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⁺⁺) 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.
As an alternative to the clipping methodology for the installation of the CBPQT\textsuperscript{4+} cyclophane, we recently investigated synthetic transformations that are compatible with CBPQT\textsuperscript{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\textsuperscript{4+} ring to nucleophiles and bases. However, we recently harnessed the mild conditions, excellent functional-group tolerance, and high efficiency (all virtues of “click chemistry”) of the Cu\textsuperscript{I}-catalyzed Huisgen 1,3-dipolar cycloaddition\cite{14,15} for the preparation of donor–acceptor rotaxanes\cite{16} and catenanes.\cite{17} In this “threading-followed-by-stoppering” approach, the association process takes advantage of the thermodynamic 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,\cite{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\textsuperscript{4+} derivatives\cite{18} the attempted synthesis of which, with the clipping method, failed completely. Furthermore, self-complexed mechanically interlocked molecules\cite{19} were prepared efficiently by reacting an alkyne-functionalized CBPQT\textsuperscript{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.\cite{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\textsuperscript{4+} ring over 1,4-triazole units placed between degenerate DNP recognition sites. The barrier to shuttling (\(\Delta G^+\)) of the CBPQT\textsuperscript{4+} ring over the triazole units may be compared with values obtained previously for other spacers.\cite{7i} 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\cite{7j} and other condensed media.\cite{7k,9k}

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\textsuperscript{4+} ring within the degenerate shuttle.

\textbf{Results and Discussion}

\textbf{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 alkyn-functionalized rods, stoppers, and CBPQT\textsuperscript{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.

\textbf{Synthesis of Rotaxane Components}

The symmetrical DNP diazide derivative 2 was synthesized in 74\% yield by treating the corresponding ditosylate 1 with NaN\textsubscript{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\textsubscript{2}CO\textsubscript{3} as a base (Scheme 2). The azide half-dumbbell-shaped DNP derivative 7 was obtained first by

\textbf{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\textsuperscript{4+} derivatives by the Cu-catalyzed azide–alkyne cycloaddition.}
converting the hydroxy group into a tosylate, followed by nucleophilic displacement with NaN₃. The hydrophobic propargyl ether stopper 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-butylphenylmagnesium bromide to give the trityl alcohol (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 BBr₃ 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.

Although the synthesis of CBPQT·4PF₆ and the corresponding tetrafluorinated derivative 13·4PF₆ have both been reported previously, a new derivative 17·4PF₆ 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 17·4PF₆ was accomplished by reacting 15 with the dicationic cyclophane precursor 16·2PF₆ in DMF under high pressure (13 kbar) with 1,5-bis(ethoxy(ethoxy))dioxy-naphthalene (DNP-DEG) as a template.


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 18·4PF₆ (Scheme 6). The DNP diazide derivative 2 was mixed with CBPQT·4PF₆, 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 [2c:CBPQT]·4PF₆. Copper(II) sulfate pentahydrate and ascorbic acid were then added, and the so-
Scheme 5. Synthesis of the alkyne-functionalized CBPQT\(^{++}\) derivative 17·4PF\(_6\). DCC = dicyclohexylcarbodiimide.

olution was stirred for 24 h. By following these mild reaction conditions, \(18\cdot4\text{PF}_6\) 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\(^{[a]d}\) 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 \(19\cdot8\text{PF}_6\) was obtained from the stoppered DNP azide 7 and bis(propargyl ether) 12 in 79% yield (Scheme 7). The branched [4]rotaxane \(21\cdot12\text{PF}_6\) 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 (≪3%) yields.

The \(^1\text{H}\)NMR spectra of \(19\cdot8\text{PF}_6\) 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 (\(\delta = 6.30–6.20\) (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...
becomes fast on the NMR timescale, and the signals for the α-bipyridinium protons coalesce to afford a single, broad signal.[28]


