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Modular Synthesis and Dynamics of a Variety of Donor–Acceptor Interlocked Compounds Prepared by Click Chemistry

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Abstract: A series of donor–acceptor [2]-, [3]-, and [4]rotaxanes and self-complexes ([1]rotaxanes) have been synthesized by a threading-followed-by-stoppering approach, in which the precursor pseudorotaxanes are fixed by using Cu^{I}-catalyzed Huisgen 1,3-dipolar cycloaddition to attach the required stoppers. This alternative approach to forming rotaxanes of the donor–acceptor type, in which the donor is a 1,5-dioxynaphthalene unit and the acceptor is the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene), proceeds with enhanced yields relative to the tried and tested synthetic strategies, which involve the clipping of the cyclophane around a preformed dumbbell containing π-electron-donating recognition sites. The new synthetic approach is amenable to application to highly convergent sequences. To extend the scope of this reaction, we constructed [2]rotaxanes in which one of the phenylene rings of the tetracationic cyclophane is perfluorinated, a feature which significantly weakens its association with π-electron-rich guests. The activation barrier for the shuttling of the cyclophane over a spacer containing two triazole rings was determined to be (15.5 ± 0.1) kcal mol^{-1} for a degenerate two-station [2]rotaxane, a value similar to that previously measured for analogous degenerate compounds containing aromatic or ethylene glycol spacers. The triazole rings do not seem to perturb the shuttling process significantly; this property bodes well for their future incorporation into bistable molecular switches.

Keywords: click chemistry · cycloaddition · host–guest systems · interlocked compounds · rotaxanes

Introduction

Template-directed synthetic protocols have facilitated the preparation of mechanically interlocked compounds such as catenanes,[1] rotaxanes,[2] knots,[3] and Borromean links.[4] The mechanical bonds[5] and noncovalent forces that hold these molecules together can also give rise to relative motions such as circumrotation[6] and shuttling,[7] which have been utilized in artificial molecular muscles[8] and molecular electronic devices.[9] Mechanically interlocked molecular compounds based on donor–acceptor interactions that incorporate cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) as the π-electron-accepting ring[10] component have been synthesized traditionally by template-directed,[11] kinetically controlled reactions[12] in which the partially formed π-acceptor ring is clipped around a dumbbell or macrocycle that contains complementary π-electron-rich recognition units. Although this clipping approach has been used extensively, the moderate yields associated with the protocol limit its practical utility mostly to the preparation of [2]rotaxanes and [2]catenanes.

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As an alternative to the clipping methodology for the installation of the $CBPQT^{4+}$ cyclophane, we recently investigated synthetic transformations that are compatible with $CBPQT^{4+}$–guest binding and so enable convergent synthetic approaches in which the final product is synthesized and catenated simultaneously. Until recently, few such transformations were known, largely because of the sensitivity of the $CBPQT^{4+}$ ring to nucleophiles and bases. However, we recently harnessed the mild conditions, excellent functional-group tolerance, and high efficiency (all virtues[13] of "click chemistry") of the Cu^{I}-catalyzed Huisgen 1,3-dipolar cycloaddition[14,15] for the preparation of donor–acceptor rotaxanes[16] and catenanes.[17] In this "threading-followed-by-stoppering" approach, the association process takes advantage of the thermodyanamic binding energy of fully formed recognition elements, and the high efficiency of the reaction allows many individual components to be joined in a single step.

Since our initial report was published,[16a] we have developed a modular toolkit of appropriately functionalized building blocks for the preparation of mechanically interlocked compounds with a focus on accessing unique topologies and structures that are particularly difficult to prepare by other methods. For example, the Cu-catalyzed azide–alkyne cycloaddition has been employed to prepare [2]rotaxanes that incorporate significantly weaker-binding fluorinated $CBPQT^{4+}$ derivatives,[18] the attempted synthesis of which, with the clipping method, failed completely. Furthermore, self-complexed mechanically interlocked molecules[19] were prepared efficiently by reacting an alkyne-functionalized $CBPQT^{4+}$ derivative with a 1,5-dioxynaphthalene (DNP) species bearing ethylene glycol chains, one functionalized with an azide and the other with a stoppering group. Self-complexing systems have a rich stereochemistry and display a variety of interesting dynamic processes.[20–26] Efficient methods for their preparation would facilitate their continued development as artificial molecular machines.

Finally, to evaluate the suitable placement of triazole rings for the design of bistable interlocked structures, we measured the rate of shuttling of the $CBPQT^{4+}$ ring over 1,4-triazole units placed between degenerate DNP recognition sites. The barrier to shuttling ($\Delta G^{\ddagger}$) of the $CBPQT^{4+}$ ring over the triazole units may be compared with values obtained previously for other spacers.[7g] Although this measurement was performed in the solution phase, we recently developed models to relate the kinetic parameters of switching in solution with those in molecular electronic devices[7i] and other condensed media.[7f,h,9f]

In this paper, we describe the highly efficient and convergent threading-followed-by-stoppering approach to the synthesis of a variety of rotaxanes with the different architectures illustrated in Figure 1; specifically, the high-yielding synthesis of [2]-, [3]-, and [4]rotaxanes, self-complexed rotaxanes (i.e., [1]rotaxanes), and a degenerate molecular shuttle. These materials and their precursors were all characterized by appropriate spectroscopic and crystallographic methods. Finally, the possibility of designing switches, in which shuttling takes place over triazole units, was evaluated based on the kinetics of the movement of the $CBPQT^{4+}$ ring within the degenerate shuttle.

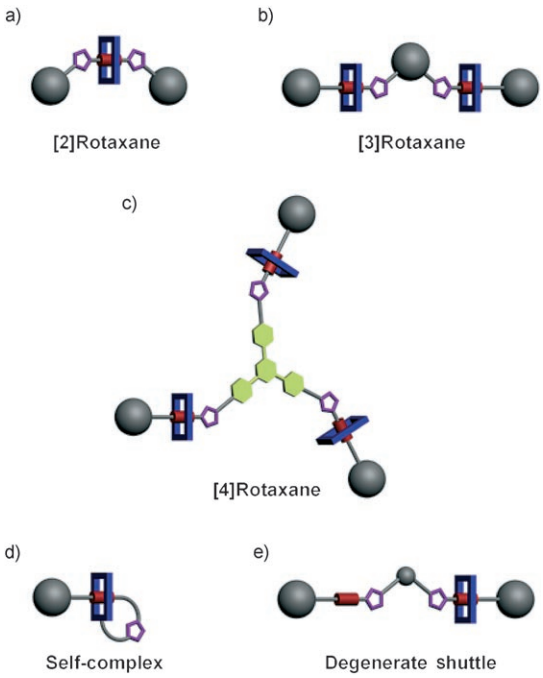


Figure 1. Schematic representation of a collection of mechanically interlocked compounds produced from a few simple azide- and alkyne-functionalized 1,5-dioxynaphthalene and $CBPQT^{4+}$ derivatives by the Cu-catalyzed azide–alkyne cycloaddition.

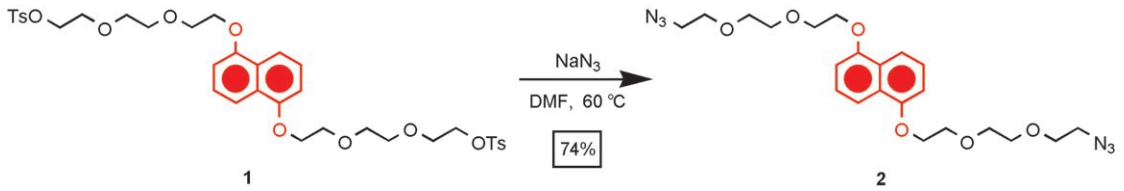
Results and Discussion

Design and Synthetic Strategy

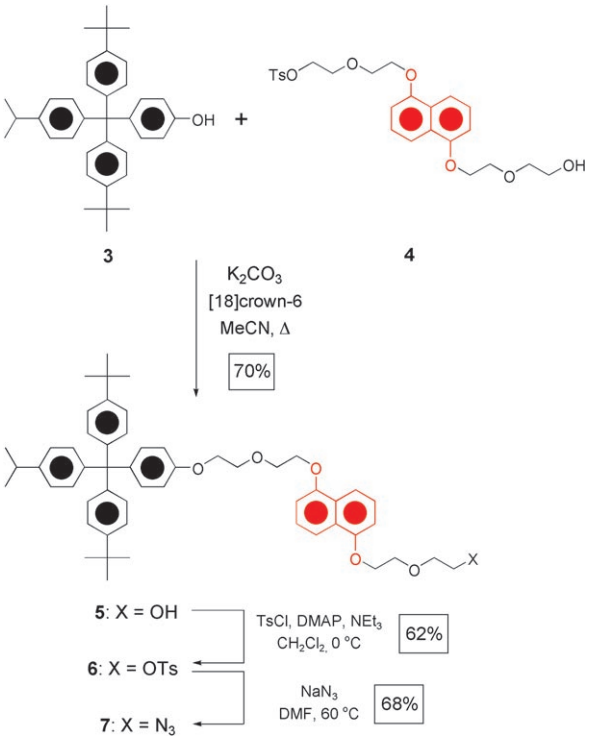
No longer constrained by the requirement of performing the clipping reaction on a fully formed template in the final step of the synthesis, retrosynthetic analysis of the architectures in Figure 1 suggested disconnection to a series of common precursors. The resulting "toolkit" of alkyne- or azide-functionalized rods, stoppers, and $CBPQT^{4+}$ derivatives provides modular access to an even wider variety of mechanically interlocked molecular compounds than is represented in Figure 1. Further complexity and new properties can be realized by designing more building blocks, a relatively simple process given the ease of incorporating azides and alkynes into most molecular structures.

Synthesis of Rotaxane Components

The symmetrical DNP diazide derivative **2** was synthesized in 74% yield by treating the corresponding ditosylate **1** with NaN_3 in *N*,*N*-dimethylformamide (DMF) (Scheme 1). The stoppered DNP derivative **5** was obtained by alkylation of the phenol **3** with the monotosylated DNP derivative **4** in the presence of K_2CO_3 as a base (Scheme 2). The azide half-dumbbell-shaped DNP derivative **7** was obtained first by



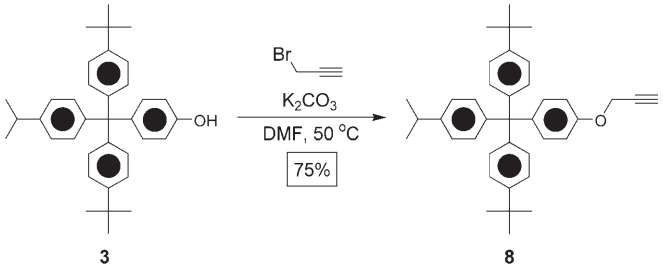
Scheme 1. Synthesis of DNP diazide **2**.



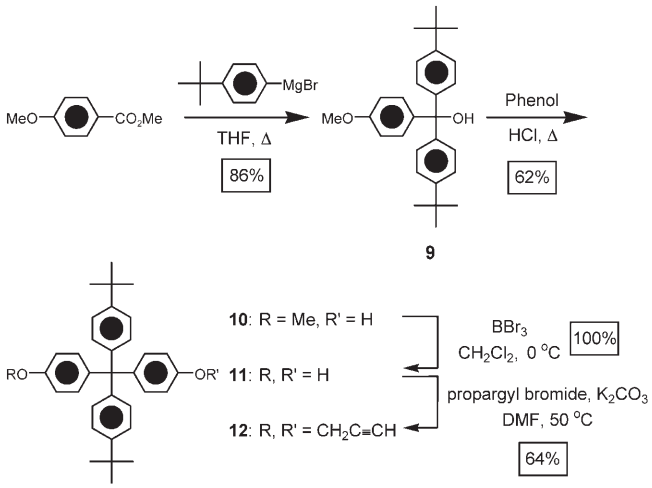
Scheme 2. Synthesis of the stoppered DNP monoazide **7**.

converting the hydroxy group into a tosylate, followed by nucleophilic displacement with NaN_3.

