ORGANIC
LETTERS

2006
Vol. 8, No. 21
4835−4838

Cyclobis(paraquat-*p*-phenylene)-Based [2]Catenanes Prepared by Kinetically Controlled Reactions Involving Alkynes

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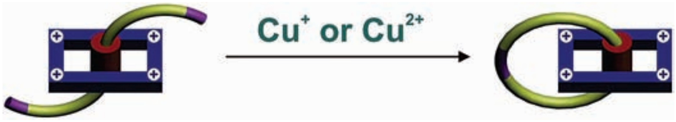
Received July 27, 2006

ABSTRACT



Charged donor–acceptor [2]catenanes, in which the π-accepting cyclobis(paraquat-*p*-phenylene) acts as a tetracationic template for the threading-followed-by-clipping of acyclic oligoethers, incorporating centrally a π-donating 1,5-dioxynaphthalene ring system and terminated either by acetylene units or by acetylene and azide functions, are the products of copper-mediated Eglinton coupling and Huisgen 1,3-dipolar cycloaddition, respectively.

[2]Catenanes are challenging synthetic targets because of their nontrivial topology and the need for molecular recognition and self-assembly processes[1] to aid and abet the efficient mechanical interlocking of the two rings. Bistable [2]-catenanes, moreover, have become key molecular components of reconfigurable switches[2] and artificial motors.[3] Ever more diverse methods for the preparation of such bistable catenanes are being pursued actively in order to facilitate the optimal realization of these and other applications.

Previous syntheses of charged donor−acceptor [2]catenanes incorporating the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene)[4] (CBPQT^{4+}), as the π-electron-accepting component, have relied on the clipping of the CBPQT^{4+} ring around preformed π-electron-donating crown ethers (Figure 1a,b). Increased flexibility in the syntheses of catenanes of this type could be achieved by the development of an approach in which the formation of the crown ether is templated by the CBPQT^{4+} ring (Figure 1c,d). This reciprocal approach has not been realized previously because of the sensitivity of CBPQT·4PF$_6$ to bases, nucleophiles, and reducing agents.[5] Provided that all the reactions are mutually compatible, the two approaches could be combined into an elegant all-in-one catenation[6,7] (Figure 1e), which would lead

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(1) For recent reviews, see: (a) Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *Top. Curr. Chem.* **2005**, *262*, 29−62. (b) Schalley, C. A.; Weilandt, T.; Brüggemann, J.; Vögtle, F. *Top. Curr. Chem.* **2004**, *248*, 141−200. (c) Stoddart, J. F.; Tseng, H.-R. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4797−4800. (d) *Molecular Catenanes, Rotaxanes and Knots*; Sauvage, J.-P., Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, 1999. (e) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154−1156. (f) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725−2828. (g) Philp, D.; Stoddart, J. F. *Synlett* **1991**, 445−458.

(2) See, inter alia: (a) Flood, A. H.; Wong, E. W.; Stoddart, J. F. *Chem. Phys.* **2006**, *324*, 280−290. (b) Kim, Y.-H.; Jang, S. S.; Goddard, W. A. *Appl. Phys. Lett.* **2006**, *88*, 163112/1−163112/3. (c) Flood, A. H.; Stoddart, J. F.; Heath J. R. *Science* **2004**, *306*, 2055−2056. (d) 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. (e) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001. (f) Álvaro, M.; Chretien, M. N.; Ferrer, B.; Fornes, V.; Garcia, H.; Scaiano, J. C. *Chem. Commun.* **2001**, *20*, 2106−2107. (g) 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.

(3) See, inter alia: (a) Braunschweig, A. B.; Northrop, B. H.; Stoddart, J. F. *J. Mater. Chem.* **2006**, *16*, 32−44. (b) Kay, E. R.; Leigh, D. A. *Top. Curr. Chem.* **2005**, *262*, 133−177. (c) Balzani, V.; Credi, A.; Ferrer, B.; Silvi, S.; Venturi, M. *Top. Curr. Chem.* **2005**, *262*, 1−27. (d) Mandl, C. P.; König, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 1622−1624. (e) Hernández, J. V.; Kay, E. R.; Leigh, D. A. *Science* **2004**, *306*, 1532−1537. (f) Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174−179.

(4) (a) Doddi, G.; Ercolani, G.; Mencarelli, P.; Piermattei, A. *J. Org. Chem.* **2005**, *70*, 3761−3764. (b) 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. (c) 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.

