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Communication between Components in Metal-Directed Assemblies of Oriented Calix[6]arene-Based Pseudorotaxanes and Rotaxanes

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Dedicated to Professor Andrea Pochini on the occasion of his retirement

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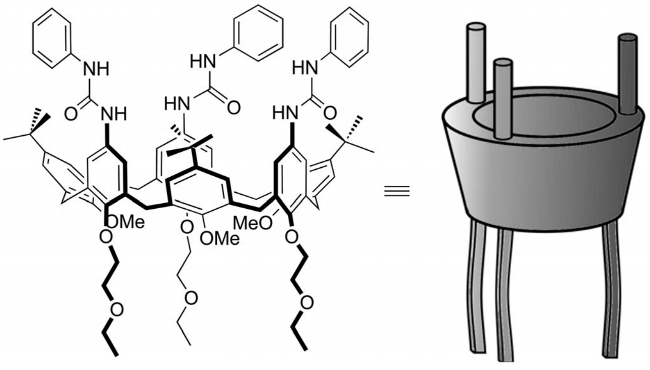
Oriented calix[6]arene-based pseudorotaxanes and rotaxanes where the axial component bears a terpyridine ligand as a stopper positioned at the upper rim of the calixarene have been synthesized. The binding ability of the terpyridine unit present in the axle toward zinc salts is affected by the presence of the wheel, its distance with respect to the calix[6]arene upper rim, and the nature of the counterion of the zinc salt employed. Metal coordination at the terpyridine unit changes the electrochemical behavior of the 4,4′-bipyridinium unit of the axle inside the wheel in both the pseudorotaxanes and rotaxanes.

Introduction

Pseudorotaxanes and rotaxanes encompass a class of devices that, under the action of external energy inputs, are able to behave as molecular level machines.[1] Recently, in view of conferring specific functional tasks, remarkable examples of rotaxanes and pseudorotaxanes endowed with an increased level of complexity where cooperative and allosteric effects play a crucial role in governing their functioning mode have been described.[2] It however appears that the increase in complexity stored in these systems parallels the increase in the number of parameters that influence their response to stimulations. Consequently, prediction of their working mode is far from trivial. Here we report preliminary data that show how the chemical properties and the response to electrochemical stimuli of oriented calix[6]arene-based pseudorotaxanes and rotaxanes are influenced by the orientation, distance among molecular components, and presence of a metal cationic effector.[3]

Results and Discussion

We have shown previously that calix[6]arene wheel **1** can act as a 3D asymmetric and heteroditopic host for the synthesis of oriented pseudorotaxanes and rotaxanes characterized by the univocal orientation of the two calixarene rims toward the two termini of the axles derived from 4,4′-dialkylviologen. With the general aim to exploit the unidirectional threading of asymmetrical axles into **1** for the construction of devices and molecular machines endowed with new properties,[4] we started a study to verify whether the orientation of the wheel rims toward one particular stopper could be employed as further a structural information element able to subtly modify their properties and/or working mode.



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Hence, we synthesized axle T(C6) (Scheme 1), where the central 4,4′-bipyridine (bipy) cationic core is functionalized with two hexyl chains, one of which bears an OH group suitable for further functionalization at one terminus and a 2,2′:6′,2′′-terpyridine (terpy) at the other. This latter unit was selected because it is bulky enough to act as stopper

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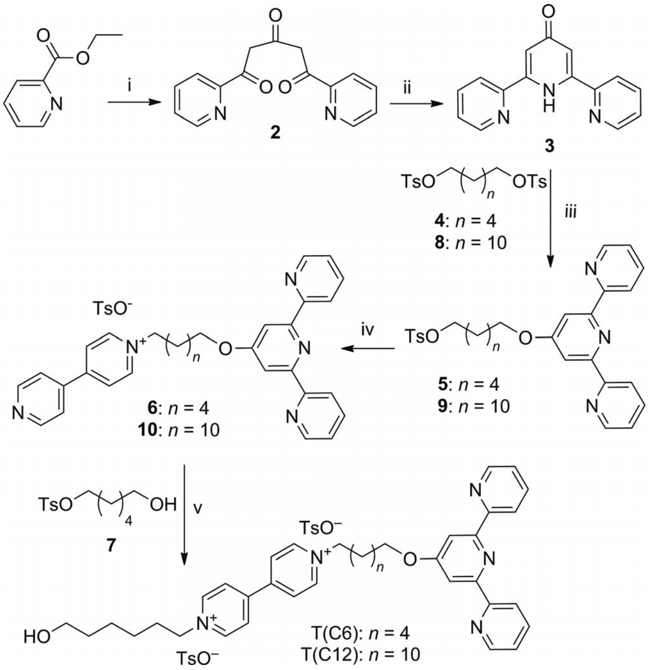
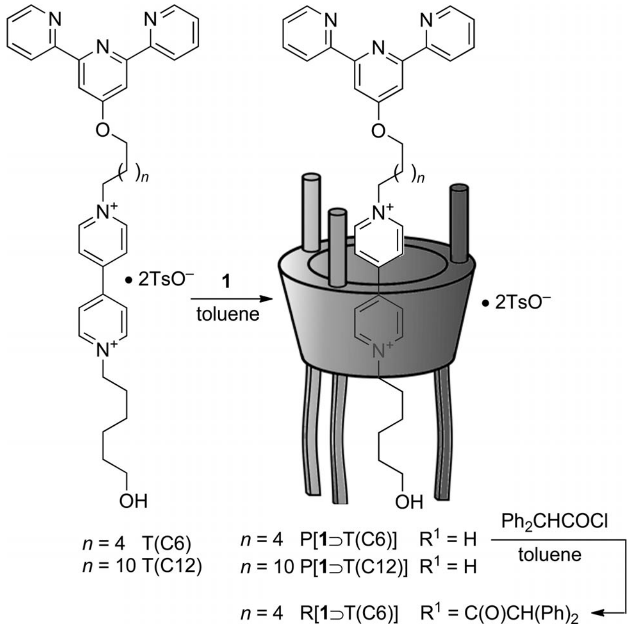
and because of its well-known ability to efficiently bind transition metal cations[5] that, in this axle, could possibly act as effectors.



