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## A chromophoric switch based on pseudorotaxanes

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In a three-component system containing dibenzo-24-crown-8 (1), diamino-dibenzo-24-crown-8 (2), and 1,2-bis(4,4'-dipyridyl)ethane ( $3^{2+}$ ), axle  $3^{2+}$  can shuttle between wheels 1 and 2 by acid-base control, accompanying color changes from yellow to red. This system could not only be taken as a chromophoric supramolecular switch, but also exhibit a function as INHIBIT logic gate.

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### I. INTRODUCTION

Much attention is currently being devoted to molecular-level systems in which the relative positions of the component parts can change as a result of some external stimulus.<sup>1,2</sup> Such systems could find applications for information processing at the molecular level<sup>3</sup> and also be viewed as the forerunners of nanoscopic machines.<sup>1(a)</sup> Appealing examples of chemical compounds where controlled mechanical movements can take place are suitably designed pseudorotaxanes, rotaxanes, and catenanes.<sup>4-7</sup> It is well known that organic ammonium ions can form adducts with crown ethers<sup>6(f),6(g)</sup> Ashton *et al.* demonstrated that suitable threadlike dialkylammonium ions can interpenetrate suitably sized crown ethers to form pseudorotaxanes, and then easily be dethreaded by adding a base.<sup>8</sup> Recently, Huang *et al.*<sup>9</sup> showed a cryptand/paraquat [2]pseudorotaxane which can be reversibly switched off (and back on) by protonation (and deprotonation) of the host, and Mendoza *et al.* reported the experimental and theoretical studies of the adsorption of fumaramide [2]rotaxane on Au and Ag surfaces.<sup>10</sup>

In the present work, we wish to report a methodology constructing a chromophoric switch, in which 1,2-bis(4,4'-dipyridyl)ethane ( $3^{2+}$ ) can shuttle between dibenzo-24-crown-8 (1) and diamino-dibenzo-24-crown-8 (2) by acid-base control. The system should be interesting because of the following: (a) there are three components of two wheels and one axle; (b) it is a molecular switch based on pseudorotaxane that both the wheel 2 and the axle  $3^{2+}$  are acid responsive; (c) it can be easily detected by the naked eye due to its dramatic color change; (d) it can function as a molecular logic gate.

### II. EXPERIMENTAL DETAILS

Starting materials were commercially available unless noted otherwise. Analytical-grade acetonitrile was dried over calcium hydride and then distilled fractionally to give the anhydrous solvent. Of the macrocyclic hosts, dibenzo-24-

crown-8 (1) (Ref. 11) and diamino-dibenzo-24-crown-8 (2) (Ref. 12) were prepared according to the literature procedures and recrystallized twice before use.  $3^{2+}$  bromide salt was prepared by the literature method.<sup>13</sup> The hexafluorophosphate salts were precipitated from water by the addition of saturated aqueous  $\text{NH}_4\text{PF}_6$  and recrystallized before use.

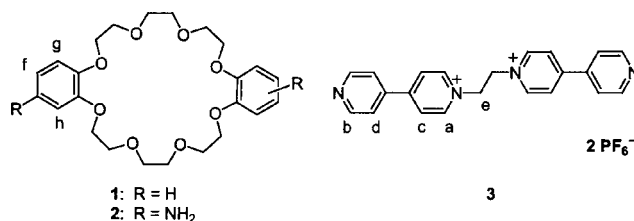
Ultraviolet-visible spectra were measured employing a Shimadzu UV-2401PC using a conventional 1 cm path ( $1 \times 0.25 \text{ cm}^2$ ) quartz cell in a thermostated compartment, which was kept at 25 °C through a Shimadzu TB-85 Thermo Bath unit. NMR spectra were recorded on a Varian Mercury VX300 instrument.

The microcalorimetric titrations were performed at atmospheric pressure and 25 °C in anhydrous acetonitrile by using Microcal VP-ITC titration microcalorimetry, which allows us to determine simultaneously the enthalpy and equilibrium constant from a single titration curve.

