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A Molecular Plug−Socket Connector

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Abstract: A monocationic plug−socket connector that is composed, at the molecular level, of three components, (1) a secondary dialkylammonium center ($CH_2NH_2^+CH_2$), which can play the role of a plug toward dibenzo[24]crown-8 (DB24C8), (2) a rigid and conducting biphenyl spacer, and (3) 1,4-benzo-1,5-naphtho[36]crown-10 (BN36C10), capable of playing the role of a socket toward a 4,4′-bipyridinium dicationic plug, was synthesized and displays the ability to act as a plug−socket connector. The fluorescent signal changes associated with the 1,5-dioxynaphthalene unit of its BN36C10 portion were monitored to investigate the association of this plug−socket connector with the complementary socket and plug compounds. The results indicate that (1) the $CH_2NH_2^+CH_2$ part of the molecular connector can thread DB24C8 in a trivial manner and (2) the BN36C10 ring of the connector can be threaded by a 1,1′-dioctyl-4,4′-bipyridinium ion only after the $CH_2NH_2^+CH_2$ site is occupied by a DB24C8 ring. The two connections of the three-component assembly are shown to be controlled reversibly by acid/base and red/ox external inputs, respectively. The results obtained represent a key step for the design and construction of a self-assembling supramolecular system in which the molecular electron source can be connected to the molecular electron drain by a molecular elongation cable.

Introduction

Molecular self-assembly,[1] a process which is central and key to nature’s forms and functions, provides[2−18] a mechanism for the construction of artificial molecular-level devices and machines. The challenge for the chemist in this field resides in the programming[7,11,13,15] of the devices and machines, that is, in the design of components, which carry within their structures all of the pieces of information necessary for the performance of certain required functions. In the course of designing and

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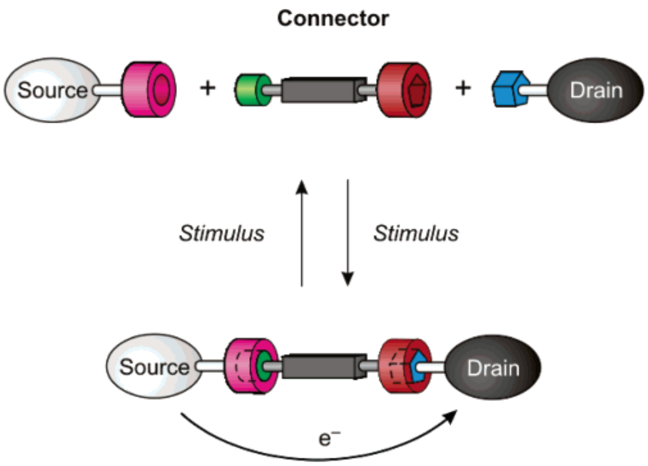
Scheme 1. The Graphic Representation of a Molecular Connector



constructing[19] a supramolecular system in which a molecular electron source can be connected (Scheme 1) to a molecular electron drain by a molecular plug−socket connector, we have synthesized and characterized the compound **1**-H$^+$ shown in Chart 1. This compound is made up of three parts, (1) a secondary dialkylammonium ($CH_2NH_2^+CH_2$) center, which can play the role of a plug,[20,21] (2) a rigid and conducting[22] biphenyl spacer, and (3) a 1,4-benzo-1,5-naphtho[36]crown-10 (BN36C10, **2**) ring that is able to play the role of a socket.[19,23] The connector **1**-H$^+$ is the most important component of a recently reported self-assembling supramolecular system which mimics[24] an electrical extension cable at the nanoscale. We have investigated, by absorption and fluorescence measurements, the connection of the two ends of this wire-type molecule with socket (DB24C8, **3**) and plug (1,1′-dioctyl-4,4′-bipyridinium, **4**$^{2+}$) compounds. The formulas of the molecular components **1**-H$^+$, **3**, and **4**$^{2+}$, together with that of the 1,4-benzo-1,5-naphtho[36]crown-10 (BN36C10) model compound **2**, are shown in Chart 1.

Results and Discussion

Design of the Molecular Connector. It has long been known[25] that crown ethers with the 18-crown-6 constitution form face-to-face complexes with primary alkylammonium ions (RNH_3^+) as a result of the stabilizing influence, primarily of three [$N^+{-}H{\cdots}O$] hydrogen bonds. More recently, it has been demonstrated[26,27] that, when the crown ether constitution is large enough, such as, a 24C8 ring minimally and ideally, suitably chosen secondary dialkylammonium ($R_2NH_2^+$) ions can thread through the ring to give [2]pseudorotaxanes,[26a] often used as precursor 1:1 complexes in the syntheses of rotaxanes[26b] and catenanes.[28] Upon deprotonation of the $CH_2NH_2^+CH_2$ center, the two strong [$N^+{-}H{\cdots}O$] hydrogen bonds that give stability to the 1:1 complex are broken, and dethreading of these [2]pseudorotaxanes takes place. This assembly/disassembly feature has been exploited previously[21] in the construction of a molecular plug−socket system for energy transfer.

Another well-known[29] recognition motif is manifest in the spontaneous threading of π-electron-rich crown ethers like BN36C10 with π-electron-deficient bipyridinium dications to form stable 1:1 complexes. This kind of supramolecular assistance has also been harnessed[30] in the synthesis of catenanes and rotaxanes. Furthermore, it is known that such [2]pseudorotaxanes can be easily dethreaded by reduction of the electron-

