgment. This work was supported by the Microelectronics Advanced Research Corporation (MARCO) and its focus center on Functional Engineered NanoArchitectonics (FENA) and the Defense Advanced Research Projects Agency (DARPA) and the center for Nanoscale Innovative Defense (CNID).

Supporting Information Available: Experimental details and spectral characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL070052U

(16) Flood, A. H.; Nygaard, S.; Laursen, B. W.; Jeppesen, J. O.; Stoddart, J. F. *Org. Lett.* **2006**, *8*, 2205−2208.
(17) (a) Bissell, R. A.; Córdova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133−137. (b) Córdova, E.; Bissell, R. A.; Kaifer, A. E. *J. Org. Chem.* **1995**, *60*, 1003−1038.
(18) Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1584−1586.