### III. RESULTS AND DISCUSSION

#### A. UV spectra

As can be seen from Fig. 1, when equivalent amounts of 1 and 2 are added to the  $\text{CH}_3\text{CN}$  solution of  $3^{2+}$ , the distinctly different photophysical behaviors are observed. The mixtures of 1 and  $3^{2+}$  as well as 2 and  $3^{2+}$ , respectively, show charge transfer (CT) bands at about 370 nm and 438 nm. The results allow them to be readily distinguished by the eye. When equivalent amounts of phenylamine (or benzene) and  $3^{2+}$  were mixed, neither color change nor CT band was observed. These observations indicate the formation of pseudorotaxanes between 1/2 and  $3^{2+}$ .



The addition of 2 mol equivalents of  $\text{CF}_3\text{COOH}$  to the  $\text{CH}_3\text{CN}$  solution of pseudorotaxane  $[2 \cdot 3]^{2+}$  leads to the suppression of the CT absorption band (2·3-2 acid in Fig. 1).

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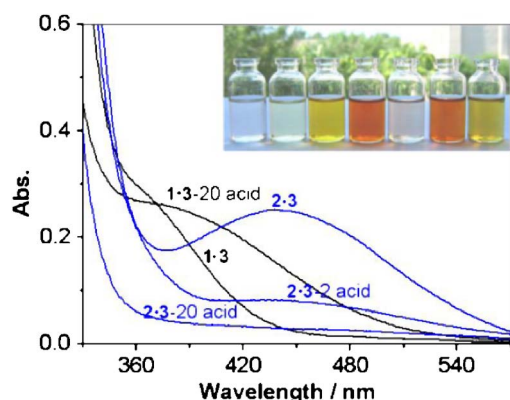


FIG. 1. (Color online) UV spectra of  $1 \cdot [3][PF_6]_2$ ,  $1 \cdot [3][PF_6]_2 + 20$  equiv.  $CF_3COOH$ ,  $2 \cdot [3][PF_6]_2$ ,  $2 \cdot [3][PF_6]_2 + 2$  equiv.  $CF_3COOH$ , and  $2 \cdot [3][PF_6]_2 + 20$  equiv.  $CF_3COOH$  in  $CH_3CN$  at  $25^\circ C$ . (The concentrations of 1, 2, and  $3^{2+}$  are 1.0 mM). Insert: Visible color changes. From left to right:  $[3][PF_6]_2$ ,  $1 \cdot [3][PF_6]_2$ ,  $1 \cdot [3][PF_6]_2 + CF_3COOH$ ,  $2 \cdot [3][PF_6]_2$ ,  $2 \cdot [3][PF_6]_2 + CF_3COOH$ ,  $1 \cdot 2 \cdot [3][PF_6]_2$ , and  $1 \cdot 2 \cdot [3][PF_6]_2 + CF_3COOH$ . (The concentrations of 1, 2, and  $3^{2+}$  are 5.0 mM).

When 20 mol equivalents of  $CF_3COOH$  are added, the CT absorption band completely disappears. To the contrary, the same experiment performed for  $[1 \cdot 3]^{2+}$  leads to an increase in the intensity of a CT absorption band with a bathochromic shift to about 390 nm. These observations indicate that the pseudorotaxane  $[2 \cdot 3]^{2+}$  gradually disassociates with the addition of  $CF_3COOH$ , while the complexation of 1 and  $3^{2+}$  becomes stronger. The above results can be explained by the protonation of both the amino groups in 2 and the pyridium groups in  $3^{2+}$ . For pseudorotaxane  $[2 \cdot 3]^{2+}$ , the protonation of the pyridium groups in  $3^{2+}$  could increase the hydrogen bond interaction of  $C-H \cdots O$  and the  $\pi$ -stacking interaction be-

