Plugging a Bipyridinium Axle into Multichromophoric Calix[6]arene Wheels Bearing Naphthyl Units at Different Rims

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Tris-(N-phenylureido)-calix[6]arene derivatives are heteroditopic non-symmetric molecular hosts that can form pseudorotaxane complexes with 4,4'-bipyridinium-type guests. Owing to the unique structural features and recognition properties of the calix[6]arene wheel, these systems are of interest for the design and synthesis of novel molecular devices and machines. We envisaged that the incorporation of photoactive units in the calixarene skeleton could lead to the development of systems the working modes of which can be governed and monitored by means of light-activated processes. Here, we report on the synthesis, structural characterization, and spectroscopic, photophysical, and electrochemical investigation of two calix[6]arene wheels decorated with three naphthyl groups anchored either to the upper or lower rim of the phenylureido calixarene platform. We found that the naphthyl units interact mutually and with the calixarene skeleton in a different fashion in the two compounds, which thus exhibit a markedly distinct photophysical behavior. For both hosts, the inclusion of a 4,4'-bipyridinium guest activates energy- and/or electron-transfer processes that lead to non-trivial luminescence changes.

1. Introduction

The suitable selection and design of molecular components are of paramount importance in determining the properties of molecular devices and to allow rational implementation of the mechanisms that govern their functions.[1–6] This is particularly true when these systems are supposed to perform a programmed task, such as, for example, sensing,[7,8] switching,[9–15] or nanoscale movements as in molecular machines.[16–18] Thus, a central factor to be considered during the design of new devices is how to connect, either covalently or non-covalently, and organize in space all the necessary molecular subunits, each of which should perform a predetermined function.[19,20] In this context, we have demonstrated that calix[6]arene 1 (Figure 1) acts as three-dimensional and heteroditopic wheel that, in low polarity media, forms oriented pseudorotaxanes and rotaxanes with dialkylviologen salts as axles.[21–23] A peculiar property of 1 is that suitable bipyridinium axles can unidirectionally transit through the calixarene annulus under the action of external stimulation.[24–27] Owing to the possibility of functionalizing the two chemically different rims, wheel 1 is also attractive as a scaffold for the construction of multicomponent species bearing covalently linked molecular subunits.

In view of our current interest in the design and synthesis of calix[6]arene prototypes of molecular machines, we envisaged that the incorporation of photoactive units in the calixarene skeleton could lead to the development of new systems the working modes of which can be governed and monitored through a wider set of control tools. The naphthyl moiety, which is extensively employed in supramolecular chemistry because of its rich and well-known photophysical behavior and its molecular recognition properties,[6,18,28–30] appears to be an ideal choice. Herein, we report the synthesis, structural characterization, and study of the spectroscopic, photophysical, and electrochemical behavior of two new calix[6]arene wheels decorated with three naphthyl groups anchored either to the upper or lower rim of the phenylureido calix[6]arene platform. We also describe their ability to form pseudorotaxane com-

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plexes with a 4,4'-bipyridinium guest and the consequences of the complexation on their peculiar physicochemical properties.

2. Results and Discussion

2.1. Synthesis and Structural Characterization of the Wheels

To study whether the photophysical properties of the naphthalene unit can be affected by its location within a defined supramolecular system, we managed to synthesize the calix[6]arene-based hosts 7 and 10 (Figure 1), which are characterized by the different positions of the three naphthyl units with respect to the aromatic cavity of the macrocycle. The three β-naphthoxy groups of 7 are linked to phenolic groups present at the macrocycle lower rim through a C6 alkyl chain acting as a spacer, whereas in 10 these units are directly attached to the three urea moieties present on the host upper rim. As suggested by previous studies, these two derivatives present all the structural features necessary to maintain their excellent recognition properties, in low-polarity solvents, towards molecular axles derived from the 1,1'-dialkyl-4,4'-bipyridinium (viologen) unit, namely, 1) a preorganized electron-rich aromatic cavity to stabilize the dicatonic unit of the axle, and 2) ureido groups that, acting as hydrogen-bond donors, can interact with the counter anions of the axle.

