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A Molecular Shuttle for Driving a Multilevel Fluorescence Switch

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Abstract: A [2]rotaxane-based molecular shuttle comprised a macrocycle mechanically interlocked to a chemical "dumbbell" has been prepared in high yields by a thermodynamically controlled, template-induced clipping procedure. This molecular shuttle has two different recognition sites, namely, $-NH_2^+-$ and amide, separated by a phenyl unit. The macrocycle exhibits high selectivity for the $-NH_2^+-$ recognition sites in the protonated form through noncovalent interactions, which include 1) $N^+-H\cdots O$ hydrogen bonds; 2) $C-H\cdots O$ interactions between the $CH_2NH_2^+CH_2$ protons on the thread and the oligo(ethylene glycol) unit in the macrocycle; 3) $\pi\cdots\pi$ stacking interaction between macrocycle and aromatic unit. Upon deprotonation of the [2]rotaxane the macrocycle glides to the amide recognition site due to the hydrogen bonds between the −CONH− group and the oligo(ethylene glycol) unit in the macrocycle. The deprotonation process requires about 10 equivalents of base (iPr$_2$NEt) in polar acetone, while the amount of base is only 1.2 equivalents in apolar tetrachloroethane. Upon addition of Li^+, the conformation of the [2]rotaxane was altered as a result of the collective interactions of 1) hydrogen bonds between pyridine nitrogen and amide hydrogen atoms; 2) coordination between the oligo(ethylene glycol) unit, amide oxygen atom and Li^+ cation. Then, when Zn^{2+} ions are added, the macrocycle returns to the deprotonated −NH− recognition site owing to coordination of the macrocycle and −NH− from the axle with the Zn^{2+} ion. All the above-mentioned movement processes are reversible through the alternate addition of TFA/iPr$_2$NEt, Li/[12]-crown-4 and Zn^{2+}/ethylenediaminetetraacetate (EDTA), by virtue of hydrogen bonding and metal-ion complexation. Significantly, the three independent movement processes are all accompanied by fluorescent responses: 1) complete repression in the protonated form; 2) low-level expression in the deprotonated form; 3) medium-level expression following addition of Li^+; 4) high-level expression on complexation with Zn^{2+}.

Keywords: fluorescence · molecular devices · rotaxanes · supramolecular chemistry · template synthesis

Introduction

Mechanically interlocked molecules such as catenanes and rotaxanes have received a great deal of attention due to their multiple controllable and reversible alternations of conformation through induced relative movement of their non-covalently interacting components on application of external stimuli.[1] Various noncovalent interactions have been employed in the construction of classical mechanically interlocked molecules: electron donor–acceptor interaction between a tetracationic cyclophane and dioxynaphthalene or tetrathiafulvalene,[2] $N^+-H\cdots O$ hydrogen bonds and $C-H\cdots O$ interactions in secondary dialkylammonium ions and recognition by crown ether macrocycles,[3] metal cation–ligand coordination in pyridine–copper architectures[4] and amide–amide hydrogen bonds in short peptides and isophthalamide macrocycles.[5] With the development of supramolecular chemistry, some weak noncovalent interactions have also been found to have the ability to stabilize the optimized conformation, such as $C-H\cdots\pi$ interactions[6] and electron-transfer processes.[7] Thus, construction of multistable molecular shuttles became possible by combination of the above interactions. The alternation of relative positions of the above-mentioned interlocked components constitutes a basic kind of mechanical switch, capable of varying physical properties such as conductivity,[8] circular dichroism[9]

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and fluorescence.[10] Some of these molecular mechanical switches have been designed specifically to perform particular functions, such as molecular muscles,[11] molecular elevators[12] and even molecular walkers.[13] However, most current artificial systems controlled by molecular shuttles are operated only as on/off switches and not in an adjustable multilevel mode. The availability of robust artificial switches which exhibit a single signal at desired levels in response to fixed doses of different inducers rather than minute concentration changes of a single inducer would be more desirable in the field of biotechnology.[14] With this in mind, we designed and constructed a multistable system to study the properties and operational mechanisms of this kind of artificial shuttles as a prelude to optimizing their performance (Figure 1).

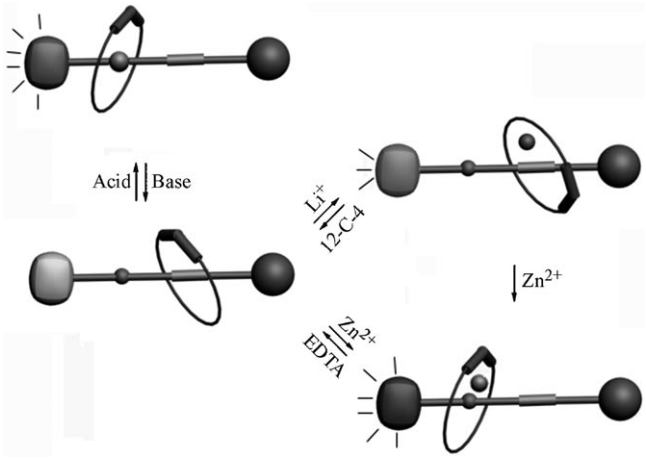
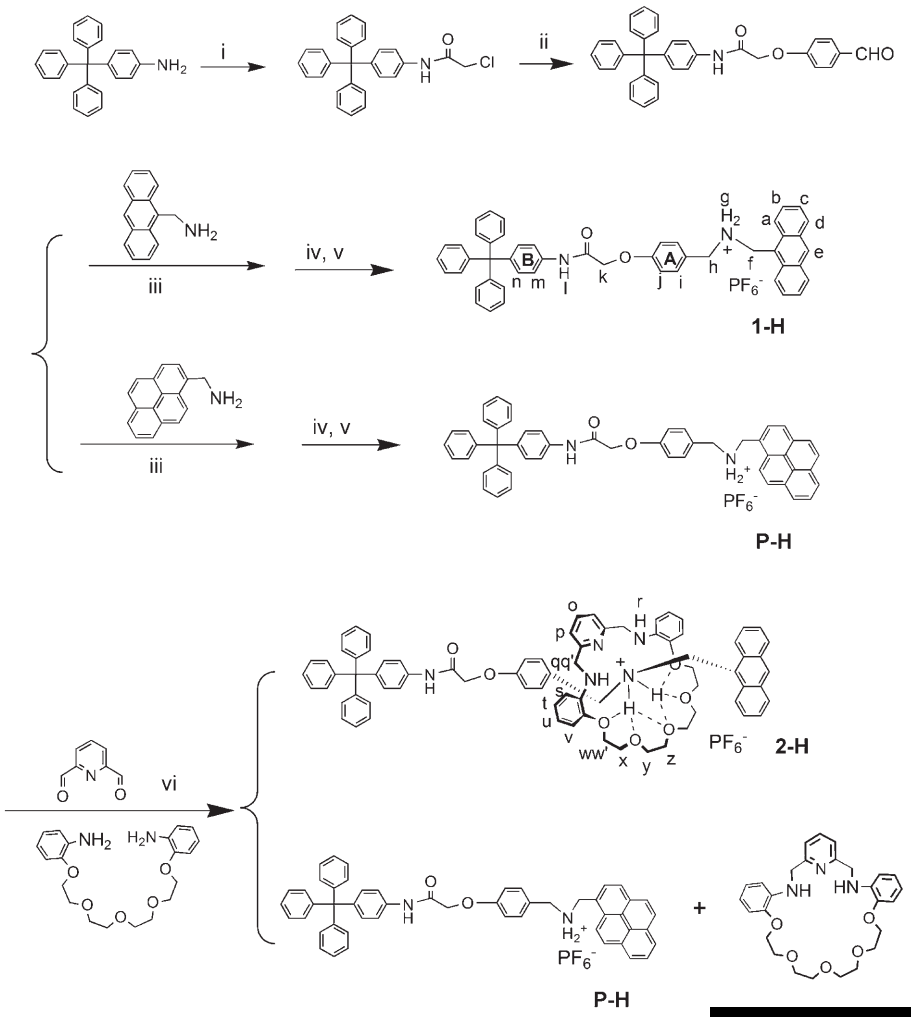