tween the host and the guest to some extent. However, the protonation of the amino groups in 2 violently decreases the electron cloud density of the catechol ring, which not only results in the electrostatic repulsion between the dicationic host and tetracationic guest, but also greatly weakens the ion-dipole interactions between the positive charge on the pyridinium nitrogen atoms and the oxygen atoms of the crown ether. Consequently, the dethreading of  $3^{2+}$  from 2 is a natural process. For pseudorotaxane  $[1 \cdot 3]^{2+}$ , the protonation happens in just  $3^{2+}$ , and hence the resulting additional hydrogen bond of  $C-H \cdots O$  and  $\pi$ -stacking interaction significantly enhance the stability of the pseudorotaxane. It is noted that the absorption values of  $[1 \cdot 3]^{2+}$  and  $[2 \cdot 3]^{2+}$  recover upon neutralization of the solution with 20 mol equivalents of  $Bu_3N$ , and the colors change to the original light yellow for  $[1 \cdot 3]^{2+}$  and red for  $[2 \cdot 3]^{2+}$ . Furthermore, the addition of  $CF_3COOH$  again results in the colors of the solution becoming yellow for  $[1 \cdot 3]^{2+}$  and colorless for  $[2 \cdot 3]^{2+}$ .

Mixing equimolar proportions of 1, 2, and  $3^{2+}$  makes the solution color become red, and the intensity of the CT band at about 440 nm increases. When 20 equivalents of  $CF_3COOH$  are added to the above solution, the CT band shifts to about 380 nm, and the solution color becomes yellow, as shown in Fig. 1. In the case of the absence of  $CF_3COOH$ , the color of the mixing solution is consistent with that of the pseudorotaxane  $[2 \cdot 3]^{2+}$ , while the color in the present of  $CF_3COOH$  is accordant with that of the pseudorotaxane  $[1 \cdot 3]^{2+}$ . The neutralization of the solution with  $Bu_3N$  is accompanied by the reappearance of red color. These observations indicate that  $3^{2+}$  can shuttle between crown ether rings of 1 and 2 by the adjustment of the acid-base, as shown in Fig. 2.