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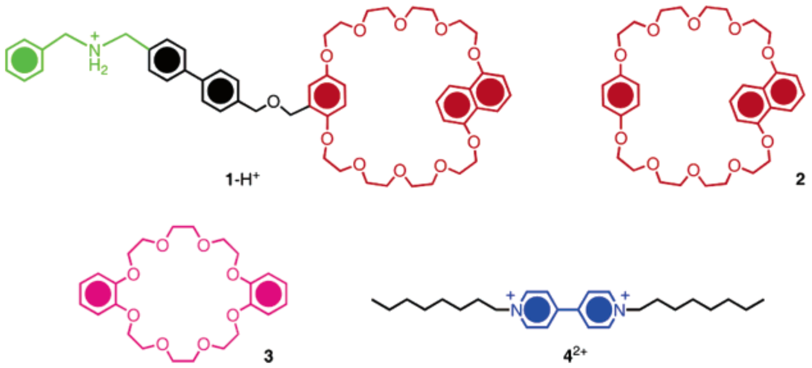
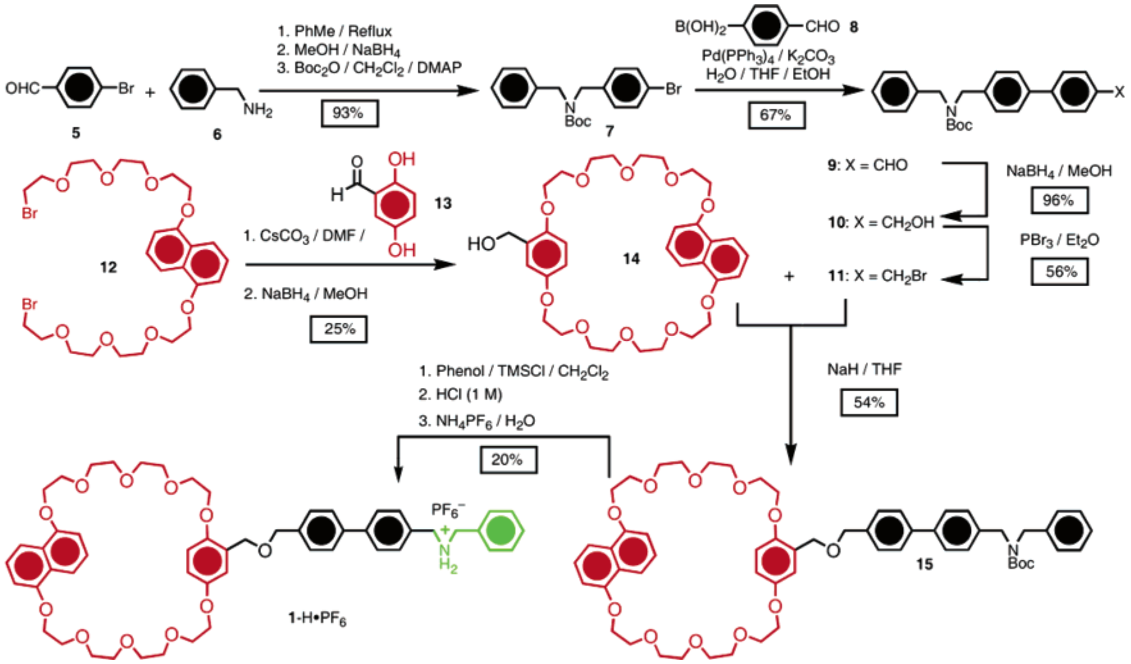
Chart 1



Scheme 2. Synthesis of the Molecular Connector **1**-H•PF_6



accepting unit and then rethreaded by its reoxidation, thereby constituting one of the simplest examples of red/ox-controlled molecular machines.[11,15,19,31−36]

By taking advantage of the complexation/decomplexation properties of these [2]pseudorotaxanes that can be subjected to acid/base control on the one hand and red/ox control on the other, as well as experience accumulated in previous investigations,[37] including an attempt to govern the photoinduced electron transfer in a triad that can be assembled/disassembled by chemical inputs,[19] we have designed **1**-H^+, a new type of connector molecule containing a $CH_2NH_2^+CH_2$ center that can play the role of a plug and a BN36C10-type unit that can play the role of a socket. The next challenge was to make **1**-H^+.

Synthesis of the Molecular Plug−Socket Connector. The synthesis of **1**-H•PF_6 is outlined in Scheme 2. Condensation of 4-bromobenzaldehyde (**5**) and benzylamine (**6**), followed by reduction of the generated imine and subsequent N-protection afforded the bromide **7**. Pd(0)-catalyzed coupling between **7** and the boronic acid **8** generated the aldehyde **9**. Reduction of **9**, followed by bromination of the resulting alcohol **10**, afforded the bromide **11**. The crown ether **14** was prepared from

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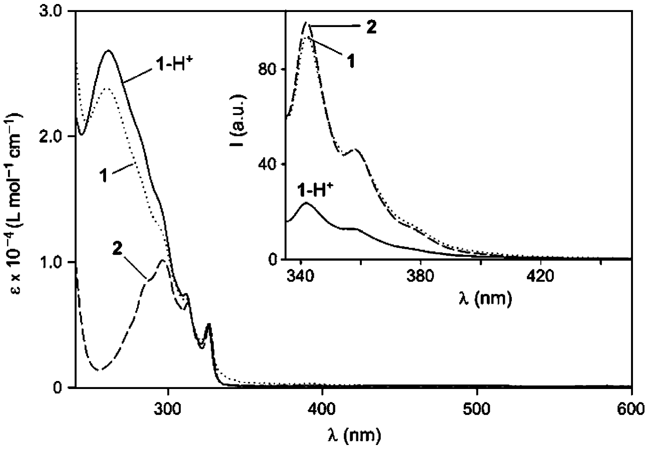

Figure 1. Absorption and (inset) fluorescence spectra of **1**-H$^+$ (full line), **1** (dotted line), and **2** (dashed line). Experimental conditions: air-equilibrated 3.0×10^{-5} mol L^{-1} solutions in CH_2Cl_2 at 298 K; excitation wavelength, 326 nm.

reduction of the macrocyclization product between dibromide **12**[38] and the aldehyde **13**. The etherification between **11** and **14** afforded **15**, which was deprotected[39] under mild conditions employing a phenol/TMSCl/CH_2Cl_2 solution. Subsequent protonation with HCl and counterion exchange afforded the title compound **1**-H·PF_6.

Absorption and Fluorescence Properties of the Molecular Plug−Socket Connector. Figure 1 shows the absorption and (inset) luminescence spectra of **1**-H$^+$, **1** (obtained by deprotonation of **1**-H$^+$ with 1 equiv of tributylamine), and of the BN36C10 reference compound **2**. Above 300 nm, the absorption spectra of the three compounds are quite similar. Comparison with the absorption spectrum of 4-phenylbenzylamine shows that the strong absorption band with $\lambda_{max} = 260$ nm of **1** and **1**-H$^+$ can be attributed to their wire-type moiety. The emission spectrum of **1** is almost identical to that of model compound **2**, assigned to the fluorescence emission of the 1,5-dioxynaphthalene unit.[40] The spectrum of **1**-H$^+$ is much weaker and, contrary to what happens for **1** and **2**, exhibits two distinct emission decays (Table 1). The absorption and emission properties of **2** are unaffected by the addition of 1 equiv of trifluoromethanesulfonic (triflic) acid or tributylamine (TBA). Upon addition of 1 equiv of triflic acid, the absorption and emission properties of **1** become identical to those of **1**-H$^+$ and are reconverted into the properties of **1** upon successive addition of 1 equiv of tributylamine. Therefore, **1** and **1**-H$^+$ can be reversibly interconverted by acid/base inputs.

The decrease in the emission intensity of **1** upon protonation shows that, in **1**-H$^+$, the fluorescence of the BN36C10-type unit is quenched by the 4-phenylbenzylammonium moiety, most likely because of an electron-transfer process from the BN36C10 singlet excited state to the 4-phenylbenzylammonium moiety. The double exponential emission decay suggests that **1**-H$^+$ is present as two different conformations originating from self-complexation between the secondary dialkylammonium center and the BN36C10-type moiety. Inspection of CPK space-filling molecular models shows (Figure 2), indeed, that both threaded and side-on self-complexation can occur. It seems likely that the electronic interaction between the BN36C10 and 4-phenylbenzylammonium units of **1**-H$^+$ is more favored for a threaded compared with a side-on structure. If this is the case, the emission lifetime data (Table 1) show that about 80% of the complexation occurs by threading.