Scheme 1. Reagents and conditions: (i) acetone, NaH, DME, reflux 4 h; (ii) NH_4OAc, EtOH abs., reflux 6 h; (iii) KOH, DMF, r.t., 90 min; (iv) 4,4′-bipyridine, CH_3CN, reflux, 48 h; (v) CH_3CN, reflux, 10 d.

A slight excess amount of solid axle T(C6) was added to a C_6D_6 solution of **1**; after mixing, the resulting deep-red suspension was filtered to remove the excess amount of undissolved salt and the resulting solution was analyzed by NMR spectroscopy. As expected,[6] the spectroscopic data showed that the oriented pseudorotaxane P[**1**⊃T(C6)] that bears the stopper at the upper rim of the wheel had formed (see Supporting Information). In a separate experiment, the threading process was carried out in toluene followed by the addition of diphenylacetyl chloride to yield the corresponding rotaxane R[**1**⊃T(C6)] (Scheme 2).

To establish whether the binding ability of the terpy unit in axle T(C6) toward metal cations was affected by the presence of the 4,4′-bipy cationic core, we used $Zn(TsO)_2$. This metal was chosen because of its well-documented preference to adopt an octahedral coordination geometry and its ability to form either 1:1 or 2:1 complexes with terpy ligands.[7] In agreement with the literature data,[8] the ^1H NMR spectra taken in $CDCl_3/CD_3OD$ (6:4) showed that T(C6) forms either the 1:1 or the 1:2 Zn/T(C6) complex, depending on the ratio between the analytes used and that these complexes are in slow exchange on the NMR time scale (Figure 1).



Scheme 2. Synthesis of oriented pseudorotaxanes P[**1**⊃T(C6)] and P[**1**⊃T(C12)] and rotaxane R[**1**⊃T(C6)].

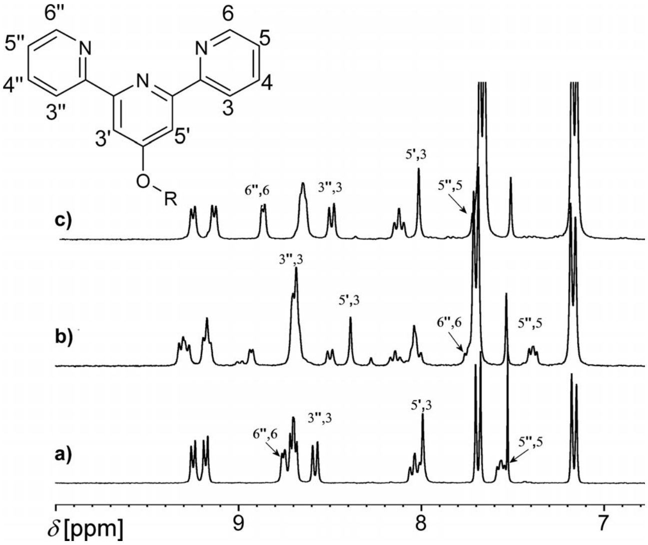
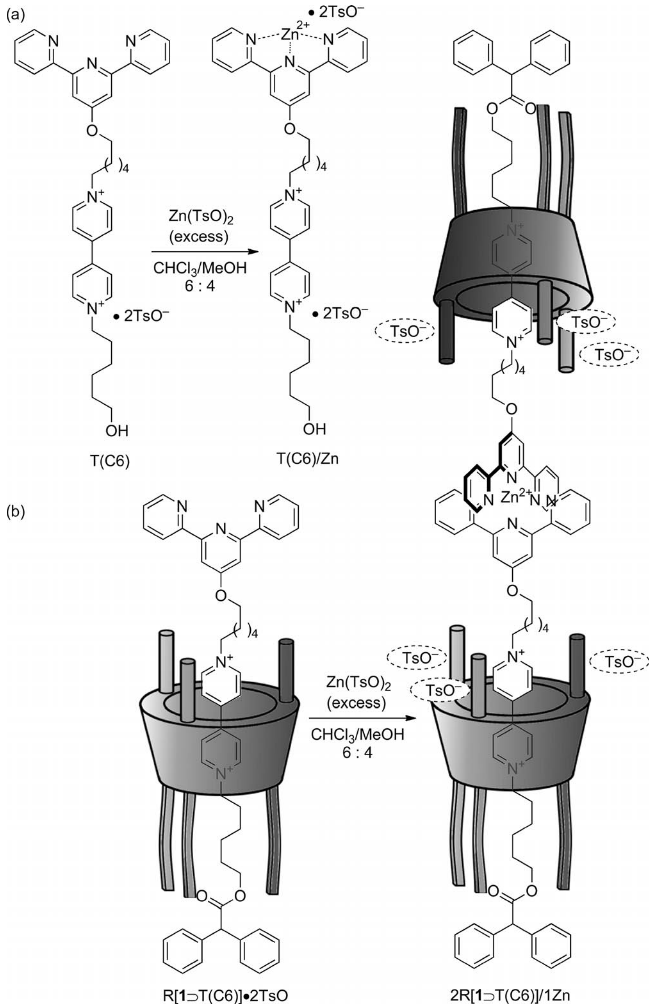