The hydrophobic propargyl ether stopper **8** was obtained in 75% yield by alkylation of **3** with propargyl bromide under Williamson etherification conditions (Scheme 3). A related compound with two phenol groups was prepared by treating methyl 4-methoxybenzoate with 4-*tert*-butylphenyl magnesium bromide to give the trityl alcohol **9** (Scheme 4). Electrophilic aromatic substitution of the phenol by **9**, catalyzed by HCl, provided the tetraarylmethane derivative **10**, which contains one methoxy and one hydroxy group. Cleavage of the methyl ether with BBr_3 proceeded in quantitative yield, and the resulting diphenol **11** was alkylated with propargyl bromide to give the bifunctional blocking unit **12** suitable for the synthesis of [3]rotaxanes.



Scheme 3. Synthesis of the propargyl ether stopper **8**.

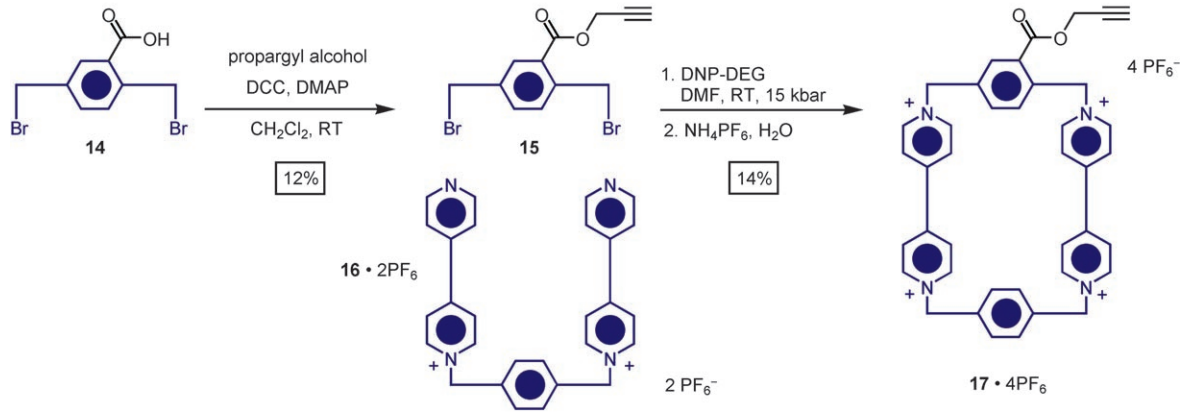


Scheme 4. Synthesis of the bis(propargyl ether) central stopper **12**.

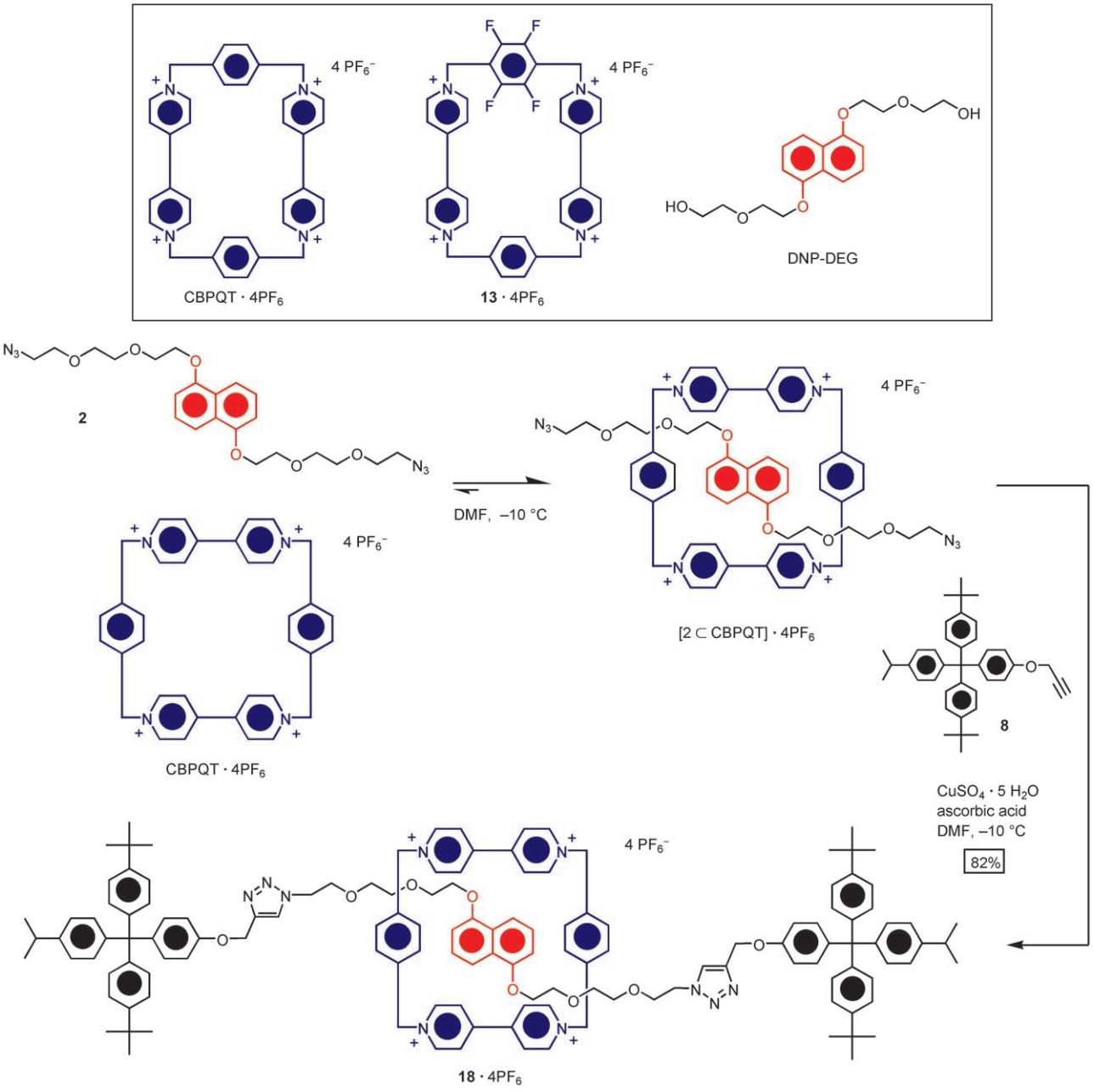
Although the synthesis of CBPQT·$4PF_6$ and the corresponding tetraflourinated derivative **13**·$4PF_6$ have both been reported previously,[18b] a new derivative **17**·$4PF_6$ with an alkyne moiety was prepared to enable synthesis of the self-complexing rotaxanes. The benzoic acid derivative **14** was esterified with propargyl alcohol under carbodiimide-mediated coupling conditions (Scheme 5). Formation of the cyclophane **17**·$4PF_6$ was accomplished by reacting **15** with the dicationic cyclophane precursor **16**·$2PF_6$ in DMF under high pressure (13 kbar) with 1,5-bis(ethoxy(ethoxy))dioxynaphthalene (DNP-DEG) as a template.

[2]-, [3]-, and [4]Rotaxanes

The general approach employed for the preparation of mechanically interlocked molecules by Cu-catalyzed azide–alkyne cycloaddition is exemplified by the synthesis of the [2]rotaxane **18**·$4PF_6$ (Scheme 6). The DNP diazide derivative **2** was mixed with CBPQT·$4PF_6$ and the propargyl ether stopper **8** in DMF (75 mM in **2**) at −10 °C. Under these conditions, the equilibrium lies almost completely in favor of the [2]pseudorotaxane [**2**⊂CBPQT]·$4PF_6$. Copper(II) sulfate pentahydrate and ascorbic acid were then added, and the so-



Scheme 5. Synthesis of the alkyne-functionalized $CBPQT^{4+}$ derivative **17**·$4PF_6$. DCC = dicyclohexylcarbodiimide.



Scheme 6. Synthesis of the [2]rotaxane **18**·$4PF_6$.

lution was stirred for 24 h. By following these mild reaction conditions, **18**·4PF$_6$ was isolated by preparative TLC in 82% yield. Formation of the corresponding dumbbell (the [2]rotaxane without the CBPQT^{4+} ring) was not observed by analytical TLC.

Encouragingly, [3]- and [4]rotaxanes can be synthesized by using the above approach with almost no decrease in yields, whereas the simultaneous clipping of multiple CBPQT^{4+} rings around synthetically advanced polyvalent templates is low-yielding. For example, doubly bistable [3]rotaxanes incorporating CBPQT^{4+} rings were used as redox-driven molecular muscles,[8d] despite the fact that clipping two CBPQT^{4+} rings around the palindromic template gave the desired [3]rotaxane in only 9% yield. By contrast, the palindromic [3]rotaxane **19**·8PF$_6$ was obtained from the stoppered DNP azide **7** and bis(propargyl ether) **12** in 79% yield (Scheme 7). The branched [4]rotaxane **21**·12PF$_6$ was prepared in 72% yield by using tris(1,3,5(4′-ethynylphenyl)-benzene)[27] **20** as the central unit. [4]Rotaxanes containing CBPQT^{4+} rings had not been reported previously: the clipping approach is expected to lead to this [4]rotaxane in very low ($\ll$3%) yields.

The ^{1}H NMR spectra of **19**·8PF$_6$ taken over a range of temperatures are representative of those of the other rotaxanes in the series (Figure 2), and their simplicity reflects the symmetry of the [3]rotaxane. The resonances characteristic of complexed DNP moieties appear at high field (δ = 6.30–6.20 (2-H, 6-H), 6.00–5.90 (3-H, 7-H), and 2.41–2.39 ppm (4-H, 8-H; not shown)). The triazole resonance remains as a strong singlet at around 8.10 ppm at all temperatures. The lack of significant changes in its chemical shift suggests that it does not compete as a station for the host, a hypothesis that will be further elaborated on later in this paper. Whereas, at low temperatures, the broad peaks for the bipyridinium protons indicate slow rotation and, in turn, slow exchange by which every individual resonance for these protons can be resolved, at higher temperatures the exchange

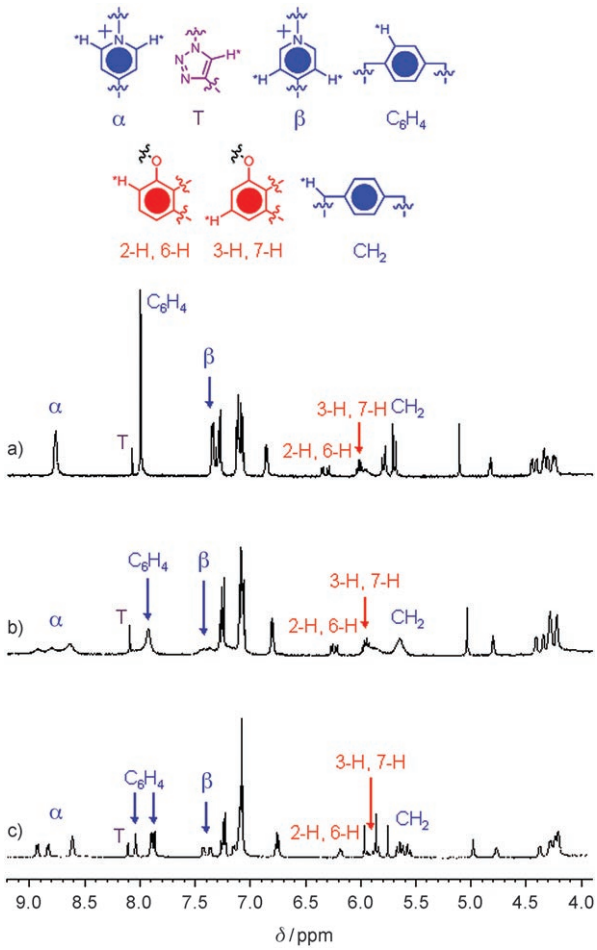
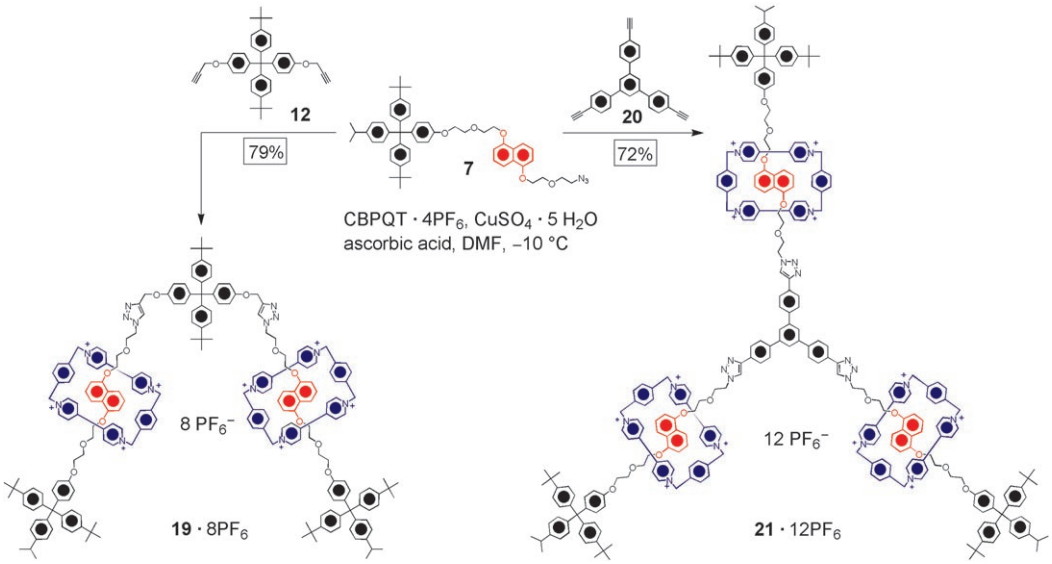


Figure 2. Section of ^{1}H NMR spectra (500 MHz, CD$_3$CN) of **19**·8PF$_6$ recorded at a) 348, b) 298, and c) 248 K. The slow rotations of the bipyridinium and phenylene units in the CBPQT^{4+} rings are reflected in their broad proton resonances at 298 K. At lower temperatures, these rotations are slowed until the signals become clearly resolved. The signals for the CBPQT^{4+} α- and β-ring protons coalesce into single, albeit broad peaks at higher temperatures.