Table 1. Luminescence Data (Air-Equilibrated Solutions, CH_2Cl_2, 298 K)

compound	I_{em}[a]	τ (ns)
2	100	7.0
1	95	6.6
1-H$^+$	23	1.3 (78%)[b] 5.6 (22%)[b]
3⊃**1**-H$^+$	30	1.9 (75%)[b] 7.0 (25%)[b]
2⊃**4**$^{2+}$	25[c]	7.0[c]
3⊃**1**-H$^+$⊃**4**$^{2+}$	13[d]	7.0[d]

[a] $\lambda_{exc} = 326$ nm; $\lambda_{em} = 345$ nm. [b] From the ratios of the pre-exponential factors of the decay curves. [c] Emission attributed to the fraction of noncomplexed crown **2** after addition of 6 equiv of **4**$^{2+}$. [d] Emission attributed to the fraction of noncomplexed **1**-H$^+$ after addition of 6 equiv of **4**$^{2+}$.

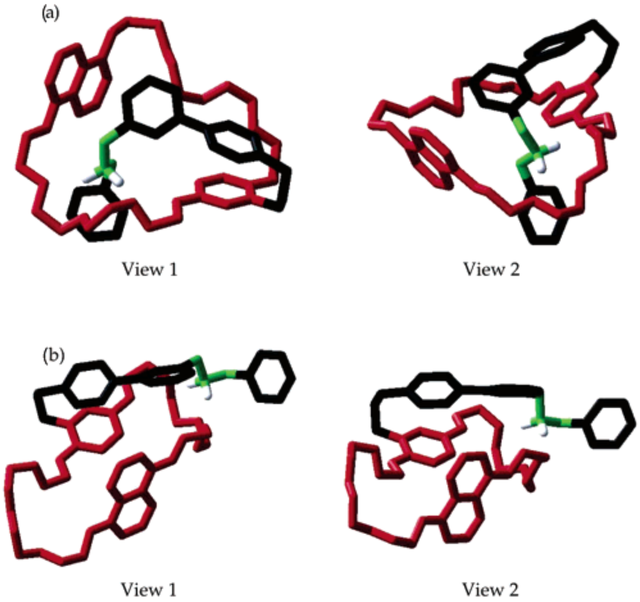

Figure 2. (a) Two perspectives of the global energy minimum conformer of **1**-H$^+$, which is the threaded self-complex, as determined by molecular force field calculations. (b) Two perspectives of the side-on self-complex, which is a local-energy-minimum conformer of **1**-H$^+$ and has been determined to be 1.1 kcal mol^{-1} less stable than the threaded self-complex. All hydrogens except those involved in hydrogen bonding have been removed for clarity.

Modeling of Molecular Plug−Socket Connector Conformers. In order to gain a more thorough understanding of the different low-energy conformers that may be adopted by **1**-H$^+$, we have undertaken a theoretical investigation of the monocationic plug−socket connector using molecular force field computations. Computations were performed using the AMBER* force field[41] and GB/SA solvent model[42] for $CHCl_3$ in the program[43] Maestro v3.0.038. A 1000-step conformational search was used to determine the lowest energy conformer of

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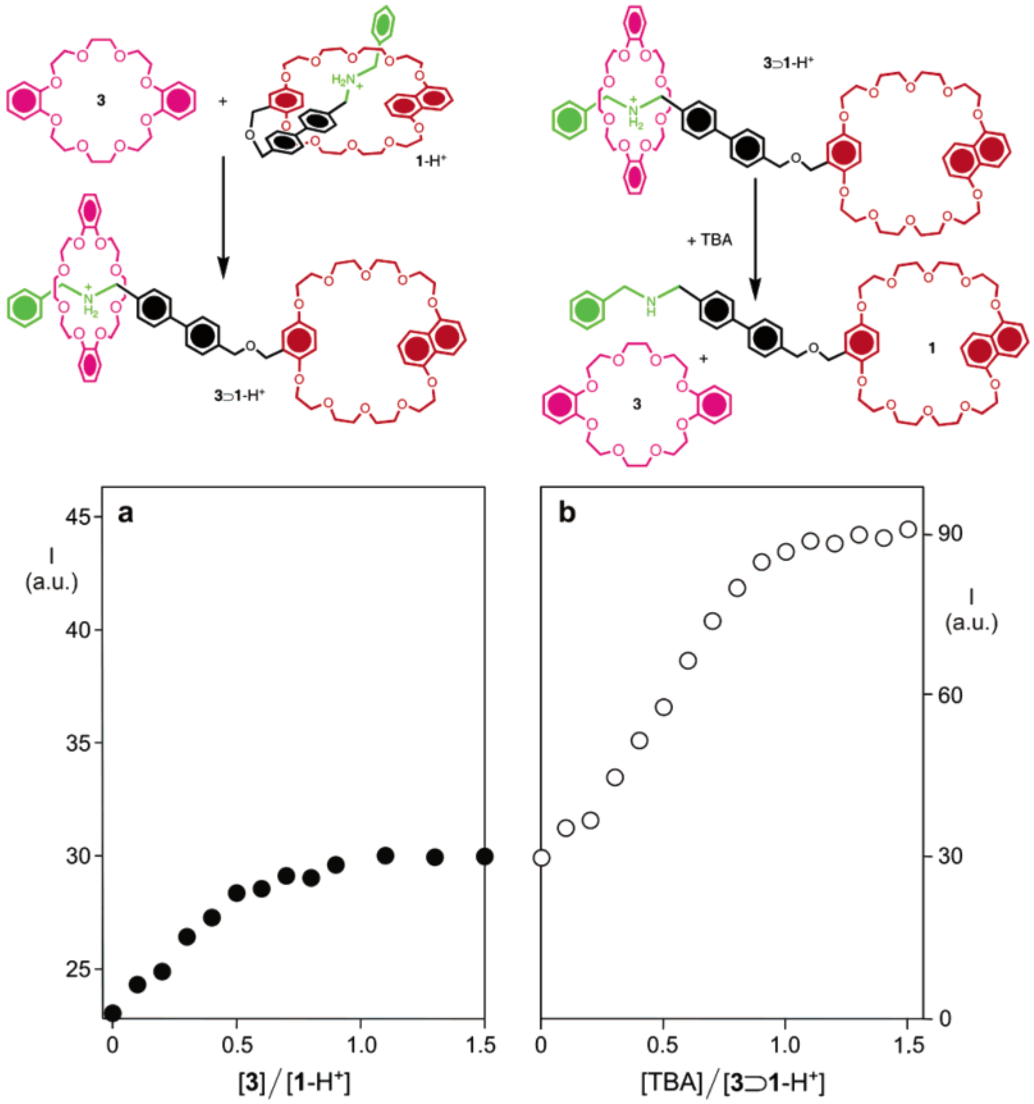

Figure 3. (a) Change in the fluorescence intensity of **1**-H$^+$ (2.0×10^{-5} mol L^{-1}) upon addition of DB24C8 (**3**). (b) Change in the fluorescence intensity of a solution containing **1**-H$^+$ (2.0×10^{-5} mol L^{-1}) and **3** (1.5 equiv) upon addition of TBA. The corresponding processes are schematized at the top of each diagram. Experimental conditions: air-equilibrated CH_2Cl_2 solution at 298 K; excitation wavelength, 326 nm; emission wavelength, 345 nm.