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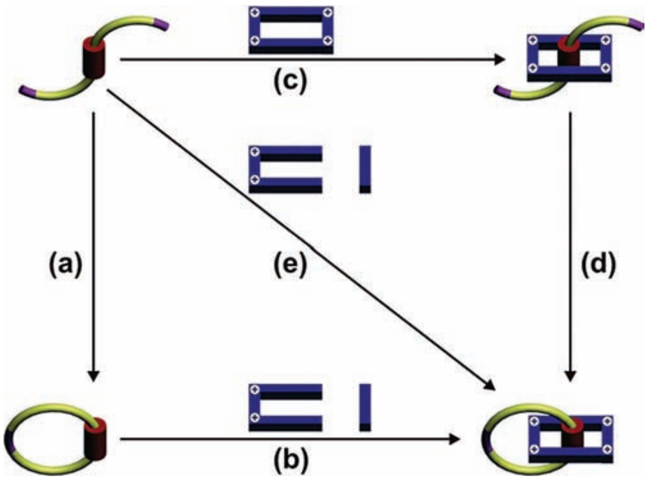

Figure 1. Some alternative conceptual strategies that can be employed in the template-directed synthesis of charged donor−acceptor [2]catenanes containing π-electron-rich crown ethers incorporating dioxy-benzene and -naphthalene units (red) and the π-electron-deficient tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}, blue). Alternative heterocatenation strategies are (i) macrocyclization (a) to give the crown ether, followed by clipping (b) to form CBPQT^{4+} and (ii) threading (c) of CBPQT^{4+} by an acyclic precursor of the crown ether, followed by clipping (d) to form the crown ether itself. An all-in-one alternative is a tandem heterocatenation (e).

to the formation of a [2]catenane from three acyclic components.

In this Letter, we report on the synthesis and characterization of charged donor−acceptor [2]catenanes by performing (i) a Cu^{2+}-mediated Eglinton coupling[8] on a [2]pseudorotaxane formed between CBPQT^{4+} and a bispropargyl ether of an acyclic oligoether derivative incorporating a 1,5-dioxynaphthalene unit and (ii) a Cu^{+}-catalyzed Huisgen 1,3-dipolar cycloaddition,[9] namely, click chemistry,[10] on a similar [2]pseudorotaxane where an azidoethyl group replaces one of the two propargyloxyethyl groups in the bis(propargyl ether) of the acyclic oligoether derivative.

An earlier variant of the Eglinton coupling,[8] the Glaser reaction,[8a] has been employed previously in the template-directed synthesis of [2]- and [3]catenanes of different types[11] and molecular composite knots.[12] Most significantly, Sanders and co-workers[6e,f] have prepared a *neutral* donor−acceptor [2]catenane by tandem heterocatenation of three acyclic components using a 3-fold Glaser coupling. To render this strategy a practical one for the preparation of *charged* donor−acceptor [2]catenanes, starting from a [2]pseudorotaxane where the ring component is CBPQT^{4+}, the catenation has to proceed under close to neutral, oxidative, and non-nucleophilic conditions at room temperature. Thus, we decided to use (i) an acyclic oligoether with a centrally and symmetrically located 1,5-dioxynaphthalene (DNP) recognition unit and terminated by alkynes (propargyl groups) and (ii) oxidative Eglinton coupling[13] of these alkynes as the basis for catenation. Since the relative movements of components in mechanically interlocked molecules can be delineated more precisely in rigid systems,[14] there is a further impetus to be able to incorporate rigid alkynes into switchable catenanes for use in molecular mechanical devices.[1b,3]

The π-electron-donating oligoether **2** was prepared (Scheme 1) by the propargylation of the known[15] 1,5-dioxynaphthalene derivative **1**. An equimolar mixture of **2** and CBPQT·4PF$_6$ in DMF constituted the intensely purple [**2** $\subset$ CBPQT]·4PF$_6$. Exposure of this [2]pseudorotaxane to 3 equiv of Cu(OAc)$_2$·H$_2$O at 23 °C for 4 d afforded the [2]catenane **3**·4PF$_6$ in 14% yield. Our concern at the long reaction time in the presence of weakly nucleophilic acetate ion encouraged us to shorten the reaction time to 20 min, while using a single-mode microwave reactor[16] with MeCN as the solvent. The result was a modest increase[17] in the yield of **3**·4PF$_6$ to 21%.