Figure 1. Graphical representation of the movement processes in the multistable molecular shuttle.

Here we describe a multilevel fluorescence switch in which acid/base- and metal-ion complexation/decomplexation-induced shuttling of the macrocycle along the thread drives changes in the interaction between the macrocycle and the fluorescent chromophore in the thread. The molecular shuttle consists of a thread bearing an anthracene group as a fluorescent probe and an aniline-containing oligo(ethylene glycol) macrocycle mechanically interlocked on the thread. The thread has two potential H-bonding stations: a secondary dialkylammonium ($-NH_2^+-$) center and an amide center, separated by a phenylene group. Under low-pH conditions, the macrocycle is assembled around an ammonium cation center through a combination of strong $N^+-H\cdots O$ hydrogen bonds and weak $C-H\cdots O$ interactions between macrocycle and thread. Addition of 1.2 equivalents of iPr$_2$NEt as base to the [2]rotaxane in apolar solution causes deprotonation of the ammonium recognition site. As a result, the hydrogen bonds between dialkylammonium and oligo(ethylene glycol) groups are switched off, and the macrocycle moves to the amide recognition site due to the hydrogen bond between them. Upon addition of 1.2 equivalents of Li^+ ions, the conformation of the [2]rotaxane is altered by a combination of Li–oligo(ethylene glycol) interaction[15] and weak hydrogen bonds between amide and pyridine groups. When 1.1 equivalents of Zn^{2+} ions are added, the pyridine/aniline moiety in the macrocycle and the amine in the thread complex with Zn^{2+}, and the macrocycle returns to the amine site. It is well known that photoinduced electron transfer takes place from the aniline and amine groups to the anthracene unit,[16] which can be influenced by the alternation of distance between them, protonation/deprotonation and metal ion complexation/decomplexation of aniline and amine groups.[5e,17] Thus, in this system, protonation/deprotonation and metal-ion complexation/decomplexation of aniline and amine, which can induce movement of the macrocycle, will all affect the fluorescent emission of the anthracene unit. By means of the above three movement processes, this shuttle enables multilevel expression of fluorescence in response to different triggers: 1) complete repression in the absence of any stimulus; 2) slight expression in response to base; 3) low-level expression following addition of Li^+; 4) high-level expression in the presence of Zn^{2+}.

Results and Discussion

Synthesis: Two threads **1-H** and **P-H** were synthesized for the construction of the [2]rotaxane and the multistable mechanical switch. According to the literature,[18] [2]rotaxanes can be prepared in high yields by a thermodynamically controlled, template-induced clipping procedure (Scheme 1), by mixing together of three components: a pyridine dialdehyde, a diamine and a dumbbell thread compound containing a $-CH_2NH_2^+CH_2-$ center. The target [2]rotaxane **2-H** was obtained in 75% yield after purification by chromatography on silica when **1-H** was used as template. A similar experiment using **P-H** as template gave independent **P-H** and macrocycle after purification by chromatography on silica, that is, the pyrene unit is not large enough to function as a bulky stopper for this macrocycle. The single-crystal structure of the macrocycle (Figure 2a) shows that the largest intramacrocycle distance is 9.222 Å, between O1 and O5, in the solid state.[18c] Though the conformation in the solid state is different from that in solution, this conformation possibly exists among the various states of free rotation in solution. In the pyrene unit, the largest distance, between H1 and H5, is 6.861 Å, slightly smaller than the cavity of the macrocycle (Figure 2b). Thus, the pyrene unit is small enough for the thread to leave the macrocycle. In Stoddart's model, a 3,5-dimethoxybenzyl group acts as a bulky stopper for the macrocycle.[18] As shown in Figure 2c, the largest distance, between H1 and H2, is 7.905 Å in the solid state, which is smaller than the cavity of the macrocycle, too. In addition, the methoxyl group can rotate freely around the C–O single bond, and this might reduce the distance between H1 and H2 to that between H1 and H5 in the pyrene unit. In their model,[18] the steric hindrance from the C–H



Scheme 1. i) 2-Chloroacetyl chloride, $Et_3N/CHCl_3$, 0 °C, 85 %; ii) 4-hydroxybenzaldehyde, K_2CO_3, acetone, KI, reflux, 8 h, 80 %; iii) EtOH, molecular sieves (4 Å), reflux, 8 h; iv) $NaBH_4$, EtOH, 25 °C, 8 h, 75 %; v) CF_3CO_2H, acetone, then NH_4PF_6, water; vi) 2,6-pyridinedicarboxaldehyde, tetraethylene glycol bis(2-aminophenyl)ether, $MeNO_2$, 10 min, then BH_3·THF, room temperature, 4 h, 70 %.

bonds in methyl groups may restrain the macrocycle on the thread.

The HRMS (N-SIMS NBA) of **2-H** (Figure 3) revealed a high intensity signal at *m*/*z* 1168.5566 corresponding to [**2-H**]$^+$, that is, loss of PF_6 ions from the salt. The ^{1}H NMR spectra of **1-H** and **2-H** in $CDCl_2CDCl_2/CD_3COCD_3$ (10/1) are shown in Figure 4. As expected for complexation, the ^{1}H NMR signals for the four protons H_f and H_g adjacent to NH_2^+ experienced a significant downfield shift of 0.5 ppm with respect to those in free **1-H**.[16a,18] The signals corresponding to phenylene protons H_i and H_j exhibited substantial downfield shift due to the shielding effect of the macrocycle (see Scheme 2). In this way, the macrocycle was probably, to some extent, sandwiching the phenylene **A** spacer so as to benefit from supplementary stabilization by means of weak π–π stacking interactions. The signals of the oligo(ethylene glycol) moiety of the macrocycle experienced downfield shift due to a combination of C–H···O and N^+–H···O hydrogen bonds. The signals of H_p, H_s and H_v on the macrocycle exhibited clear upfield shifts in **2-H**, which can be attributed to the shielding effect of phenylene ring **A**. This confirms a mutual shielding effect between phenylene ring **A** and the pyridine aniline moiety in the macrocycle. Thus, the ^{1}H NMR spectra support formation of rotaxane **2-H** and selective binding of the macrocycle with the $-NH_2^+-$ center.