Calixarene 7 was obtained through a convergent synthetic approach (Scheme 1); the naphthyl-containing alkylating agent 3 was obtained in high yield by reacting 2-naphthol with an excess of 1,6-hexanediol ditosylate (2) in acetonitrile at reflux. A similar procedure was adopted to functionalize the phenolic groups at the lower rim of the known calix[6]arene 4 to yield 5. The nitro groups of 5 were then quantitatively reduced to amines in methanol at reflux by using hydrazine monohydrate as the reducing agent and Pd/C as the catalyst. The phenylureido moieties were finally introduced on the macrocycle upper rim by reacting 6 with phenyl isocyanate in dry dichloromethane to yield 7 with 16% overall yield. Calixarene 10 was synthesized in two steps starting from the known trinitro calix[6]arene derivative 8 (Scheme 1). The nitro groups were quantitatively reduced by using the same route adopted for 5. The resulting triamino derivative was not isolated but immediately reacted with 1-naphthyl isocyanate to obtain 10 in 48% overall yield.

The 1H NMR analysis of 7 reveals that this macrocycle adopts, on the NMR timescale in solutions of low-polarity solvents such as CDCl₃, CD₂Cl₂ (see the Supporting Information), and [D₆]benzene, a pseudo cone conformation in which the three alternate phenolic rings bearing the phenylureido units define a trigonal prism, whereas the remaining three, bearing the tert-butyl groups, are oriented with their methoxy groups pointing towards the center of the cavity. This geometrical arrangement generates few diagnostic signals such as the unusual upfield shift (approximately 2.9 ppm) of the resonance of the methoxy groups and the two doublets at δ = 4.4 and 3.6 ppm (J = 15.6 Hz), related to the bridging methylene groups of the macrocycle. The 1H NMR spectrum of 10 shows very broad resonances in CDCl₃ and [D₆]benzene (see Figure 2c), which is evidence for the higher mobility of this host with respect to 7.
containing wheel 7 (see the Supporting Information). These findings suggest that the methoxy groups of both 7 and 10 are no longer affected by the shielding of the aromatic cavity because of the threading of the axle into the macrocycle. Another symptomatic observation is the large downfield shift (approximately 3 ppm) experienced by the protons of the ureido groups (NH) located at the upper rim of the hosts (see Figure 2b). This shift is consistent with the participation of the ureido groups in the complexation process by binding the counter anions of the axle. Other evidence for the pseudorotaxane formation were gathered by monitoring the chemical shift of the signals of the axle (Figure 2a), in particular those corresponding to the aromatic and N—CH₃ protons (8), which experience a noticeable upfield shift (up to 2.5 ppm) caused by the strong shielding effect exerted by the aromatic cavity of the calix[6]arene. It is important to note that in both pseudorotaxane complexes, the calix[6]arene hosts maintain their pseudo cone conformation on the NMR timescale. This arrangement is witnessed by the presence in the spectra (see Figure 2b and the Supporting Information) of the typical AX system of two doublets relative to the protons belonging to the hosts methylene bridging units at approximately 4.5 and 3.5 ppm (H₆ and H₇ in Figure 2b). The latter is overlapped with other calixarenes resonances, but it can be easily identified through 2D NMR measurements (see the Supporting Information).

2.3. Spectroscopic and Photophysical Experiments on Wheel 7 and its Pseudorotaxane 7$\cdot$DOV$\cdot$2TsO

The absorption and luminescence data for the calixarene host 7, the guest DOV, their pseudorotaxane complex 7$\cdot$DOV$\cdot$2TsO, and the model compounds for the calixarene scaffold (1) and for the naphthalene chromophore (2-methoxynaphthalene, 2-MN) are reported in Table 1.