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(5) We have only recently achieved this "supramolecular umpolung" in the syntheses of [*n*]rotaxanes incorporating CBPQT^{4+} rings using click chemistry. See: Dichtel, W. R.; Miljanić, O. Š.; Spruell, J. M.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10388−10390.

(6) Early examples of this synthetic approach were limited to [2]catenanes with identical rings (homo-catenation): (a) Johnston, A. G.; Leigh, D. A.; Pritchard, R. J.; Deegan, M. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1209−1212. (b) Vögtle, F.; Meier, S.; Hoss, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1619−1622. (c) Hunter, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 5303−5311. (d) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J. P. *Tetrahedron Lett.* **1983**, *24*, 5095−5098. The approach presented in Figure 1e is a hetero-catenation, in which the two rings in the [2]catenane differ. See: (e) Hamilton, D. G.; Prodi, L.; Feeder, N.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1057−1065. (f) Hamilton, D. G.; Feeder, N.; Prodi, L.; Teat, S. J.; Clegg, W.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1998**, *120*, 1096−1097.

(7) Brown, C. L.; Philp, D.; Stoddart, J. F. *Synlett* **1991**, 459−461.

(8) For an authoritative review of Glaser, Eglinton, and related alkyne couplings, see: (a) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2632−2657. For the original report, see: (b) Eglinton, G.; Galbraith, A. R. *Chem. Ind. (London)* **1956**, 737−738.

(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) Lwowski, W. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, Chapter 5. (d) Bastide, J.; Hamelin, J.; Texier, F.; Ven, V. Q. *Bull. Chem. Soc. Fr.* **1973**, 2555−2579. (e) Bastide, J.; Hamelin, J.; Texier, F.; Ven, V. Q. *Bull. Chem. 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) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021. (c) Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057−3064.

(11) (a) Godt, A. *Eur. J. Org. Chem.* **2004**, 1639−1645. (b) Duda, S.; Godt, A. *Eur. J. Org. Chem.* **2003**, 3412−3420. (c) Ünsal, Ö.; Godt, A. *Chem.−Eur. J.* **1999**, *5*, 1728−1733. (d) Hamilton, D. G.; Sanders, J. K. M.; Davies, J. E.; Clégg, W.; Teat, S. J. *Chem. Commun.* **1997**, 897−898. (e) Dietrich-Buchecker, C. O.; Hemmert, C.; Khémiss, A.-K.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 8002−8008. (f) Dietrich-Buchecker, C. O.; Khémiss, A.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1986**, 1376−1378. See also: (g) Gunter, M. J.; Farquhar, S. M. *Org. Biomol. Chem.* **2003**, *1*, 3450−3457.

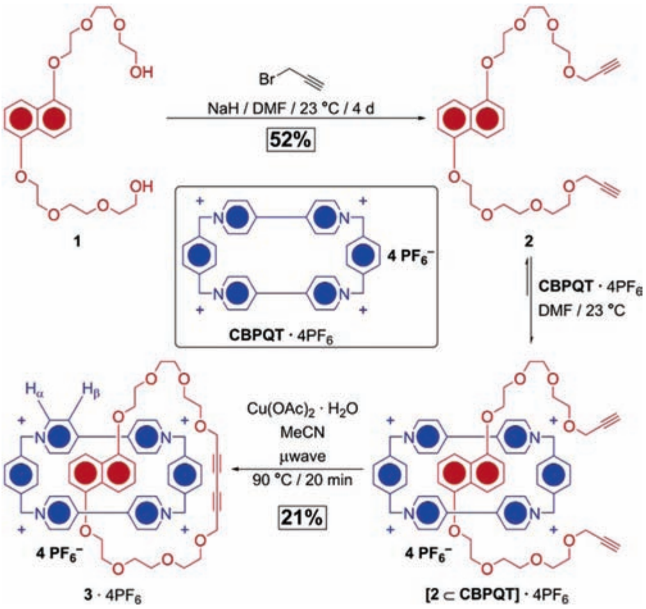
(12) Carina, R. F.; Dietrich-Buchecker, C.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1996**, *118*, 9110−9116.