Scheme 7. Synthesis of the [3]rotaxane **19**·8PF$_6$ and the [4]rotaxane **21**·12PF$_6$.

becomes fast on the NMR timescale, and the signals for the α-bipyridinium protons coalesce to afford a single, broad signal.[28]

F_4CBPQT^{4+} [2]Rotaxane Synthesis and Characterization

The association between the fluorinated CBPQT^{4+} **13**·4PF$_6$ and DNP is greatly attenuated relative to CBPQT^{4+} itself, a feature which led us to test the scope of this approach towards more weakly binding components. The attempted synthesis of a [2]rotaxane by reacting **23**·2PF$_6$ and 1,4-bis(bromomethyl)benzene for two weeks in the presence of the stoppered DNP derivative **22** resulted in none of the desired [2]rotaxane (Scheme 8a). By subjecting **2** and **13**·4PF$_6$ to azide–alkyne cycloaddition conditions, the [2]rotaxane **24**·4PF$_6$ was isolated in 11% yield (Scheme 8b), along with significant quantities of the corresponding dumbbell compound and free **13**·4PF$_6$. The yield of **24**·4PF$_6$ was increased to 37% by running the reaction in the presence of 3 equivalents of **13**·4PF$_6$. The ability to improve the yield of the rotaxane by adjusting the ratio of added cyclophane is another advantage of the threading-followed-by-stoppering approach, especially given the failure of the clipping methodology for this particular structure type.

To gain a better understanding of how the incorporation of one perflourinated aromatic ring into the CBPQT^{4+} scaffold affects the strength of its interaction with a DNP unit, the binding of **13**·4PF$_6$ to DNP-DEG was investigated in the solid state. X-ray crystallography of **13**·4PF$_6$ was used to determine the effects of the four fluorine atoms on the shape of the cyclophane in the absence as well as the presence of a DNP-DEG guest (Figure 3). Single crystals of **13**·4PF$_6$ suitable for X-ray diffraction were obtained by vapor diffusion of *i*Pr$_2$O into a solution of **13**·4PF$_6$ in MeCN. In the solid state, the presence of the four fluorine atoms causes the two adjacent pyridinium rings to twist 33° out of the plane formed by the four N$^+$ atoms, whereas the pair of pyridinium rings

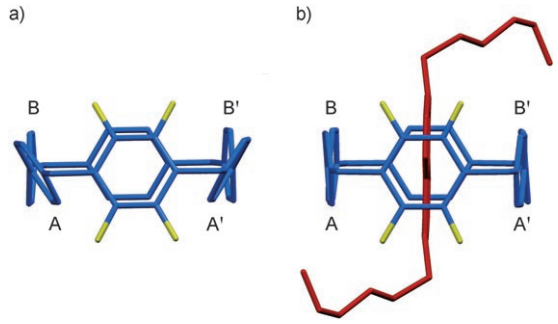
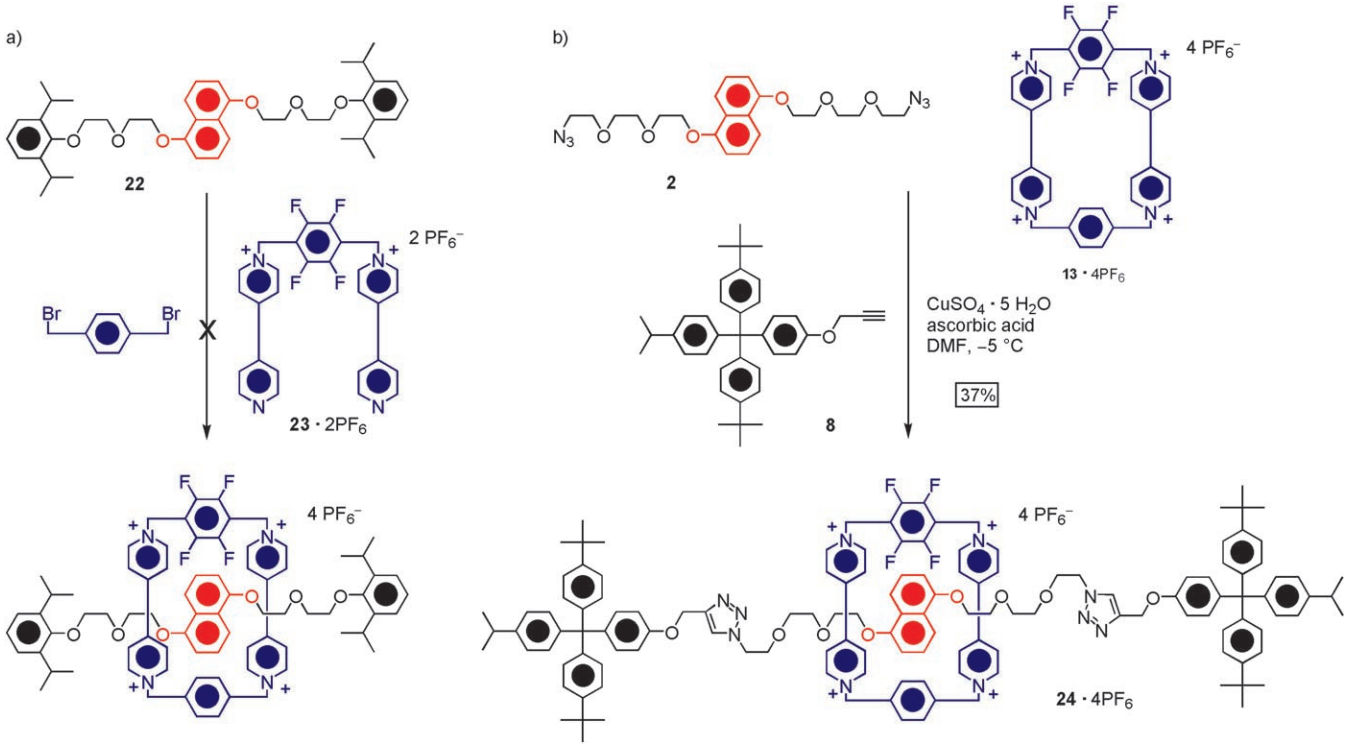


Figure 3. a) View along the axis of the F_4-substituted xylene ring of **13**·4PF$_6$. In the uncomplexed cyclophane, the pyridinium rings nearest the perfluorinated benzene (A and A′) are twisted 33° out of the plane formed by the four nitrogen atoms. b) In the pseudorotaxane [DNP⊂**13**]·4PF$_6$, the A and A′ pyridinium rings are nearly coplanar with B and B′. The π···π interactions have centroid–centroid distances of 3.77 Å. The C–H···O interactions occur with the third and second oxygen atoms on the glycol chain (H···O 2.83 Å, C–H···O 143° and H···O 2.50 Å, C–H···O 141°, respectively). A C–H···π interaction (2.54 Å) forms between the centroid of the *p*-xylyl rings and 4-H/8-H of the DNP ring.



Scheme 8. a) Unsuccessful preparation of an F_4CBPQT^{4+}-containing rotaxane by the clipping method. b) Synthesis of the F_4CBPQT^{4+}-containing [2]rotaxane **24**·4PF$_6$.

adjacent to the paraphenylene unit is only twisted 3° out of the plane. The torsion of the bipyridinium rings significantly decreases the size of the binding cavity relative to that of the parent host $CBPQT^{4+}$, a factor that may explain its decreased ability to form host–guest complexes.

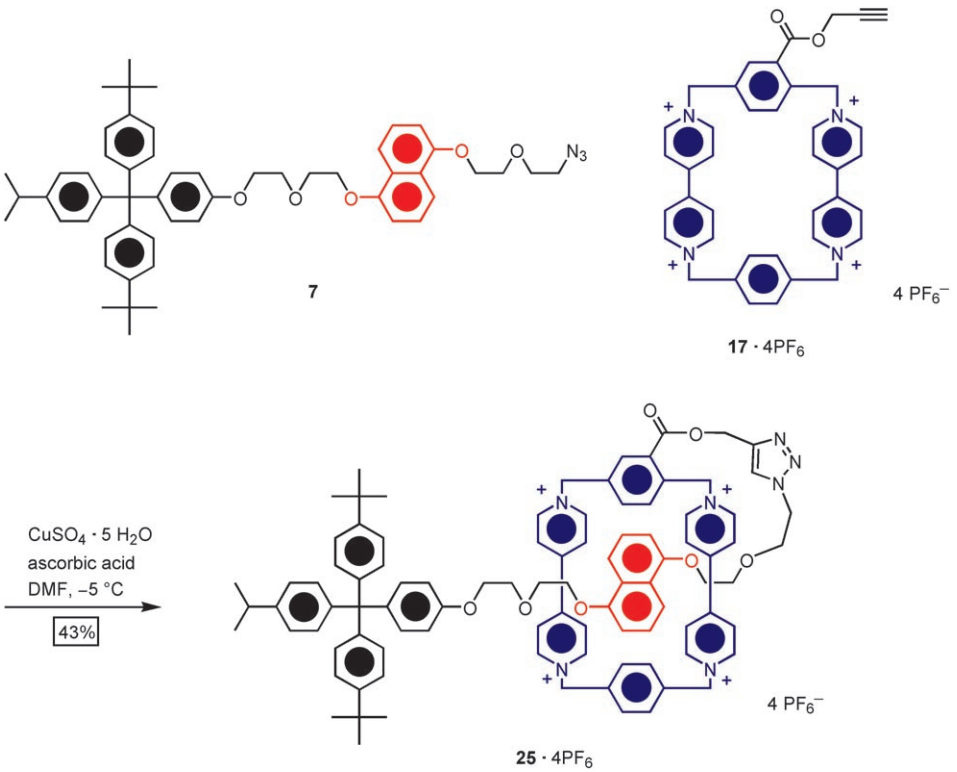
Crystals of the [2]pseudorotaxane [DNP-DEG⊂**13**]·$4PF_6$ were also obtained by vapor diffusion of iPr_2O into a 3:1 solution of DNP-DEG/**13**·$4PF_6$ dissolved in MeCN. The complex (Figure 3b) is stabilized by π···π, C–H···π, and C–H···O interactions between the host and guest. Because the crystal lattice has an inversion center, the electron density corresponding to the four fluorine atoms is equally distributed among the eight positions available on the *p*-xylyl rings. Upon complexation, rings A and A′ rotate almost into planarity with B and B′ so that a π···π interaction associated with a face-to-face distance of 3.77 Å can occur. Additionally, this geometry also allows for the formation of C–H···O interactions with both the third oxygen atom of the glycol substituents (H···O 2.83 Å, C–H···O 143°) and the second oxygen atom (H···O 2.50 Å, C–H···O 141°), thus stabilizing the [2]pseudorotaxane in the solid state. The final stabilizing force is a C–H···π interaction (H···π 2.54 Å) that forms between the *p*-xylyl ring and 4-H/8-H of the 1,5-dihydroxynaphthalene ring. On the basis of these crystal structures, we hypothesize that the energetic cost of twisting the pyridinium rings of the cyclophane back to coplanarity results in a weakened association between **13**·$4PF_6$ and DNP-DEG.[29]