The association between the fluorinated CBPQT⁺⁺ 13-4PF₆ and DNP is greatly attenuated relative to CBPQT⁺⁺ 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 23-2PF₆ 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 13-4PF₆ to azide-alkyne cycloaddition conditions, the [2]rotaxane 24-4PF₆ was isolated in 11% yield (Scheme 8b), along with significant quantities of the corresponding dumbbell compound and free 13-4PF₆. The yield of 24-4PF₆ was increased to 37% by running the reaction in the presence of 3 equivalents of 13-4PF₆. 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 perfluorinated aromatic ring into the CBPQT⁺⁺ scaffold affects the strength of its interaction with a DNP unit, the binding of 13-4PF₆ to DNP-DEG was investigated in the solid state. X-ray crystallography of 13-4PF₆ 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 13-4PF₆ suitable for X-ray diffraction were obtained by vapor diffusion of iPr₂O into a solution of 13-4PF₆ in MeCN. In the solid state, the presence of the four fluoride 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](image_url)

**Figure 3.** a) View along the axis of the F₄-substituted xylene ring of 13-4PF₆. 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]4PF₆, 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°, 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-xyllyl rings and 4-H/8-H of the DNP ring.

**Scheme 8.** a) Unsuccessful preparation of an F₄CBPQT⁺⁺-containing rotaxane by the clipping method. b) Synthesis of the F₄CBPQT⁺⁺-containing [2]rotaxane 24-4PF₆.
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 CBPQT4+, a factor that may explain its decreased ability to form host–guest complexes.

Crystals of the [2]pseudorotaxane [DNP-DEG·13·4PF6] were also obtained by vapor diffusion of iPr2O into a 3:1 solution of DNP-DEG/13·4PF6 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 13·4PF6 and DNP-DEG.[29]

To quantify this effect in solution, the thermodynamic parameters for the binding of DNP-DEG and 13·4PF6 were measured by isothermal titration microcalorimetry[60] (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 13·4PF6 (0.5 mM, MeCN). The association constant (K) of (690±220) M⁻¹ obtained is significantly lower than that of (36400±250) M⁻¹ obtained for the parent system [DNP-DEG·CBPQT]·4PF6 under similar conditions.[7]

### Synthesis and Characterization of Self-Complexing Systems

A self-complex[19] was prepared in 43% yield by subjecting the alkyne-functionalized CBPQT4+ derivative 17·4PF6 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 ¹³C 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 25·4PF6 (Figure 4). The intensity of the charge-transfer band (λmax = 512 nm, ε = 700 M⁻¹ cm⁻¹)[32] between the DNP and CBPQT4+ moieties in the absorption spectrum of 25·4PF6 was investigated over a range of concentrations. The linear change in absorbance with respect to the change in concentration of 25·4PF6 confirms the proposed interlocked structure, in which the DNP moiety does not dethread from the CBPQT4+ binding site.

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·4PF₆ to Cu-catalyzed cyclization conditions (Scheme 10). Purification by preparative TLC afforded 27·4PF₆ in 16% yield.

The shuttling process of 27·4PF₆ was investigated by variable temperature ¹H NMR spectroscopy in CD₃COCD₃ (Figure 5). In this [2]rotaxane, the CBPQT⁺ 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 ¹H 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 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) and corresponds to a shuttling frequency of 22 Hz at 23 °C.
We have demonstrated the utility of CuI-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<sup>+</sup><sub>4</sub> derivatives, including the parent macrocycle, the weaker-binding fluorinated derivative 13-4PF<sub>6</sub> and the alkylene-bearing 17-4PF<sub>6</sub>, 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<sup>+</sup> 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.

**1H** and **13C 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 **13C NMR** spectra were recorded with simultaneous decoupling of hydrogen nuclei.