1-H$^+$, which was found (Figure 2a) to be the threaded self-complex. The slightly higher energy side-on self-complex (Figure 2b) was also located. A 500 ps molecular dynamics simulation at an elevated temperature of 400 K was then used to equilibrate both the threaded and side-on self-complexes. Full energy minimization of 500 randomly sampled conformers generated during each molecular dynamics simulation gave the global minimum threaded structure and local minimum side-on self-complex (Figure 2). The threaded self-complex, which is able to form two bifurcated hydrogen bonds with the macrocyclic polyether, is found to be 1.1 kcal mol^{-1} more stable than the side-on self-complex, which is only able to form two hydrogen bonds with the macrocycle. This energetic difference corresponds to a relative ratio of 84:16 in favor of the threaded conformer. This theoretically predicted value is in good agreement with experimental emission lifetime data and supports the conclusions that (1) there are two distinct low-energy conformations available to **1**-H$^+$ and that (2) the threaded self-complex is the more stable of the two.

Two-Component Supramolecular System 3⊃1-H$^+$. Titration of **1**-H$^+$ (2.0×10^{-5} mol L^{-1}) with the dibenzocrown ether **3** caused an increase in the fluorescence of the BN36C10 unit of **1**-H$^+$. A plateau is reached (Figure 3a) after addition of 1 equiv of **3**, indicating that the dibenzocrown ether **3** interacts with **1**-H$^+$ to give a remarkably stable ($K > 10^5$ L mol^{-1}) 1:1 adduct.[26c] This is an expected result since **1**-H$^+$ contains a dialkylammonium ion center that is known to thread dibenzo[24]crown-8.[20,26] Therefore, **3** prevents self-complexation of **1**-H$^+$, giving rise to a supramolecular entity **3**⊃**1**-H$^+$. Under such conditions, the fluorescence of the BN36C10 unit of **1**-H$^+$ shows two distinct decay times, different from those exhibited by **1**-H$^+$ alone (Table 1). This result suggests that **3**⊃**1**-H$^+$ is present in two distinct conformations.

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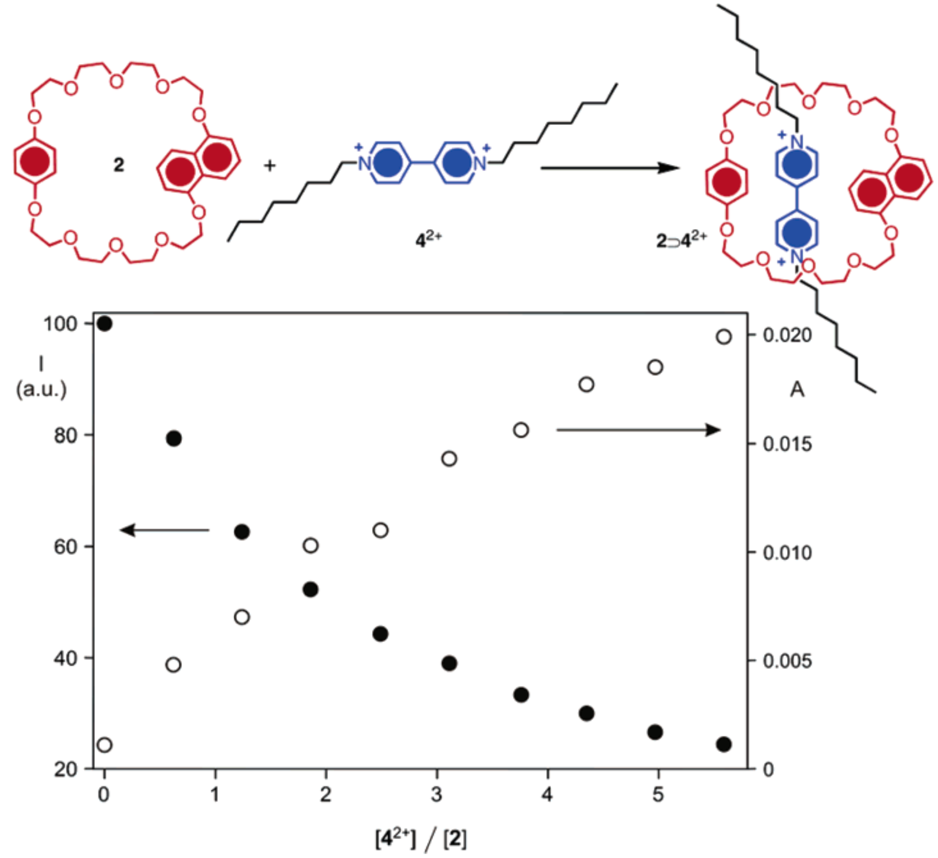

Figure 4. Changes observed in the emission spectrum at 345 nm (●) and in the absorption spectrum at 500 nm (○) of a solution containing the BN36C10 model compound **2** (3.0×10^{-5} mol L^{-1}) upon titration with 1,1′-dioctyl-4,4′-bipyridinium ion (**4**$^{2+}$). The corresponding process is schematized at the top of the diagram. Experimental conditions: air-equilibrated CH_2Cl_2 solution at 298 K; excitation wavelength, 326 nm. Solubility reasons prevented the addition of more than 6 equiv of compound **4**$^{2+}$.

Titration of the $\mathbf{3}\supset\mathbf{1}$-H$^+$ supramolecular entity with tributylamine causes an increase in the intensity of the BN36C10 fluorescence (Figure 3b) that, upon addition of a stoichiometric amount of base, reaches a value equal to that previously found for the unprotonated species **1**. Formation of **1** is confirmed by the disappearance of the double emission decay and the recovering of the monoexponential decay with τ = 6.6 ns. Successive addition of a stoichiometric amount of triflic acid leads back to the emission intensity and decay times of the $\mathbf{3}\supset\mathbf{1}$-H$^+$ species. These results show that the adduct between **3** and **1**-H$^+$ can be reversibly assembled/disassembled by acid/base inputs.