To quantify this effect in solution, the thermodynamic parameters for the binding of DNP-DEG and **13**·$4PF_6$ were measured by isothermal titration microcalorimetry[30] (ITC) in MeCN at 298 K. A solution of DNP-DEG (4.5 mM, MeCN) was titrated in 5-μL aliquots into a solution of **13**·$4PF_6$ (0.5 mM, MeCN). The association constant (K_a) of $(690 \pm 220)\ M^{-1}$ obtained is significantly lower than that of $(36400 \pm 250)\ M^{-1}$ obtained for the parent system [DNP-DEG⊂CBPQT]·$4PF_6$ under similar conditions.[7i]

Synthesis and Characterization of Self-Complexing Systems

A self-complex[19] was prepared in 43% yield by subjecting the alkyne-functionalized $CBPQT^{4+}$ derivative **17**·$4PF_6$ and the DNP-containing thread **7** to cycloaddition conditions (Scheme 9). The existence of the self-complex was confirmed by high-resolution mass spectrometry, as well as by ^1H and ^{13}C NMR spectroscopy. The presence of a new peak in the ^1H NMR spectrum that corresponds to the triazole proton, as well as the fact that the spectrum showed little change over a broad range of temperatures, confirms that the molecule is a self-complexing one.[31]

UV/Vis spectroscopic analysis proves the self-complexed nature of **25**·$4PF_6$ (Figure 4). The intensity of the charge-transfer band ($\lambda_{max} = 512$ nm, $\varepsilon \cong 700\ M^{-1}cm^{-1}$)[32] between the DNP and $CBPQT^{4+}$ moieties in the absorption spectrum of **25**·$4PF_6$ was investigated over a range of concentrations. The linear change in absorbance with respect to the change in concentration of **25**·$4PF_6$ confirms the proposed interlocked structure, in which the DNP moiety does not dethread from the $CBPQT^{4+}$ binding site.



Scheme 9. Synthesis of the self-complexed rotaxane **25**·$4PF_6$.

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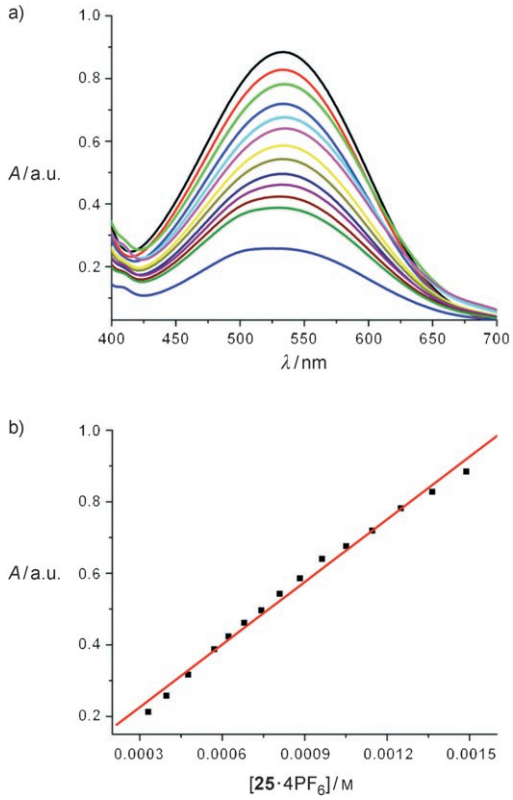
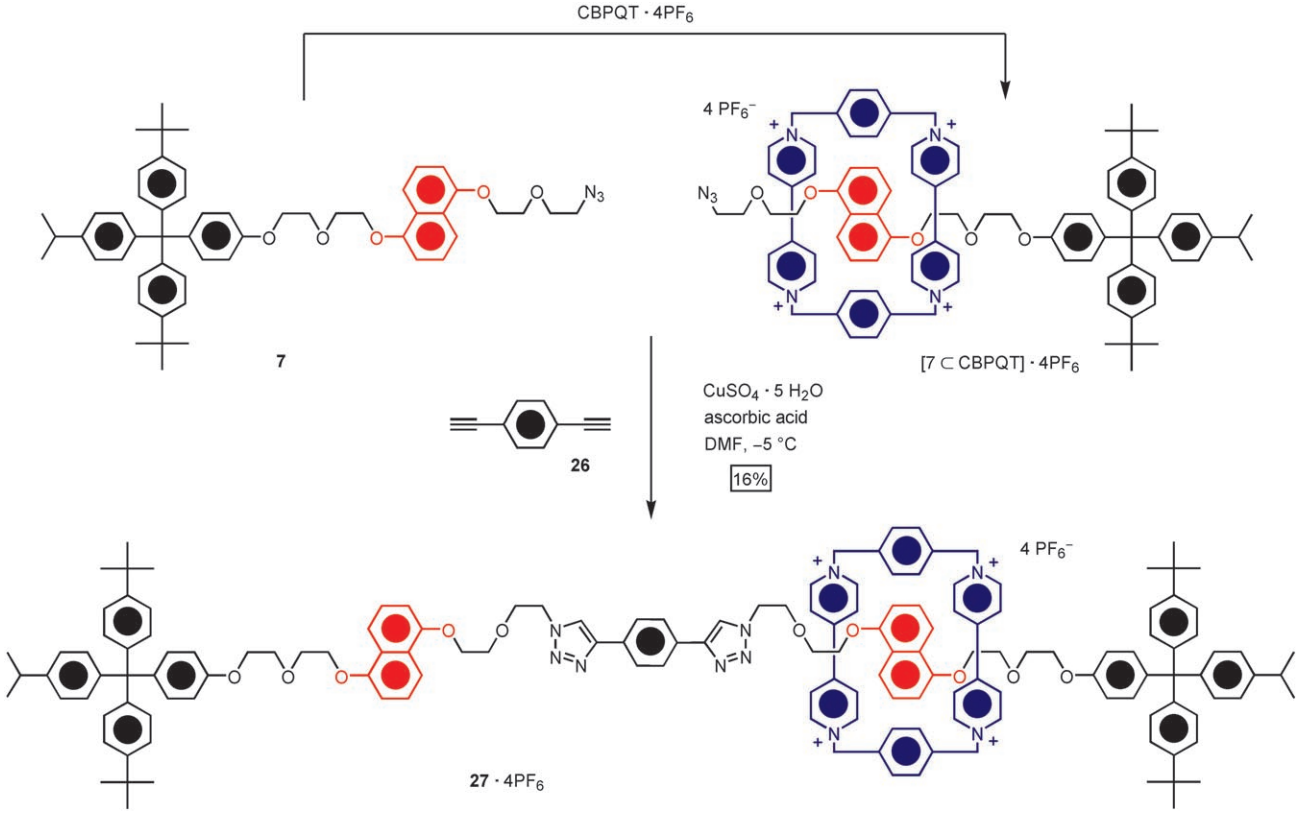


Figure 4. a) UV/Vis spectra of the charge-transfer band of **25**·4PF$_6$ recorded over a range of concentrations. b) The intensity of the charge-transfer band varies linearly with concentration, thus confirming that the self-complexed interlocked structure does not dissociate upon dilution.

Synthesis and Shuttling Rate of a Degenerate Molecular Shuttle

Finally, a degenerate molecular shuttle was prepared in 15% yield by subjecting two equivalents of **7** with one equivalent each of 1,4-diethynylbenzene and CBPQT·4PF$_6$ to Cu-catalyzed cyclization conditions (Scheme 10). Purification by preparative TLC afforded **27**·4PF$_6$ in 16% yield.

The shuttling process of **27**·4PF$_6$ was investigated by variable temperature ^{1}H NMR spectroscopy in CD_3COCD_3 (Figure 5). In this [2]rotaxane, the CBPQT^{4+} ring shuttles between the two identical stations by passing over a spacer containing two triazole rings. The shuttling process is slow on the NMR timescale at lower temperatures, a feature which causes many of the resonances in the ^{1}H NMR spectrum to separate into pairs of signals of equal intensity. This separation is most easily observed by tracking the resonances of the alkyl protons on the hydrophobic stoppers at low temperature. As the temperature is increased, the shuttling rate becomes faster than the NMR timescale, and the two sets of signals coalesce. A semiquantitative prediction of the energy barrier to this shuttling process was accomplished by using the variable-temperature coalescence method,[33] and it was found to be (15.5±0.1) kcal mol^{-1}. This value is similar to those obtained for triphenylene and tetraethylene glycol spacers ((15.0±0.2) and (15.5±0.1) kcal mol^{-1}, respectively)[7g] and corresponds to a shuttling frequency of 22 Hz at 23 °C.



Scheme 10. Synthesis of the [2]rotaxane degenerate shuttle **27**·4PF$_6$.

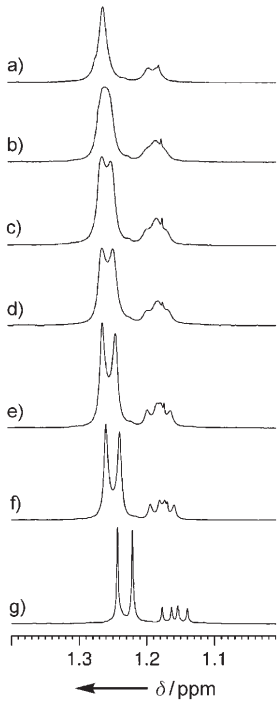


Figure 5. Section of variable-temperature ^{1}H NMR spectra (500 MHz, CD_3COCD_3) of the methyl protons in the degenerate molecular shuttle **27**·4PF$_6$. a) 315 K, b) 309 K, c) 306 K, d) 302 K, e) 300 K, f) 296 K, g) 261 K.

Conclusions

We have demonstrated the utility of Cu^I-catalyzed Huisgen 1,3-dipolar cycloaddition for the preparation of donor–acceptor rotaxanes and self-complexes. Because of the potential of this reaction for making a variety of diverse topologically interesting compounds, we have created a modular set of components to prepare a variety of mechanically interlocked molecules. The symmetrical DNP derivative **2** bearing two azide-terminated glycol chains and the asymmetric derivative **7** bearing one stopper and one azide group serve as universal precursors to symmetrical and nonsymmetrical mechanically interlocked molecules, respectively. Furthermore, several different CBPQT^{4+} derivatives, including the parent macrocycle, the weaker-binding fluorinated derivative **13**·4PF$_6$, and the alkyne-bearing **17**·4PF$_6$, can be used interchangeably, with seemingly no limit imposed on the preparation of other alkyne- and azide-functionalized components.

Higher-order rotaxanes, whose synthesis would have proceeded in prohibitively low yields with the clipping approach, have been made with ease and in high yields by employing this methodology. Significantly, we have also found that the triazoles formed as a result of the cycloaddition reaction do not serve as competing recognition sites, nor do they hinder significantly the rate of shuttling of the CBPQT^{4+} ring between degenerate recognition sites. The modularity, convergent nature, and high yield of this approach lead us to believe that it will continue to be the method of choice in obtaining previously inaccessible molecular machines and topologically challenging compounds.

Experimental Section

General

All reagents were purchased from commercial suppliers (Aldrich or Fisher) and were used without further purification. Dry solvents were used as received from a Dri-Solv solvent system purchased from EMD Chemicals. TLC was carried out on aluminum sheets precoated with silica gel 60 (Merck 40–60 μm, 230–400 mesh). Melting points were measured on an Electrothermal 9100 melting-point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 or AV-600 spectrometer. NMR spectra were calibrated by using the residual peak of the nondeuterated solvent as internal standard. All ^{13}C NMR spectra were recorded with simultaneous decoupling of hydrogen nuclei. Electrospray ionization (ESI) mass spectra were recorded on a Finnigan LCQ ion-trap mass spectrometer with MeCN/H_2O (1:1) as the mobile phase. High-resolution fast atom bombardment (HR-FAB) mass spectra were obtained on a JEOL JMS-600H high-resolution mass spectrometer equipped with an FAB probe. Isothermal titration microcalorimetry (ITC) was carried out on a Microcal VP-ITC titration microcalorimeter. Aliquots (3–7 μL) of degassed solutions of the guest in MeCN were titrated with stirring into solutions of the host at 298 K. The enthalpy of dilution for each titration was measured by determining the heat released by the injection of the guest into MeCN in the absence of the host, and the enthalpy of dilution was subtracted from the enthalpy of the titration to determine the enthalpy of complexation. Software provided by Microcal LLC was used to calculate the thermodynamic parameters of the titration ($\Delta G°$, K_a, $\Delta S°$, $\Delta H°$) based on a one-site binding model.