The UV/Visible absorption spectra of 7 in CH₂Cl₂ (Figure 3) show the typical bands of the aromatic systems of the calixarene skeleton in the 240–300 nm region, whereas the features occurring between 280 and 340 nm are assigned to π→π* transitions of the 2-alkoxynaphthalene units at the macrocycle lower rim. The absorption spectrum of 7 matches well with
the sum of the absorption spectra of its chromophoric components (1 plus 3 × 2-MN) in the 280–340 nm region, indicating the absence of interactions between the pendant naphthalene units in the ground state. On the other hand, the absorption of 7 is substantially more intense than the sum of its chromophoric components in the 240–280 nm region. As the naphthalene units and the wheel skeleton are electronically insulated by the long alkyl chains, we hypothesize that the change in the calixarene absorption bands arises from conformational effects exerted on the diphenylureido units of the wheel by the bulky substituents at the lower rim. In CH$_2$Cl$_2$ at room temperature, compound 7 shows a luminescence band ($\lambda_{\text{max}} = 350$ nm) that is safely assigned to the fluorescence of the alkoxyanaphthalene units (Table 1 and Figure 3, inset). The emission quantum yield ($\Phi = 0.12$) and lifetime ($\tau = 5.0$ ns) values are identical within errors to those of the 2-MN model. In a rigid matrix at 77 K, 7 shows both the structured fluorescence ($\lambda_{\text{max}} = 350$ nm) and phosphorescence ($\lambda_{\text{max}} = 465$ nm) bands of the alkoxyanaphthalene units (see the Supporting Information). The corrected excitation spectrum$^{[36, 37]}$ of 7 ($\lambda_{\text{em}} = 350$ nm) at room temperature matches with the absorption spectrum of the same compound only between 310 and 340 nm, whereas it is significantly weaker in the 230–310 nm region. Conversely, the excitation spectrum of 7 exhibits a good overlap with the absorption spectrum of 2-MN in the whole spectral region monitored (see the Supporting Information).

This observation indicates that the energy transfer from the excited states located on the calixarene skeleton to the excited singlet level of the pendant naphthalene units is inefficient. Unfortunately, an estimation of the residual fluorescence intensity arising from the calixarene annulus ($\lambda_{\text{max}} = 340$ nm, Table 1) is prevented because such an emission band is covered by the much more intense naphthalene-type fluorescence ($\lambda_{\text{max}} = 350$ nm). The application of the Förster model$^{[36, 37]}$ suggests that the low energy-transfer efficiency is determined by the very poor overlap between the calixarene-type (donor) emission and the naphthalene-type (acceptor) absorption, together with the small quantum yield of the calixarene-type emission. In summary, the naphthalene units appended at the lower rim of the wheel as in 7 are photophysically independent both of one another and of the calixarene chromophore.

The addition of DOV×2TsO to a solution of 7 causes changes in the UV absorption bands of the molecular components and the appearance of broad absorption features in the 350–600 nm region ($\lambda_{\text{max}} = 460$ nm, Table 1), arising from charge-transfer (CT) interactions between the $\pi$-electron-rich aromatic units of the calixarene and the $\pi$-electron-poor 4,4’-bipyridinium moiety of the guest (see the Supporting Information$^{[23, 24, 26, 27]}$). In the same experiment, the fluorescence band of 7 is quenched as a function of the amount of DOV×2TsO added (Figure 4). The absorption and luminescence data collected in the titration experiments could be satisfactorily fitted with a 1:1 binding model, yielding a value of the association constant $K = 7.0 \pm 0.2$. These results are consistent with the NMR data and with previous observations on related compounds$^{[23, 24, 26, 27]}$ and confirm the formation of a pseudorotaxane in which DOV×2TsO is threaded into the cavity of 7 with its bipyridinium unit located close to the aromatic units of the calixarene.

In the light of these observations, it is worth discussing the effect of the DOV×2TsO guest on the photophysics of the calixarene. From the residual emission intensity of 7 at the end of the titration, one can calculate the quenching rate constant according to Equation (1):