Two-Component Supramolecular System $\mathbf{2}\supset\mathbf{4}^{2+}$. Viologen-type molecules (i.e, 1,1′-dimethyl-4,4′-bipyridinium ions) are known to thread aromatic crown ethers by virtue of π-electron donor−acceptor and hydrogen-bonding interactions.[19,23] Formation of such pseudorotaxane structures causes the quenching of the fluorescence of the crown ether and the appearance of a broad and weak charge-transfer absorption band in the visible region.[26d,40]

In preliminary experiments, we found that titration of the BN36C10 reference compound **2** (3.0×10^{-5} mol L^{-1}) with 1,1′-dioctyl-4,4′-bipyridinium (**4**$^{2+}$) causes the quenching of the fluorescence intensity of **2**, accompanied by the appearance of an absorption band with a maximum at 500 nm (Figure 4). It should be noted that dynamic quenching of the fluorescent excited state of **2** by **4**$^{2+}$ can be excluded because of the short excited-state lifetime of **2** (τ = 7 ns) and the low concentration of **4**$^{2+}$ ($\leq 2.0 \times 10^{-4}$ mol L^{-1}). These results indicate the formation of an adduct between the electron-donating crown ether **2** and the electron-accepting **4**$^{2+}$ species, as already known to occur upon threading bipyridinium-type units into crown ethers incorporating benzo and naphtho substituents.[19,23,40,44] Fitting of the titration curves (Figure 4) yielded a value of 21 000 ± 1000 L mol^{-1} for the association constant and a molar absorption coefficient of ca. 1000 L mol^{-1} cm^{-1} for the maximum of the charge-transfer band, in good agreement with previously reported values.[40,45] Addition of Zn or Ag powder to deaerated solutions of the adduct $\mathbf{2}\supset\mathbf{4}^{2+}$ caused a complete revival of the fluorescence of **2** and the appearance of the strong absorption bands characteristic of the one-electron reduced form of the bipyridinium unit.[46] When dioxygen was allowed to enter the solution, the changes caused in the absorption spectrum by the addition of the metal were reversed. These results show that **4**$^{2+}$ threads **2** and that the threading/dethreading process can be redox controlled.

Two-Component Supramolecular System $\mathbf{1}\supset\mathbf{4}^{2+}$. Upon titration of **1**-H$^+$ (5.0×10^{-5} mol L^{-1}) with **4**$^{2+}$, no quenching of the fluorescence of the BN36C10-type moiety was observed

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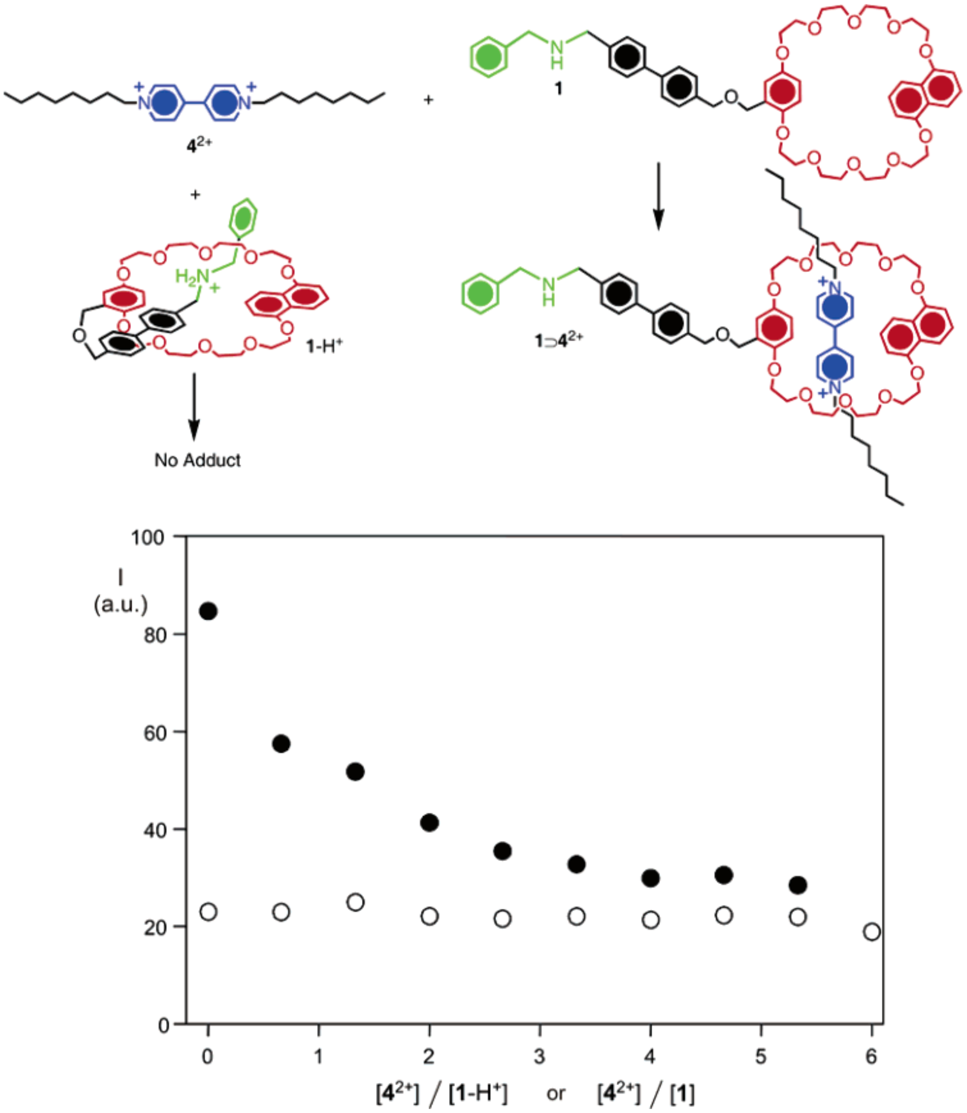

Figure 5. Changes in the fluorescence intensity of a 3.0×10^{-5} mol L^{-1} solution of **1**-H$^+$ (○) and **1** (●) upon titration with $\mathbf{4}^{2+}$. The corresponding processes are schematized at the top of the diagram. Experimental conditions: air-equilibrated CH_2Cl_2 solution at 298 K; excitation wavelength, 326 nm; emission wavelength, 345 nm.

(Figure 5), showing that $\mathbf{4}^{2+}$ does not thread the crown-ether moiety of **1**-H$^+$. The most likely explanation is that **1**-H$^+$ is self-complexed (vide supra), and therefore, its macrocyclic cavity is not available for intermolecular complexation. In fact, if titration is performed in the presence of 1 equiv of tributylamine (that causes deprotonation of **1**-H$^+$ and the consequent disruption of the self-complexed species), the fluorescence intensity of the BN36C10-type moiety decreases upon increasing the $\mathbf{4}^{2+}$ concentration (Figure 5), and an absorption band with maximum around 500 nm appears. These results indicate[26d,40] that $\mathbf{4}^{2+}$ does thread the crown-ether moiety of the unprotonated species **1**. The association constant is substantially the same as that for $\mathbf{2}\supset\mathbf{4}^{2+}$ (vide supra). Successive addition of triflic acid caused opposite spectral changes, showing that back self-complexation of **1**-H$^+$ kicks out $\mathbf{4}^{2+}$.