**Syntheses**

2: 1.5-Bis[2-(2-(toluene-4-−sulfonyl)ethoxy)ethoxy]ethoxy)naphthalene (I)<sup>16</sup> (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<sub>2</sub>Cl<sub>2</sub>, and the aqueous phase was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic extracts were washed with brine, dried (MgSO<sub>4</sub>), and the solvent was evaporated. The crude product was subjected to chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtO (7:3) to give 2 (96 mg, 74%) as a pale-yellow solid. 1H NMR (500 MHz, CDCl<sub>3</sub>, 25°C, TMS): δ = 7.86 (d, <sup>1</sup>J<sub>HH</sub> = 9 Hz, 2H, DNP Ar-H p-O), 7.25 (s, <sup>1</sup>J<sub>HH</sub> = 10 Hz, 2H, DNP Ar-H o-O), 6.84 (d, <sup>1</sup>J<sub>HH</sub> = 8 Hz, 2H, DNP Ar-H o-O), 3.82 (t, <sup>1</sup>J<sub>HH</sub> = 5 Hz, 4H, DNP-OCH<sub>2</sub>), 3.37 ppm (t, <sup>1</sup>J<sub>HH</sub> = 5 Hz, 2H, DNPAr-H p-O), 3.73 (m, 2H, HOC<sub>2</sub>H<sub>2</sub>), 2.88 (sept, <sup>1</sup>J<sub>HH</sub> = 7.8 Hz, 6H, <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25°C); δ = 143.4, 142.9, 141.9, 134.3, 131.5, 129.4, 128.7, 127.6, 125.3, 124.9, 124.5, 123.3, 122.9, 120.0, 115.6, 60.6, 50.6 ppm; HRMS (FAB): m/z calcd for C<sub>31</sub>H<sub>29</sub>N<sub>15</sub>O<sub>8</sub>; 474.2226; found: 474.2226.

5: Tetraarylmethane 3 (1.500 g, 3.057 mmol), 4<sup>8</sup> (1.799 g, 3.688 mmol), K<sub>2</sub>CO<sub>3</sub> (1.690 g, 12.23 mmol), and [18]crown-6 (0.040 g, 0.153 mmol) were dissolved partially in MeCN (50 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<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/ether ether = 85:15) of the crude product gave 5 (1.725 g, 70%) as an amorphous white solid. 1H NMR (500 MHz, CDCl<sub>3</sub>, 25°C, TMS): δ = 7.88 (d, <sup>1</sup>J<sub>HH</sub> = 9 Hz, 1H, DNP Ar-H o-O), 7.86 (d, <sup>1</sup>J<sub>HH</sub> = 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-dBu), 7.11–7.07 (m, 10H, stopper meta Ar-H and meta-Ph), 6.85 (d, <sup>1</sup>J<sub>HH</sub> = 8 Hz, 1H, DNP Ar-H o-O), 6.84 (d, <sup>1</sup>J<sub>HH</sub> = 8 Hz, 1H, DNP Ar-H p-O), 6.80 (d, <sup>1</sup>J<sub>HH</sub> = 9 Hz, 2H, stopper Ar-H o-O), 4.33–4.29 (m, 4H, both DNP-OCH<sub>2</sub>), 4.16 (t, <sup>1</sup>J<sub>HH</sub> = 5 Hz, 2H, stopper-OCH<sub>2</sub>), 4.07 (t, <sup>1</sup>J<sub>HH</sub> = 5 Hz, 2H, stopper-OCH<sub>2</sub>), 4.02–3.97 (m, 4H, both DNP-OCH<sub>2</sub>CH<sub>3</sub>), 3.80–3.77 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 3.19 ppm (d, <sup>1</sup>J<sub>HH</sub> = 7 Hz, 6H, dPr-H); <sup>13</sup>C NMR (125 MHz,
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4.16 (t, 3.4, 33.4, 23.9 ppm; HRMS (FAB): m/z calculated for C_{34}H_{38}O_{2}: 481.2307; found: 481.2308).

6: Alcohol 5 (0.300 g, 0.071 mmol), 4-dimethylaminopyridine (DMAP), 0.005 g, 0.037 mmol, and triethylamine (0.261 mL, 1.854 mmol) were dissolved in CH_{2}Cl_{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_{2}Cl_{2} (50 mL), washed with H_{2}O (2 × 50 mL), saturated NH_{4}Cl (2 × 50 mL), and brine (1 × 50 mL), dried (MgSO_{4}), and the solvent evaporated. The crude product was passed through a small plug of SiO_{2}; to CH_{2}Cl_{2} to obtain pure 6 (0.221 g, 62%).