$$
k_q = 1/\tau_0 (\Phi_0/\Phi - 1)
$$

where $\tau_0$ and $\Phi_0$ are the luminescence lifetime and quantum yields of 7 in the absence of DOV×2TsO, and $\Phi$ is the luminescence quantum yield of the complex. According to the
data listed in Table 1, $k_i = 3.8 \times 10^4 \, \text{s}^{-1}$. The quenching of the naphthalene-type emission of 7 by DOV×2TsO can involve two distinct mechanisms: mechanism i) energy transfer from the singlet excited state localized on an alkoxynaphthalene unit to the lower lying charge-transfer levels as a result of the calixarene–bipyridinium interaction, and mechanism ii) electron transfer from the alkoxynaphthalene singlet excited state to the encapsulated bipyridinium unit. Because of the good overlap between the naphthalene emission and the visible charge-transfer absorption and the large luminescence quantum yield of the donor, the Förster radius (i.e. the donor-acceptor distance at which the energy-transfer efficiency is 50%) is as long as 5.4 nm. Considering that the maximum distance between the naphthalene substituents and the center of the calixarene cavity is 1.5 nm, the energy-transfer process (mechanism i) is expected to be very efficient. Moreover, from the available excited-state energy and the potential values for oxidation of the donor and reduction of the acceptor (see above), one can estimate that the photoinduced electron transfer (mechanism ii) is highly exergonic ($\Delta G < -1.8 \, \text{eV}$).

To gain more insight into the luminescence quenching mechanism, we performed emission experiments in a rigid matrix at 77 K. Under these conditions, the solvent reorganization energy is small and highly exergonic electron-transfer processes such as that mentioned above, which may fall into the Marcus inverted region, can become slow (13, 19). Both the naphthalene-type fluorescence and phosphorescence bands observed for 7 in CH$_2$Cl$_2$/CHCl$_3$ 1:1 at 77 K are absent in the spectrum of the 7:DOV×2TsO complex (see the Supporting Information). The occurrence of such a strong quenching in a rigid medium at low temperature is consistent with an electron transfer from the naphthalene excited singlet to the charge-transfer (CT) levels. Laser flash photolysis experiments with ns excitation pulses, carried out in solution at room temperature, revealed no trace of the bipyridinium radical cation, which would be a product of the electron-transfer reaction. It cannot be excluded, however, that a fast back-electron transfer process prevents the accumulation of the bipyridinium radical cation on the ns timescale.

2.4. Spectroscopic and Photophysical Experiments on Wheel 10 and its Pseudorotaxane 10:DOV×2TsO

The absorption and luminescence data for the calixarene host 10, the pseudorotaxane 10:DOV×2TsO, and the model chromophoric compound for the calixarene (N-1-naphthyl-N'-phenylurea, 1-NPU) are reported in Table 2. The absorption spectrum of 10 in CH$_2$Cl$_2$ (Figure 3) shows the bands typical of the naphthyl-phenylureido chromophore in the near UV region. The spectrum is very similar to the sum of the spectra of its chromophoric components (3×1-NPU), which suggests that the interactions between the pendant naphthalene units are negligible in the ground state.

The luminescence band of 10 in CH$_2$Cl$_2$ at room temperature is less intense, much broader, and shifted to longer wavelengths in comparison with that of the 1-NPU model (Table 2 and Figure 5, inset). The excitation spectrum of 10 ($\lambda_{em} =$ 410 nm, see the Supporting Information) is similar to its absorption spectrum. The emission band, however, shows a biexponential decay with $\tau_1 = 2.8$ ns and $\tau_2 = 18$ ns. The shorter lifetime is comparable with that of 1-NPU ($\tau = 1.6$ ns) and its contribution to the overall decay decreases as the monitored emission wavelength is moved towards the lower energy side (Figure 3, inset). Based on these observations and in the light of the structure of 10, it can be concluded that its emission has a dual nature: a higher energy and shorter lived component assigned to the individual naphthyl-phenylureido chromophores, and a lower energy and longer lived component attributed to the formation of excimers between the pendant naphthalene moieties. This hypothesis is confirmed by the fact that in rigid matrix at 77 K, in which the formation of excimers is prevented, both the fluorescence ($\lambda_{em} =$ 360 nm) and phosphorescence ($\lambda_{em} =$ 540 nm) bands of 10 coincide with those of 1-NPU (see the Supporting Information).