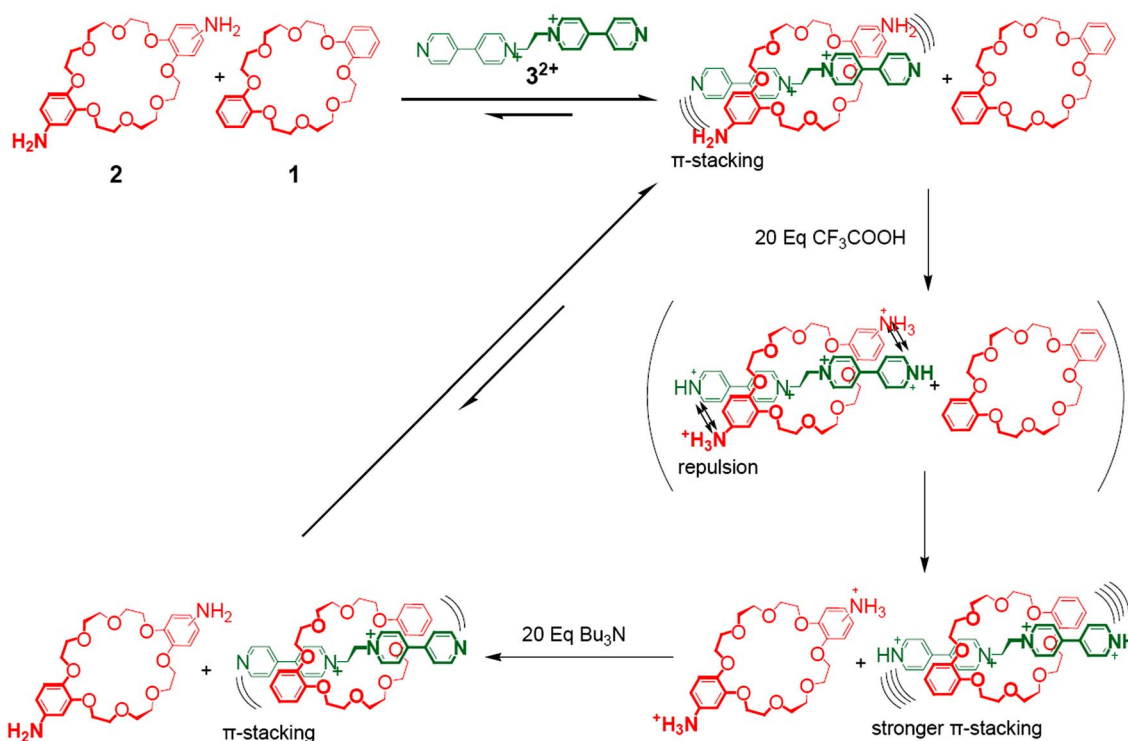


FIG. 2. (Color online) The acid/base controlled dethreading and rethreading of the  $[2]$ pseudorotaxane  $1/2/3^{2+}$  in  $CH_3CN$  solution.