Figure 1. ^1H NMR ($CDCl_3/CD_3OD$ = 6:4, 300 MHz) stack plot (expanded region) of T(C6) with $Zn(TsO)_2$: (a) T(C6), (b) T(C6) + 0.5 equiv. $Zn(TsO)_2$, (c) T(C6) + 2 equiv. $Zn(TsO)_2$.

Because P[**1**⊃T(C6)] could not be employed in the $CDCl_3/CD_3OD$ mixture because of extensive dethreading of the axle from the wheel, C_6D_6 was used as the solvent to evaluate the binding features of the terpy unit in P[**1**⊃T(C6)] toward Zn^{2+}. The spectra obtained upon addition of an excess amount of solid $Zn(TsO)_2$ to P[**1**⊃T(C6)], in spite of the extensive broadening of several signals, suggests that the species that form, because of the upfield shifts experienced by the terpy protons, are compatible with a unique 2:1 adduct, where the two terpy units assume an orthogonal orientation around the Zn^{2+} ion.[8c] Further support for this stoichiometry was gained by comparing, in C_6D_6, the diffusion coefficient (*D*) of P[**1**⊃T(C6)] ($D = 2.68 \pm 0.02 \times 10^{-10}\ m^2 s^{-1}$) with that measured after the addition of an excess amount of solid $Zn(TsO)_2$ ($D = 2.09 \pm 0.05 \times 10^{-10}\ m^2 s^{-1}$), which confirmed the formation of the 2P[**1**⊃T(C6)]/1Zn complex.[9]

Quantitative data were obtained through UV/Vis techniques by titrating T(C6) with $Zn(TsO)_2$ in $CHCl_3/CH_3OH$ (6:4). Data treatment showed the formation of both the 1:1 and 2:1 complexes with binding constants $\log K_{1:1} = 6.7 \pm 0.3$ and $\log\beta = 12.3 \pm 0.3$, respectively. When R[**1**$\supset$T(C6)] was employed as the ligand for $Zn(TsO)_2$, it emerged that only one complex formed, with $\log\beta = 10.7 \pm 0.3$, consistent with a stoichiometry R[**1**$\supset$T(C6)]/Zn^{2+} = 2:1. This stoichiometry does not change even in the presence of a large excess of Zn^{2+} or by reversing the addition order of one species to the other (see Supporting Information). On the other hand, when $Zn(BF_4)_2$ was titrated with R[**1**$\supset$T(C6)], both the 1R[**1**$\supset$T(C6)]/1Zn and the 2R[**1**$\supset$T(C6)]/1Zn complexes form ($\log K_{1:1} = 7.3 \pm 0.3$, $\log\beta = 12.7 \pm 0.3$, respectively). This particular behavior could be explained by considering that when the more coordinating tosylate was employed, the perfect match between the six tosylate anions and the six ureido binding sites of the two wheels in the 2R[**1**$\supset$T(C6)]/1Zn and 2P[**1**$\supset$T(C6)]/1Zn species drives the formation of these 2:1 complexes (Scheme 3).[10]



Scheme 3. Different behavior of (a) axle T(C6) and (b) R[**1**$\supset$T(C6)] in the presence of an excess amount of $Zn(TsO)_2$.

A consequent question that emerged was whether the complexation of the Zn^{2+} ion at the terpy unit could have an effect on the ability of the whole R[**1**$\supset$T(C6)] and P[**1**$\supset$T(C6)] systems to work as molecular machines. To address this issue, the electroactivity of the bipy group in the different systems was examined by cyclic voltammetry (CV). Experiments were carried out in CH_2Cl_2 containing TBAP as a supporting electrolyte before and upon progressive addition of Zn^{2+} (0.5 to 3 equiv.) to the solution. Representative data are given in Figure 2 and Table 1. As expected, all the metal-free systems, T(C6), P[**1**$\supset$T(C6)], and R[**1**$\supset$T(C6)], showed the same behavior as that of similar previously reported systems (Figure 2a).[11] Namely, the free T(C6) axle and the R[**1**$\supset$T(C6)] rotaxane were both characterized by two monoelectronic reversible reduction waves at $E_{1/2}' = -0.68$ V vs. Ag^+/Ag and $E_{1/2}'' = -1.17$ V (axle)[12] and at $E_{1/2}' = -1.02$ V and $E_{1/2}'' = -1.42$ V (rotaxane). As expected, when included in the cavity of the wheel, the axle becomes more difficult to reduce and large negative shifts (ca. –400 mV) for the reduction waves were thus logically observed. For the same reason, in the case of the P[**1**$\supset$T(C6)] pseudorotaxane, the first reduction wave was observed at a lower potential ($E_{pc}' = -1.02$ V). However, in this latter system the 1 e^- reduction of the bipy unit destabilizes the axle–wheel complex, which results in fast dethreading of the axle from **1**. For this reason, this first reduction wave is irreversible and both the second system ($E_{1/2}' = -1.13$ V) and first oxidation peak ($E_{pa}' = -0.62$ V) observed

