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Synthesis of a Novel Triptycene-Based Molecular Tweezer and Its Complexation with Paraquat Derivatives

Xiao-Xia Peng,[†,‡] Hai-Yan Lu,[†] Tao Han,[†] and Chuan-Feng Chen*,[†]

Beijing National Laboratory for Molecular Sciences, Laboratory of Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and Graduate School, Chinese Academy of Sciences, Beijing 100049, China

cchen@iccas.ac.cn

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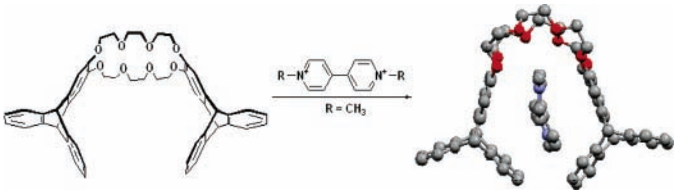
ABSTRACT



A novel triptycene–based molecular tweezer has been synthesized, and its complexation with paraquat derivatives in solution and in the solid state has been studied. Due to its electron-rich cavity, the molecular tweezer could form stable complexes with paraquat derivatives with different functional groups. Moreover, it was also found that formation of the complexes was caused by a charge transfer interaction and the complexes dissociated upon two one-electron reduction of the bipyridinium ring.

The design of novel efficient synthetic receptors with the capability for strongly and selectively binding a substrate is a permanent and challenging topic in the development of new supramolecular systems with specific structures and properities.[1] Recently, molecular tweezers,[2] which are composed of a tether and two flat, generally aromatic pincers, have attracted increasing interest for their specific structures, convenient synthesis, and wide potential applications in biological and supramolecular chemistry.[3]

Triptycene,[4] with its unique three-dimensional rigid structure and electron-rich property, has been found to be a useful building block for the construction of novel receptors.[5] We deduced that with triptycene as the building block, novel molecular tweezers could also be formed. Herein, we report the synthesis and binding properties of a novel tweezer-like receptor **1**, which is composed of two triptycene units linked by two crown ether chains (Figure 1). Due to its electron-rich cavity, the receptor **1** could form stable complexes with the paraquat derivatives[6] with different functional groups in

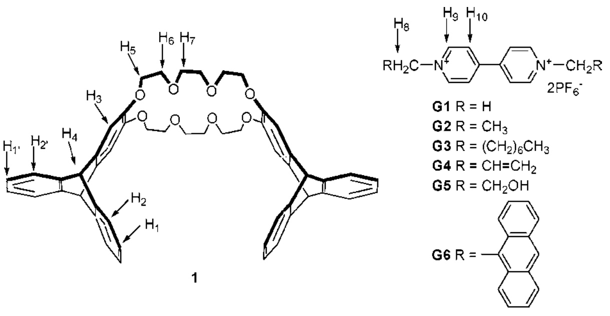


Figure 1. Structure and proton designations of the receptor **1** and guests $\mathbf{G_1}$−$\mathbf{G_6}$.

[†] Institute of Chemistry.

[‡] Graduate School, Chinese Academy of Sciences.

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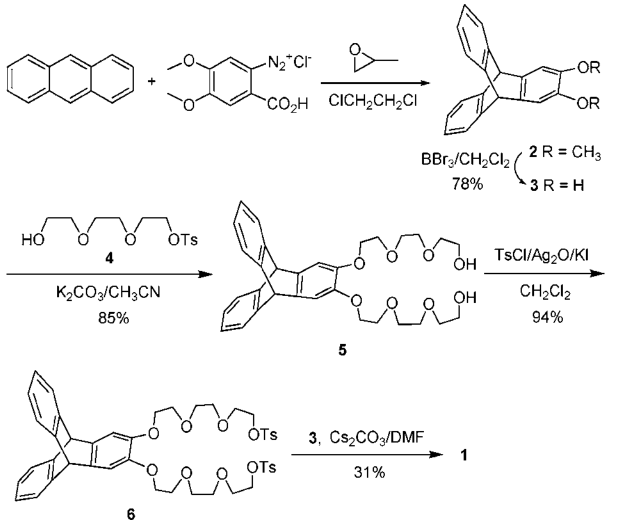
solution and in the solid state. Moreover, it was also found that formation of the complexes could be caused by a charge-transfer interaction and the complexes could dissociate upon two one-electron reductions of the bipyridinium salt.