(13) While the original Eglinton conditions employed Cu(OAc)$_2$ in amines at high temperatures,[8a] examples of coupling in nonbasic solvents have been reported. See: (a) Meissner, U.; Meissner, B.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 916−918. (b) Berscheid, R.; Vögtle, F. *Synthesis* **1992**, 58−62. Since in our hands oxidative coupling of Ph−C≡C−H proceeded at 23 °C to give Ph−C≡C−C≡C−Ph in 72% yield, high temperatures were shown also to be not essential.

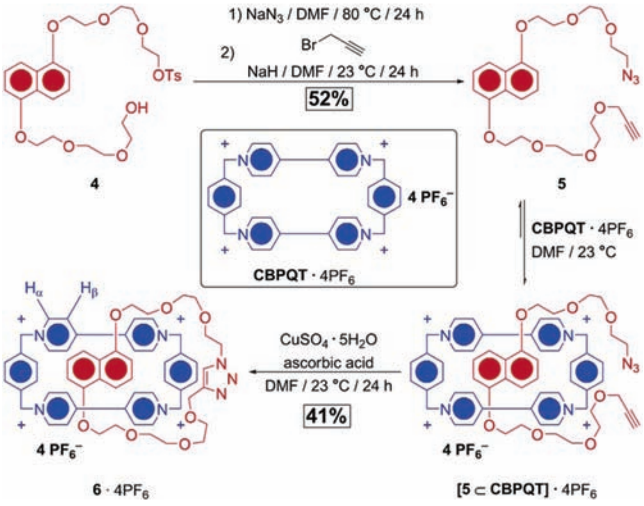
(14) (a) Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H. R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C. M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9745−9759. (b) Huang, T. J.; Brough, B.; Ho, C.-M.; Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Tseng, H.-R.; Stoddart, J. F.; Baller, M.; Magonov, S. *Appl. Phys. Lett.* **2004**, *85*, 5391−5393.

(15) Ashton, P. R.; Huff, J.; Menzer, S.; Parsons, I. W.; Preece, J. A.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J. *Chem.−Eur. J.* **1996**, *2*, 31−44.

Scheme 1



Scheme 2



Inspired by the success of the synthetic strategy outlined conceptually in Figure 1c,d, we turned our attention to other reactions that might be amenable to the same strategy. The high regioselectivity and mild conditions associated with the Cu$^+$-catalyzed Huisgen 1,3-dipolar cycloaddition have led to its use in a variety of applications in supramolecular[18,19] and materials[20] chemistry. Recently, we demonstrated[5] that this reaction, popularized by Sharpless[10a,b] under the banner of click chemistry, is tolerant of the CBPQT^{4+} ring during the template-directed syntheses of [*n*]rotaxanes. The template-directed synthesis of a [2]catenane, which relies on an intramolecular application of the click reactions, requires the initial formation (Scheme 2) of a [2]pseudorotaxane between a π-electron-donating oligoether such as **5** and the CBPQT^{4+} ring. The monotosylate[21] **4** of **1** was reacted with NaN$_3$ and the free hydroxyl group was propargylated[22] to yield **5** in a 52% yield overall. On mixing **5** with CBPQT·4PF$_6$ in equimolar amounts, the solution turned a deep purple color, indicative of the formation of the pseudorotaxane [**5** ⊂ CBPQT]·4PF$_6$. Treating this complex with CuSO$_4$·5H$_2$O and ascorbic acid provided (Scheme 2) the [2]catenane **6**·4PF$_6$ in 41% yield. This yield is more or less independent of the concentration, suggesting that the [2]pseudorotaxane [**5** ⊂ CBPQT]·4PF$_6$ possesses a certain level of preorganization,[23] which favors catenation over polymerization.

The [2]catenanes **3**·4PF$_6$ and **6**·4PF$_6$ are both purple solids, soluble in polar organic solvents (MeCN, Me$_2$CO, DMF, MeOH) and insoluble in H$_2$O and less polar organic solvents. The higher solubility of these two [2]catenanes in MeOH and Me$_2$CO, relative to that of CBPQT·4PF$_6$, facilitated their purification. The FAB mass spectra revealed diagnostic peaks at *m*/*z* 1453, 1308, and 1163 (**3**·4PF$_6$) and 1442, 1297, and 1152 (**6**·4PF$_6$), corresponding to the loss of one, two, and three PF$_6^-$ counterions, successively. Additional peaks at *m*/*z* 955, 810, and 655 (in the mass spectra of both catenanes) could be assigned to CBPQT·4PF$_6$ fragment ions, commensurate with the loss of the catenated rings.[24] Figure 2 illustrates this interpretation for **3**·4PF$_6$.