Three-Component Supramolecular System $\mathbf{3}\supset\mathbf{1}$-H$^+\supset\mathbf{4}^{2+}$. Titration of **1**-H$^+$ with $\mathbf{4}^{2+}$ does not cause (Figure 5) any change in the emission spectrum, indicating that threading of the crown-ether moiety of **1**-H$^+$ by $\mathbf{4}^{2+}$ does not take place because **1**-H$^+$ is self-complexed. We have seen that disassembling of the self-complexed structure of **1**-H$^+$ can be obtained not only by deprotonation but also by surrounding the ammonium moiety of **1**-H$^+$ with the dibenzocrown ether **3**. Titration with $\mathbf{4}^{2+}$ of a solution of **1**-H$^+$ containing 1.5 equiv of **3** caused[47] the quenching of the fluorescence intensity of the BN36C10-type unit and the increase of absorbance at 500 nm (Figure 6). These results show that, when the $CH_2NH_2^+CH_2$ center in **1**-H$^+$ is surrounded by **3**, $\mathbf{4}^{2+}$ threads the crown-ether moiety of **1**-H$^+$. The association constant is estimated to be on the order of 10^4 L mol^{-1} from the fitting of the titration plots. Addition of Zn or Ag powder to the deaerated solution at the end of the titration caused a revival of the BN36C10-type unit fluorescence intensity and the appearance of the strong absorption bands of the monoreduced bipyridinium unit. In conclusion, the crown unit of **1**-H$^+$ can play the role of a socket toward $\mathbf{4}^{2+}$ when the ammonium function is plugged in the crown ether **3**.

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(47) Titration experiments showed that the association between **3** and $\mathbf{4}^{2+}$ is negligible under the conditions employed.

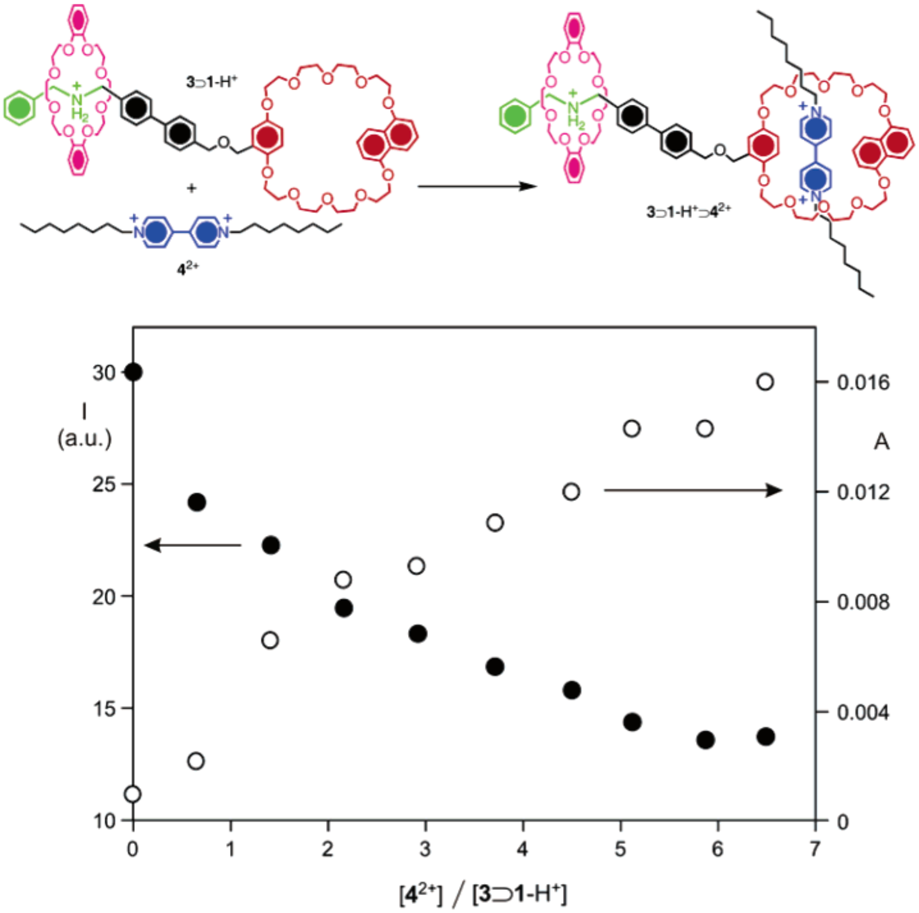

Figure 6. Changes observed in the emission spectrum at 345 nm (●) and in the absorption spectrum at 500 nm (○) of a 3.0 × 10^{-5} mol L^{-1} solution of **1**-H^+ in the presence of 1.5 equiv of DB24C8 (**3**) upon titration with $\mathbf{4}^{2+}$. The corresponding process is schematized at the top of the diagram. Experimental conditions: air-equilibrated CH_2Cl_2 solution at 298 K; excitation wavelength, 326 nm.

Conclusions

We have designed, synthesized, and characterized a compound (**1**-H^+) that exhibits a fluorescence signal associated with the dioxynaphthalene unit of its crown-ether moiety. Fluorescence studies performed in CH_2Cl_2 solution show that **1**-H^+ is present as two different conformers, originating from self-complexation between the $CH_2NH_2^+CH_2$ center and the crown-ether moiety. Upon addition of a stoichiometric amount of tributylamine, **1**-H^+ is converted into its unprotonated form **1**; subsequent addition of triflic acid causes reversible conversion to the initial **1**-H^+ species. The secondary $CH_2NH_2^+CH_2$ center in **1**-H^+ threads the DB24C8 crown ether **3** (Figure 2) and is under conditions such that the crown-ether moiety of **1**-H^+ can be threaded by 1,1′-dioctyl-4,4′-bipyridinium ion $\mathbf{4}^{2+}$ (Figure 5). Therefore, **1**-H^+, **2**, and $\mathbf{4}^{2+}$ can self-assemble, giving rise to the triad $\mathbf{3}\supset\mathbf{1}$-$H^+\supset\mathbf{4}^{2+}$. Both of the self-assembling processes are reversible and can be controlled by external inputs; assembling/disassembling between **1**-H^+ and **3** is acid/base controlled, and that between **1**-H^+ and $\mathbf{4}^{2+}$ is redox controlled. In the $\mathbf{3}\supset\mathbf{1}$-$H^+\supset\mathbf{4}^{2+}$ triad, the central component **1**-H^+ performs as a connector between a socket-type component (crown ether **3**) and a plug-type component (1,1′-dioctyl-4,4′-bipyridinium ion). The results obtained in this work represent a fundamental premise for the construction[24] of more complex self-assembling supramolecular systems in which a molecular electron source can be connected with a molecular electron drain by a molecular elongation cable.