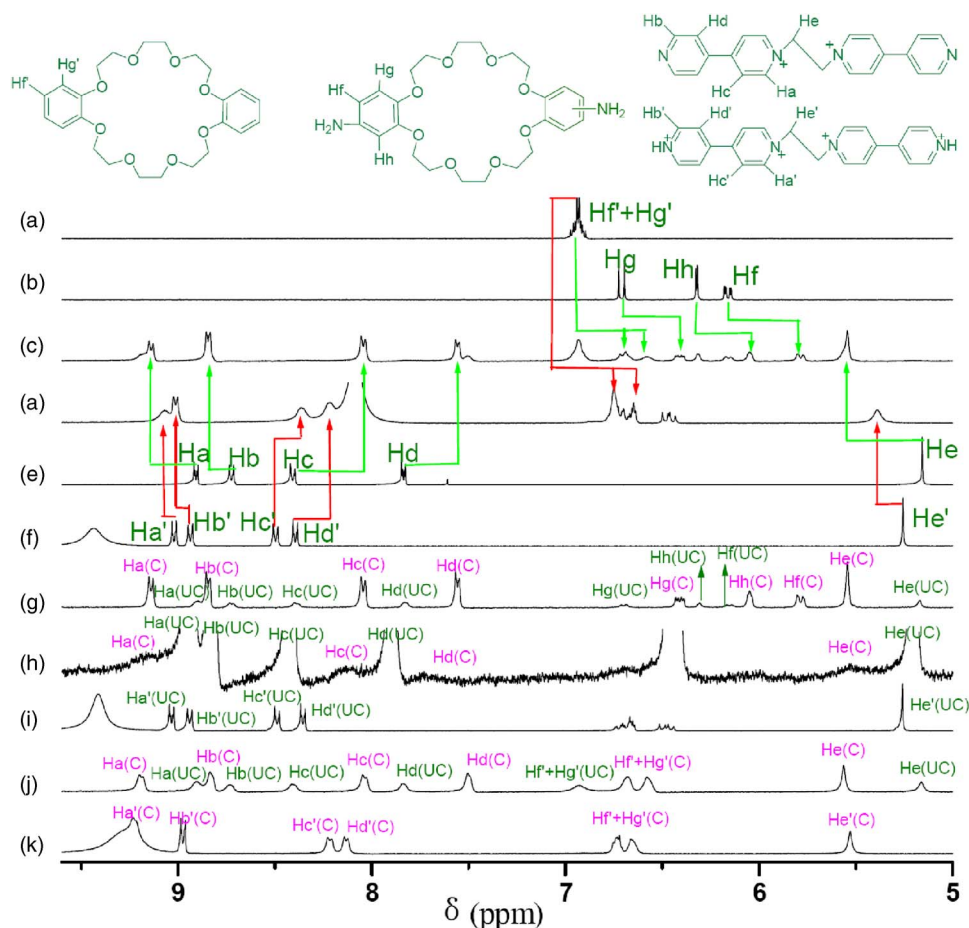


FIG. 3. (Color online) 300 MHz  $^1\text{H}$  NMR spectra of  $\text{CD}_3\text{CN}$  samples containing: (a) 5.0 mM 1, (b) 5.0 mM 2, (c) 5.0 mM 1+5.0 mM 2+5.0 mM  $[\text{3}][\text{PF}_6]_2$ , (d) 5.0 mM 1+5.0 mM 2+5.0 mM  $[\text{3}][\text{PF}_6]_2$ +20 equiv.  $\text{CF}_3\text{COOH}$ , (e) 5.0 mM  $[\text{3}][\text{PF}_6]_2$ , (f)  $[\text{3}][\text{PF}_6]_2$ +20 equiv.  $\text{CF}_3\text{COOH}$ , (g) 5.0 mM  $[\text{3}][\text{PF}_6]_2$ +5.0 mM 2, (h) 5.0 mM  $[\text{3}][\text{PF}_6]_2$ +5.0 mM 2+2 equiv.  $\text{CF}_3\text{COOH}$ , (i) 5.0 mM  $[\text{3}][\text{PF}_6]_2$ +5.0 mM 2+20 equiv.  $\text{CF}_3\text{COOH}$ , (j) 5.0 mM  $[\text{3}][\text{PF}_6]_2$ +5.0 mM 1, and (k) 5.0 mM  $[\text{3}][\text{PF}_6]_2$ +5.0 mM 1+20 equiv.  $\text{CF}_3\text{COOH}$ .

The above threading/unthreading processes for  $3^{2+}$  and the shuttle movement of  $3^{2+}$  between the two rings of 1 and 2 can be described as three INHIBIT (INH) logic gates.  $\text{CF}_3\text{COOH}$  and  $\text{Bu}_3\text{N}$  are assigned as the inputs, and the intensity of the absorbance of the  $1/3^{2+}$  system at 420 nm, that of the  $2/3^{2+}$  system at 438 nm, and that of the  $1/2/3^{2+}$  system at 480 nm are considered as the outputs. Truth tables of INH logic gates for  $1/3^{2+}$ ,  $2/3^{2+}$ , and  $1/2/3^{2+}$  and the logic scheme are shown in the EPAPS.<sup>15</sup>

## B. $^1\text{H}$ NMR spectra

The switching process of  $[2]\text{pseudorotaxane}$   $[1\cdot 3]^{2+}$  and  $[2\cdot 3]^{2+}$  and the tricomponent system  $1/2/3^{2+}$  can also be monitored by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR spectra of a solution of 2 and  $3^{2+}$  following the addition of 2 and 20 equivalents of  $\text{CF}_3\text{COOH}$ , together with only  $3^{2+}$  in the absence and the presence of  $\text{CF}_3\text{COOH}$ , are shown in Figs. 3(b) and 3(e)–3(i). After the addition of two equivalents of  $\text{CF}_3\text{COOH}$ , a majority of the resonances associated with  $[2\cdot 3]^{2+}$  disappears, the corresponding intensity of the resonances of  $3^{2+}$  increases. In the spectrum of the solution that contains 20 equivalents of  $\text{CF}_3\text{COOH}$ , the resonances associated with  $[2\cdot 3]^{2+}$  completely disappears, and only the resonances of the protonated 2 and  $3^{2+}$  are observed. This is an unambiguous confirmation of the dethreading process. The rethreading process can be reversed quantitatively by the ad-

dition of 20 equivalents of  $\text{Bu}_3\text{N}$ , which is attributed to the deprotonation of 2 and  $3^{2+}$  restoring the original equilibrium between 2,  $3^{2+}$ , and  $[2\cdot 3]^{2+}$ .

In the case of pseudorotaxane  $[1\cdot 3]^{2+}$ , it is interesting that the complexation ability increases upon addition of acid, which is contrary to pseudorotaxane  $[2\cdot 3]^{2+}$ . Addition of 20 equivalents of  $\text{CF}_3\text{COOH}$  causes all of the guest axle threads into the DB24C8 wheel [Figs. 3(a), 3(e), 3(f), 3(j), and 3(k)], leading to a deeper color from light yellow to yellow. This is also reasonable since protonation of  $3^{2+}$  causes stronger  $\pi$ -stacking interactions between the electron-rich catechol rings of the crown ether and the electron-poorer aromatic rings of the pyridinium salt. Similarly, the addition of 20 equivalents of  $\text{Bu}_3\text{N}$  restores to the original state.