The ^{1}H NMR spectra recorded in CD$_3$CN were also informative: in both cases, the protons associated with the DNP unit were appreciably shielded compared to their free

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(16) For reviews of microwave-assisted reactions, see: (a) Kappe, O. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 6250−6284. (b) Lindstrom, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron Lett.* **2001**, *57*, 9225−9283.

(17) The success of this synthetic route prompted us to assess the viability of tandem heterocatenation (Figure 1e). The efficient (>60% yield) preparation of CBPQT·4PF$_6$ involves the reaction between 1,4-bis(bromomethyl)benzene (**A**) and 1,1′-[1,4-phenylene bis(methylene)]-bis-4,4′-bipyridinium hexafluorophosphate (**B**·2PF$_6$) in the presence of DNP derivatives as cyclization templates (see ref 4b and Supporting Information). This fact suggested to us that it might be possible to use **2** as a template in the formation of CBPQT^{4+}, while it simultaneously cyclizes to form **3**$^{4+}$. Leaving a mixture of **A**, **B**·2PF$_6$, and **2** in DMF exposed to Cu(OAc)$_2$·H$_2$O for 4 d gave the catenane **3**·4PF$_6$ in 5% yield after counterion exchange (NH$_4$PF$_6$). While this outcome was the expected one, the efficiency of the approach leaves a lot to be desired.

(18) For previous examples of the use of a Cu$^+$-catalyzed Huisgen 1,3-dipolar cycloaddition in the template-directed syntheses of rotaxanes, see: (a) Aucagne, V.; Hänni, K. D.; Leigh, D. A.; Lusby, P. J.; Walker, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 2186−2187. (b) Mobian, P.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **2006**, *47*, 4907−4909.

(19) Previously, [2]- and [3]rotaxanes have been self-assembled from secondary dialkylammonium salts and crown ethers by using uncatalyzed Huisgen 1,3-dipolar cycloadditions to attach stoppers to the ends of the threads of [2]- and [3]pseudorotaxanes. See: (a) Badjić, J. D.; Balzani, V.; Credi, A.; Lowe, J. N.; Silvi, S.; Stoddart, J. F. *Chem.−Eur. J.* **2004**, *10*, 1926−1935. (b) Cao, J.; Fyfe, M. C. T.; Stoddart, J. F.; Cousins, G. R. L.; Glink, P. T. *J. Org. Chem.* **2000**, *65*, 1937−1946. (c) Ashton, P. R.; Glink, P. T.; Stoddart, J. F.; Menzer, S.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Tetrahedron Lett.* **1996**, *37*, 6217−6220. (d) Ashton, P. R.; Glink, P. T.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem.−Eur. J.* **1996**, *2*, 729−736.

(20) Hawker, C. J.; Wooley, K. L. *Science* **2005**, *309*, 1200−1205.

(21) Liu, Y.; Saha, S.; Vignon, S. A.; Flood, A. H.; Stoddart, J. F. *Synthesis* **2005**, 3437−3445.

(22) Based on: Hotha, S.; Anegundi, R. I.; Natu, A. A. *Tetrahedron Lett.* **2005**, *46*, 4585−4588.

(23) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039−1057.

(24) (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Menzer, S.; Pérez-García, L.; Prodi, L.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11171−11197. (b) Vetter, W.; Schill, G. *Tetrahedron* **1967**, *23*, 3079−3093.

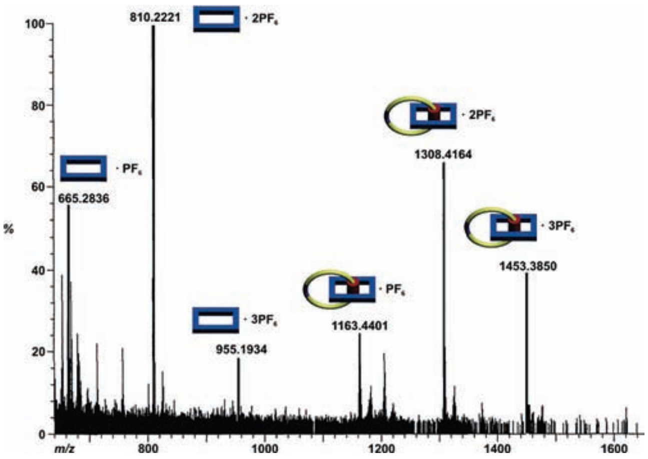

Figure 2. FAB mass spectrum of the [2]catenane **3**·$4PF_6$.