H NMR (500 MHz, CDCl_{3}, 25°C): δ = 7.98 (d, 9H, 2H, 1H, DNP Ar-H), 7.25–7.20 (m, 4H, stopper all Ar-H), 7.10–7.04 (m, 1H, stopper all meta Ar-H and o-Pr), 6.85 (d, 9H = 8 Hz, 1H, DNP Ar-H o-Pr), 6.80 (d, 9H = 8 Hz, 1H, DNP Ar-H p-0), 6.78 (d, 9H = 8 Hz, 1H, DNP Ar-H p-0), 6.32 (t, 9H = 5 Hz, 2H), 4.24–4.14 (m, 6H, 4OH, 4OH Ar-H p-Pr), 3.99 (t, 9H = 5 Hz, 2H), 3.91 (t, 9H = 5 Hz, 2H), 3.83 (t, 9H = 5 Hz, 2H), 2.87 (sept, 9H = 7 Hz, 1H, pr-Pr), 2.35 (s, 3H, OTs-CH_{3}), 1.29 (s, 18H, Bu), 1.24 ppm (d, 9H = 7 Hz, 6H, pr-Pr-CH_{3}); HRMS (FAB): m/z calculated for C_{34}H_{38}O_{2}: 496.2479; found: 496.4833.

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 solvents evaporated. The resulting solid was sonicated in CH_{2}Cl_{2}, and the soluble fractions were fractionated by chromatography (SiO_{2}; CH_{2}Cl_{2}) to yield 7 (0.155 g, 68%) as an amorphous white powder, H NMR (400 MHz, CDCl_{3}, 25°C): δ = 7.89 (d, 9H = 8 Hz, 1H, DNP Ar-H p-0), 7.87 (d, 9H = 8 Hz, 1H, DNP Ar-H p-0), 7.38–7.29 (m, 2H, DNP Ar-H m-0), 7.25–7.20 (m, 4H, stopper Ar-H o-Pr), 7.12–7.06 (m, 10H, stopper all meta Ar-H and o-Pr), 6.85 (d, 9H = 8 Hz, 1H, DNP Ar-H o-Pr), 6.84 (d, 9H = 8 Hz, 1H, DNP Ar-H o-Pr), 6.80 (d, 9H = 8 Hz, 1H, stopper Ar-H o-Pr), 4.34–4.29 (m, 4H, 4OH t, 9H = 5 Hz, 2H), 4.07 (t, 9H = 5 Hz, 2H), 4.03–3.97 (m, 4H, 4OH t, 9H = 5 Hz, 2H), 3.44 (t, 9H = 5 Hz, 2H), 3.40 (m, 18H, Bu), 2.12 ppm (q, 9H = 7 Hz, 6H, pr-Pr-CH_{3}); HRMS (FAB): m/z calculated for C_{34}H_{38}O_{2}: 478.2872; found: 478.2866; elemental analysis: calcd (% for C_{34}H_{38}O_{2}: C 85.31, H 8.00; found: C 85.31, H 7.86; 8H, 69.3, 68.9, 67.9, 67.8, 67.2, 63.0, 34.2, 33.3, 31.3, 29.3 ppm; HRMS (FAB): m/z calculated for C_{34}H_{38}O_{2}: C 84.89, H 8.15.

10: A solution of BBr_{3} (1.0 mL) in CH_{2}Cl_{2} (23.0 mL, 23.0 mmol) was added dropwise to a solution of 10 (5.00 g, 14.0 mmol) in CH_{2}Cl_{2} (350 mL) at 0°C. The reaction mixture was warmed to room temperature and stirred for 2 h under argon. MeOH (5 mL) and then H_{2}O (200 mL) were added to quench the reaction. The organic layer was separated and collected. The aqueous layer was treated with CH_{2}Cl_{2} (200 mL) and 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. H NMR (500 MHz, CDCl_{3}, 25°C): δ = 7.23 (d, 9H = 9 Hz, 4H, Ar-H), 7.07 (d, 9H = 9 Hz, 4H, Ar-H), 6.70 (d, 9H = 9 Hz, 4H, Ar-H), 6.07 (d, 9H = 9 Hz, 4H, Ar-H), 6.01 ppm (s, 18H, CH_{3}); 13C NMR (125 MHz, CDCl_{3}): δ = 151.5, 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 calculated for C_{34}H_{38}O_{2}: 646.2715; found: 646.2721.