On the other hand, since chemical exchange is slow on the NMR time scale and peaks are observed for both complexed and uncomplexed species in this current system, the stability constants ( $K_S$ ) of  $3^{2+}$  with 2 and 1 could be determined from Figs. 3(g) and 3(j). The  $K_S$  values obtained are  $(1.4 \pm 0.1) \times 10^3 \text{M}^{-1}$  for  $[1\cdot 3]^{2+}$  and  $(4.5 \pm 0.1) \times 10^3 \text{M}^{-1}$  for  $[2\cdot 3]^{2+}$ .

The  $^1\text{H}$  NMR spectra of an equimolar solution of 1, 2, and  $3^{2+}$  also show separate signals for complexed and uncomplexed species [Figs. 3(a)–3(f)]. About 75% of complexed axle  $3^{2+}$  thread into wheel 2, and only 25% into 1, which is reasonable because the substitution of amino for hydrogen in 1, affording 2, significantly increases the  $K_S$  values upon about 3.2 times, ascribing extra  $\pi$ -stacking in-

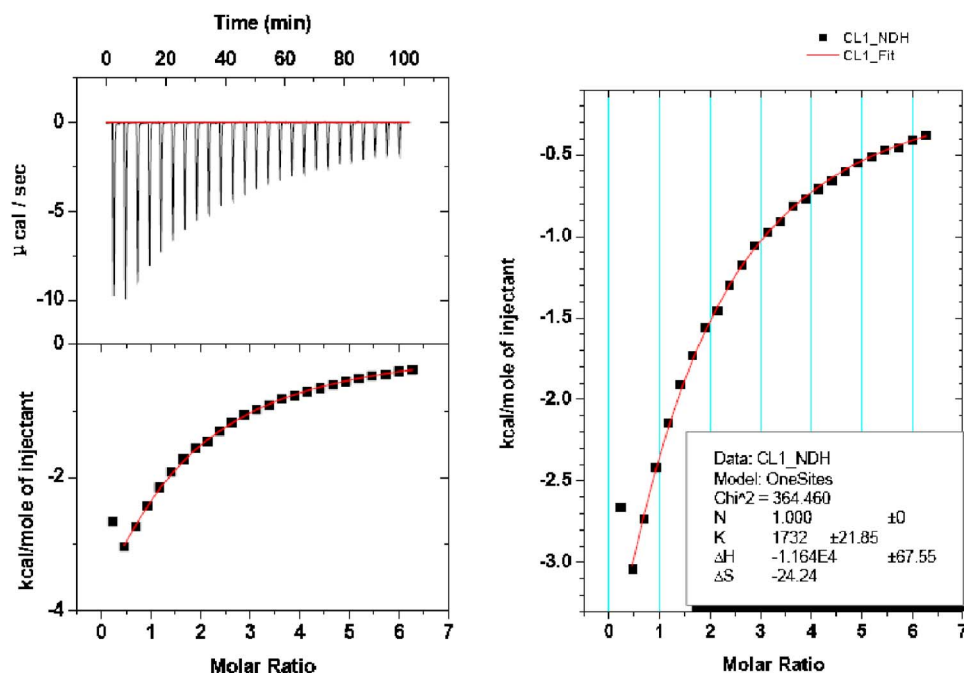


FIG. 4. (Color online) Calorimetric titrations of host 1 (0.25 mM) with  $3^{2+}$  (8.30 mM) in  $\text{CH}_3\text{CN}$  at 25 °C. Left: Raw data for sequential 10  $\mu\text{l}$  injections of guest  $3^{2+}$  solution into crown ether 1 solution. (b) Heats of reaction as obtained from the integration of the calorimetric traces. Right: “Net” heat effect of 1 with  $3^{2+}$  obtained by subtracting the heat of dilution from the heat of reaction, which was analyzed by computer simulation using the “one set of binding sites” model.