The addition of DOV×2TsO to a solution of 10 causes absorption spectral changes consistent with the formation of a 1:1 complex, as discussed above for host 7. In particular, a weak shoulder on the lower energy side of the more intense UV bands, assigned to calixarene–bipyridinium CT interactions,
DOV is observed (Table 2 and the Supporting Information). The emission changes of 10 upon titration with DOV×2TsO (Figure 6) consist of a decrease in the band intensity accompanied by a change in shape; namely, the band becomes sharper and its maximum exhibits a blueshift. From the titration curves obtained from absorption and luminescence data and fitted with a 1:1 binding model, a lower limiting value of the association constant $K = 7.5$ was obtained. Once again, these findings are consistent with the NMR results and confirm that DOV×2TsO is threaded into wheel 10 in a pseudorotaxane fashion. Notably, at the end of the titration, the shape of the residual emission band of the calixarene is very similar to that of 1-NPU but its decay is still described by a biesponential function (Table 2). As observed for the uncomplexed calixarene 10, the contribution of the two lifetime components to the overall decay depends on the observation wavelength: the weight of the longer lifetime increases at lower energies. On the basis of the discussion made for 10, we assign $\tau_1$ (1.5 ns) and $\tau_2$ (3.4 ns) to emission from the naphthalene monomer and excimer species, respectively, in the complex. Both lifetimes are shorter than the corresponding values measured for 10 (Table 2), indicating that both the excited monomer (singlet) and dimer (excimer) levels are quenched in the presence of DOV×2TsO. The similarity of the luminescence band of the 10:DOV×2TsO complex with that of the 1-NPU model, which arises from a substantial disappearance of the contribution from the excimer emission, is consistent with the presence of a specific quenching pathway involving the excimers. It can also be hypothesized that the alkyl tail of the threaded DOV×2TsO guest can hinder the approach of two nearby naphthalene units by increasing the steric crowding at the upper rim of the calixarene, thus discouraging the formation of excimers.

As previously discussed for 7, the emission quenching mechanism of 10 upon complexation with DOV×2TsO can be an energy transfer from the excited naphthyl-type units (monomers or dimers) to lower lying charge-transfer states owing to the calixarene–bipyridinium interaction, and/or an electron transfer from the excited naphthalenes to the bipyridinium guest, which is highly exergonic also in the case of 10. In contrast with the results obtained for host 7, the emission spectra of the 10:DOV×2TsO complex at 77 K exhibit the fluorescence and phosphorescence bands of 10 (see the Supporting Information). Unfortunately, the luminescence intensities measured in the frozen solvent cannot be quantitatively compared and on the basis of our data we cannot extend the discussion any further.

2.5. Electrochemical Experiments

The association of the calixarenes with DOV×2TsO can also be probed by electrochemical techniques. The voltammetric patterns of hosts 7 and 10 in CH₂Cl₂ exhibit no reduction processes and several chemically irreversible oxidation processes with onset at about +1.1 V versus the saturated calomel electrode (SCE), assigned to the oxidation of the naphthalene units and the alkoxybenzene rings of the calixarene skeleton. Because of their irreversible nature, these processes will not be further discussed. DOV×2TsO shows the typical reversible monoelectronic reductions of the 4,4′-bipyridinium unit ($E_{1/2}^{\text{red}} = -0.27$ V, $E_{1/2}^{\text{red}} = -0.81$ V versus SCE, see Figure 7 and the Supporting Information) and no oxidation. The inclusion of DOV×2TsO into either 7 or 10 causes a large negative shift of the first reduction potential, although the second process occurs at the same potential as for the free guest (see Figure 7 and the Supporting Information). These results indicate that 1) the bipyridinium unit becomes more difficult to reduce because it is stabilized inside the calixarene wheel, and 2) the one-electron reduction of DOV×2TsO promotes its dethreading from the host, in line with the behavior of several related bipyridinium-containing pseudorotaxanes. The large peak-to-peak separation and the scan-rate dependence of the first reduction

![Figure 6](image_url1)  
**Figure 6.** Luminescence spectral changes ($\lambda_{ex} = 330$ nm) upon addition of increasing amounts of DOV×2TsO to a 4.0×10⁻¹⁰ M solution of 10. The inset shows the titration curve obtained by plotting the emission intensity at 408 nm as a function of the DOV×2TsO equivalents; the full line is the data fitting corresponding to a 1:1 binding model. Conditions: air-equilibrated CH₂Cl₂, room temperature.