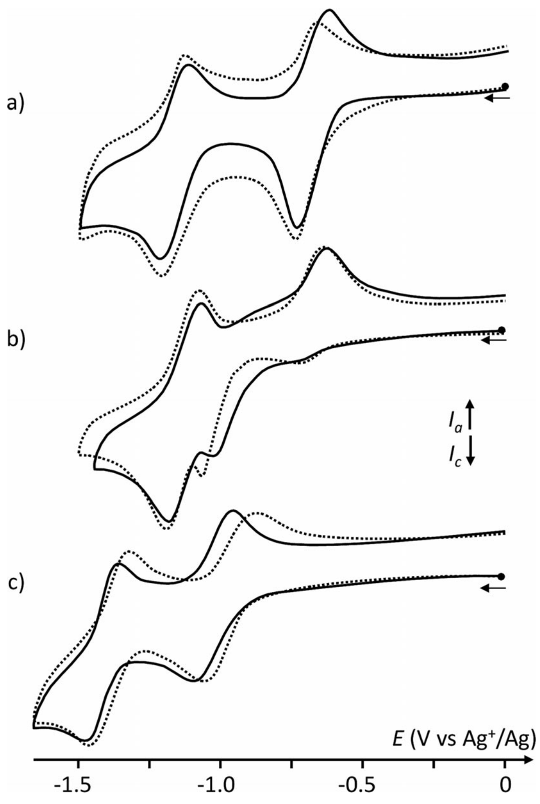


Figure 2. Cyclic voltammograms of (a) T(C6), (b) P[**1**$\supset$T(C6)], and (c) R[**1**$\supset$T(C6)] in CH_2Cl_2 + 0.5 M TBAP.[14] Scan rate: 100 mV/s. Full line: no Zn^{2+}, dashed line: 1 equiv. of Zn^{2+} added.

Table 1. Electrochemical data of T(C6), P[**1**⊃T(C6)], R[**1**⊃T(C6)], and P[**1**⊃T(C12)] in the presence of $Zn(TsO)_2$ (0–1 equiv.).[a,b]

Equiv.	T(C6)	P[**1**⊃T(C6)]	R[**1**⊃T(C6)]	P[**1**⊃T(C12)]
0	$E_{1/2}' = -0.68$ $E_{1/2}'' = -1.17$	$E_{pc}' = -1.02$ $E_{pa}' = -0.62$ $E_{1/2}'' = -1.13$	$E_{1/2}' = -1.02$ $E_{1/2}'' = -1.42$	$E_{pc}' = -0.99$ $E_{pa}' = -0.59$ $E_{1/2}'' = -1.08$
1	$E_{1/2}' = -0.69$ $E_{1/2}'' = -1.17$	$E_{pc}' = -1.05$ $E_{pa}' = -0.62$ $E_{1/2}'' = -1.13$	$E_{1/2}' = -0.97$ $E_{1/2}'' = -1.40$	$E_{pc}' = -0.99$ $E_{pa}' = -0.59$ $E_{1/2}'' = -1.08$

[a] Volts vs. Ag^+/Ag. Scan rate: 100 mV/s. [b] E' and E'' correspond to the first and second electron transfer of the viologen unit, respectively.

during the reverse scan are close to those observed for the free T(C6) axle (Figure 2b).

Upon addition of Zn^{2+} to the solution (0.5 to 3 equiv. as TsO^- salt),[13] no significant modification of the CV curve was observed for the T(C6) axle, indicating that the complexation of the metal ion has no influence on the redox behavior of the viologen unit. By contrast, in the case of the P[**1**⊃T(C6)] system, the presence of Zn^{2+} induced a negative decay in the first reduction wave (–20 to –30 mV). This shift could be interpreted by the fact that the dethreading process of the axle is more difficult to realize when Zn^{2+} is bound to the terpy unit. These results, together with the UV/Vis data, suggest that the bipy core communicates through the calixarene component with the terpy–Zn domain.

Quite unexpectedly, in the case of the 2R[**1**⊃T(C6)]/1Zn rotaxane, a positive shift (up to +50 mV) of the two reversible waves was observed. Again, the redox potential of the bipy unit is affected, although in the opposite direction, by the presence of the metal ion bound at the terpy unit. This behavior could be tentatively explained by invoking a possible steric effect exerted by the diphenylacetyl stopper that imposes a closer proximity of the wheel upper rim to the terpy–Zn^{2+} stopper.[15] It could be hypothesized that, contrary to 2P[**1**⊃T(C6)]/1Zn where the Brownian motion of the wheel could take place along both arms of the axle, the conformational situation in 2R[**1**⊃T(C6)]/1Zn could result in the protrusion of the bipy unit from the lower rim of the calixarene that could thus be more easily reduced.