Experimental Section

Materials and General Procedures. Reagents were purchased from Aldrich. BN36C10 (**2**) was available from previous work. DB24C8 (**3**) and 4-phenylbenzylamine were obtained from Aldrich. The 1,1′-dioctyl-4,4′-bipyridium hexafluorophosphate salt **4**·2PF_6 was a gift from Professor A. Arduni (University of Parma). The compound **12**[38] was prepared according to literature procedures. Solvents were purified according to literature procedures.[48] Thin-layer chromatography (TLC) was carried out using aluminum sheets, precoated with silica gel 60F (Merck 5554). The plates were inspected by UV light prior to development with iodine vapor. Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker Avance500, Avance 600, or ARX500, using the deuterated solvent as the lock and the residual protonated solvent as the internal standard. All chemical shifts are quoted using the δ scale, and all coupling constants (J) are expressed in Hertz (Hz). Electrospray mass spectra (ESI−MS) were measured on a VG ProSpec triple-focusing mass spectrometer.

7: 4-Bromobenzaldehyde (**5**) (2.50 g, 23.4 mmol) and benzylamine (**6**) (4.32 g, 23.4 mmol) were heated together in refluxing PhMe (100 mL) for 30 min. The reaction mixture was

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cooled to room temperature, and the solvent was evaporated off in vacuo. The residue was redissolved in MeOH (150 mL). $NaBH_4$ (1.7 g, 46.8 mmol) was added, and the mixture was heated under reflux for 1 h. The reaction mixture was partitioned in 2N HCl/CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layer was dried ($MgSO_4$) and filtered, and the filtrate was evaporated to dryness. The obtained oil was stirred together with Boc_2O (5.53 g, 25.4 mmol) and DMAP (0.12 g, 0.1 mmol) in CH_2Cl_2 (100 mL) for 1 h at room temperature. The solution was evaporated, and the residue was subjected to column chromatography (SiO_2−EtOAc/hexanes 1:10) to give compound **7** (4.70 g, 93%) as a colorless liquid, which slowly solidified upon storage. Mp: 64−66 °C. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.59 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 7.7$ Hz, 2H), 7.36−7.22 (m, 7H), 4.74 (s, 2H), 4.46 (br s, 2H), 4.38 (br s, 2H), 1.92 (s, 1H), 1.52 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 156.0, 140.1, 139.9, 139.7, 137.9 (br), 137.0 (br), 128.5, 128.3 (br), 127.9 (br), 127.8 (br), 127.4, 127.1 (br), 127.1, 80.1, 64.9, 49.3 (br), 48.9 (br), 48.6 (br), 28.4. HRMS (ESI) (m/z): $[M - \mathrm{Boc}]^+$ calcd for $C_{19}H_{22}BrNO_2$, 274.0231; found, 274.0439.

10: A mixture of bromide **7** (2.00 g, 5.30 mmol), boronic acid **8** (0.88 g, 5.85 mmol), $Pd(PPh_3)_4$ (0.31 g, 27 μmol), and K_2CO_3 (1.47 g, 10.7 mmol) in degassed $EtOH/H_2O$/THF (8/6/50 mL) was stirred under reflux for 2 h. The resulting solution was cooled down, evaporated, and partitioned in H_2O/CH_2Cl_2. The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was evaporated to get a residue, which was subjected to column chromatography (SiO_2−EtOAc/hexanes 1:10) to give **9** (1.40 g, 67%) as a colorless oil. The oil was dissolved in MeOH (30 mL). $NaBH_4$ (0.19 g, 5.03 mmol) was added, and the solution was heated under reflux for 2 h. The reaction mixture was evaporated and subjected to column chromatography (SiO_2−EtOAC/hexanes 1:3) to give **10** as a colorless oil (1.35 g, 96%), which slowly solidified upon vacuum. Mp: 91−92 °C. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.59 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 7.7$ Hz, 2H), 7.36−7.22 (m, 7H), 4.74 (s, 2H), 4.46 (br s, 2H), 4.38 (br s, 2H), 1.92 (s, 1H), 1.52 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 156.0, 140.1, 139.9, 139.7, 137.9 (br), 137.0 (br), 128.5, 128.3 (br), 127.9 (br), 127.8 (br), 127.4, 127.1 (br), 127.1, 80.1, 64.9, 49.3 (br), 48.9 (br), 48.6 (br), 28.4. HRMS (ESI) (m/z): $[M + \mathrm{Na}]^+$ calcd for $C_{26}H_{29}NO_3$, 426.2040; found, 426.2064.

11: PBr_3 (0.15 g, 0.55 mmol) was added dropwise into the solution of **10** (0.20 g, 0.50 mmol) in Et_2O (5 mL), and the mixture was stirred at room temperature for 1 h. The resulting suspension was filtered, and the filtrate was evaporated to dryness. The residue was partitioned in H_2O/CH_2Cl_2. The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was evaporated to give a sticky oil (0.13 g, 56%), which was used directly for the next step without further purification.

14: Cesium carbonate (17.2 g, 89 mmol) was stirred in dry DMF (180 mL). After the temperature was raised up to 100 °C, a solution of the dibromide **12** (5.70 g, 8.92 mmol) and the aldehyde **13** (1.23 g, 8.92 mmol) in dry DMF (180 mL) was added over 72 h. After cooling down to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. Purification of the resulting brown oil by column chromatography (SiO_2−EtOAC/hexanes 3:1) gave a yellow oil (1.4 g). This yellow oil was dissolved in MeOH (25 mL). $NaBH_4$ (0.13 g, 3.50 mmol) was added, and the mixture was heated under reflux for 2 h. After cooling down to room temperature, the solvent was evaporated, and the residue was extracted with CH_2Cl_2. After filtration, the filtrate was concentrated to give **14** (1.40 g, 25% for two steps) as a white solid. Mp: 52−54 °C. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.88 (dd, $J = 8.5$, 4.5 Hz, 2H), 7.31 (q, $J = 8.2$, 2H), 6.75 (d, $J = 8.1$ Hz, 2H), 6.62 (d, $J = 7.5$ Hz, 1H), 6.59 (dd, $J = 8.5$, 2.9 Hz, 1H), 6.45 (d, $J = 8.5$ Hz, 1H), 4.47 (d, $J = 5.0$ Hz, 2H), 4.24−4.21 (m, 4H), 3.99 (t, $J = 4.8$ Hz, 2H), 3.97 (t, $J = 4.8$ Hz, 2H), 3.85−3.65 (m, 24H). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 154.2, 154.1, 152.9, 150.7, 131.3, 126.6, 126.5, 125.1, 125.0, 115.0, 114.5, 114.4, 114.1, 113.5, 105.6, 70.9, 70.7, 70.7, 70.7, 70.6, 70.6, 70.3, 69.6, 69.5, 68.6, 67.9, 67.7, 61.4. HRMS (ESI) (m/z): $[M + \mathrm{Na}]^+$ calcd for $C_{33}H_{44}O_{11}$, 639.2761,; found, 639.2776.