Syntheses

2: 1,5-Bis[2-(2-(2-(toluene-4—sulfonyl)ethoxy)ethoxy)ethoxy]naphthalene (**1**)[34] (0.200 g, 0.273 mmol) and sodium azide (0.355 g, 5.458 mmol) were dissolved in DMF (2.7 mL) and heated at 60 °C for 12 h. The crude reaction mixture was partitioned between water (100 mL) and CH_2Cl_2, and the aqueous phase was washed with CH_2Cl_2 (3×50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and the solvent was evaporated. The crude product was subjected to chromatography (SiO_2, CH_2Cl_2/Et_2O=7:3) to give **2** (96 mg, 74%) as a pale-yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=7.86 (d, $^3J_{H,H}$=9 Hz, 2H, DNP Ar-H *p*-O), 7.35 (t, $^3J_{H,H}$=9 Hz, 2H, DNP Ar-H *m*-O), 6.84 (d, $^3J_{H,H}$=8 Hz, 2H, DNP Ar-H *o*-O), 4.31 (t, $^3J_{H,H}$=5 Hz, 4H, DNP-OCH_2), 4.00 (t, $^3J_{H,H}$=5 Hz, 4H), 3.82 (t, $^3J_{H,H}$=9 Hz, 4H), 3.74–3.64 (m, 8H), 3.37 ppm (t, $^3J_{H,H}$=5 Hz, 4H, CH_2N_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=154.2, 126.7, 125.0, 114.5, 105.6, 71.0, 70.7, 70.0, 69.8, 67.8, 50.6 ppm; HRMS (FAB): *m/z* calcd for $C_{22}H_{30}N_6O_6$: 474.2227; found: 474.2226.

5: Tetraarylmethane **3** (1.500 g, 3.057 mmol), **4**[35] (1.799 g, 3.668 mmol), K_2CO_3 (1.690 g, 12.23 mmol), and [18]crown-6 (0.040 g, 0.153 mmol) were dissolved partially in MeCN (30 mL). The heterogeneous solution was heated at reflux with vigorous stirring for 12 h. The reaction mixture was filtered through celite, and the solvent was evaporated. Flash chromatography (SiO_2, CH_2Cl_2/diethyl ether=85:15) of the crude product gave **5** (1.725 g, 70%) as an amorphous white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=7.88 (d, $^3J_{H,H}$=9 Hz, 1H, DNP *p*-O), 7.86 (d, $^3J_{H,H}$=9 Hz, 1H, DNP Ar-H *p*-O), 7.38–7.27 (m, 2H, DNP Ar-H *m*-O), 7.25–7.21 (m, 4H, stopper Ar-H *o*-*t*Bu), 7.11–7.07 (m, 10H, stopper all *meta* Ar-H and *o*-*i*Pr), 6.85 (d, $^3J_{H,H}$=8 Hz, 1H, DNP Ar-H *o*-O), 6.84 (d, $^3J_{H,H}$=8 Hz, 1H, DNP Ar-H *o*-O), 6.80 (d, $^3J_{H,H}$=9 Hz, 2H, stopper Ar-H *o*-O), 4.33–4.29 (m, 4H, both DNP-OCH_2), 4.16 (t, $^3J_{H,H}$=5 Hz, 2H, stopper-OCH_2), 4.07 (t, $^3J_{H,H}$=5 Hz, 2H, stopper-OCH_2CH_2), 4.02–3.97 (m, 4H, both DNP-OCH_2CH_2), 3.80–3.77 (m, 2H, $HOCH_2CH_2$), 3.76–3.73 (m, 2H, $HOCH_2$), 2.88 (sept, $^3J_{H,H}$=7 Hz, 1H, *i*Pr-H), 1.31 (s, 18H, *t*Bu), 1.24 ppm (d, $^3J_{H,H}$=7 Hz, 6H, *i*Pr-CH_3); ^{13}C NMR (125 MHz,

$CDCl_3$, 25 °C): δ = 156.4, 154.3, 154.1, 148.2, 145.9, 144.5, 144.0, 139.7, 132.1, 130.9, 130.6, 128.9, 128.8, 126.7, 126.6, 125.1, 125.1, 125.0, 124.0, 114.7, 114.4, 113.0, 105.7, 72.5, 70.0, 69.9, 69.7, 67.9, 67.8, 67.2, 63.0, 61.8, 34.2, 33.4, 23.9 ppm; HRMS (FAB): *m/z* calcd for $C_{54}H_{64}O_6$: 808.4703; found: 808.4701.

6: Alcohol **5** (0.300 g, 0371 mmol), 4-dimethylaminopyridine (DMAP; 0.005 g, 0.037 mmol), and triethylamine (0.261 mL, 1.854 mmol) were dissolved in CH_2Cl_2 (3.7 mL). The solution was cooled to 0 °C, and *p*-toluenesulfonyl chloride (0.085 g, 0.445 mmol) was added. The solution was allowed to warm slowly to room temperature with stirring for 12 h. The reaction mixture was poured into CH_2Cl_2 (50 mL), washed with H_2O (2 × 50 mL), saturated NH_4Cl (2 × 50 mL), and brine (1 × 50 mL), dried ($MgSO_4$), filtered, and the solvent evaporated. The crude product was passed through a short plug of SiO_2 in CH_2Cl_2 to obtain pure **6** (0.221 g, 62 %). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.83 (d, $^3J_{H,H}$ = 9 Hz, 1H, DNP *p*-O), 7.79 (d, $^3J_{H,H}$ = 9 Hz, 1H, DNP Ar-H *p*-O), 7.78 (d, $^3J_{H,H}$ = 8 Hz, 2H, tosylate Ar-H *o*-S), 7.37–7.27 (m, 2H, DNP Ar-H *m*-O), 7.25–7.20 (m, 4H, stopper Ar-H *o*-*t*Bu), 7.10–7.04 (m, 10H, stopper all *meta* Ar-H and *o*-*i*Pr), 6.85 (d, $^3J_{H,H}$ = 8 Hz, 1H, DNP Ar-H *o*-O), 6.80 (d, $^3J_{H,H}$ = 9 Hz, 2H, stopper Ar-H *o*-O), 6.78 (d, $^3J_{H,H}$ = 8 Hz, 1H, DNP Ar-H *o*-O), 4.32 (t, $^3J_{H,H}$ = 5 Hz, 2H), 4.24–4.14 (m, 6H), 4.07 (t, $^3J_{H,H}$ = 5 Hz, 2H), 3.99 (t, $^3J_{H,H}$ = 5 Hz, 2H), 3.91 (t, $^3J_{H,H}$ = 5 Hz, 2H), 3.83 (t, $^3J_{H,H}$ = 5 Hz, 2H), 2.87 (sept, $^3J_{H,H}$ = 7 Hz, 1H, *i*Pr-H), 2.35 (s, 3H, OTs-CH_3), 1.29 (s, 18H, *t*Bu), 1.24 ppm (d, $^3J_{H,H}$ = 7 Hz, 6H, *i*Pr-CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 156.4, 154.2, 154.0, 148.2, 145.9, 144.7, 144.5, 144.1, 139.7, 132.1, 130.9, 130.6, 129.7, 128.9, 127.9, 126.7, 126.6, 125.1, 125.0, 124.0, 114.7, 114.4, 113.0, 105.7, 105.6, 70.0, 69.8, 69.3, 68.9, 67.9, 67.8, 67.2, 63.0, 34.2, 33.3, 31.3, 29.6, 23.9, 21.5 ppm; HRMS (FAB): *m/z* calcd for $C_{61}H_{70}O_8S$: 962.4791; found: 962.4833.

7: Tosylate **6** (0.275 g, 0.285 mmol) and sodium azide (0.186 g, 2.855 mmol) were stirred in DMF (3.81 mL) at 50 °C for 6 h. The reaction mixture was filtered through celite and the solvent evaporated. The resulting solid was sonicated in CH_2Cl_2, and the soluble fractions were subjected to chromatography (SiO_2, CH_2Cl_2) to yield **7** (0.155 g, 68 %) as an amorphous white powder. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.89 (d, $^3J_{H,H}$ = 8 Hz, 1H, DNP *p*-O), 7.87 (d, $^3J_{H,H}$ = 8 Hz, 1H, DNP Ar-H *p*-O), 7.38–7.29 (m, 2H, DNP Ar-H *m*-O), 7.25–7.20 (m, 4H, stopper Ar-H *o*-*t*Bu), 7.12–7.06 (m, 10H, stopper all *meta* Ar-H and *o*-*i*Pr), 6.85 (d, $^3J_{H,H}$ = 8 Hz, 1H, DNP Ar-H *o*-O), 6.84 (d, $^3J_{H,H}$ = 8 Hz, 1H, DNP Ar-H *o*-O), 6.80 (d, $^3J_{H,H}$ = 9 Hz, 2H, stopper Ar-H *o*-O), 4.34–4.29 (m, 4H), 4.16 (t, $^3J_{H,H}$ = 5 Hz, 2H), 4.07 (t, $^3J_{H,H}$ = 5 Hz, 2H), 4.03–3.97 (m, 4H), 3.84 (t, $^3J_{H,H}$ = 5 Hz, 2H), 3.44 (t, $^3J_{H,H}$ = 5 Hz, 2H, CH_2N_3), 2.88 (sept, $^3J_{H,H}$ = 7 Hz, 1H, *i*Pr-H), 1.30 (s, 18H, *t*Bu), 1.24 ppm (d, $^3J_{H,H}$ = 7 Hz, 6H, *i*Pr-CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 156.5, 154.2, 154.1, 148.2, 145.9, 144.5, 144.0, 139.7, 132.1, 130.9, 130.6, 126.7, 126.6, 125.1, 125.1, 125.0, 124.0, 114.7, 114.5, 113.0, 105.6, 70.3, 70.0, 69.9, 69.8, 67.9, 67.2, 63.0, 50.7, 34.2, 33.3, 31.3, 23.9 ppm; HRMS (FAB): *m/z* calcd for $C_{54}H_{63}N_3O_5$: 873.4768; found: 873.4736.

8: Tetraarylmethane **3**[36] (0.750 g, 1.528 mmol) and K_2CO_3 (0.634 g, 4.585 mmol) were suspended in DMF (7.6 mL). Propargyl bromide (0.6 g of an 80 wt % solution in xylenes, 3.47 mmol) was added, and the solution was heated to 50 °C for 12 h. The reaction mixture was poured into EtOAc (75 mL), washed with $NaHSO_4$ (1 M, 75 mL), H_2O (2 × 75 mL), and brine (75 mL), and dried ($MgSO_4$). The solution was transferred onto silica gel by rotary evaporation, loaded onto a silica-gel column, and subjected to chromatography (EtOAc/hexanes = 1:9) to give **8** (0.602 g, 75 % yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.22 (d, $^2J_{H,H}$ = 9 Hz, 4H, Ar-H *o*-*t*Bu), 7.12 (d, $^2J_{H,H}$ = 7 Hz, 2H, Ar-H, Ar-H *o*-*i*Pr), 7.13–7.03 (m, 8H, all *meta* Ar-H), 6.85 (d, $^2J_{H,H}$ = 6 Hz, 2H, Ar-H *o*-O), 4.66 (d, $^2J_{H,H}$ = 2 Hz, OCH_2), 2.88 (sept, $^2J_{H,H}$ = 7 Hz, 1H, $CH(CH_3)_2$), 2.52 (t, $^2J_{H,H}$ = 2 Hz, 1H, CCH), 1.30 (s, 18H, *t*Bu), 1.24 ppm (d, $^2J_{H,H}$ = 7 Hz, 6H, *i*Pr); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.4, 148.2, 146.0, 144.4, 144.0, 140.4, 132.2, 130.9, 130.6, 125.1, 124.0, 113.2, 78.7, 75.3, 63.1, 55.7, 34.2, 33.4, 31.3, 23.9 ppm; HRMS (FAB): *m/z* calcd for $C_{39}H_{45}O$: 529.3470; found: 529.3449.

