A chromophoric switch based on pseudorotaxanes

Yu Liu, Chun-Ju Li, Heng-Yi Zhang, Li-Hua Wang, Qian Luo, and Ge Wang
Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People’s Republic of China

(Received 30 October 2006; accepted 21 December 2006; published online 12 February 2007)

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 (32+), axle 32+ 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.


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. Such systems could find applications for information processing at the molecular level and also be viewed as the forerunners of nanoscopic machines. Appealing examples of chemical compounds where controlled mechanical movements can take place are suitably designed pseudorotaxanes, rotaxanes, and catenanes. It is well known that organic ammonium ions can form adducts with crown ethers. 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. Recently, Huang et al. showed a cryptand/paraquat [2]pseudorotaxane which can be reversibly switched off and 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.

In the present work, we wish to report a methodology constructing a chromophoric switch, in which 1,2-bis(4,4′-dipyridyl)ethane (32+) 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 32+ 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-

© 2007 American Institute of Physics.
When 20 mol equivalents of CF₃COOH are added, the CT absorption band completely disappears. To the contrary, the same experiment performed for [1·3][PF₆]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 [1·3][PF₆]₂ gradually disassociates with the addition of CF₃COOH, while the complexation of 1 and 3²⁺ becomes stronger. The above results can be explained by the protonation of both the amino groups in 2 and the pyridium groups in 3²⁺. For pseudorotaxane [2·3]²⁺, the protonation of the pyridium groups in 3²⁺ could increase the hydrogen bond interaction of C–H···O and the π-stacking interaction between 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 dicaticonic host and tetracaticonic 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 3²⁺ from 2 is a natural process. For pseudorotaxane [1·3]²⁺, the protonation happens in just 3²⁺, and hence the resulting additional hydrogen bond of C–H···O and π-stacking interaction significantly enhance the stability of the pseudorotaxane. It is noted that the absorption values of [1·3][PF₆]₂ and [2·3][PF₆]₂ recover upon neutralization of the solution with 20 mol equivalents of Bu₃N, and the colors change to the original light yellow for [1·3][PF₆]₂ and red for [2·3][PF₆]₂. Furthermore, the addition of CF₃COOH again results in the colors of the solution becoming yellow for [1·3][PF₆]₂ and colorless for [2·3][PF₆]₂.

Mixing equimolar proportions of 1, 2, and 3²⁺ makes the solution color become red, and the intensity of the CT band at about 440 nm increases. When 20 equivalents of CF₃COOH 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 CF₃COOH, the color of the mixing solution is consistent with that of the pseudorotaxane [2·3][PF₆]₂, while the color in the present of CF₃COOH is accordant with that of the pseudorotaxane [1·3][PF₆]₂. The neutralization of the solution with Bu₃N is accompanied by the reappearance of red color. These observations indicate that 3²⁺ can shuttle between crown ether rings of 1 and 2 by the adjustment of the acid-base, as shown in Fig. 2.
The above threading/unthreading processes for \(3^{2+}\) and the shullte movement of \(3^{2+}\) between the two rings of 1 and 2 can be described as three INHIBIT (INH) logic gates. CF\(_3\)COOH and Bu\(_3\)N are assigned as the inputs, and the unambiguous confirmation of the dethreading process. The solution of 2 and 3 following the addition of 2 and 20 equivalents of CF\(_3\)COOH, the resonances associated with the protonated 2 and 3 are observed. This is an unambiguous confirmation of the dethreading process. The retreading process can be reversed quantitatively by the addition of 20 equivalents of Bu\(_3\)N, which is attributed to the deprotonation of 2 and 3 restoring the original equilibrium between 2, 3, and [2-3]\(^{2+}\).