Scheme 1. Synthesis of the Receptor **1**



Synthesis of the receptor **1** is outlined in Scheme 1. First, triptycene derivative **2**[7] was obtained by treating anthrancene with 4,5-dimethoxybenzenediazonium-2-carboxylate in 1,2-dichloroethane in the presence of 1,2-epoxypropane. Demethylation of **2** with BBr_3 in CH_2Cl_2 gave the compound **3** in 78% yield. Triptycene derivative **5** was then achieved in 85% yield by the reaction of 8-tosyloxy-3,6-dioxaoctanol **4** and compound **3** in CH_3CN in the presence of K_2CO_3. By the treatment of compound **5** with TsCl in CH_2Cl_2 in the presence of Ag_2O and KI, the ester product **6** was obtained in 94% yield. Finally, the target molecule **1** was produced in 31% yield by the reaction of **6** and **3** in DMF in the presence of Cs_2CO_3. All new compounds were confirmed by ^{1}H NMR, ^{13}C NMR, MS spectra, and elemental analysis.[8]

We first investigated the complex ability of receptor **1** toward paraquat derivatives in solution. Consequently, mixing **1** and guest **G1** (2 mM each) in chloroform and acetonitrile (1:1) showed a swift color change from pale yellow to a light red-brown, which might be due to the charge transfer between the electron-rich aromatic ring of **1** and the bipyridinium ring of **G1**. Similar phenomena also took place for other guests. As shown in Figure 2, the ^{1}H NMR spectrum of a mixture of **1** and **G1** in $CDCl_3$ and CD_3CN (1/1) showed a great difference with those for **1** and **G1** (Figure 2). The H_9 and H_{10} proton signals of **G1** shifted significantly upfield, which might be due to the strong shielding effect of the aromatic rings of **1**. Similarly, the proton H_3 of aromatic ring linked with the crown ether chains and the proton H_4 also showed considerable upfield shifts. Although there are no obvious changes for the protons H_1 and H_2 of **1**, obvious changes were observed for the crown protons H_5−H_7. These observations all suggested that a new complex between **1** and **G1** was formed. The ^{1}H NMR spectroscopic titrations further gave a quantitative estimate for the complex of **1** and **G1** by monitoring the changes of the chemical shift of the proton H_3. The results showed that a 1:1 complex **1·G1** was formed by a mole ratio plot. Accordingly, the association constant between **1** and **G1** was calculated to be $K_{a1\cdot G1} = 4.08 \times 10^3\ M^{-1}$ by the Scatchard plot,[5c,9] which is bigger than that of the complex between dibenzo[24]crown-8 and the paraquat.[10]

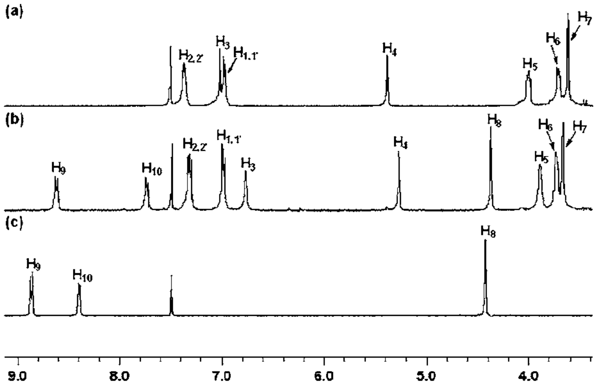


Figure 2. Partial ^{1}H NMR spectra (300 MHz, 1:1 $CDCl_3/CD_3CN$, 298 K) of (a) free **1**, (b) **1** and 1.0 equiv of **G1**, and (c) free guest **G1**. $[\mathbf{1}]_0 = 2.0$ mM.

Furthermore, we tested the complexation of receptor **1** toward paraquat derivatives **G2**−**G6** by NMR approach. The results showed that similar to the complex **1·G1**, the alkyl substituted paraquat derivatives **G2** and **G3** could also form 1:1 complex with the receptor **1**. For the guests containing terminal vinyl group, hydroxyl, and anthracyl group, a similar but slightly weak complexation with receptor **1** was observed.

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Table 1. Half-Wave Potentials ($E_{1/2}$/V vs SCE)[a] and Association Constants

	bpy^{2+} → bpy^{+}	bpy^{+} → bpy	K_a[b] (M^{-1})
[**G1**]$^{2+}$	−0.697	−1.179	
1·[**G1**]$^{2+}$	−0.622	−1.049	4.08 × 10^{3}
[**G2**]$^{2+}$	−0.385	−0.871	
1·[**G2**]$^{2+}$	−0.338	−0.813	2.98 × 10^{3}
[**G3**]$^{2+}$	−0.343	−0.826	
1· [**G3**]$^{2+}$	−0.270	−0.751	3.09 × 10^{3}
[**G4**]$^{2+}$	−0.324	−0.783	
1·[**G4**]$^{2+}$	−0.245	−0.695	1.22 × 10^{3}
[**G5**]$^{2+}$	*c*	*c*	
1·[**G5**]$^{2+}$	−	−	9.86 × 10^{2}
[**G6**]$^{2+}$	−0.314	−0.776	
1·[**G6**]$^{2+}$	−0.250	−0.693	3.44 × 10^{3}

[a] Solvent: CH_2Cl_2/CH_3CN (9:1), $[NBu_4]PF_6$ 0.1M, [G]/[**1**] = 1:4, [G] = 1.25 × 10^{-3} M. [b] From the ^1H NMR titration experiments. Solvent: $CDCl_3/CD_3CN$ (1:1). [c] Adsorption on the electrode surface.