To verify whether these reduction potential variations of the axle were the consequence of the proximity of the upper rim of the wheel with the terpy unit, the T(C12) axle, where the span between the terpy unit and the 4,4′-bipy is 12 carbon atoms, was synthesized and then submitted to threading with **1** to yield P[**1**⊃T(C12)]. The CV behavior of P[**1**⊃T(C12)] was similar to that observed for P[**1**⊃T(C6)], however, no significant change in the CV curve was observed for P[**1**⊃T(C12)] upon addition of Zn ions. This result clearly indicates that, in this system, the upper rim of the wheel and the terpy–Zn unit no longer "communicate" because of the increased distance.

Conclusions

Taken all together, these data suggest that metal coordination, distance between binding sites, and orientation induce a reciprocal exchange of chemical information among the different domains in both P[**1**⊃T(C6)] and R[**1**⊃T(C6)]. Studies to rationalize these effects and transfer these acquisitions to the construction of a new generation of metal–organic rotaxane frameworks, in which these cascade effects can be applied to subtly tune properties and functions, are undergoing in our laboratories.

Experimental Section

General: Toluene and DMF were dried by using standard procedures. All other reagents were of reagent-grade quality, obtained from commercial suppliers, and were used without further purification. ^1H and ^{13}C NMR spectra were recorded at 300 or 400 and 75 or 100 MHz, respectively. Chemical shifts are expressed in ppm using the residual solvent signals as an internal reference. MS and HRMS analyses were determined in the ESI mode with a Micromass ZMD and a LTQ ORBITRAP XL Thermo, respectively. Compounds **2**,[16] **3**,[17] **4**,[18] **7**,[6] and **8**[19] were synthesized according to literature procedures.

General Procedure for the Synthesis of 5 and 9: In a 250-mL, two-necked, round-bottomed flask, compound **3** (1.0 g, 4 mmol) and KOH (0.7 g, 12 mmol) were dissolved in dry DMF (50 mL). The resulting solution was stirred at room temperature for 20 min, and then the appropriate ditosylate **4** or **8** (25.2 mmol) dissolved in dry DMF (30 mL) was added. After stirring for 90 min at room temperature, the reaction was quenched by the addition of water. The white precipitate formed was recovered by suction filtration and dissolved in ethyl acetate (30 mL). The organic phase was extracted with 10% HCl (2 × 20 mL). The combined aqueous extract was adjusted to pH 8, and the white precipitate formed was extracted with ethyl acetate (3 × 15 mL). The organic phase was dried with anhydrous Na_2SO_4, and the solvent was evaporated to dryness under reduced pressure. The desired terpyridine was obtained pure after recrystallization from CH_3CN as a white solid. Data for **5**: Yield: 1.0 g (50%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.69 (dd, ^3J = 4.5 Hz, ^4J = 0.6 Hz, 2 H), 8.62 (d, J = 8.1 Hz, 2 H), 8.00 (s, 2 H), 7.9–7.7 (m, 4 H), 7.33 (m, 4 H), 4.18 (t, J = 6.3 Hz, 2 H), 4.05 (t, J = 6.3 Hz, 2 H), 2.43 (s, 3 H), 1.8–1.7 (m, 4 H), 1.5–1.4 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 25.0, 25.3, 28.7, 29.0, 67.8, 70.4, 107.3, 121.3, 123.7, 129.8, 136.7, 138.0, 144.3, 149.0, 156.2, 157.1, 167.2 ppm. MS (ESI): *m/z* (%) = 526 (100) $[M + Na]^+$. M.p. 134–135 °C. Data for **9**: 1.2 g (55%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, J = 4.5 Hz, 2 H), 8.62 (d, J = 7.8 Hz, 2 H), 8.05 (s, 2 H), 7.85 (t, J = 6.5 Hz, 2 H), 7.79 (d, J = 8.4 Hz, 2 H), 7.33 (m, 4 H), 4.23 (t, J = 6.3 Hz, 2 H), 4.02 (t, J = 6.3 Hz, 2 H), 2.44 (s, 3 H), 1.9–1.8 (m, 2 H), 1.8 (br. s, 2 H), 1.7–1.6 (m, 2 H), 1.4–1.2 (m, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 24.9, 25.5, 28.4, 28.6, 28.9, 29.0, 29.1, 67.8, 70.4, 106.8, 120.8, 123.6, 129.5, 136.7, 138.0, 144.3, 148.6, 155.5, 156.6, 166.9 ppm. MS (ESI): *m*/*z* (%) = 610 (50) [M + Na]$^+$. M.p. 99.5–100.8 °C.