Clear evidence for the formation of the [2]rotaxane was also obtained from electrochemical experiments in acetonitrile solution (Figure 5). The macrocycle exhibited two successive irreversible one-electron reduction waves around 0.97 and 1.28 V relative to a silver-wire electrode. When the macrocycle locked around the axle, the two oxidation potentials become less positive by about 170 and 50 mV, respectively, which can

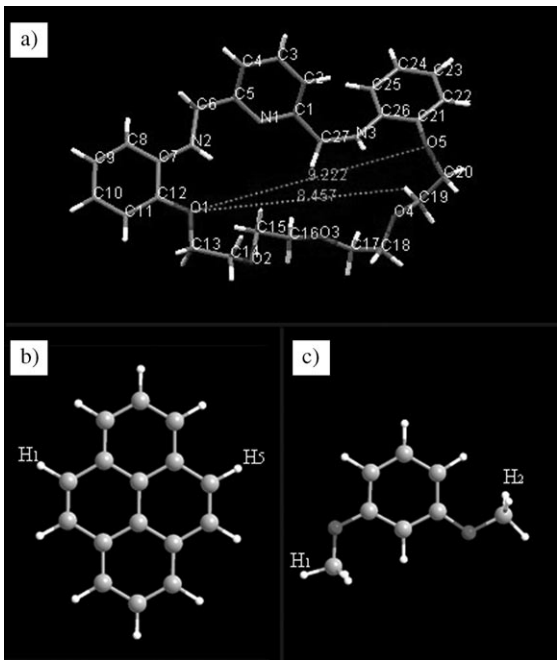


Figure 2. a) Solid-state structure of the macrocycle (CCDC-263073–CCDC-263075 from The Cambridge Crystallographic Data Centre).[18c] b) and c) Models of pyrene and 3,5-dimethoxybenzyl groups (The MM2 force field was used to calculate the minimum-energy conformation).

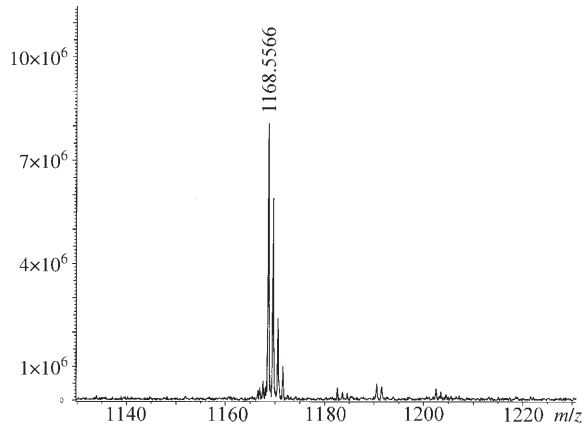


Figure 3. HRMS (N-SIMS NBA) of **2-H**.

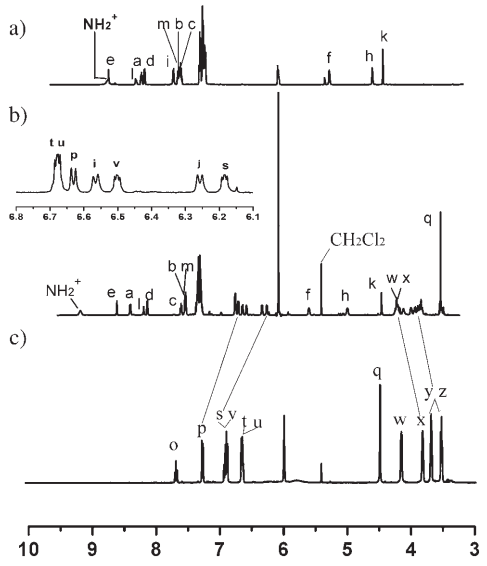


Figure 4. Partial ^{1}H NMR spectra (600 MHz, 298 K, 10^{-3} M, $CDCl_2CDCl_2$/CD_3COCD_3 10/1) of **1-H** (a), **2-H** (b) and macrocycle (c).

be ascribed to the electronic interaction between the macrocycle and the dialkylammonium center.[3] The reduction potential of the anthracene axle did not exhibit any clear difference during formation of the [2]rotaxane.

Movement processes: Switching of the ring between different recognition sites can be monitored by ^{1}H NMR, NOESY, UV/Vis and fluorescence spectroscopy.

NMR spectroscopy: The ^{1}H NMR titration of **2-H** with *i*Pr_2NEt in CD_3COCD_3 is outlined in Figure 6. Upon addition of *i*Pr_2NEt, two single peaks for the four protons H_f and H_g adjacent to NH_2^+ shift upfield from $\delta = 5.53$ and 5.23 to 4.87 and 4.62 ppm, respectively, which indicates deprotonation of the dialkylammonium group and breaking of C–H···O hydrogen bonds. The upfield shift of the methylene resonance ($\delta(H_k) = 0.62$ ppm) near the amide station in **2** is

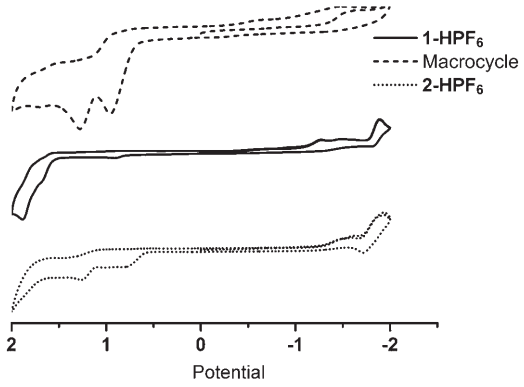


Figure 5. Cyclic voltammetric (CV) curves for **1-H**, macrocycle, and **2-H**. CV experiments were performed at room temperature in dried acetonitrile solutions containing 0.04 M $TBAPF_6$ as supporting electrolyte. A three-electrode configuration consisting of a glassy carbon working electrode, a Pt counterelectrode and an Ag wire quasi-reference electrode was used.

characteristic of aromatic shielding from the encapsulating macrocycle. At the same time, the signals assigned to H_e experienced an upfield shift from $\delta = 8.54$ to 8.49 ppm, due to reduced withdrawal of electrons on deprotonation of the dialkylammonium center. The signal for H_a shifted downfield by 0.13 ppm in the rotaxane as a result of the loss of aromatic shielding from the encapsulating macrocycle. All these features indicate that the macrocycle migrates from the dialkylammonium center to the amide center upon addition of *i*Pr_2NEt in acetone.