interactions and ion-dipole interactions between pyridinium  $3^{2+}$  and electron-rich amino-catechol rings in 2. Upon addition of 20 equivalents of  $\text{CF}_3\text{COOH}$ , the resonances associated with  $[2 \cdot 3]^{2+}$  disappear, and the resonances of  $[1 \cdot 3]^{2+}$  increase, corresponding to 100% resultant complex of  $[1 \cdot 3]^{2+}$ . The original state can be reversed quantitatively by the addition of 20 equivalents of  $\text{Bu}_3\text{N}$ . To the best of our knowledge, this is the first acid-base controlled chromophoric molecular switch, in which the same axle molecule can shuttle between different wheels.

### C. Complexation thermodynamics

In order to investigate the switching mechanisms and illuminate quantitatively the role of acid to the binding behavior of 1/2 with  $3^{2+}$ , microcalorimetry titration has been performed in the absence and the presence of  $\text{CF}_3\text{COOH}$  to give the complex stability constants ( $K_S$ ) and the standard free energy ( $\Delta G^\circ$ ), enthalpy changes ( $\Delta H^\circ$ ), and entropy changes ( $T\Delta S^\circ$ ) (Fig. 4 and Table I). The reaction enthalpy between 2 with  $3^{2+}$  in the presence of  $\text{CF}_3\text{COOH}$  is too

small to determine the  $K_S$  value by titration microcalorimetry, suggesting that there is no complexation between 2 with  $3^{4+}$ . In the case of 1 and  $3^{2+}$  in the presence of  $\text{CF}_3\text{COOH}$ , the experimental curve does not fit the simple 1:1 model and the simplest choice to give a satisfactory fit is a stepwise 1:2 complexation model, which has been validated by its crystal structures.<sup>14</sup>

As indicated in Table I, in the absence of  $\text{CF}_3\text{COOH}$ , the substitution of amino for hydrogen in 1, affording 2, significantly increases the  $K_S$  values upon 2.5 times, ascribing extra  $\pi$ -stacking interactions and ion-dipole interactions between pyridinium  $3^{2+}$  and electron-rich amino-catechol rings in 2.<sup>15</sup> The enhanced binding ability is apparently controlled by the enthalpy changes because the enthalpy change ( $\Delta H_{2,3}^\circ - \Delta H_{1,3}^\circ = -3.1 \text{ kJ mol}^{-1}$ ) is more remarkable than the entropy changes ( $T\Delta S_{2,3}^\circ - T\Delta S_{1,3}^\circ = -0.9 \text{ kJ mol}^{-1}$ ).

In the presence of  $\text{CF}_3\text{COOH}$ , the enthalpy change values in each step are almost equal ( $-\Delta H_1^\circ = 25.7 \text{ kJ mol}^{-1}$  and  $-\Delta H_2^\circ = 25.2 \text{ kJ mol}^{-1}$ ), but their entropy changes are distinctly different, which results in the first binding affinity being much stronger than the second one. On the other hand,

TABLE I. Complex stability constant ( $K_S/M^{-1}$ ) and thermodynamic parameters (in  $\text{kJ mol}^{-1}$ ) for complexation of hosts 1 and 2 with guest  $3^{2+}$  in anhydrous acetonitrile in the absence and the presence of  $\text{CF}_3\text{COOH}$  at 298.15 K.