9: 4-*tert*-Butylphenyl bromide (24.5 mL, 30.1 g, 141.4 mmol) was added slowly to freshly cleaned magnesium turnings (3.50 g, 144 mmol; cleaned by sonication in Et_2O) in THF (65 mL) under an Ar atmosphere. The solution was heated at reflux for 4 h until the solid Mg had disappeared. The Grignard reagent was cooled to 0 °C, and a solution of methyl 4-methoxybenzoate (10.0 g, 60.2 mmol) in a minimum amount of THF was added by cannula. The mixture was heated at reflux for 1 h before being taken up in CH_2Cl_2 (100 mL), washed with saturated NH_4Cl (3 × 100 mL), dried ($MgSO_4$), and the solvent was evaporated. The crude product was recrystallized from hexanes to yield **9** (20.8 g, 86 %) as white crystals. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.33–7.31 (m, 4H, H-Ar), 7.21–7.18 (m, 6H, H-Ar), 6.84 (d, $^3J_{H,H}$ = 9 Hz, 2H, Ar-H), 3.80 (s, 3H, OCH_3), 1.32 ppm (s, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 149.8, 144.1, 139.5, 129.0, 127.4, 124.6, 113.0, 81.3, 55.1, 34.3, 31.3 ppm; HRMS (FAB): *m/z* calcd for $C_{28}H_{34}O_2$: 402.2559; found 402.2567; elemental analysis: calcd (%) for $C_{28}H_{34}O_2$: C 83.54, H 8.51; found: C 83.74, H 8.18.

10: Trityl alcohol **9** (10.00 g, 24.2 mmol) and phenol (45.4 g, 483 mmol) were mixed neat and heated to 80 °C until the phenol melted. Concentrated HCl (1.1 mL) was added, and the solution was heated to 100 °C for 5 h. The reaction mixture was taken up in PhMe, washed with aqueous NaOH (0.5 M, 7 × 75 mL), dried ($MgSO_4$), and the solvent evaporated to give the crude product as a yellow oil. Chromatography (SiO_2, 25 % hexanes in CH_2Cl_2) afforded **10** (6.06 g, 62 %) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.24–7.22 (m, 4H, Ar-H), 7.10–7.04 (m, 8H, Ar-H), 6.77 (d, $^3J_{H,H}$ = 9 Hz, 2H, Ar-H), 6.70 (d, $^3J_{H,H}$ = 9 Hz, 2H, Ar-H), 4.63 (s, 1H, OH), 3.79 (s, 3H, OCH_3), 1.30 ppm (s, 18H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 153.3, 148.4, 144.2, 139.9, 139.7, 132.4, 132.2, 130.6, 129.1, 124.1, 114.0, 112.5, 62.8, 55.2, 34.3, 31.4 ppm; HRMS (FAB): *m/z* calcd for $C_{34}H_{38}O_2$: 478.2872; found: 478.2886; elemental analysis: calcd (%) for $C_{34}H_{38}O_2$: C 85.31, H 8.00; found: C 84.89, H 8.15.

11: A solution of BBr_3 (1 M) in CH_2Cl_2 (23.0 mL, 23.0 mmol) was added dropwise to a solution of **10** (5.00 g, 10.4 mmol) in CH_2Cl_2 (350 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 36 h under argon. MeOH (5 mL) and then H_2O (200 mL) were added to quench the reaction. The organic layer was separated and collected. The aqueous layer was washed with CH_2Cl_2 (3 × 200 mL), and the combined organic layers were dried ($MgSO_4$). Removal of the solvent in vacuo afforded **11** (4.85 g, 100 %) as an orange powder that required no further purification. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.23 (d, $^3J_{H,H}$ = 9 Hz, 4H, Ar-H), 7.07 (d, $^3J_{H,H}$ = 9 Hz, 4H, Ar-H), 7.04 (d, $^3J_{H,H}$ = 9 Hz, 4H, Ar-H), 6.70 (d, $^3J_{H,H}$ = 9 Hz, 4H, Ar-H), 1.30 ppm (s, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.1, 148.3, 144.0, 139.8, 132.3, 130.5, 124.0, 113.9, 62.7, 34.2, 31.3 ppm; HRMS (FAB): *m/z* calcd for $C_{33}H_{36}O_2$: 464.2715; found: 464.2721.

12: Propargyl bromide (80 % *w*/*w* solution in xylenes, 4.80 g, 32.3 mmol) and K_2CO_3 (2.68 g, 19.4 mmol) were added to a solution of **11** (1.50 g, 3.23 mmol) in DMF (20 mL). The reaction mixture was heated to 50 °C and stirred for 40 h under Ar. The reaction mixture was taken up in EtOAc (150 mL), washed with $NaHSO_4$ (1 M, 1 × 150 mL), H_2O (2 × 100 mL), and brine (2 × 100 mL), dried ($MgSO_4$), and evaporated onto SiO_2. Chromatography (SiO_2, 10 % EtOAc in hexanes) afforded **12** (1.12 g, 64 %) as an off-white powder. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.24 (d, $^3J_{H,H}$ = 9 Hz, 4H, Ar-H), 7.10 (d, $^3J_{H,H}$ = 9 Hz, 4H, Ar-H), 7.07 (d, $^3J_{H,H}$ = 9 Hz, 4H, Ar-H), 6.85 (d, $^3J_{H,H}$ = 9 Hz, 4H, Ar-H), 4.66 (d, $^4J_{H,H}$ = 2 Hz, 4H, CH_2), 2.52 (t, $^4J_{H,H}$ = 2 Hz, 2H, acetylene-H), 1.30 ppm (s, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.4, 148.3, 143.9, 140.3, 132.0, 130.5, 124.0, 113.3, 78.7, 75.3, 62.7, 55.7, 34.2, 31.3 ppm; HRMS (FAB): *m/z* calcd for $C_{39}H_{40}O_2$: 540.3028; found: 540.3042.

15: Propargyl alcohol (3.00 g, 54 mmol), DMAP (0.19 g, 1.5 mmol), and **14** (5.00 g, 15.3 mmol) were mixed in CH_2Cl_2 (60 mL). After the solution was stirred for 10 min, DCC (4.70 g, 23 mmol) in CH_2Cl_2 (20 mL) was added dropwise with stirring. After 24 h, the solution was filtered to remove the white precipitate, and the solvent was evaporated under vacuum. The solid was redissolved in Et_2O (100 mL), filtered again, and the solvent was evaporated. The solid was purified by column chromatography (SiO_2, CH_2Cl_2/hexanes = 4:1) to afford **15** (650 mg, 1.78 mmol, 12 %) as a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.02 (d, $^4J_{H,H}$ = 2 Hz, 1H, aryl-H *o*-CO_2R), 7.57 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2 Hz, 1H, aryl-H *p*-CO_2R), 7.48 (d, $^3J_{H,H}$ = 8 Hz, 1H, aryl-H *m*-CO_2R), 4.95 (d, $^4J_{H,H}$ = 2 Hz, 2H, propargyl-CH_2), 4.94 (s, 2H, CH_2Br), 4.52 (s, 2H, CH_2Br), 2.61 ppm

(t, $^4J_{H,H}$=2 Hz, 1H, alkyne-H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ=164.8, 139.5, 138.6, 138.6, 133.2, 132.2, 131.7, 128.6, 77.2, 74.9, 34.8, 31.8, 30.6 ppm; MS (EI): *m/z* calcd for $C_{12}H_{10}Br_2O_2$: 345.9; found: 346 $[M]^+$, 265 $[M-Br]^+$.

17·4PF$_6$: Dicationic cyclophane precursor **16**·2PF$_6$ (0.733 g, 1.03 mmol) was added to a solution of **15** (0.359 g, 1.03 mmol) and DNP-DEG (1.04 g, 3.09 mmol) dissolved in DMF. The reaction mixture was subjected to high pressure (13 kbar) for 4 days. The solvent was removed from the resulting purple solution under vacuum, and the purple oil was subjected to liquid–liquid extraction (1% (*w/v*) aq. NH_4Cl by $CHCl_3$) until the solution became colorless. The solvent was removed from the aqueous portion, and the resulting solid was subjected to column chromatography (SiO_2, MeOH/$MeNO_2$/NH_4Cl (2 M)=7:1:2). The eluent was removed in vacuo, the solid was dissolved in hot H_2O, and a saturated aqueous solution of NH_4PF_6 was added until no further precipitate was observed. The precipitate was recovered by filtration to afford **17**·4PF$_6$ (170 mg, 0.14 mmol, 14%) as a white solid. ^{1}H NMR (500 MHz, CD_3CN, 25°C) δ=8.97–8.87 (br s, 8H, α-CBPQT^{4+}), 8.28 (s, 1H, aryl-H *o*-CO_2R), 8.26–8.17 (m, 6H, β-CBPQT^{4+}), 8.13 (d, *J*=5 Hz, 2H, β-CBPQT^{4+}), 7.73 (d, $^3J_{H,H}$=7 Hz, 1H, aryl-H *p*-CO_2R), 7.61 (d, $^3J_{H,H}$=7 Hz, 1H, aryl-H *m*-CO_2R), 7.58 (s, 4H, unsubstituted aryl-H), 6.18 (s, 2H, CBPQT^{4+} benzyl-H), 5.89 (s, 2H, CBPQT^{4+} benzyl-H), 5.79 (s, 4H, CBPQT^{4+} benzyl-H), 5.02 (d, $^4J_{H,H}$=2 Hz, 2H, propargyl CH_2), 3.00 ppm (t, $^4J_{H,H}$=2 Hz, 1H, alkyne-H); ^{13}C NMR (125 MHz, CD_3CN): δ=165.0, 149.8, 149.6, 149.5, 149.4, 145.2, 145.1, 145.0, 143.8, 136.3, 136.0, 135.8, 134.2, 133.5, 132.5, 130.3, 130.1, 129.6, 127.4, 127.3, 127.2, 126.7, 77.1, 76.2, 64.6, 64.5, 63.9, 61.4, 53.4 ppm; HRMS (FAB): *m/z* calcd for $C_{40}H_{34}O_2N_4P_3F_{18}$: 1037.1607 $[M-PF_6]^+$; found: 1037.1607.

18·4PF$_6$: Diazide DNP derivative **2** (0.0070 g, 0.015 mmol), CBPQT·4PF$_6$ (0.017 g, 0.015 mmol), and **8** (0.016 g, 0.031 mmol) were dissolved in DMF (0.160 mL) at −10°C to form a deep-red solution. Stock solutions of $CuSO_4$·5H_2O in DMF (0.074 M, 20 μL) and ascorbic acid in DMF (0.148 M, 20 μL) were added. The solution was stirred at −10°C for 24 h, after which the solvent was evaporated. The red residue was redissolved in Me_2CO, and the [2]rotaxane was purified by preparative TLC with a solution of NH_4PF_6 (1% *w/v*) in Me_2CO as the mobile phase. The rotaxane was recovered from the silica gel by washing with an excess of eluent. The Me_2CO was concentrated to a minimum volume, and the product was precipitated from this solution by the addition of an excess of cold water. The [2]rotaxane **18**·4PF$_6$ (0.033 g, 84%) was isolated as a purple solid. ^{1}H NMR (500 MHz, CD_3COCD_3, 52°C): δ=9.21 (br s, 8H, α-CBPQT^{4+}), 8.29 (s, 8H, aryl-CBPQT^{4+}), 8.02 (s, 2H, triazole-H), 7.75 (br s, 8H, β-CBPQT^{4+}), 7.29 (d, $^3J_{H,H}$=7 Hz, 8H, stopper Ar-H *o*-*t*Bu), 7.16–7.05 (m, 20H, stopper all *meta* Ar-H, *o*-*i*Pr Ar-H), 6.84 (d, $^3J_{H,H}$=9 Hz , 4H, stopper Ar-H *o*-O), 6.49 (d, $^3J_{H,H}$=8 Hz, 2H, DNP *o*-O), 6.26 (t, $^3J_{H,H}$=8 Hz, 2H, DNP *m*-O), 6.02 (br s, 8H, CBPQT^{4+} benzyl-H), 4.97 (s, 4H, stopper-OCH_2), 4.61 (t, $^3J_{H,H}$=5 Hz, 4H), 4.53–4.47 (m, 4H), 4.33–4.27 (br m, 4H), 4.15 (t, $^3J_{H,H}$=5 Hz, 4H), 4.11–4.06 (m, 4H), 4.03–3.98 (m, 4H), 2.89 (sept, $^3J_{H,H}$=7 Hz, 2H, stopper *i*Pr-H), 2.80 (d, $^3J_{H,H}$=8 Hz, 2H, DNP *p*-O), 1.31 (s, 36H, *t*Bu), 1.23 ppm (d, $^3J_{H,H}$=7 Hz, 12H, *i*Pr-CH_3); ^{13}C NMR (125 MHz, CD_3COCD_3, 52°C): 149.6, 147.3, 146.7, 145.8, 145.4, 137.9, 133.1, 132.6, 131.9, 131.7, 129.3, 126.3, 125.8, 125.2, 114.6, 110.0, 105.9, 72.1, 71.8, 71.1, 70.5, 69.3, 66.6, 64.3, 62.6, 35.0, 34.3, 31.8, 24.3 ppm; MS (ESI; MeCN/H_2O=1:1, 0.1% AcOH): *m/z*=1170.9 $[M-2PF_6]^{2+}$, 723.3 $[M-3PF_6]^{3+}$, 512.9 $[M-4PF_6]^{4+}$.