The fraction of **2** is about 61% when 2 equivalents of *i*Pr_2NEt are added, and increases to 86 and about 91% on addition of 6 and 10 equivalents of *i*Pr_2NEt, respectively. This indicates that the complexation constant between the dialkylammonium group and *i*Pr_2NEt is not very large under these conditions, which might be due to the high polarity of acetone. When $CDCl_2CDCl_2/CD_3COCD_3$ (10/1) was used as solvent in a neutralization experiment, approximately 1.2 equivalents of *i*Pr_2NEt were needed to neutralize the dialkylammonium center completely. These results show that the complexation constant is smaller in more polar solvents.[3]

The ^{1}H NMR spectra of **2-H**, **2** and **1** in $CDCl_2CDCl_2$/CD_3COCD_3 (10/1) are shown in Figure 7. Upon addition of 1.2 equivalents of *i*Pr_2NEt to **2-H**, the dialkylammonium group was neutralized and the hydrogen bonds between macrocycle and ammonium group were switched off. The signals for H_f and H_h shifted upfield by 0.92 and 0.24 ppm, respectively, which indicates deprotonation of the dialkylammonium center and breaking of the C–H···O hydrogen bonds. Two characteristics reflect the site of the macrocycle on the thread: 1) the characteristic resonances for the methylene protons H_k adjacent to the amide group experienced a significant upfield shift of 0.71 ppm compared with free thread **1**, which should be due to the shielding effect of the macrocycle; 2) substantial downfield shift by 0.51 ppm was observed for the signal of H_l from the amide compared with

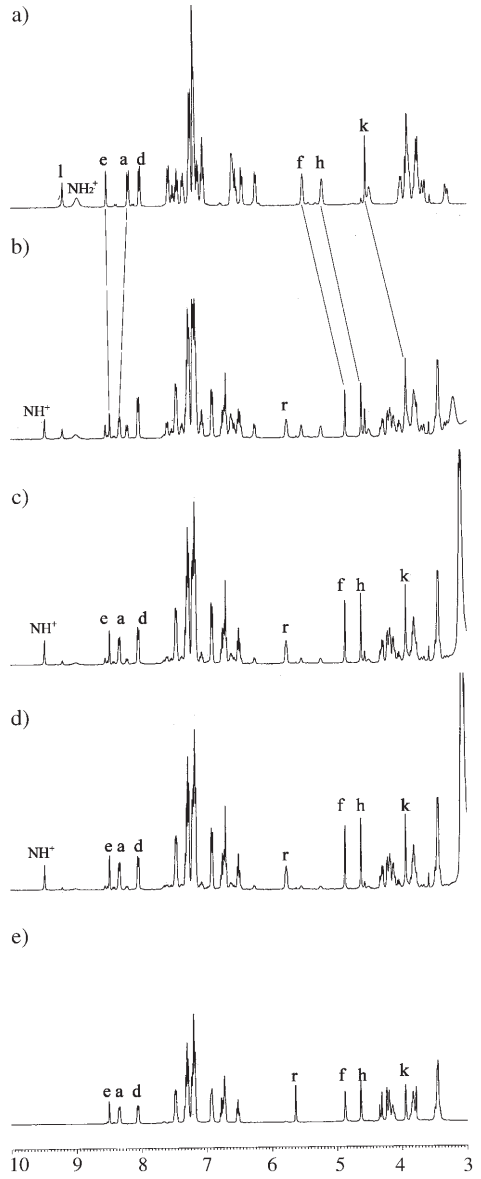


Figure 6. Partial ^{1}H NMR spectra (400 MHz, 298 K, 10^{-3} M, CD_3COCD_3) of **2-H** (a), **2-H**+2 equiv iPr$_2$NEt (b), **2-H**+6 equiv iPr$_2$NEt (c), **2-H**+ 10 equiv iPr$_2$NEt (d), and **2** (e).

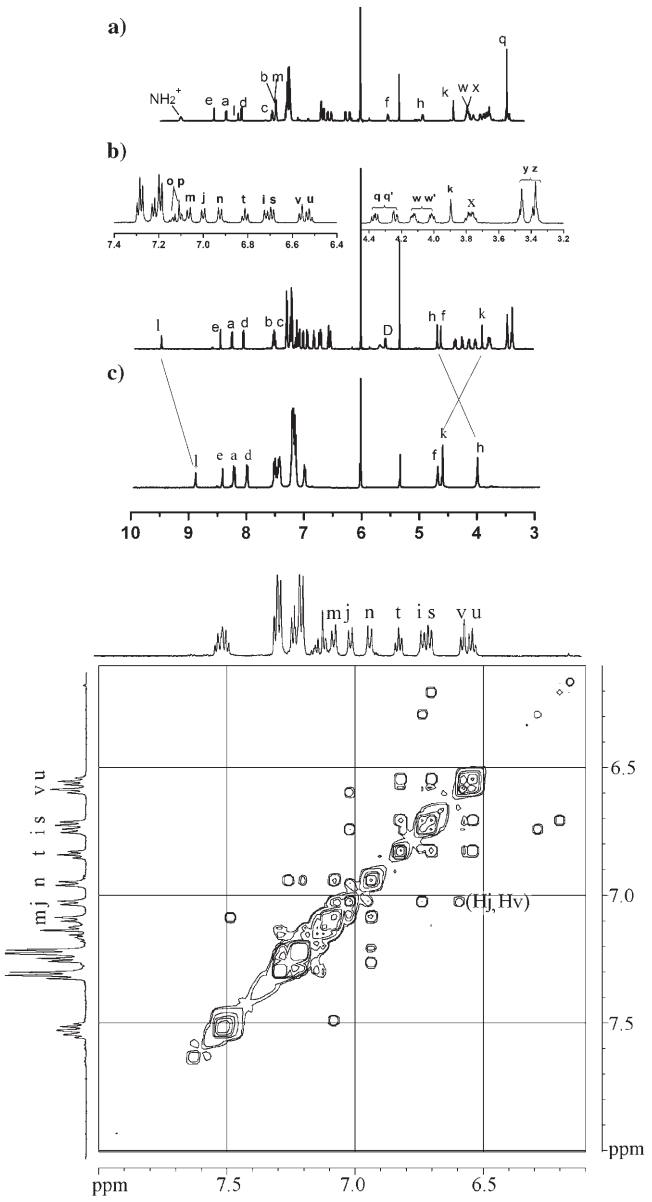


Figure 7. Partial ^{1}H NMR spectra (600 MHz, 298 K, 10^{-3} M, $CDCl_2CDCl_2$/CD_3COCD_3 10/1) of **2-H** (a), **2** (b), and **1** (c). Partial NOESY spectrum of **2** (bottom).

that in free thread **1**, which can be ascribed to the hydrogen bond between macrocycle and amide.[19] Both features support that the macrocycle moves to the amide recognition site due to the hydrogen bonds between them.[19]

The signals for $H_{q/q'}$ and $H_{w/w'}$ separated into two different sets of signals as a consequence of losing their planes of symmetry orthogonal to the principal axis in the molecular shuttle.[3] The signals for phenylene ring **A** protons H_i and H_j in **2** shifted downfield by 0.16 and 0.73 ppm compared to those in **2-H**, but still less than $\delta = 7.0$ ppm. This suggests that the shielding effect of the macrocycle was reduced due to the movement of the macrocycle, but still existed to some extent. Meanwhile, the NOESY spectrum exhibited cross-peaks between the signals for H_j of phenylene ring **A** and H_v of aniline (Figure 7), which indicate that they are adjacent to each other in space. The above two features support formation of a stable conformation in which the macrocycle encircles the amide site, while the pyridine aniline moiety shields phenylene unit **A**, and the oligo(ethylene glycol) section encircles the hydrogen atom of the amide group (shown for **2** in Scheme 2).