According to the Scatchard plot, the association constants between **1** and the guests were further calculated.[8] As shown in Table 1, the substituted groups in the bipyridinium salts had no obvious influence on the stabilities of the complexes, in which the driving forces might be mainly attributed to the noncovalent interactions between the molecular tweezer **1** and the bipyridinium ring of the guests.

The electrospray ionization mass spectra provided another evidence for formation of 1:1 stable complexes between **1** and paraquat derivatives **G1**−**G6**. As a result, the strong peaks at *m*/*z* 493.7, 507.7, 591.9, 519.7, 523.7, and 670.0 for [**1**·**G1**−2PF$_6$]$^{2+}$, [**1**·**G2**−2PF$_6$]$^{2+}$, [**1**·**G3**−2PF$_6$]$^{2+}$, [**1**·**G4**−2PF$_6$]$^{2+}$, [**1**·**G5**−2PF$_6$]$^{2+}$, and [**1**·**G6**−2PF$_6$]$^{2+}$, respectively, were all observed.[8]

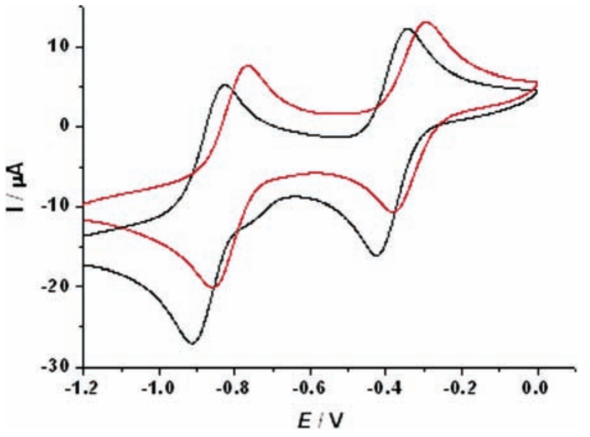

Figure 3. CV curves for a solution of **[G2]**$^{2+}$ (1.25 × 10^{-3} M) in CH_2Cl_2/CH_3CN (9:1)−$(NBu_4)PF_6$ (0.1 M) in the absence (black line) and presence (red line) of the receptor **1** (5.0 × 10^{-3} M). Scan rate: 0.2 Vs^{-1}.

Because the guests contain the well-known 4, 4′-bipyridinium electroactive unit, their electrochemical behavior in the absence and presence of the receptor **1** was also studied. As expected, the **[G]**$^{2+}$ showed two reversible one-electron reduction processes. The half-wave potential values are summarized in Table 1, and the cyclic voltammetric (CV) curve for **[G2]**$^{2+}$ was shown in Figure 3. It was found that the CV patterns for reduction of the paraquat derivatives were remarkably affected by the presence of **1**, which showed that the formation of the complexes involved an interaction between **1** and the bipyridinium salts. In particular, both the cathodic and anodic peaks corresponding to the first and second one-electron reduction process of the bipyridinium core moved to less negative values upon the addition of **1**, which is different from that in the presence of other hosts.[3a,b,11] Such a behavior suggested that formation of the complexes between **1** and the paraquat derivatives was caused by a charge transfer interaction and the complexes