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_{2}Cl_{2} (60 mL). After the solution was stirred for 10 min, DCC (4.70 g, 23 mmol) in CH_{2}Cl_{2} (20 mL) was added dropwise with stirring. After 2 h, the solution was filtered to remove the white precipitate, and the solvent was evaporated under vacuum. The solid was redissolved in EtOAc (100 mL), filtered again, and the solvent was evaporated. The solid was purified by column chromatography (SiO_{2}; CH_{2}Cl_{2}/hexanes (2:1) to afford 15 (3.78 g, 12%) as a white solid. H NMR (500 MHz, CDCl_{3}, 25°C): δ = 8.02 (d, 9H = 2 Hz, 1H, aryl-H o-CO_{2}R), 7.57 (d, 9H = 8 Hz, 2H, aryl-H p-CO_{2}R), 7.48 (d, 9H = 8 Hz, 1H, aryl-H m-CO_{2}R), 4.95 (d, 9H = 2 Hz, propargyl-CH_{3}), 4.94 (s, 2H, CH_{2}Br), 4.52 (s, 2H, CH_{2}Br), 2.61 ppm.


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of CuSO₄·5H₂O in DMF (0.074 644 76.2, 64.6, 64.5, 63.9, 61.4, 53.4ppm; HRMS (FAB): 18·

product was recovered from the silica gel by washing with an excess of aqueous solution of NH₄PF₆ was added until no further precipitate was

0.0178mmol, 1.2equiv per alkyne), and

General azide–alkyne cycloaddition procedure (1:1, 0.1% AcOH): 8.02 (s, 2H, DNP

m/z = 589.9 [M–6PF₆]⁺, 484.9 [M–7PF₆]⁺. 21-DPF: The above procedure was followed with 20m (0.004g, 0.011mol) as the alkylamine-containing precursor. Preliminary TRLC provided the 21-DPF (47.5 mg, 72%) as a purple solid. H NMR (500 MHz, CD3COCD3, 25°C): δ = 9.17 (brs, 24H, 3H–BCPQT4), 8.61 (s, 3H, tri-azole), 8.28 (24H, 4H–BCPQT4), 8.00–7.61 (m, 39H, 4βH–BCPQT4), all central Ar–H, 7.26 (3H, 2H, stopper –O), 6.22 (overlapping t, δ = 7.8 Hz, 6H, both DNP m–o), 6.05–5.90 (br m, 24H, 4βH–BCPQT4* benzyl-H), 4.00 (t, δ = 8.0 Hz, 6H, stopper–OCH3), 4.59–4.53 (m, 12H), 4.53–4.47 (m, 12H), 4.46–4.39 (m, 12H), 4.32 (t, δ = 7.8 Hz, 6H, triazole-NCH₃), 2.86 (sept, δ = 7.4 Hz, 3H, stopper–ipr), 2.55 (t, δ = 3.8 Hz, 3H, DNP m–p), 1.28 (brs, δ = 7.2 Hz, 12H, Pr–CH₃); 13C NMR (125 MHz, CD3COCD3, 25°C) 156.2, 150.8, 148.4, 147.2, 146.2, 145.2, 144.7, 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, 124.3, 124.2, 121.5, 113.8, 108.4, 104.4, 104.2, 70.35, 69.9, 69.7, 68.1, 68.0, 65.0, 62.95, 53.8, 33.1, 30.4, 23.1 ppm; MS (EI; McCN=O=H=1.1, 0.1% AcOH): m/z = 1915.2, 69.8 [M–6PF₆]⁺, 140.03 [M–4PF₆]⁺, 1061.3 [M–9PF₆]⁺, 885.3 [M–8PF₆]⁺, 738.1 [M–7PF₆]⁺, 6277.6 [M–8PF₆]⁺, 541.8 [M–9PF₆]⁺. 24-IPF: Fluorinated [2]rotaxane 24-IPF was obtained under the same conditions used for the preparation of 18-IPF, by using 2 (0.005g, 0.013mol), 13-IPF (3 equiv. 0.039g, 0.003mol), 8 (0.012g, 0.031mol), and stock solutions of CuSO₄·5H₂O in DMF (0.074m, 20µL) and ascorbic acid in DMF (0.148m, 20µL). The [2]rotaxane 24-IPF (1.07mg, 37%) was isolated as a purple solid. H NMR (500 MHz, CD3COCD3, 25°C): δ = 9.31–9.24 (m, 4H, 4βH–BCPQT4), 9.19–9.13 (m, 4H, e–BCPQT4) 8.29 (s, 4H, arylic=–BCPQT4), 7.99 (s, 2H, tri-azole), 7.95–7.86 (m, 4H, β–BCPQT4*), 7.84–7.76 (m, 4H, β–BCPQT4*), 7.29 (d, δ = 7.9 Hz, 8H, stopper Ar–H) 7.24 (t, δ = 7.9 Hz, 2H, DNP m–p), 1.31 (br s, 6H, β–DNP), 1.23 ppm (d, δ = 7.2 Hz, 2H, DNP p–p), 1.31 (s, 36H, β–Bu), 1.23 ppm (d, δ = 7.2 Hz, 12H, Pr–CH₃); MS (ESI; McCN=O=H=1.1, 0.1% AcOH): m/z = 2065.5 [M–2PF₆]⁺, 756.0 [M–3PF₆]⁺, 550.8 [M–4PF₆]⁺, HRMS (ESI) m/z calculated for C₁₉₂H₂₂₉F₄N₁₀O₄P₂⁺: 2065.5272 [M–2PF₆]⁺; found 2065.5267. 25-IPF: Azide DNP derivative 7 (18 mg, 0.022mol) and 17-IPF (25 mg, 0.022mol) were dissolved in DMF (0.20mL) at -5°C. Stock solutions of CuSO₄·5H₂O in DMF (0.074m, 20µL) and ascorbic acid in DMF (0.148m, 20µL) 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 Me2CO, and the 2]rotaxane was purified by preparative TLC with NH4PF6 (1% w/v) in Me2CO as the mobile phase. The rotaxane product was recovered from the silica gel by washing with an excess of eluent. The Me2CO was concentrated to a minimum volume, and the product was precipitated by the addition of an excess of cold water. The self-complex [2]rotaxane was purified by preparative TLC with NH4PF6 (1% w/v) in Me2CO as the mobile phase. The rotaxane product was recovered from the silica gel by washing with an excess of eluent. The Me2CO was concentrated to a minimum volume, and the product was precipitated by the addition of an excess of cold water. The 