When 1.2 equivalents of Li^+ were added to a solution of **2** at room temperature, dramatic changes in the ^{1}H NMR spectrum were observed (Figure 8). The single peak corresponding to the methylene protons H_k shifted downfield by 1.5 ppm compared with that in **2**, and by 0.75 ppm compared with that in the free thread. The signals for the oligo(ethylene glycol) unit shifted downfield, too. These phenomena

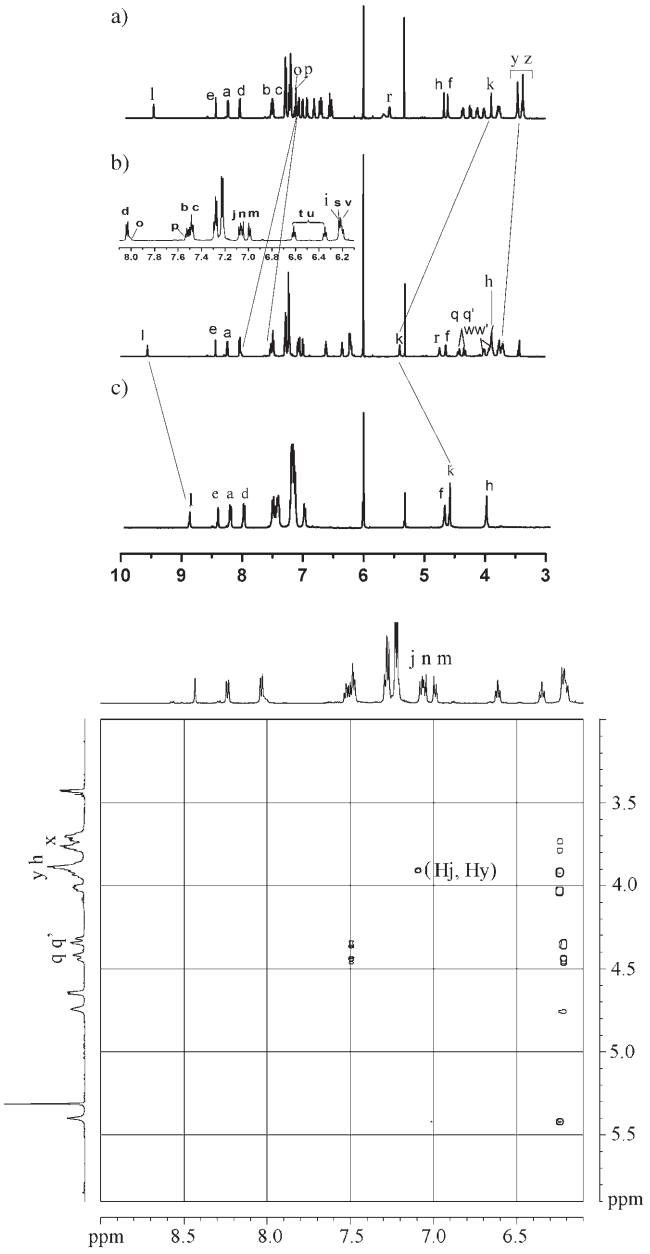


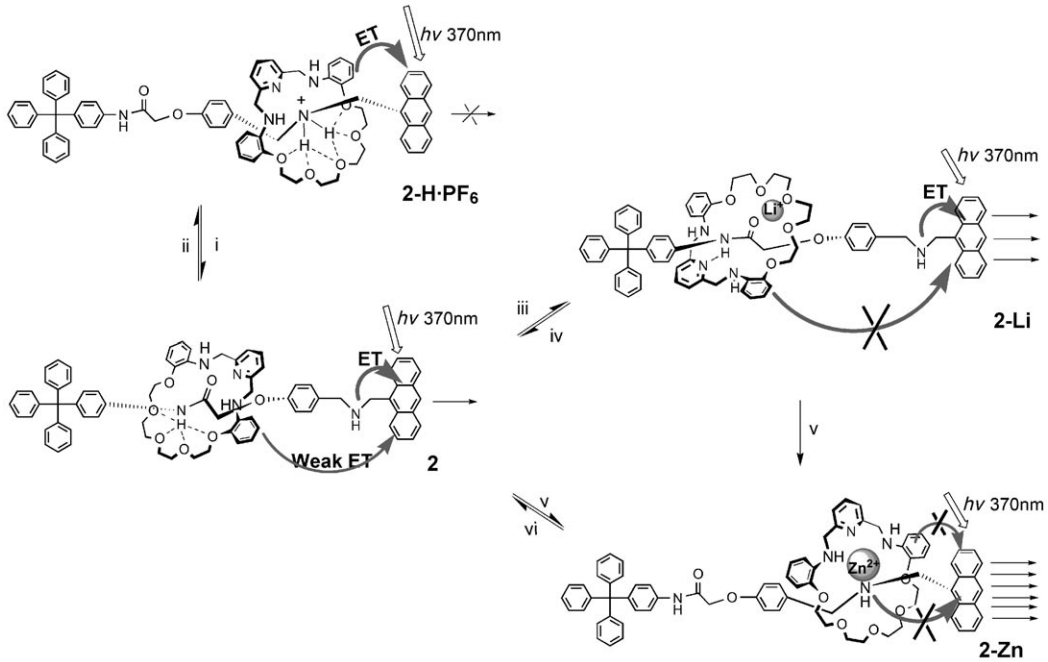
Figure 8. Partial ^{1}H NMR spectra (600 MHz, 298 K, 10^{-3} M, $CDCl_2CDCl_2$/CD_3COCD_3, v/v, 10/1) of **2** (a), **2-Li** (b), and **1** (c). Partial NOESY spectrum of **2-Li** (bottom).

can be attributed to coordinative interaction between the oligo(ethylene glycol) moiety on the macrocycle, the amide oxygen atom and the Li^+ ion.[15] Upon addition of Li^+, the oligo(ethylene glycol) moiety of the macrocycle and the amide oxygen atom encircle the Li^+ ion and coordinate to it, which leads to clear downfield shifts of H_k and the protons of the oligo(ethylene glycol) moiety. In addition, the signals for pyridine protons H_o and H_p shifted downfield by 0.85 and 0.42 ppm, respectively. This could be attributed to the strengthened hydrogen bonds between pyridine nitrogen and amide hydrogen atoms as a result of the conformational change of the macrocycle on coordination to Li^+.[15a] Moreover, a NOESY experiment showed cross-peaks between the signals for H_j of phenylene ring **A** and those for H_y of the oligo(ethylene glycol) unit (Figure 8), which indicate that phenylene ring **A** and oligo(ethylene glycol) unit are close to each other in space. This steric interaction could lead to weak C–H···π interaction between them, which would induce significant splitting of the signals for H_i and H_j in *p*-phenylene unit **A**.[6] As shown in Figure 8b, the two "doublets" for H_i and H_j shifted by −0.5 and 0.08 ppm, respectively, compared with those in **2**, and the splitting increased from 0.28 to 0.86 ppm. This enlarged splitting of the signals for H_i and H_j in *p*-phenylene unit **A** verifies the existence of the C–H···π interaction. All these changes in chemical shift suggested that the macrocycle still encircled the amide site. However, the oligo(ethylene glycol) section is closer to phenylene unit **A**, and the pyridine/aniline moiety encircles the amide hydrogen atom in this state. These features required alternation of conformation of the [2]rotaxane to some extent (see **2-Li** in Scheme 2).