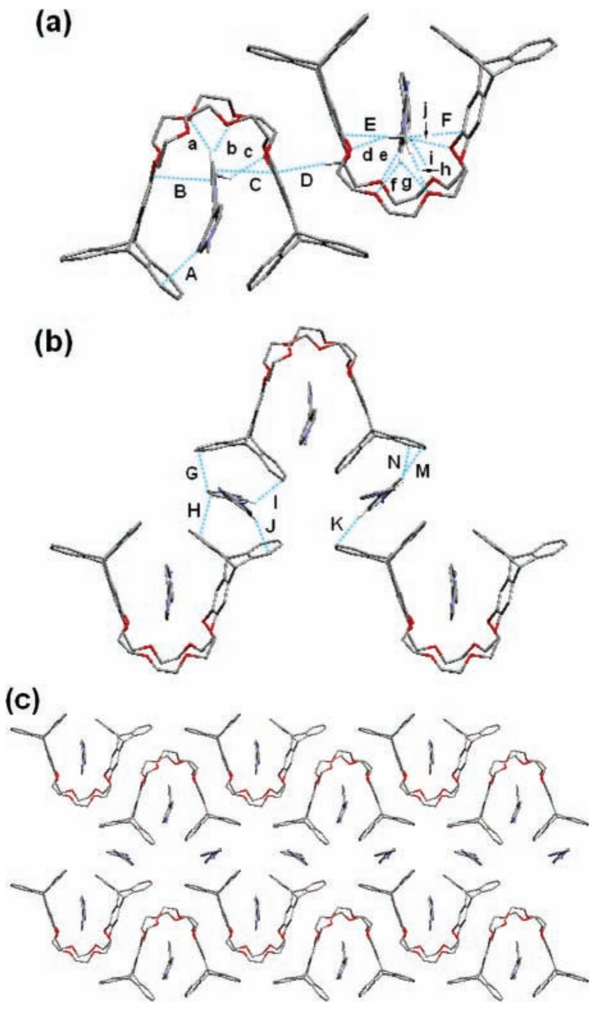

Figure 4. Two views (a) and (b) of the crystal structure of the complex **1·G1**. Hydrogen bond distances (Å): *a* = 2.31; *b* = 2.53; *c* = 2.61; *d* = 2.62; *e* = 2.60; *f* = 2.54; *g* = 2.71; *h* = 2.45; *i* = 2.49; *j* = 2.70. (c) Crystal packing of the complex viewed along the *c*-axis. Solvent molecules, PF$_6^-$ counterions, and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

dissociated upon two one-electron reduction of the bipyridinium ring.

Further support for the formation of the complex **1·G1** came from its X-ray diffraction results.[12] It was found that compared to a simple dibenzo[24]crown-8,[10] the host **1** showed completely different binding properties with the paraquat **G1** in the solid state. As shown in Figure 4a, in one crystal cell, there are two tweezer-like molecules with different orientation, and each molecule tweezered a bipyridinium guest by different complexation modes. In one case, there existed not only multiple hydrogen bonds between the polyether oxygen atoms and protons of methyl group and aromatic protons in **G1**, but also a C−H···π interaction with distance of 2.75 Å (A) and $\pi-\pi$ stacking interactions between phenyl rings of triptycene units and the bipyridinium ring with distances of 3.28 (B) and 3.36 Å (C). While in another case, multiple hydrogen bonds between the receptor **1** and the guest **G1**, and $\pi-\pi$ stacking interactions between phenyl rings of triptycene units and the bipyridinium ring with distances of 3.34 (E) and 3.34 Å (F) were only observed. Due to the multiple noncovalent interactions, the complex **1·G1** showed a high stability. Moreover, the guest in the complex was very closed to the dibenzocrown-8 moiety, and no obvious interactions between the guest and the other aromatic rings of triptycene units were observed. These results are consistent with those of the complex in solution.

Interestingly, it was also found that a C−H···π interaction with distance of 2.78 Å (D) between the two adjacent molecules existed. In particular, due to the unique structural property of triptycene unit, the adjacent receptors could be connected with each other by the complexation with the paraquat salts (Figure 4b), in which the driven forces were multiple $\pi-\pi$ stacking (G and H) and C−H···π interactions (I−M) between the bipyridinium ring and phenyl rings of triptycene units. Consequently, a waveform strcture was formed, which could further result in a 2D layer viewed along the *c*-axis (Figure 4c) and 3D microporous network.[8]

In summary, we have synthesized a novel triptycene-based molecular tweezer and demonstrated that it could form stable complexes with paraquat derivatives with different groups in solution and in the solid state. Moreover, it was also found that formation of the complexes was caused by a charge transfer interaction and the complexes dissociated upon two one-electron reduction of the bipyridinium ring. More applications of the molecular tweezer in supramolecular chemistry are underway.

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Supporting Information Available: Experimental procedures and characterization data for the receptor and the complexes. Cyclic voltammetry curves. The crystal structure for the complex **1·G1** and its CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for 2(**1·G1**)·2**G1**·6CH_3CN·H_2O: chemical formula sum $C_{164}H_{172}F_{48}N_{14}O_{17}P_8$; $M_r = 3770.92$; monoclinic; space group $P1n1$; $a = 20.390(4)$ Å, $b = 18.300(4)$ Å, $c = 22.938(5)$ Å; $\beta = 92.504(4)$; $V = 8551(3)$ Å^3; $Z = 2$; $T = 113(2)$ K; 23425 reflections collected, 19402 independent, giving $R_1 = 0.0913$, w$R_2 = 0.2487$ for observed unique reflection ($I > 2\sigma(I)$) and $R_1 = 0.1033$, w$R_2 = 0.2654$ for all data.