General Procedure for the Synthesis of 6 and 10: In a 100-mL, two-necked, round-bottomed flask, the appropriate terpyridine derivative **5** or **9** (1.4 mmol) and 4,4′-bipyridine (0.65 g, 4.2 mmol) were dissolved in CH_3CN (50 mL). The resulting solution was heated at reflux for 2 d, then the solvent was evaporated under reduce pressure. The sticky residue was triturated with ethyl acetate (3 × 20 mL) until the tosylate salt precipitated from the trituration solvent. The solid was recovered by suction filtration and recrystallized from CH_3CN to afford product **6** or **10** as a white solid. Data for **6**: 0.8 g (85%). ^{1}H NMR (300 MHz, CD_3OD): δ = 9.11 (d, *J* = 5.1 Hz, 2 H), 8.76 (d, *J* = 3.3 Hz, 2 H), 8.65 (d, *J* = 3.3 Hz, 2 H), 8.59 (d, *J* = 6.0 Hz, 2 H), 8.45 (d, *J* = 4.8, 2 H), 7.98 (d, *J* = 6.9, 2 H), 7.89 (s, 2 H), 7.70 (d, *J* = 6.3 Hz, 2 H), 7.5–7.4 (m, 2 H), 7.21 (d, *J* = 6.0 Hz, 2 H), 4.71 (t, *J* = 5.7 Hz, 2 H), 4.25 (t, *J* = 4.5 Hz, 2 H), 2.34 (s, 3 H), 2.2–2.0 (m, 4 H), 1.7–1.5 (m, 4 H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 19.1, 25.1, 25.2, 28.2, 30.8, 61.2, 67.8, 106.9, 114.0, 121.5, 122.0, 124.1, 125.5, 125.6, 128.4, 137.3, 140.2, 142.0, 145.1, 148.6, 150.3, 153.0, 155.6, 156.8, 167.2 ppm. MS (ESI): *m*/*z* (%) = 488 (100) [M – TsO]$^+$. M.p. 117–120 °C. Data for **10**: Yield: 0.9 g (80%). ^{1}H NMR (300 MHz, CD_3OD): δ = 9.08 (d, *J* = 7 Hz, 2 H), 8.80 (d, *J* = 5.0 Hz, 2 H), 8.65 (d, *J* = 3.3 Hz, 2 H), 8.59 (d, *J* = 7.8 Hz, 2 H), 8.47 (d, *J* = 7 Hz, 2 H), 8.0–7.9 (m, 4 H), 7.93 (s, 2 H), 7.70 (d, *J* = 6.0 Hz, 2 H), 7.47 (t, *J* = 6.9 Hz, 2 H), 7.21 (d, *J* = 6.0 Hz, 2 H), 4.64 (t, *J* = 5.7 Hz, 2 H), 4.23 (t, *J* = 4.5 Hz, 2 H), 2.35 (s, 3 H), 2.1–2.0 (m, 4 H), 1.9–1.8 (m, 2 H), 1.6–1.5 (m, 2 H), 1.4–1.3 (m, 14 H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 19.9, 25.6, 25.8, 28.6, 28.7, 28.9, 29.0, 29.1, 29.2, 31.2, 61.4, 68.1, 107.3, 121.6, 122.1, 124.1, 125.5, 125.7, 128.4, 137.3, 140.2, 142.2, 145.1, 148.6, 150.4, 153.6, 155.8, 156.9, 167.4 ppm. MS (ESI): *m*/*z* (%) = 573 (100) [M – TsO]$^+$. M.p. 91.5–93.5 °C.

General Procedure for the Synthesis of T(C6) and T(C12): In a 100-mL, two-necked, round-bottomed flask, compound **6** (0.85 g, 1.3 mmol) or **10** (0.96 g, 1.3 mmol) and compound **7** (0.35 g, 1.3 mmol) were dissolved in CH_3CN (50mL), and the solution was heated at refluxed for 10 d. Then the solvent was evaporated under reduce pressure, and the residue obtained was triturated with EtOAc (3 × 20 mL) until T(C6) and T(C12) precipitated from the trituration solvent. The solid was recovered by suction filtration and purified by recrystallization from CH_3CN to afford product T(C6) or T(C12) as a white solid. Data for T(C6): Yield: 0.5 g (41%). ^{1}H NMR (300 MHz, CD_3OD): δ = 9.30 (d, *J* = 5.1 Hz, 4 H), 9.20 (d, *J* = 8.2 Hz, 2 H), 8.70–8.61 (m, 8 H), 8.03 (d, *J* = 9.3 Hz, 2 H), 7.89 (s, 2 H), 7.97 (s, 2 H), 7.70 (d, *J* = 8.1 Hz, 4 H), 7.52 (m, 2 H), 7.22 (d, *J* = 7.8 Hz, 4 H), 4.8–4.6 (m, 4 H), 4.30 (t, *J* = 4.5 Hz, 2 H), 3.57 (t, *J* = 6.0 Hz, 2 H), 2.34 (s, 6 H), 2.2–2.1 (m, 4 H), 2.0–1.9 (m, 4 H), 1.7–1.6 (m, 10 H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 166.4, 155.5, 153.4, 148.5, 145.3, 145.0, 142.2, 139.5, 138.4, 129.3, 126.4, 126.2, 125.3, 125.0, 121.0, 107.4, 62.0, 61.9, 61.4, 30.9, 30.5, 30.3, 27.4, 25.0, 24.4, 20.4 ppm. MS (ESI): *m*/*z* (%) = 589 (45) [M – 2TsO – H]$^+$, 294 (100) [M – 2TsO]$^{2+}$. M.p. 127–129 °C. Data for T(C12): 0.72 g (55%). ^{1}H NMR (400 MHz, CD_3OD): δ = 9.14 (d, *J* = 4.1 Hz, 4 H), 8.6–8.4 (m, 8 H), 7.9–7.8 (m, 4 H), 7.67 (d, *J* = 8 Hz, 4 H), 7.4–7.3 (m, 2 H), 7.11 (d, *J* = 8 Hz, 4 H), 4.7–4.5 (m, 4 H), 4.2–4.1 (m, 2 H), 3.5–3.4 (m, 2 H), 2.26 (s, 6 H), 2.1–2.0 (m, 4 H), 1.9–1.8 (m, 2 H), 1.5–1.2 (m, 22 H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 167.4, 156.9, 155.8, 149.6, 145.6, 142.2, 140.3, 137.3, 128.4, 126.9, 125.5, 124.1, 121.6, 107.1, 68.1, 61.9, 61.2, 31.8, 31.1, 31.0, 29.2, 29.1, 29.0, 28.7, 28.6, 25.8, 25.6, 25.5, 25.0, 19.9 ppm. MS (ESI): *m*/*z* (%) = 337 (100) [M – 2TsO]$^{2+}$. M.p. 103.5–105.5 °C.