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Synthesis and Dynamics of Donor–Acceptor Interlocked Compounds


[28] In our initial report,[36] the assignments of the CBPQT4+ and phenylene resonances were transposed for compounds 18-4PF6, 198PF6, and 21-12PF6. We confirmed the correct assignments by observing correlations between the CBPQT4+ α and β resonances in a COSY experiment performed in CD3COCD3 at 245 K.

[29] The benzylic positions of α,α-dibromo-p-tetrafluoroxylenyl show enhanced reactivity to nucleophile substitution because of the +M effect (donation of electrons into the perfluoroarene π system).[36]

Though this phenomenon may also explain the reduced binding affinity between 13-4PF6 and electron-rich guests, catenanes that incorporate 13-4PF6 as the acceptor and DNP- or hydroquinone-containing crown ethers as the donor exhibit stronger charge-transfer interactions than the corresponding catenanes that contain CBPQT4+ itself.[39] Thus, the reduced binding affinity of 13-4PF6 is likely to be the result of the increased steric demand of the perfluoroarene ring.


[31] The self-complexing compound 25-4PF6 exists as a possible mixture of four diastereomers 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-xylene unit. It has not been determined whether the two enantiomeric pairs (A and A, B and B, respectively) can interconvert.


[33] Variable-temperature 1H NMR spectroscopic coalescence method for 27-4PF6: The rate of shifting for the DNP-containing degenerate shuttle 27-4PF6 was estimated by determining the average value of the νex (15 s−1) of the peak separations for the two signals arising from the tert-butylenyl groups in the stoppers at low temperatures. This information was inserted into the equation kex= (νex/2) to determine the rate of exchange, kex. An estimate (309 K) for the coalescence temperature, Tc, along with kex were inserted into the Eyring equation, AGCrt = −RTln(kex/kT), in which R is the gas constant, h is the Planck constant, and k is the Boltzmann constant. The calculated ΔGCr value of (15.1±0.1) kcal mol−1 is similar to those obtained in other similar systems.[76]