When 1.1 equivalents of Zn^{2+} ions were added to **2-Li**, the four protons H_f and H_h adjacent to −NH− experienced significant downfield shifts of 0.82 and 0.23 ppm compared with those of **2-Li**. As shown in Figure 9b, the signals corresponding to pyridine and aniline all exhibited clear downfield shifts compared with the free macrocycle,[18] which can be attributed to coordination between the pyridine/aniline moiety and Zn^{2+}. The remarkable downfield shift of four protons H_f and H_h adjacent to −NH− also indicated coordination between dialkylamine (−NH−) and Zn^{2+}. Thus, the ^{1}H NMR spectra support selective binding of the pyridine/aniline moiety in the macrocycle and −NH− of the thread with the Zn^{2+} ion and formation of rotaxane **2-Zn** (see Scheme 2).

Optical properties: Figure 10 depicts UV/Vis spectra of **1** and **2** under different stimuli. Only the anthracene moiety absorbs in the spectral region above 300 nm, and hence all changes in the UV/Vis spectra in this region are due to alteration of electronic state of the anthracene unit. The absorption features of neutral thread **1** are similar to those of neutral rotaxane **2**, that is, there is no obvious interaction between macrocycle and anthracene unit in the ground state in this conformation. When Zn^{2+} or TFA was added to solutions of **1** and **2**, three absorption peaks arising from the anthracene unit experienced a red shift of 4 nm, which can be ascribed to restriction of the interaction between lone-pair electrons of amine and anthracene units in the ground state due to complexation or protonation.

Clear evidence for multilevel switching with different inputs was obtained from fluorescence experiments in CH_2Cl_2/THF (10/1). As shown in Figure 11a, **1-H** exhibited strong emission at 423 nm, while the neutral form **1** exhibited weak emission around 413 nm. This quenching effect can be attributed to photoinduced electron transfer (PET) from amine (−NH−) to anthracene.[16,17] The anthracene fluorescence of **2-H** was quenched completely, due to strong PET from the aniline unit of the macrocycle to anthracene. Upon



Scheme 2. Movement processes of the multistable molecular shuttle under different stimuli. i) iPr$_2$NEt; ii) CF_3CO_2H; iii) $LiClO_4$; iv) [12]crown-4; v) Zn-$(ClO_4)_2$; vi) EDTA.

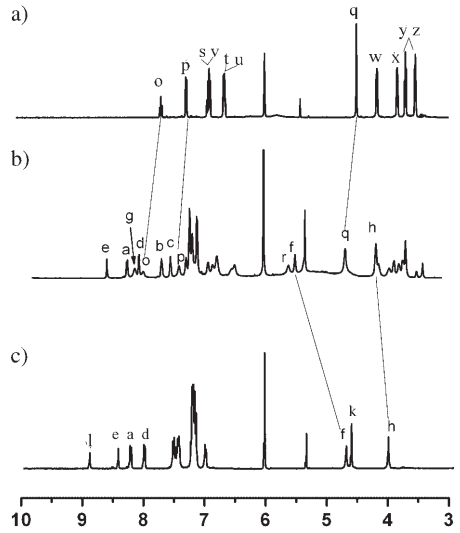


Figure 9. Partial ^{1}H NMR spectra (600 MHz, 298 K, 10^{-3} M, $CDCl_2CDCl_2$/CD_3COCD_3, 10/1) of macrocycle (a), **2-Zn** (b), and **1** (c).

addition of 1.2 equivalents of iPr$_2$NEt to **2-H**, the emission of the anthracene moiety increased slightly but was still less than that of **1**, which indicated the PET from aniline to anthracene moiety was restricted to some extent due to the elongated distance. The similar fluorescence intensity of **2-Li** to that of neutral **1** implies that PET from aniline to anthracene was completely quenched in this state. This might be due to further elongation of the spatial distance between them or blockage of PET by the presence of Li^+. Upon addition of Zn^{2+} ions to **2**, the fluorescence intensity was re-

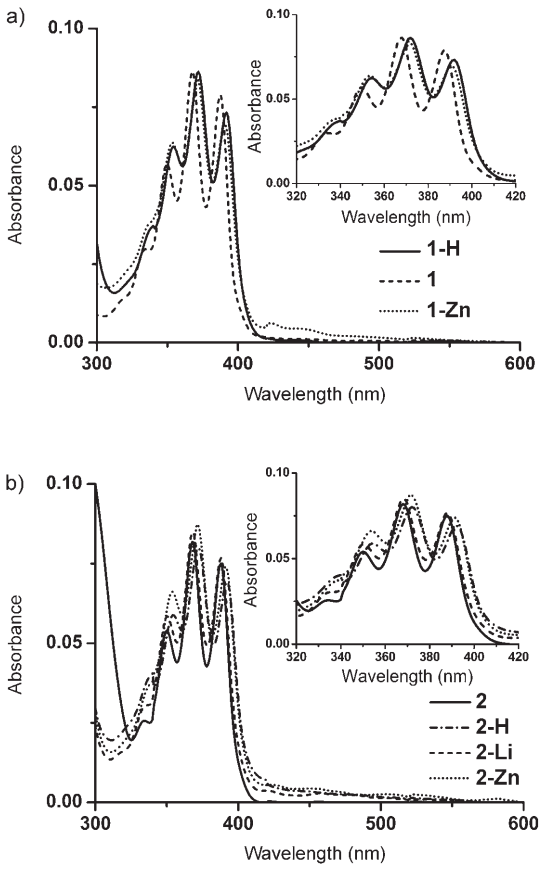


Figure 10. Absorption spectra of **1-H**, **1**, **1-Zn**, **2-H**, **2**, **2-Li**, and **2-Zn** in CH_2Cl_2/THF (10/1, 1×10^{-5} M) at room temperature.