![Figure 7](image_url2)  
**Figure 7.** Cyclic voltammograms recorded upon reduction of DOV×2TsO (approximately 4.0×10⁻¹⁰ M) in the absence (dashed line) and in the presence (full line) of 1.5 equivalents of calixarene 10 to ensure full complexation (SCE), assigned to the oxidation of the naphthalene units and the alkoxybenzene rings of the calixarene skeleton. Because of their irreversible nature, these processes will not be further discussed. DOV×2TsO shows the typical reversible monoelectronic reductions of the 4,4′-bipyridinium unit ($E_{1/2}^{\text{red}} = -0.27$ V, $E_{1/2}^{\text{red}} = -0.81$ V versus SCE, see Figure 7 and the Supporting Information) and no oxidation. The inclusion of DOV×2TsO into either 7 or 10 causes a large negative shift of the first reduction potential, although the second process occurs at the same potential as for the free guest (see Figure 7 and the Supporting Information). These results indicate that 1) the bipyridinium unit becomes more difficult to reduce because it is stabilized inside the calixarene wheel, and 2) the one-electron reduction of DOV×2TsO promotes its dethreading from the host, in line with the behavior of several related bipyridinium-containing pseudorotaxanes. The large peak-to-peak separation and the scan-rate dependence of the first reduction...
process of the 7–DOV × 2TsO and 10–DOV × 2TsO complexes indicate that the complexation/decomplexation reactions occur on the voltammetric timescale; these aspects have been discussed in detail elsewhere.[22]

3. Conclusions

We have reported the synthesis, structural characterization, and study of the spectroscopic, photophysical, and electrochemical behavior of two new calix[6]arenes wheels 7 and 10 decorated with three naphthyl groups anchored either to the upper or lower rim of the phenyleureido calix[6]arene platform. We also describe their ability to form pseudorotaxane complexes with a 4,4′-bipyridinium guest (DOV × 2TsO) and the consequences of the complexation on their peculiar physicochemical properties. In particular, in the case of calixarene 7, the three naphthyl units connected to the lower rim do not interact with each other in the ground or excited states, and do not exchange electronic energy with the calixarene skeleton. The presence of a DOV × 2TsO guest inside the wheel, however, enables photoinduced energy and/or electron-transfer processes to occur from the peripheral chromophores to the cavity. The behavior of calixarene 10, in which the three naphthalene moieties are linked to the ureido moieties at the upper rim, is markedly different. The naphthyl units do not exhibit significant interactions in the ground state but they can form excimer species characterized by a redshifted luminescence band and a longer lifetime. The threading of DOV × 2TsO into the calixarene can activate energy- and/or electron-transfer pathways that cause the quenching of both the monomeric and, to a relatively higher extent, the excimeric naphthyl-type emission of 10. For both calixarenes, the bipyridinium guest can be reversibly de-threaded/rethreaded from the host by reduction/oxidation of DOV × 2TsO in a potential region in which the host is not electroactive, thus providing a way to modulate the photophysical properties of the multichromophoric calixarenes by means of electrochemical stimuli. The investigated systems constitute a compelling example of the potential of calix[6]arenes for arranging functional molecular units with precise structural control around an efficient three-dimensional host. The resulting multicomponent species are of interest for the construction of novel molecular devices, machines, and motors that can take particular advantage of the topologically and chemically different rims of the calixarene cavity.