General azide–alkyne cycloaddition procedure (**19**·8PF$_6$): DNP derivative **7** (0.013 g, 0.0155 mmol, 1.05 equiv per alkyne), CBPQT^{4+} (0.0195 g, 0.0178 mmol, 1.2 equiv per alkyne), and **12** (0.0040 g, 0.0074 mmol) were dissolved in DMF (0.090 mL) at −10°C to form a deep-red solution. Stock solutions of $CuSO_4$·5H_2O in DMF (0.036 M, 20 μL, 0.05 equiv per alkyne) and ascorbic acid in DMF (0.072 M, 20 μL, 0.1 equiv per alkyne) were added. The solution was stirred at −10°C for 24 h, at which time the solvent was evaporated. The red residue was redissolved in Me_2CO, and the crude [2]rotaxane was purified by preparative TLC with a solution of NH_4PF_6 (2% *w/v*) in Me_2CO as the mobile phase. The rotaxane product was recovered from the silica gel by washing with an excess of Me_2CO/NH_4PF_6. The Me_2CO was concentrated to a minimum volume, and the product was precipitated by the addition of an excess of cold water. The [3]rotaxane **19**·8PF$_6$ (0.033 g, 84%) was isolated by filtration as a purple solid and dried under high vacuum overnight. ^{1}H NMR (500 MHz, CD_3CN, 75°C): δ=8.77 (br s, 16H, α-CBPQT^{4+}), 8.07 (s, 2H, triazole-H), 7.99 (s, 16H, aryl-CBPQT^{4+}), 7.37–7.24 (m, 28H, β-CBPQT^{4+}, all stopper Ar-H *o*-*t*Bu), 7.15–7.04 (m, 28H, stopper *m*-Ar-H, stopper Ar-H *o*-*i*Pr), 6.88–6.82 (m, 8H, stopper Ar-H *o*-O), 6.41 (d, $^3J_{H,H}$=8 Hz, 2H, DNP *o*-O), 6.37 (d, $^3J_{H,H}$=8 Hz, 2H, DNP *o*-O), 6.08–5.88 (m, 4H, DNP *m*-O), 5.79 (d, $^2J_{H,H}$=13 Hz, 8H, CBPQT^{4+} benzyl-H), 5.79 (d, $^2J_{H,H}$=13 Hz, 8H, CBPQT^{4+} benzyl-H), 5.11 (s, 4H, triazole-OCH_2), 4.83 (t, $^3J_{H,H}$=5 Hz, 4H, triazole-CH_2), 4.46–4.39 (br m, 8H), 4.36–4.28 (br m, 12H), 4.27–4.21 (m, 8H), 2.88 (sept, $^3J_{H,H}$=7 Hz, 2H, stopper *i*Pr-H), 2.56 (d, $^3J_{H,H}$=8 Hz, 2H, DNP *p*-O), 2.55 (d, $^3J_{H,H}$=8 Hz, 2H, DNP *p*-O), 1.31 (s, 18H, central *t*Bu), 1.29 (s, 36H, external *t*Bu), 1.22 ppm (d, $^3J_{H,H}$=7 Hz, 12H, stopper *i*Pr); ^{13}C NMR (125 MHz, CD_3COCD_3, 25°C): δ=156.2, 156.1, 150.9, 148.5, 148.4, 146.2, 145.2, 144.7, 144.3, 144.3, 143.8, 140.1, 140.0, 136.4, 131.8, 131.6, 131.2, 130.3, 130.0, 128.0, 127.9, 126.1 125.4, 124.6, 124.3, 124.2, 124.2, 113.5, 113.4, 108.2, 104.4, 104.3, 70.4, 69.8, 69.6, 68.2, 68.0, 65.0, 62.9, 62.6, 61.1, 50.5, 33.8, 33.8, 33.1, 30.5, 30.4, 23.1 ppm; MS (ESI; MeCN/H_2O=1:1, 0.1% AcOH): *m/z*=1324.6 $[M-3PF_6]^{3+}$, 957.3 $[M-4PF_6]^{4+}$, 736.9 $[M-5PF_6]^{5+}$, 589.9 $[M-6PF_6]^{6+}$, 484.9 $[M-7PF_6]^{7+}$.

21·12PF$_6$: The above procedure was followed with **20**[27] (0.0040 g, 0.011 mmol) as the alkyne-containing component. Preparative TLC provided the **21**·12PF$_6$ (47.5 mg, 72%) as a purple solid. ^{1}H NMR (500 MHz, CD_3COCD_3, 52°C): δ=9.17 (br s, 24H, α-CBPQT^{4+}), 8.61 (s, 3H, triazole-H), 8.28 (s, 24H, aryl-CBPQT^{4+}), 8.00–7.61 (m, 39H, β-CBPQT^{4+}, all central Ar-H), 7.26 (d, $^3J_{H,H}$=7 Hz, 12H, stopper Ar-H *o*-*t*Bu), 7.14–7.00 (m, 30H, stopper all *meta* Ar-H, *o*-*i*Pr Ar-H), 6.88 (d, $^3J_{H,H}$=9 Hz , 6H, stopper Ar-H *o*-O), 6.49 (d, $^3J_{H,H}$=8 Hz, 6H, DNP *o*-O), 6.22 (overlapping t, $^3J_{H,H}$=8 Hz, 6H, both DNP *m*-O), 6.20–5.90 (br m, 24H, CBPQT^{4+} benzyl-H), 4.00 (t, $^3J_{H,H}$=8 Hz, 6H, stopper-OCH_2), 4.59–4.53 (m, 12H), 4.53–4.47 (m, 12H), 4.46–4.39 (m, 12H), 4.32 (t, $^3J_{H,H}$=5 Hz, 6H, triazole-NCH_2), 2.86 (sept, $^3J_{H,H}$=7 Hz, 3H, stopper *i*Pr-H), 2.55 (br s, 3H, DNP *p*-O), 1.28 (s, 54H, *t*Bu), 1.20 ppm (d, $^3J_{H,H}$=7 Hz, 12H, *i*Pr-CH_3); ^{13}C NMR (125 MHz, CD_3COCD_3, 25°C):156.2, 150.8, 148.4, 147.2, 146.2, 145.2, 144.7, 144.3, 143.6, 141.4, 140.2, 140.0, 136.3, 131.8, 131.2, 130.3, 130.0, 127.9, 127.9, 127.7, 126.2, 125.7, 125.4, 124.6, 124.3, 124.2, 121.5, 113.4, 108.2, 104.4, 104.2, 70.35, 69.9, 69.7, 68.1, 68.0, 65.0, 62.9,50.5, 33.8, 33.1, 30.4, 23.1 ppm; MS (ESI; MeCN/H_2O=1:1, 0.1% AcOH): *m/z*=1915.2 $[M-3PF_6]^{3+}$, 1400.3 $[M-4PF_6]^{4+}$, 1091.3 $[M-5PF_6]^{5+}$, 885.3 $[M-6PF_6]^{6+}$, 738.1 $[M-7PF_6]^{7+}$, 627.7 $[M-8PF_6]^{8+}$, 541.8 $[M-9PF_6]^{9+}$.

24·4 PF$_6$: Fluorinated [2]rotaxane **24**·4PF$_6$ was obtained under the same conditions used for the preparation of **18**·4PF$_6$ by using **2** (0.0050 g, 0.011 mmol), **13**·4PF$_6$ (3 equiv, 0.039 g, 0.033 mmol), **8** (0.012 g, 0.031 mmol), and stock solutions of $CuSO_4$·5H_2O in DMF (0.074 M, 20 μL) and ascorbic acid in DMF (0.148 M, 20 μL). The [2]rotaxane **24**·4PF$_6$ (10.7 mg, 37%) was isolated as a purple solid. ^{1}H NMR (500 MHz, CD_3COCD_3, 51°C): δ=9.31–9.24 (m, 4H, α-CBPQT^{4+}), 9.19–9.13 (m, 4H, α-CBPQT^{4+}) 8.29 (s, 4H, aryl-CBPQT^{4+}), 7.99 (s, 2H, triazole-H), 7.95–7.86 (m, 4H, β-CBPQT^{4+}), 7.84–7.76 (m, 4H, β-CBPQT^{4+}), 7.29 (d, $^3J_{H,H}$=7 Hz, 8H, stopper Ar-H *o*-*t*Bu), 7.15–7.06 (m, 20H, stopper all *meta* Ar-H plus *o*-*i*Pr Ar-H), 6.84 (d, $^3J_{H,H}$=9 Hz , 4H, stopper Ar-H *o*-O), 6.65 (d, $^3J_{H,H}$=8 Hz, 2H, DNP *o*-O), 6.44 (br s, 4H, F_4CBPQT^{4+} benzyl-H), 6.31 (t, $^3J_{H,H}$=8 Hz, 2H, DNP *m*-O), 6.06 (br s, 4H, H_4CBPQT^{4+} benzyl-H), 4.97 (s, 4H, stopper-OCH_2), 4.63–4.54 (br m, 8H), 4.26–4.20 (br m, 4H), 4.09 (t, $^3J_{H,H}$=5 Hz, 4H), 4.04–3.97 (m, 4H), 3.97–3.92 (m, 4H), 3.37 (d, $^3J_{H,H}$=8 Hz, 1H, DNP *p*-O), 2.89 (sept, $^3J_{H,H}$=7 Hz, 2H, stopper *i*Pr-H), 2.72 (d, $^3J_{H,H}$=8 Hz, 2H, DNP *p*-O), 1.31 (s, 36H, *t*Bu), 1.23 ppm (d, $^3J_{H,H}$=7 Hz, 12H, *i*Pr-CH_3); MS (ESI; MeCN/H_2O=1:1, 0.1% AcOH): *m/z*=1206.5 $[M-2PF_6]^{2+}$, 756.0 $[M-3PF_6]^{3+}$, 530.8 $[M-4PF_6]^{4+}$; HRMS (ESI): *m/z* calcd for $C_{136}H_{146}F_{16}N_{10}O_8P_2^{2+}$: 1206.5272 $[M-2PF_6]^{2+}$; found: 1206.5267.