General Procedure for the Synthesis of P[1⊃T(C6)] and P[1⊃T(C12)]: In a 50-mL, two-necked, round-bottomed flask, calix[6]arene wheel **1** (0.15 g, 0.10 mmol) was dissolved in toluene (20 mL) and compound T(C6) (0.10 g, 0.11 mmol) or T(C12) (0.12 g, 0.11 mmol) was added. The solution assumed gradually a deep-red color and it was stirred at room temperature for 30 min. The solution was filtered, and the solvent was evaporated under reduce pressure. The pseudorotaxane P[**1**⊃T(C6)] or P[**1**⊃T(C12)] was obtained as a red solid. Data for P[**1**⊃T(C6)]: Yield: 0.23 g (95%). ^{1}H NMR (300 MHz, C_6D_6): δ = 9.5 (br. s, 6 H), 8.93 (d, *J* = 7.8 Hz, 2 H), 8.73 (s, 2 H), 8.69 (d, *J* = 4.5 Hz, 2 H), 8.28 (d, *J* = 7.5 Hz, 4 H), 8.1–8.0 (m, 10 H), 7.7–7.6 (m, 12 H), 7.46 (d, *J* = 7.8 Hz, 2 H), 7.2–7.1 (m, 6 H), 7.00 (d, *J* = 8.1 Hz, 4 H), 6.9–6.8 (m, 9 H), 4.66 (d, *J* = 14.7 Hz, 6 H), 4.03 (s, 9 H), 3.9–3.8 (m, 10 H), 3.8–3.6 (m, 10 H), 3.5–3.4 (m, 12 H), 2.35 (br. s, 2 H), 2.06 (s, 6 H), 1.9–1.6 (m, 32 H), 1.5–1.3 (m, 11 H), 1.1–0.9 (m, 4 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 169.7, 157.6, 156.5, 152.9, 149.1, 138.9, 136.3, 133.8, 126.5, 123.5, 121.3, 121.0, 118.1, 116.7, 107.8, 72.2, 69.9, 67.6, 66.5, 66.3, 59.7, 44.6, 39.2, 31.6, 31.3, 29.8, 29.2, 26.9, 22.8, 20.8, 20.2, 15.1, 13.9 ppm. MS (ESI): *m*/*z* (%) = 1027 (45) [M – 2TsO]$^{2+}$. $C_{141}H_{165}N_{11}O_{20}S_2$ (2398.04): calcd. C 70.62, H 6.94, N 6.43, S 2.67; found C 70.40, H 7.15, N 6.34, S 2.85. M.p. 152.7–154.1 °C. Data for P[**1**⊃T(C12)]: Yield: 0.25 g (95%). ^{1}H NMR (400 MHz, C_6D_6): δ = 9.5 (br. s, 6 H), 8.93 (d, *J* = 7.8 Hz, 2 H), 8.73 (m, 4 H), 8.28 (d, *J* = 7.5 Hz, 4 H), 8.1–7.9 (m, 10 H), 7.8–7.6 (m, 12 H), 7.5–7.4 (m, 2 H), 7.2–7.1 (m, 6 H), 7.00 (d, *J* = 8.1 Hz, 4 H), 6.95 (br. s, 2 H), 6.90–6.7 (m, 7 H), 4.66 (d, *J* = 14.7 Hz, 6 H), 4.03 (s, 9 H), 4.0–3.9 (m, 10 H), 3.8–3.6 (m, 10 H), 3.5–3.4 (m, 12 H), 2.2 (br. s, 2 H), 2.1 (s, 6 H), 1.9–1.6 (m, 33 H), 1.5–1.3 (m, 25 H), 1.1–1.0 (m, 4 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 167.6, 157.3, 156.5, 152.8, 149.0, 148.0, 144.2, 143.1, 136.2, 133.8, 132.2, 129.3, 128.7, 126.5, 124.8, 123.4, 121.1, 118.1, 116.7, 116.1, 107.8, 72.2, 69.9, 67.9, 66.3, 62.2, 61.0, 60.7, 34.6, 33.5, 31.5, 29.7, 29.6, 29.4, 29.2, 28.9, 26.1, 25.9, 20.8, 15.1 ppm. HRMS: calcd. for [M – TsO]$^+$ 2310.25249; found 2310.24756 (100). M.p. 143.9–146.2 °C.