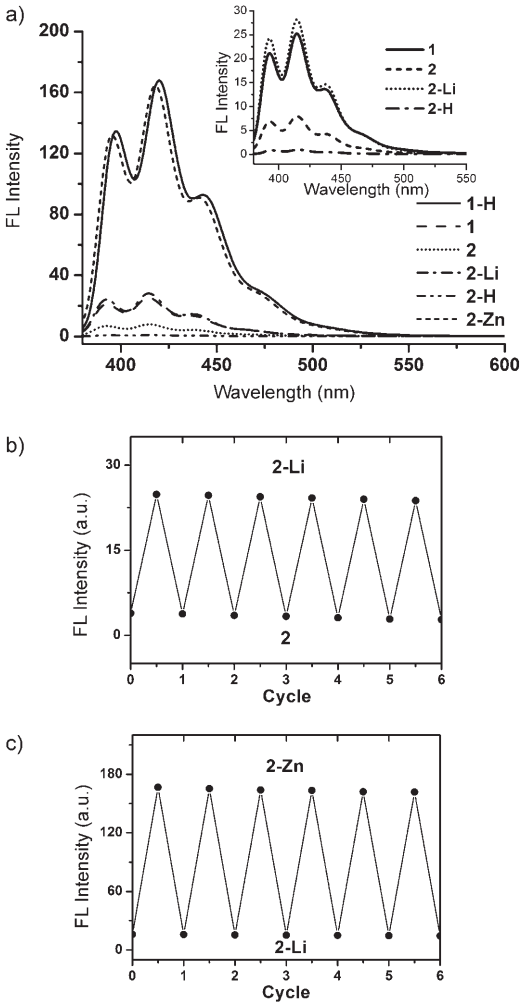


Figure 11. a) Fluorescence spectra of **1-H**, **1**, **2-H**, **2**, **2-Li**, and **2-Zn** in CH_2Cl_2/THF (10/1, 1×10^{-5} M) at room temperature ($\lambda_{ex}=370$ nm). The inset shows the magnified fluorescence spectra of **1**, **2**, **2-Li**, and **2-H**. Fluorescence-intensity changes at 414 nm (b) and 422 nm (c) after alternating additions of Li (half integers)/[12]crown-4 (integers) and Zn (half integers)/EDTA (integers) to **2** and **2-Li** over six complete cycles, respectively ($\lambda_{ex}=370$ nm).

covered and became as large as that of **1-H**$^+$, and this suggests complete abolishment of PET from amine and aniline to anthracene. In particular, when 1.2 equivalents of Zn^{2+} were introduced into a solution of **2-Li**, the fluorescence intensity also recovered and became equal to that of **1-H**$^+$. This might due to the much stronger complexation ability between the pyridine/aniline moiety and Zn^{2+} relative to that between oligo(ethylene glycol) unit and Li^+. By means of the above three movement processes, this shuttle enables multilevel expression of fluorescence in response to different triggers: 1) complete repression in the absence of any stimulus; 2) slight expression in response to base; 3) low-level expression following addition of Li^+; 4) high-level expression in the presence of Zn^{2+}.

The observations in fluorescence experiments were in accordance with the ^{1}H NMR spectra. Upon deprotonation of **2-H**, the macrocycle moved from the dialkylammonium ($-NH_2^+-$) center to the amide station, and thus the distance between aniline and anthracene moieties was enlarged. In **2**, PET from secondary dialkylamine to anthracene was recovered and the PET from aniline to anthracene was decreased. Therefore, the fluorescent emission of **2** was less than that of free thread **1**, in which only PET from secondary dialkylamine to anthracene occurs. In this conformation, the pyridine/aniline moiety was more adjacent to the phenylene unit **A** of the thread, and the oligo(ethylene glycol) moiety was centered around the amide hydrogen atom in space. Upon addition of Li^+ ions, the conformation of this [2]rotaxane was altered, and the pyridine/aniline moiety turned towards the amide hydrogen atom, which further increased the distance between aniline and anthracene moieties and decreased the PET process between them (Scheme 2). The PET from secondary dialkylamine to anthracene was not affected in this process. In the fluorescence spectra, the fluorescence intensity of **2-Li** is similar to that of neutral thread **1**, that is, PET from aniline on the macrocycle to anthracene was quenched completely. Similar to previous reports, the electron lone pair of the amino group next to the anthracene unit can not quench the emission completely.[16d] Thus, emission quenching of anthracene by the macrocycle may be of greater importance than that by the dialkylamine, because PET from aniline to anthracene unit may be stronger. When Zn^{2+} ions are added, the pyridine/aniline moiety of the macrocycle and the dialkylamine group in the thread coordinate to the Zn center, which would completely eliminate PET from aniline and dialkylamine to anthracene and recover the emission entirely.[16,17] In the fluorescence spectra, **2-Zn** exhibited intensive fluorescent emission similar to that of **1-H**, which indicated that no PET process was present. Thus, the fluorescence behavior supports the model proposed from the analysis of the ^{1}H NMR spectra. These movement processes can be repeated many times without degradation by alternate addition of TFA/*i*Pr_2NEt, Li/[12]crown-4 and Zn^{2+}/EDTA, which are all perceived through changes in fluorescence (Figure 11 b and c).

Conclusion

We have presented a multistable molecular shuttle with three successive independent movement processes driven by acid/base and metal-ion complexation/decomplexation, which are all accompanied by fluorescent responses. By means of the three movement processes, this shuttle enables multilevel expression of fluorescence in one system in response to different triggers. In addition, this artificial multilevel molecular shuttle provides a model for interconnection of different noncovalent interactions, namely, hydrogen bonding and metal-ion complexation, to achieve multistable controllable systems with regular responses.

Experimental Section

Unless stated otherwise, all reagents and anhydrous solvents were purchased and used without further purification. Column chromatography: SiO_2 (200–300 mesh). TLC glass plates coated with SiO_2 F254 were visualized by UV light. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 or 600 MHz instrument at a constant temperature of 25 °C. Chemical shifts are reported in parts per million from low to high field and referenced to TMS. MALDI-TOF mass spectra were recorded on a Bruker Biflex III MALDI-TOF spectrometer. UV/Vis spectra were measured on a Hitachi U-3010 spectrometer. Fluorescence excitation and emission spectra were recorded using a Hitachi F-4500 FL fluorimeter at a constant temperature of 25 °C; the slit was set at 5 nm when measuring in different solvents.

2-Chloro-*N*-(4-tritylphenyl)acetamide: 2-Chloroacetyl chloride (0.67 g, 6 mmol) was added to a solution of 4-tritylbenzenamine (2 g, 5.9 mmol) and Et_3N (1 mL) in $CHCl_3$ at 0 °C. Then the mixture was stirred at room temperature for 8 h and washed with distilled water (3×50 mL). The collected organic layers were dried over $NaSO_4$, and the chloroform was removed in vacuo to give the product 2-chloro-*N*-(4-tritylphenyl)acetamide (2.05 g, 85 %) after purification by flash chromatography (CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (s, 1H), 7.42 (d, 2H, J = 9 Hz), 7.27–7.15 (m, 17H), 4.17 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.8, 146.6, 143.9, 134.5, 131.9, 131.1 127.6, 126.0, 119.2, 64.7, 42.9 ppm; EI-MS: m/z 411; elemental analysis (%) calcd for $C_{27}H_{22}ClNO$: C 78.73, H 5.38, N 3.40; found: C 78.68, H 5.41, N 3.41.