(non-catenated) analogues, indicating the encircling of the DNP moiety by the $CBPQT^{4+}$ and ruling out[25] the possibility that the $-C\equiv C-C\equiv C-$ fragment (in **3**·$4PF_6$) or the triazole ring (in **6**·$4PF_6$) resides within the cavity of the $CBPQT^{4+}$ ring. Whereas **3**·$4PF_6$ showed just one set of three signals for H-2/6, H-3/7, and H-4/8 in the DNP unit, reflecting the fact that its local C_2 symmetry commutes with the crown ether component, **6**·$4PF_6$ showed five (out of the theoretical six, since two signals were accidentally isochronous) separate resonances for the DNP protons, rendered heterotopic by the fact that the substituted triazole ring destroys the DNP unit's local C_2 symmetry. The signals for the bipyridinium units in the $CBPQT^{4+}$ component of **3**·$4PF_6$ and **6**·$4PF_6$ are consistent with these symmetry considerations. In **3**·$4PF_6$ the pirouetting of the crown ether component around the $CBPQT^{4+}$ ring is rapid, leading to the observation of two resonances[26] each for H-α and H-β. On the other hand, in the smaller [2]catenane **6**·$4PF_6$ we glean evidence for eight resonances each for H-α and H-β (although not all 16 signals were resolved[27] clearly), suggesting that the pirouetting motion is slow on the NMR time scale. Also noteworthy is the chemical shift of the triazole ring proton in **6**·$4PF_6$ at δ = 7.05 ppm, lower by $\Delta\delta = -1.55$ ppm relative to the corresponding resonance[5] for the triazole ring proton in the [*n*]rotaxanes. This observation can be rationalized by invoking shielding of this proton by the bipyridinium units of the $CBPQT^{4+}$ ring.

In conclusion, we have demonstrated that the synthesis of charged donor−acceptor [2]catenanes can be achieved using a strategy in which the π-accepting $CBPQT^{4+}$ ring component acts as a template for the formation of the π-donating crown ether component. Both Eglinton coupling of acetylene functions and Huisgen 1,3-dipolar cycloadditions of azide and acetylene functions can be employed in the threading-followed-by-clipping approach, illustrated in Figure 1c,d. Although the yields are generally not competitive with the traditional threading-followed-by-clipping approach (Figure 1a,b), the brevity and simplicity of the synthetic routes in Schemes 1 and 2 are distinctively attractive. Moreover, we view the synthetic achievements, reported in this Letter, as an adequate demonstration that the complexes [**2** $\subset$ CBPQT]·$4PF_6$ and [**5** $\subset$ CBPQT]·$4PF_6$ can be used as noncovalently bonded, supramolecular synthons, along with classical covalent bond-forming reactions in organic chemistry. Conditions, of course, have to be chosen so as not to impair the stabilities of the complexes or threaten the constitutional integrity of their components. Given the vast array of mild catalytic methods developed in the past decades, this is a challenge well within reach.

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 Innovation for Defense (CNID). We thank Prof. Michael E. Jung and Ms. Hiufung V. Chu (UCLA) for assistance with microwave-promoted reactions.

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.

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[25] For **6**·$4PF_6$, this observation is additionally supported by the finding that in related [2]catenanes that contain a 1,2,4-substituted triazole ring, $CBPQT^{4+}$ preferentially encircles the DNP and not the triazole moiety: (a) Alcalde, E.; Pérez-García, L.; Ramos, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Mendeleev Commun.* **2004**, 233−235. (b) Alcalde, E.; Pérez-García, L.; Ramos, S.; Stoddart, J. F.; Vignon, S. A.; White, A. J. P.; Williams, D. J. *Mendeleev Commun.* **2003**, 100−102.

[26] Signals were observed at δ 9.07 and 8.61 ppm (H-α protons) and 7.42 and 7.23 (H-β protons). See Supporting Information for the complete ^{1}H NMR spectrum.

[27] For the better resolved H-α protons, signals were observed at δ 9.15, 8.86, 8.83, 8.73, 8.73, 8.68, 8.65, and 8.51 ppm. See Supporting Information for the complete ^{1}H NMR spectrum.