25·4PF$_6$: Azide DNP derivative **7** (18 mg, 0.022 mmol) and **17**·4PF$_6$ (25 mg, 0.022 mmol) were dissolved in DMF (0.20 mL) at −5°C. Stock solutions of $CuSO_4$·5H_2O in DMF (0.074 M, 20 μL) and ascorbic acid in DMF (0.148 M, 20 μL) were added. The solution was stirred at −5°C for 24 h, after which the solvent was evaporated. The purple residue was re-

dissolved in Me_2CO, and the [2]rotaxane was purified by preparative TLC with NH_4PF_6 (1% *w/v*) in Me_2CO as the mobile phase. The rotaxane product was recovered from the silica gel by washing with an excess of eluent. The Me_2CO was concentrated to a minimum volume, and the product was precipitated by the addition of an excess of cold water. The self-complex **25**·4PF_6 (18 mg, 43%) was isolated as a purple solid. ^{1}H NMR (500 MHz, CD_3COCD_3, 25 °C): δ = 9.43 (t, $^3J_{H,H}$ = 6 Hz, 2H, α-CBPQT^{4+}), 9.38 (t, $^3J_{H,H}$ = 8 Hz, 2H, α-CBPQT^{4+}), 9.33 (d, $^3J_{H,H}$ = 7 Hz, 1H, α-CBPQT^{4+}), 9.26 (d, $^3J_{H,H}$ = 7 Hz, 1H, α-CBPQT^{4+}), 9.21 (d, $^3J_{H,H}$ = 7 Hz, 1H, α-CBPQT^{4+}), 9.18 (d, $^3J_{H,H}$ = 6 Hz, 1H, α-CBPQT^{4+}), 8.85 (d, $^3J_{H,H}$ = 2 Hz, 1H, aryl-CBPQT^{4+}), 8.72 (dd, $^3J_{H,H}$ = 2, 9 Hz, 1H, aryl-CBPQT^{4+}), 8.61 (d, $^3J_{H,H}$ = 9 Hz, 1H, aryl-CBPQT^{4+}), 8.47 (s, 1H, triazole-H), 8.42 (d, $^3J_{H,H}$ = 8 Hz, 1H, aryl-CBPQT^{4+}), 8.37 (d, $^3J_{H,H}$ = 8 Hz, 1H, aryl-CBPQT^{4+}), 8.26 (dd, $^3J_{H,H}$ = 2, 9 Hz, 2H, aryl-CBPQT^{4+}), 7.90–7.76 (m, 6H, β-CBPQT^{4+}), 7.55 (dd, $^3J_{H,H}$ = 2, 7 Hz, 1H, β-CBPQT^{4+}), 7.29–7.18 (m, 6H, stopper aryl-H *o*-*t*Bu), 7.13 (d, $^3J_{H,H}$ = 10 Hz, 2H, stopper *o*-*i*Pr aryl-H), 7.04–6.98 (m, 8H, all stopper *meta* aryl-H), 6.84 (d, $^3J_{H,H}$ = 9 Hz, 2H, stopper aryl-H *o*-O), 6.53 (d, $^3J_{H,H}$ = 9 Hz, 1H), 6.38 (d, $^3J_{H,H}$ = 12 Hz, 1H), 6.34 (t, $^3J_{H,H}$ = 7 Hz, 1H), 6.18 (d, $^3J_{H,H}$ = 13 Hz, 1H), 6.08–6.01 (m, 5H), 5.87 (d, $^3J_{H,H}$ = 13 Hz, 1H), 5.75 (s, 1H), 5.72 (s, 1H), 5.38 (d, $^3J_{H,H}$ = 13 Hz, 1H), 4.95–4.86 (m, 1H), 4.74–4.65 (m, 2H), 4.62–4.40 (m, 9H), 4.33 (t, $^3J_{H,H}$ = 5 Hz, 2H), 4.25–4.13 (m, 2H), 2.81 (sept, $^3J_{H,H}$ = 7 Hz, 1H, *i*Pr-H), 2.62–2.53 (m, 2H, DNP aryl-H *m*-O), 1.22 (s, 18H, *t*Bu), 1.15 ppm (d, $^3J_{H,H}$ = 7 Hz, 6H, *i*Pr-CH_3); ^{13}C NMR (125 MHz, CD_3COCD_3, 298 °C): δ = 156.4, 152.4, 151.1, 148.3, 146.7, 146.4, 146.2, 146.0, 145.3, 145.3, 145.2, 144.5, 144.1, 143.7, 143.6, 142.3, 140.0, 137.3, 137.2, 137.0, 137.0, 137.6, 134.8, 132.1, 131.4, 130.9, 130.6, 130.3, 127.8, 127.2, 126.9, 126.6, 126.4, 126.2, 125.6, 125.3, 125.2, 125.2, 125.0, 125.0, 124.5, 124.2, 124.1, 113.3, 109.3, 109.3, 105.0, 105.0, 71.4, 70.4, 70.0, 68.3, 68.1, 67.9, 65.2, 65.0, 64.5, 62.9, 61.5, 57.3, 50.2, 33.8, 33.5, 33.1, 30.6, 23.2 ppm; MS (ESI; MeCN/H_2O = 1:1, 0.1% AcOH): *m/z* = 862.8 $[M-2PF_6]^{2+}$, 526.9 $[M-3PF_6]^{3+}$.

27·4PF_6: Azide DNP derivative **7** (100 mg, 0.117 mmol, 2.0 equiv), CBPQT·4PF_6 (64 mg, 0.059 mmol, 1.0 equiv), and **26** (7.4 mg, 0.059 mmol, 1.0 equiv) were dissolved in DMF (0.5 mL) at −5 °C to form a deep-purple solution. Stock solutions of $CuSO_4$·5H_2O in DMF (0.074 M, 80 μL) and ascorbic acid in DMF (0.148 M, 80 μL) were added. The solution was stirred at −5 °C for 24 h, after which the solvent was evaporated. The purple residue was redissolved in Me_2CO, and the [2]rotaxane was purified by preparative TLC with NH_4PF_6 (1% *w/v*) in Me_2CO as the mobile phase. The rotaxane product was recovered from the silica gel by washing with an excess of eluent. The Me_2CO was concentrated to a minimum volume, and the product was precipitated by the addition of an excess of cold water. The degenerate [2]rotaxane **27**·4PF_6 (0.030 g, 15.5%) was isolated as a purple solid. ^{1}H NMR (500 MHz, CD_3COCD_3, −2 °C): δ = 9.36 (d, $^3J_{H,H}$ = 6 Hz, 2H), 9.25 (d, $^3J_{H,H}$ = 6 Hz, 2H), 9.16 (d, $^3J_{H,H}$ = 6 Hz, 2H), 9.09 (d, $^3J_{H,H}$ = 7 Hz, 2H), 8.64 (s, 1H), 8.38 (s, 2H), 8.35 (s, 1H), 8.24 (s, 2H), 8.20 (s, 3H), 7.57–7.54 (m, 10H), 7.29–7.19 (m, 9H), 7.15–7.00 (m, 17H), 6.91–6.82 (m, 4H), 6.83 (s, 1H), 6.81 (s, 1H), 6.37 (t, $^3J_{H,H}$ = 7 Hz, 2H), 6.23–6.13 (m, 4H), 6.11–6.04 (m, 4H), 5.93 (d, $^3J_{H,H}$ = 13 Hz, 2H), 4.97 (s, 2H), 4.66 (t, $^3J_{H,H}$ = 5 Hz, 2H), 4.51–4.38 (m, 12H), 4.42 (s, 2H), 4.24 (s, 4H), 4.13 (t, $^3J_{H,H}$ = 4 Hz, 2H), 4.08 (t, $^3J_{H,H}$ = 4 Hz, 2H), 4.01 (s, 4H), 3.70 (t, $^3J_{H,H}$ = 4 Hz, 2H), 2.82 (overlapping sept, $^3J_{H,H}$ = 7 Hz, 2H), 2.65 (d, $^3J_{H,H}$ = 8 Hz, 1H), 2.64 (d, $^3J_{H,H}$ = 8 Hz, 1H), 1.24 (s, 18H), 1.22 (s, 18H), 1.17 (d, $^3J_{H,H}$ = 7 Hz, 6H), 1.15 ppm (d, $^3J_{H,H}$ = 7 Hz, 6H); MS (ESI; MeCN/H_2O = 1:1, 0.1% AcOH): *m/z* = 1302.1 $[M-2PF_6]^{2+}$, 819.7 $[M-3PF_6]^{3+}$; HRMS (ESI): *m/z* calcd for $C_{154}H_{164}F_{12}N_{10}O_{10}P_2^{2+}$: 1301.5960 $[M-2PF_6]^{2+}$; found: 1301.5946.

Crystal-Structure Determination and Refinement

X-ray diffraction intensity data were collected with a Bruker Smart 1000 CCD-based X-ray diffractometer. The frames for the data collection were integrated with the Bruker SAINT program system by using a narrow-frame integration algorithm. The structures were solved by direct methods and refined based on F^2 with the SHELXTL software package.[37] CCDC-624271 (**13**·4PF_6) and -624272 ([DNP-DEG⊂**13**]·4PF_6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **13**·4PF_6: $[C_{36}H_{28}F_4N_4](PF_6)_4$, M = 1377.77, monoclinic, $P2_1m$, a = 9.857(2), b = 20.966(4), c = 13.980(3) Å, β = 100.197(2)°, V = 2843.3(10) Å^3, Z = 2, ρ_{calcd} = 1.609 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 0.268 mm^{-1}, T = 100(2) K, colorless blocks; 7071 independent measured reflections, 5520 independent observed reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 57°), F^2 refinement, R_1 = 0.041, wR_2 = 0.097, 465 parameters.

Crystal data for [DNP-DEG⊂**13**]·4PF_6: $[C_{54}H_{52}F_4N_4O_6](PF_6)_4$, M = 1673.09, triclinic, $P\bar{1}$, a = 10.6685(16), b = 11.6101(17), c = 15.344(2) Å, α = 109.7120(10), β = 90.064(2), γ = 103.1320(10)°, V = 1736.1(4) Å^3, Z = 1, ρ_{calcd} = 1.599 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 0.241 mm^{-1}, T = 100(2) K, red platelets; 8290 independent measured reflections, 5927 independent observed reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°), F^2 refinement, R_1 = 0.058, wR_2 = 0.130, 539 parameters.

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[28] In our initial report,[16a] the assignments of the $CBPQT^{4+}$ β and phenylene resonances were transposed for compounds **18**·$4PF_6$, **19**·$8PF_6$, and **21**·$12PF_6$. We confirmed the corrected assignments by observing correlations between the $CBPQT^{4+}$ α and β resonances in a COSY experiment performed in CD_3COCD_3 at 245 K.

[29] The benzylic positions of α,α′-dibromo-*p*-tetrafluoroxylene show enhanced reactivity to nucleophilic substitution because of the +M effect (donation of electrons into the perfluoroarene π system).[18a] Though this phenomenon may also explain the reduced binding affinity between **13**·$4PF_6$ and electron-rich guests, catenanes that incorporate **13**·$4PF_6$ as the acceptor and DNP- or hydroquinone-containing crown ethers as the donor exhibit stronger charge-transfer interactions than the corresponding catenanes that contain $CBPQT^{4+}$ itself.[18b] Thus, the reduced binding affinity of **13**·$4PF_6$ is likely to be the result of the increased steric demand of the perfluoroarene ring.

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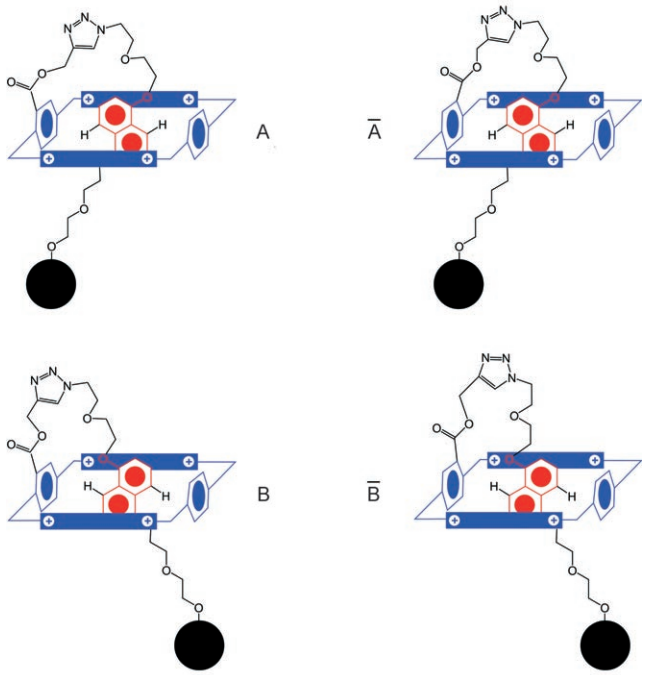
[31] The self-complexing compound **25**·$4PF_6$ exists as a possible mixture of four diastereoisomers as the result of the planar chirality associated with the DNP ring system and the helical chirality arising from the relative position of the benzoic ester substitution on the unsymmetrically substituted *p*-xylylene unit. It has not been determined whether the two enantiomeric pairs (A and Ā, B and B̄, respectively) can interconvert.



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