In the case of pseudorotaxane [1-3]\(^{2+}\), it is interesting that the complexation ability increases upon addition of acid, which is contrary to pseudorotaxane [2-3]\(^{2+}\). Addition of 20 equivalents of CF\(_3\)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 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 Bu\(_3\)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 with 2 and 1 could be determined from Figs. 3(g) and 3(j). The \(K_S\) values obtained are \((1.4\pm0.1)\times10^3\)M\(^{-1}\) for [1-3]\(^{2+}\) and \((4.5\pm0.1)\times10^3\)M\(^{-1}\) for [2-3]\(^{2+}\).

The \(^1\)H NMR spectra of an equimolar solution of 1, 2, and 3 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 about 3.2 times, ascribing extra \(\pi\)-stacking in-

### B. \(^1\)H NMR spectra

The switching process of [2]pseudorotaxane [1-3]\(^{2+}\) and [2-3]\(^{2+}\) and the tricomponent system 1/2/3\(^{2+}\) can also be monitored by \(^1\)H NMR spectroscopy. \(^1\)H NMR spectra of a solution of 2 and 3\(^{2+}\) following the addition of 2 and 20 equivalents of CF\(_3\)COOH, together with only 3\(^{2+}\) in the absence and the presence of CF\(_3\)COOH, are shown in Figs. 3(b) and 3(e)–3(i). After the addition of two equivalents of CF\(_3\)COOH, a majority of the resonances associated with [2-3]\(^{2+}\) disappears, the corresponding intensity of the resonances of 3 increases. In the spectrum of the solution that contains 20 equivalents of CF\(_3\)COOH, the resonances associated with [2-3]\(^{2+}\) 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 retreading process can be reversed quantitatively by the addition of 20 equivalents of Bu\(_3\)N, which is attributed to the deprotonation of 2 and 3\(^{2+}\) restoring the original equilibrium between 2, 3, and [2-3]\(^{2+}\).

FIG. 3. (Color online) 300 MHz \(^1\)H NMR spectra of CD\(_3\)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 [3][PF\(_6\)]\(^{-}\), (d) 5.0 mM 1+5.0 mM 2+5.0 mM [3][PF\(_6\)]\(^{-}\)+20 equiv. CF\(_3\)COOH, (e) 5.0 mM [3][PF\(_6\)]\(^{-}\}, (f) [3][PF\(_6\)]\(^{-}\}+20 equiv. CF\(_3\)COOH, (g) 5.0 mM [3][PF\(_6\)]\(^{-}\}+5.0 mM 2, (h) 5.0 mM [3][PF\(_6\)]\(^{-}\}+5.0 mM 2+2 equiv. CF\(_3\)COOH, (i) 5.0 mM [3][PF\(_6\)]\(^{-}\}+5.0 mM 2+5.0 mM 1, and (k) 5.0 mM [3][PF\(_6\)]\(^{-}\}+5.0 mM 1+20 equiv. CF\(_3\)COOH.
interactions and ion-dipole interactions between pyridinium 32⁺ and electron-richer amino-catechol rings in 2. Upon addition of 20 equivalents of CF₃COOH, the resonances associated with [2·3]²⁺ disappear, and the resonances of [1·3]²⁺ increase, corresponding to 100% resultant complex of [1·3]²⁺. The original state can be reversed quantitatively 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.

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 3²⁺, microcalorimetry titration has been performed in the absence and the presence of CF₃COOH to give the complex stability constants (Kₛ) and the standard free energy (ΔG), enthalpy changes (ΔH), and entropy changes (ΔS) (Fig. 4 and Table I). The reaction enthalpy between 2 with 3²⁺ in the presence of CF₃COOH is too small to determine the Kₛ value by titration microcalorimetry, suggesting that there is no complexation between 2 with 3²⁺. In the case of 1 and 3²⁺ in the presence of CF₃COOH, 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.¹⁴

As indicated in Table I, in the absence of CF₃COOH, the substitution of amino for hydrogen in 1, affording 2, significantly increases the Kₛ values upon 2.5 times, ascribing extra π-stacking interactions and ion-dipole interactions between pyridinium 3²⁺ and electron-richer amino-catechol rings in 2.¹⁵ The enhanced binding ability is apparently controlled by the enthalpy changes because the enthalpy change (ΔH₁·3⁻¹=25.7 kJ mol⁻¹) is more remarkable than the entropy changes (ΔS₁·3⁻¹=−3.1 kJ mol⁻¹).