Synthesis of R[1⊃T(C6)]: In a 50-mL, two-necked, round-bottomed flask P[**1**⊃T(C6)] (0.10 g, 0.04 mmol) was dissolved in toluene (20 mL) and diphenylacetyl chloride (0.011 g, 0.05 mmol) and NEt_3 (6.0 mg, 0.06 mmol) were added. The solution was stirred at room temperature for 12 h. The solvent was then removed under reduce pressure, and the crude solid was purified by flash chromatography (CH_2Cl_2/CH_3OH, 95: 5). Product R[**1**⊃T(C6)] was obtained as a red solid (0.05 g, 50%). ^{1}H NMR (300 MHz, C_6D_6): δ = 9.5 (br. s, 6 H), 8.90 (d, *J* = 7.8 Hz, 2 H), 8.70 (s, 2 H), 8.67 (d, *J* = 4.2 Hz, 2 H), 8.25 (d, *J* = 7.5 Hz, 4 H), 8.1–7.9 (m, 10 H), 7.8–7.6 (m, 6 H), 7.50 (d, *J* = 7.2 Hz, 2 H), 7.5–7.4 (m, 2 H), 7.2–7.1 (m, 12 H), 7.00 (d, *J* = 7.8 Hz, 4 H), 6.9–6.7 (m, 9 H), 5.20 (s, 1 H), 4.66 (d, *J* = 14.7 Hz, 6 H), 4.4–4.3 (m, 2 H), 3.99 (s, 9 H), 3.9–3.85 (m, 8 H), 3.8–3.6 (m, 10 H), 3.5–3.4 (m, 12 H), 2.1 (br. s, 2 H), 2.05 (s, 6 H), 1.88 (s, 2 H), 1.80 (s, 24 H), 1.7–1.5 (m, 6 H), 1.2–1.1 (m, 11 H), 1.1–0.9 (m, 4 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 167.5, 157.5, 156.4, 153.0, 149.0, 148.0, 143.1, 142.9, 141.0, 139.5, 139.0, 137.5, 136.1, 133.7, 132.0, 126.4, 125.5, 123.4, 122.0, 121.0, 118.0, 116.7, 114.0, 107.7, 72.5, 69.9, 67.5, 67.0, 66.3, 61.0, 60.9, 59.0, 57.2, 50.0, 38.2, 34.5, 33.3, 32.6, 31.9, 31.5, 31.3, 29.8, 29.7, 29.4, 29.0, 28.9, 28.7, 28.6, 28.5, 28.0, 26.8, 22.7, 20.8, 20.2, 15.2, 14.0 ppm. MS (ES): *m*/*z* (%) = 1125 [M – 2TsO]$^{2+}$. $C_{155}H_{175}N_{11}O_{21}S_2$ (2592.27): calcd. C 71.82, H 6.80, N 5.94, S 2.47; found C 72.10, H 6.75, N 6.02, S 2.65. M.p. 157.7–159.3 °C.

UV Titrations: Spectroscopic measurements were carried out by using a Perkin-Helmer Lambda Bio 20 spectrophotometer. Small aliquots of a solution ($c = 2 \times 10^{-4}$ M in CH_3Cl/CH_3OH, 6:4) of the titrant {T(C6) or R[**1**⊃T(C6)]} were added to a solution ($c = 1 \times 10^{-5}$ M in CH_3Cl/CH_3OH, 6:4) of the Zn^{2+} salt contained in a quartz cuvette (and vice versa, path length = 1 cm) and maintained at 300 K through an external thermostat. The binding constants were calculated with the Specfit/32 software selecting different binding models[20] and sampling the spectroscopic data collected in the 280–350 nm wavelength range.

NMR Diffusion Experiments: DOSY experiments were carried out in $CDCl_3$ at 300 K by using a stimulated echo sequence with bipolar gradients.[21] The diffusion coefficient D of the species diffusing in solution was determined by monitoring the intensity decay of at least six resonances present in the NMR spectrum of the specie as a function of gradient strength applied to the sample. The fitting of the attenuation profiles was carried out using the equation:

$$I = I_0 e^{-D\gamma^2 g^2 \delta^2 [\Delta-(\delta/3)-(\tau/2)]}$$

where I is the intensity of the observed resonance (attenuated), I_0 the intensity of the reference resonance (unattenuated), D the diffusion coefficient, γ the gyromagnetic ratio, g the gradient strength, δ the gradient pulse length, Δ the diffusion time, and τ the dephasing and rephasing correction time. For each sample, 16 experiments were carried out, in which the gradient strength g was varied from 5 to 95% of the maximum gradient intensity (5.35 G/mm).

Electrochemical Measurements: Electrochemical experiments were conducted in a conventional three-electrode cell under an argon atmosphere at 293 K by using a CH Instrument (CHI660B). Measurements were done with solutions of the compounds (ca. 0.5 mM) in CH_2Cl_2 containing tetra-*n*-butylammonium perchlorate (TBAP, 0.1 M) as supporting electrolyte. The reference electrode was Ag/$AgNO_3$ (10 mM in CH_3CN containing 0.1 M $TBABF_4$). The working electrode was a carbon disc (3 mm in diameter) polished with 1 µm diamond paste before each record and the counter electrode was a platinum wire.

Supporting Information (see footnote on the first page of this article): Full NMR characterization of new compounds T(C6), T(C12), P[**1**⊃T(C6)], R[**1**⊃T(C6)], and P[**1**⊃T(C12)]; collection of UV/Vis spectra for the titrations of zinc salts with T(C6) and R[**1**⊃T(C6)]; cyclic voltammogram of P[**1**⊃T(C12)].

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[14] It should be noted that the electrochemical experiments were carried out in the presence of a large amount of tetrabutylammonium perchlorate (TBAP) used as supporting electrolyte, which minimizes the role of the TsO^- anion in the binding process and no significant changes in the voltammograms could be observed when $Zn(TsO)_2$ was replaced by the corresponding BF_4^- salt.

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