Reaction	$N^d$	$K_S$	$-\Delta G^\circ$	$-\Delta H^\circ$	$T\Delta S^\circ$
$1 + 3^{2+} = [1 \cdot 3]^{2+a}$	5	$1659 \pm 45$	$18.4 \pm 0.1$	$48.5 \pm 0.4$	$-30.1 \pm 0.4$
$2 + 3^{2+} = [2 \cdot 3]^{2+b}$	2	$4142 \pm 147$	$20.6 \pm 0.1$	$51.6 \pm 1.5$	$-31.0 \pm 1.6$
$1 + 3^{4+} = [1 \cdot 3]^{4+c}$	2	$15\,550 \pm 1600$	$23.8 \pm 0.3$	$25.7 \pm 0.8$	$-1.9 \pm 1.0$
$[1 \cdot 3]^{4+} + 1 = [1_2 \cdot 3]^{4+c}$	2	$2433 \pm 8$	$19.3 \pm 0.1$	$25.2 \pm 0.7$	$-5.9 \pm 0.7$
$2 + 3^{4+c}$	1	<sup>e</sup>			

<sup>a</sup>[1]=0.25–0.50 mM, [ $3^{2+}$ ]=6.60–8.30 mM, or [1]=3.12 mM; [ $3^{2+}$ ]=0.17 mM in  $\text{CH}_3\text{CN}$  solution.

<sup>b</sup>[2]=0.56 mM, [ $3^{2+}$ ]=6.60 mM in  $\text{CH}_3\text{CN}$  solution.

<sup>c</sup>[1]=[2]=8.00 mM in  $\text{CH}_3\text{CN}$  solution; [ $3^{2+}$ ]=0.50 mM  $\text{CH}_3\text{CN}$  solution in the presence of 10 mM  $\text{CF}_3\text{COOH}$ .

<sup>d</sup>Number of titration runs performed.

<sup>e</sup>Equilibrium constant is too small to be determined by titration microcalorimetry.

any of the  $K_S$  values in two steps is larger than the original one in the absence of  $\text{CF}_3\text{COOH}$ , suggesting that acid can help significantly the complexation of 1 with 3. It is interesting to note that any of the enthalpy changes in the presence of  $\text{CF}_3\text{COOH}$  are lower than that in the absence of  $\text{CF}_3\text{COOH}$  ( $-\Delta\Delta H^\circ = -23.3 \sim -22.8 \text{ kJ mol}^{-1}$ ) for the complexation of 1 with 3, while the corresponding entropy changes are much larger from original  $-30.2$  to  $-1.9$  and  $-5.9 \text{ kJ mol}^{-1}$ . These observations imply that the increased binding abilities in the presence of an acid do not result from the contribution of the enthalpy term, but come from the entropy term. Herein, it should be emphasized that pyridinium salts with different valencies, i.e., dicationic  $3^{2+}$  and tetracationic  $3^{4+}$ , were employed in the absence and the presence of  $\text{CF}_3\text{COOH}$ , respectively. The contrasting thermodynamic behavior may be attributed to the nature of the pyridinium salts used and also to the ability of ligation by 1, both of which are related to the entropy factors such as solvation/desolvation and structural freezing upon complexation and the enthalpy factors such as solvation/desolvation. In acetonitrile, tetracationic  $3^{4+}$  might dissociate to some extent to give heavily solvated tetracationic pyridinium ions through ion-dipole interactions. Then, the complexation with 1 not only requires fairly extensive desolvation of both cation and ligand upon complexation, but also needs to absorb more energy for desolvation of cation, affording the large entropy changes and small enthalpy changes, as observed in Table I. In contrast, dicationic  $3^{2+}$  are not completely dissociated in acetonitrile, forming contact ion pairs, and therefore the solvation to dicationic pyridinium salt is not so heavy or tight as the tetracationic one, which probably reduces the entropic contributions to the complex stabilities of 1. Hence, it is concluded that the complexation of 3 with 1 is obviously enthalpy driven in the absence and the presence of  $\text{CF}_3\text{COOH}$ , but both the increased binding abilities in the presence of the acid and the difference of the binding affinity in two steps are critically governed by the entropy term.

#### IV. CONCLUSIONS

In summary, we have demonstrated an acid-base controlled chromophoric switch, in which same axle molecule can shuttle between different wheels under control of protonation or deprotonation of both the wheel and the axle. The described system therefore represents a prototype at the supramolecular level for both a simple molecular machine and a logic gate.

#### ACKNOWLEDGMENTS

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