2-(4-Formylphenoxy)-*N*-(4-tritylphenyl)acetamide: 2-Chloro-*N*-(4-tritylphenyl)acetamide (2 g, 4.8 mmol) and 4-hydroxybenzaldehyde (610 mg, 5 mmol) were dissolved in acetone, and then anhydrous potassium carbonate (1.38 g, 10 mmol) and [18]crown-6 (132 mg, 0.5 mmol) were added. The reaction mixture was refluxed gently for about 8 h and then cooled to room temperature. After acetone was removed under reduced pressure, the residue was dissolved in $CHCl_3$ and the solution washed with water, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by chromatography on SiO_2 with CH_2Cl_2/*n*-hexane (1/1) to give pure 2-(4-formylphenoxy)-*N*-(4-tritylphenyl)acetamide (1.92 g, 80 % yield) as slightly yellow powder. ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.93 (s, 1H), 8.11 (s, 1H), 7.90 (d, 2H, J = 7.97 Hz), 7.45 (d, 2H, J = 8.00 Hz), 7.26–7.10 (m, 17H), 7.11 (d, 2H, J = 8.06 Hz), 4.69 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 198.2, 163.5, 147.2, 146.1, 143.5, 134.5, 131.9, 131.1 127.6, 126.5, 126.0, 119.2, 64.4, 42.1 ppm; EI-MS: m/z 497; elemental analysis (%) calcd for $C_{34}H_{27}NO_3$: C 82.07, H 5.47, N 2.81; found: C 82.04, H 5.51, N 2.87.

1-H·PF$_6$: 2-(4-Formylphenoxy)-*N*-(4-tritylphenyl)acetamide (1.0 g, 2.0 mmol) was added to a degassed solution of 9-aminomethylanthracene (414 mg, 2.0 mmol) in anhydrous EtOH/$CHCl_3$(80 mL, 3/1). Then molecular sieves were added, and the resulting mixture was heated at 80 °C for 8 h. After cooling to room temperature, the molecular sieves were filtered off and washed with $CHCl_3$. Then $NaBH_4$ (1 g, 27 mmol) was added to the filtrate at 0 °C, which was stirred for 8 h after warming to room temperature. Water (10 mL) was added carefully to quench the excess $NaBH_4$. The solvent was then evaporated off, and the residue was partitioned between water and $CHCl_3$. The organic extracts were dried and the solvent was removed in vacuo. Then the residue was dissolved in Me_2CO and a few drops of TFA were added to the solution. The solvent was evaporated off, the oily residue was dissolved in a mixture of H_2O and Me_2CO and a saturated aqueous solution of NH_4PF_6 was added. The Me_2CO was then removed and the aqueous solution was extracted with CH_2Cl_2 several times. The organic extracts were dried ($MgSO_4$) and the solvent concentrated to dryness to yield axle **1-H·PF$_6$** (1.1 g, 70 %) as a light yellow powder. ^1H NMR (CD_3COCD_3, 400 MHz, 298 K): δ = 9.35 (s, 1H), 8.8 (s, 2H), 8.30 (d, 2H, J = 8.78 Hz), 8.19 (d, 2H, J = 8.78 Hz), 7.74 (d, 2H, J = 8.25 Hz), 7.70–7.56 (m, 6H), 7.280 (m, 6H), 7.21–7.15 (m, 15H), 5.69 (s, 2H), 4.98 (s, 2H), 4.75 ppm (s, 2H); ^{13}C NMR (CD_3COCD_3, 100 MHz, 298 K): δ = 166.3, 159.1, 146.9, 142.6, 136.2, 132.4, 131.4, 131.3, 131.0, 130.9, 130.7, 129.5, 127.6, 126.1, 125.6, 123.9, 123.3, 121.7, 119.0, 115.4, 67.4, 64.5, 54.1, 52.0, 43.2 ppm; MS (MALDI-TOF): m/z 688 [**1-H·PF$_6$**−PF_6]; elemental analysis (%) calcd: C 70.50, H 4.95, N 3.36; found: C 70.47, H 4.99, N 3.34.

P-H·PF$_6$ was synthesized from 2-(4-formylphenoxy)-*N*-(4-tritylphenyl)-acetamide and pyrenyl-1-methanamine by using a similar procedure as described for the preparation of **1-H·PF$_6$**. ^1H NMR (CD_3COCD_3, 400 MHz, 298 K): δ 8.17 (d, 1H, J = 8.0 Hz), 8.14–7.95 (m, 9H), 7.44 (d, 2H, J = 8.51 Hz), 7.23–7.11 (m, 19H), 6.82 (d, 2H, J = 8.51 Hz), 5.3 (s, 2H), 4.5 (s, 2H), 4.47 ppm (s, 2H); ^{13}C NMR ([D_6]DMSO, 100 MHz, 298 K): δ = 166.5, 156.1, 146.4, 141.6, 136.08, 132.9, 130.75, 130.42, 130.33, 129.9, 129.47, 128.57, 127.46, 127.27, 126.97, 125.9, 125.7, 124.8, 124.47, 124.13, 124.05, 118.9, 114.47, 67.33, 64.06, 50.89 ppm; MS (MALDI-TOF): m/z 711 [**1-H·PF$_6$**−PF_6].

Rotaxane 2-H·PF$_6$: A solution of 2,6-pyridinedicarboxaldehyde (29 mg, 0.2 mmol), tetraethylene glycol bis(2-aminophenyl)ether (80 mg, 0.2 mmol) and **1-H·PF$_6$** (166 mg, 0.2 mmol) in CH_3NO_2 (10 mL) was stirred at room temperature for 10 min. BH_3·THF (1.0 M in THF, 1 mL, 1 mmol) was added to the mixture, which was left stirring at room temperature for 4 h. The solvent was then evaporated off and the residue was partitioned between 2 M aqueous NaOH and $CHCl_3$. The organic extracts were dried and the solvent evaporated again. The residue was dissolved in Me_2CO, and a few drops of TFA were added to the solution. The solvent was evaporated off, the residual oil was dissolved in a mixture of H_2O and Me_2CO and a saturated aqueous solution of NH_4PF_6 was added. The Me_2CO was then removed and the aqueous solution was extracted with CH_2Cl_2 several times. The organic extracts were dried ($MgSO_4$) and concentrated to dryness to yield [2]rotaxane **2-H·PF$_6$** (181 mg, 70 %) as a white powder. ^1H NMR (CD_3COCD_3, 400 MHz, 298 K): δ = 9.26 (s, 1H), 9.0 (br, 2H), 8.55 (s, 1H), 8.21 (d, 2H, J = 8.72 Hz), 8.04 (d, 2H, J = 8.72 Hz), 7.59 (d, 2H, J = 8.16 Hz), 7.52 (t, 1H), 7.47 (t, 2H), 7.37 (t, 2H), 7.29–7.13 (m, 19H), 7.07 (t, 4H, J = 8.76 Hz), 6.62–6.60 (br, 6H), 6.48 (d, 2H), 6.27 (d, 2H), 5.53 (s, 2H), 5.23 (s, 2H), 4.56 (s, 2H), 4.51 (s, 2H), 4.02 (m, 2H), 3.95 (m, 8H), 3.78 (m, 6H), 3.68 (d, 2H, J = 14.8 Hz), 3.32 ppm (d, 2H, J = 12.6 Hz); HRMS (N-SIMS NBA): m/z 1168.5566, [**2-H·PF$_6$**−PF_6]; MS (MALDI-TOF): m/z 1168 [**2-H·PF$_6$**−PF_6]; elemental analysis (%) calcd: C 69.45, H 5.67, N 5.33; found C 69.43, H 5.71, N 5.31.

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