15: A solution of **14** (0.17 g, 0.28 mmol) in THF (2 mL) was added into a suspension of NaH (20 mg, 0.73 mmol) in THF (5 mL). The mixture was stirred under reflux for 0.5 h. After cooled down, a solution of **11** (0.13 g, 0.28 mmol) in THF (2 mL) was added dropwise, and the mixture was heated under reflux overnight. The reaction mixture was filtered, and the filtrate was evaporated to give a residue, which was subjected to column chromatography (SiO_2−EtOAC/hexanes 3:1) to give **15** (0.15 g, 54%) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.87 (dd, $J = 8.5$, 4.5 Hz, 2H), 7.56 (dd, $J = 8.5$, 2.6 Hz, 4H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 7.5$ Hz, 2H), 7.30−7.23 (m, 5H), 6.96 (d, $J = 2.9$ Hz, 2H), 6.71 (d, $J = 8.1$ Hz, 2H), 6.69 (d, $J = 7.5$ Hz, 1H), 6.65 (dd, $J = 8.5$, 2.9 Hz, 1H), 6.46 (d, $J = 8.5$ Hz, 1H), 4.55 (s, 2H), 4.53 (s, 2H), 4.48 (br s, 2H), 4.39 (br s, 2H), 4.21−4.19 (m, 4H), 3.99 (t, $J = 4.8$ Hz, 2H), 3.96 (t, $J = 4.8$ Hz, 2H), 3.90 (t, $J = 4.8$ Hz, 2H), 3.84 (t, $J = 4.8$ Hz, 2H), 3.81−3.66 (m, 20H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 155.9, 154.3, 154.2, 152.9, 150.4, 139.9, 137.7, 128.4, 128.2, 128.0, 127.1, 127.1, 126.8, 126.7, 126.6, 125.0, 125.0, 115.2, 114.5, 114.5, 113.7, 112.8, 105.5, 80.0, 72.0, 72.9, 70.8, 70.8, 70.8, 70.7, 70.6, 69.7, 69.7, 69.6, 68.4, 67.9, 67.9, 67.9, 66.9, 28.4. HRMS (ESI) (m/z): $[M + \mathrm{Na}]^+$ calcd for $C_{59}H_{71}NO_{13}$, 1024.4780; found, 1024.4818.

1-H·PF$_6$: A solution (10 mL) of phenol/trimethylsilyl chloride (1:3 M) in CH_2Cl_2 was added to **15** (60 mg, 60 μmol), and the mixture was stirred at room temperature for 5 min. The solution was washed with aqueous NaOH solution (1 M, 3 × 10 mL), and the organic layer was evaporated to dryness. The residue was redissolved in Me_2CO (5 mL), and HCl (1 M, 10 mL) was added, followed by the addition of saturated NH_4PF_6 solution. The mixture was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was evaporated, and the residue was subjected to preparative TLC (SiO_2−CH_2Cl_2/MeOH 10:1) to give **1**-H·PF_6 (13 mg, 20%; difficulty in extracting the ionic product off the TLC plate likely accounts for the relatively low yield). ^1H NMR (CD_3COCD_3, 600 MHz, 298 K): δ 7.83 (dd, $J = 9.1$, 3.6 Hz, 2H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.62 (d, $J = 8.2$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 7.5$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.37 (t, $J = 7.5$ Hz, 2H), 7.30 (t, $J = 8.2$ Hz, 2H), 7.28 (t, $J = 7.8$ Hz, 2H), 6.96 (s, 1H), 6.80 (d, $J = 7.8$ Hz, 2H), 6.62 (s, 2H), 4.58 (s, 2H), 4.53 (s, 2H), 4.21 (m, 4H), 3.99−3.95 (m, 8H), 3.93 (t, $J = 5.0$ Hz, 2H), 3.90 (t, $J = 5.0$ Hz, 2H), 3.77−3.63 (m, 20H). HRMS (ESI) (m/z): $[M - PF_6]^+$ calcd for $C_{54}H_{64}F_6NO_{11}P$, 902.4474; found, 902.4474.

Absorption and Fluorescence Spectroscopy. The absorption and fluorescence experiments have been performed at 298 K in air-equilibrated CH_2Cl_2 (Merck Uvasol), unless otherwise stated. The investigations were carried out in dilute solutions (2.0×10^{-5}−2.0×10^{-4} mol L^{-1}) in order to avoid intermolecular complexation among **1**-H^+ species (vide infra) and dynamic quenching processes. The emission intensity values, when necessary, were corrected to take into account inner filter effects, geometrical factors (for solutions of different absorbances at the excitation wavelength), and reabsorption of the emitted light.[49] UV−vis absorption spectra were recorded with a Perkin−Elmer λ40 spectrophotometer. Luminescence spectra were obtained with a Perkin−Elmer LS-50 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Excitation was performed at 326 nm, which is an isosbestic point of the chromophoric groups involved (vide infra). Luminescence lifetimes were measured by the time-correlated single-photon counting technique with Edinburgh Instruments TCSPC equipment. The exciting light was produced by a gas arc lamp (Model nF900, filled with D_2) that delivered pulses of about 1 ns (fwmh). The light emitted was filtered by using a cutoff filter. The detector was a cooled Hamamatsu R928 photomultiplier. The experimental error on molar absorption coefficients, fluorescence intensities, and fluorescence lifetimes is estimated to be ±5%.

Computational Procedure. Molecular force field calculations were performed using the program Maestro v3.0.038.[43] The AMBER* force field[41] and GB/SA solvent model[42] for $CHCl_3$ were used along with an extended cutoff for nonbonded interactions. An initial Monte Carlo multiple minimization (MCMM) conformational search involving the generation and minimization of 1000 starting conformations by application of random variations to the internal coordinates was used to locate the global energy minimum of **1**-H^+. The maximum number of iterations for each energy minimization in the search was set to 2000, and the energetic window for saving structures was 1000 kJ/mol. Both threaded and side-on self-complexes were found, with the threaded conformer being the more stable. The 500 ps molecular dynamics simulations (1.5 fs time step) at a temperature of 400 K were then used to relax both conformers. The SHAKE algorithm was employed on all bonds to hydrogens, and 500 randomly selected structures generated from each molecular dynamics simulation were energy minimized to full convergence at 298K using the PRCG algorithm,[43] resulting in fully relaxed conformations of the threaded as well as side-on self-complexes. The modeling procedure did not take into account the influence of the PF_6^- counterion, as its position in solution will be random, and subtle variations in counterion position will average out and not affect the relative energetic difference between the threaded and side-on self-complexes.

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Supporting Information Available: Complete ref 37a. This material is available free of charge via the Internet at http://pubs.acs.org.

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