In the presence of CF₃COOH, the enthalpy change values in each step are almost equal (ΔH₁·3⁻¹=25.7 kJ mol⁻¹ and ΔH₂·₃⁻¹=25.2 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 (Kₛ/M⁻¹) and thermodynamic parameters (in kJ mol⁻¹) for complexation of hosts 1 and 2 with guest 3²⁺ in anhydrous acetonitrile in the absence and the presence of CF₃COOH at 298.15 K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>N</th>
<th>Kₛ</th>
<th>−ΔG°</th>
<th>−ΔH°</th>
<th>−ΔS°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1·3⁻¹</td>
<td>5</td>
<td>1659±45</td>
<td>18.4±0.1</td>
<td>48.5±0.4</td>
<td>−30.1±0.4</td>
</tr>
<tr>
<td>2·3⁻¹</td>
<td>2</td>
<td>4142±147</td>
<td>20.6±0.1</td>
<td>51.6±1.5</td>
<td>−31.0±1.6</td>
</tr>
<tr>
<td>1·3⁻¹</td>
<td>2</td>
<td>15550±1600</td>
<td>23.8±0.3</td>
<td>25.7±0.8</td>
<td>−1.9±1.0</td>
</tr>
<tr>
<td>[1·3]²⁻+1·3⁻¹</td>
<td>2</td>
<td>2433±8</td>
<td>19.3±0.1</td>
<td>25.2±0.7</td>
<td>−5.9±0.7</td>
</tr>
</tbody>
</table>
| 2·3⁻¹ | 1     | 0.25–0.50 mM | [3²⁺]=6.60–8.30 mM, or [1]=3.12 mM; [3²⁺]=0.17 mM in CH₃CN solution.
| 2·3⁻¹ | 2     | 0.56 mM | [3²⁺]=6.60 mM in CH₃CN solution.
| 2·3⁻¹ | 8.00 mM in CH₃CN solution; [3²⁺]=0.50 mM CH₃CN solution in the presence of 10 mM CF₃COOH.
| 2·3⁻¹ | 0.25–0.50 mM | [3²⁺]=6.60–8.30 mM, or [1]=3.12 mM; [3²⁺]=0.17 mM in CH₃CN solution.
| 2·3⁻¹ | 0.56 mM | [3²⁺]=6.60 mM in CH₃CN solution.
| 2·3⁻¹ | 8.00 mM in CH₃CN solution; [3²⁺]=0.50 mM CH₃CN solution in the presence of 10 mM CF₃COOH.
| 2·3⁻¹ | 0.25–0.50 mM | [3²⁺]=6.60–8.30 mM, or [1]=3.12 mM; [3²⁺]=0.17 mM in CH₃CN solution.

FIG. 4. (Color online) Calorimetric titrations of host 1 (0.25 mM) with 3²⁺ (8.30 mM) in CH₃CN at 25 °C. Left: Raw data for sequential 10 μl injections of guest 3²⁺ 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 3⁻¹ 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.
any of the \( K_S \) values in two steps is larger than the original one in the absence of CF\(_3\)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 CF\(_3\)COOH are lower than that in the absence of CF\(_3\)COOH \((-\Delta H^\circ = -23.3 \sim -22.8 \text{kJ mol}^{-1}\) 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 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 34\(^+\) might dissociate to some extent to desolvation and structural freezing upon complexation and the enthalpy driven in the absence and the presence of CF\(_3\)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

This work was supported by NNSFC (Nos. 90306009, 20421202, and 20372038) and TJNSF (No. 05YFJMJC06500).


15 See EPAPS Document No. E-JCPSA6-126-706705 for INHIBIT logic gates, UV spectra, and calorimetric titration of pseudorotaxanes. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).