Experimental Section

General

NMR spectra were recorded by using the residual solvent signal as an internal reference. Melting points are uncorrected. Mass analyses were carried out in the ESI mode. Axle DOV × 2TsO[21] compound 2,[44] calix[5]arenes 1,[34] 4,[15] and 8[16] were synthesized according to literature procedures. All the other reagents were of reagent grade quality obtained from commercial suppliers and were used without further purification. Deuterated benzene was used as the solvent in most NMR experiments because a better resolution of the signals, especially in the low-field portion of the spectra, is afforded. Absorption and luminescence spectra were recorded at room temperature with a PerkinElmer lambda45 spectrophotometer and LSSS spectrophotometer by using 1 cm quartz cuvettes. Emission spectra at 77 K were obtained from a frozen solution contained in a quartz tube immersed in a quartz Dewar filled with liquid nitrogen. Luminescence lifetimes were measured with an Edinburg Instrument FLS920 time-correlated single-photon counting equipment. Luminescence quantum yields were determined by the optically dilute method by using naphthalene in air-equilibrated cyclohexane (Φo = 0.036) as a standard.[45] Spectroscopic titrations were performed by adding small aliquots (typically 20 μL) of a concentrated solution of DOV × 2TsO to a dilute solution of the calixarene. The titration curves were fitted according to a 1:1 association model by using the SPECFIT software.[46] Cyclic voltammetric experiments were carried out at room temperature in Ar-purged dichloromethane with an Autolab30 multipurpose instrument interfaced to a PC. A glassy carbon working electrode, a Pt wire counter electrode, and an Ag wire pseudoreference electrode were employed; ferrocene (E1/2 = +0.460 V versus SCE)[47] was present as an internal standard. The concentration of the compounds under examination was between 3 × 10−4 and 5 × 10−4 M; tetrabutylammonium hexafluorophosphate (0.03 to 0.05 m) was the supporting electrolyte. The potential scan rate was typically varied from 0.02 to 1 V·s−1.

Synthesis of 6-(Naphthalen-2-yl)hexyl tosylate (3)

In a 250 mL round-bottom flask, K2CO3 (2.9 g, 20.8 mmol) was added to a solution of 2-naphthol (1.5 g, 10.4 mmol) and 1,6-hexanediol ditosylate 2 (13.3 g, 31.2 mmol) in CH3CN (100 mL). The resulting heterogeneous reaction mixture was heated at reflux for 36 h. After cooling to room temperature, the solvent was evaporated to dryness under reduced pressure and the sticky residue was washed with a 10% w/v solution of HCl (200 mL), then dried with anhydrous sodium sulfate and evaporated to dryness under reduced pressure. The oily residue was purified by column chromatography on silica gel (n-hexane/ethyl acetate 7:3) to yield 3.0 g of 3 (72%) as a white solid. M.p. = 71–72 °C; 1H NMR (CDCl3, 400 MHz; δ = 7.80 (d, 2H, J = 7.6 Hz), 7.46 (t, 2H, J = 8.0 Hz), 7.36 (2H, J = 7.6 Hz), 7.28 (s, 1H), 7.14 (d, 1H, J = 7.2 Hz), 4.10–4.05 (m, 4H), 2.41 (s, 3H), 1.76 (q, 2H, J = 9.2 Hz), 1.68 (q, 2H, J = 9.2 Hz), 1.52–1.44 ppm (m, 4H); 13C NMR (100 MHz; δ = 157.0, 144.7, 134.6, 133.2, 129.8, 129.3, 128.9, 127.9, 127.6, 126.7, 126.3, 123.5, 118.9, 106.6, 70.5, 67.7, 29.0, 28.8, 25.5, 25.2, 21.6 ppm; MS (ESI) m/z: 421.3 [M+Na]+; elemental analysis calcd (%) for C26H18O2S: C 69.32, H 6.58; found: C 69.28, H 6.60.

Synthesis of Calix[6]arene (5)

In a 100 mL sealed glass autoclave, a heterogeneous mixture of compounds 4 (0.8 g, 0.8 mmol), 3 (1.0 g, 2.5 mmol), and K2CO3 (0.5 g, 3.7 mmol) in CH3CN (60 mL) was heated at reflux under vigorous stirring for 72 h. After cooling to room temperature, the solvent was evaporated to dryness under reduced pressure. The solid residue was taken up with ethyl acetate (80 mL) and the resulting organic phase was washed with a 10% w/v solution of HCl (80 mL) and water (2 × 80 mL). The separated organic phase was dried over anhydrous sodium sulfate, filtered to remove the drying agent, and the solvent evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel.
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