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Complexation of a Pentiptycene-Based Tweezer-Like Receptor with Paraquat Derivatives: Ion-Controlled Binding and Release of the Guests

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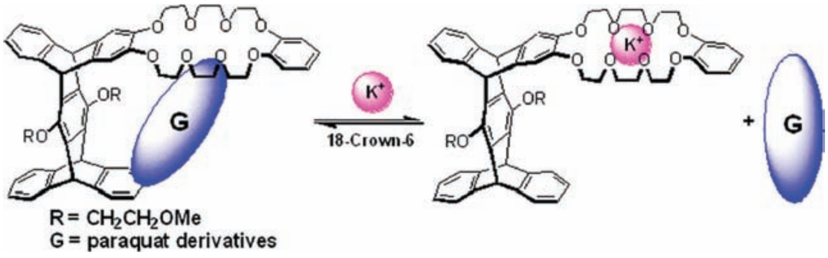
ABSTRACT



A new tweezer-like receptor containing a pentiptycene unit and a benzene ring linked by two crown ether chains has been synthesized. It could form stable complexes with paraquat derivatives with different functional groups in solution and in the solid state. It was found that the complexes dissociated upon two one-electron reduction of the bipyridinium ring. Moreover, binding and release of the guest molecules could also be easily controlled by the addition and removal of potassium ion.

In host−guest chemistry, the design and synthesis of novel efficient receptors are a permanent and challenging topic.[1] During the past decade, tweezer-like receptors,[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]

Pentiptycene,[4] with its unique rigid, aromatic, and H-shaped scaffold, has found specific applications in materials science and molecular machines.[4,5] However, most of the applications were based on the central ring functionalized pentiptycene derivatives. On the other hand, compared with those of triptycenes,[6] little is still known about pentiptycene-

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based receptors and their applications in host−guest chemistry,[7] although the H-shaped scaffold of pentiptycene is inherently different from the Y-shaped scaffold of triptycene. Recently, we[8] reported a series of peripheral functionalized pentiptycene derivatives that could be used as new building blocks and subsequently provided us opportunity to develop new supramolecular systems based on novel pentiptycene-derived receptors. Herein, we report the synthesis of a novel tweezer-like receptor **1** containing a pentiptycene unit and a benzene ring linked by two crown ether chains (Figure 1) and its complexion with the paraquat derivatives with different functional groups in solution and in the solid state. It was found that the complexes dissociated upon two one-electron reductions of the bipyridinium ring. Moreover, the binding and release of the guests could also be easily controlled by the addition and removal of potassium ion.

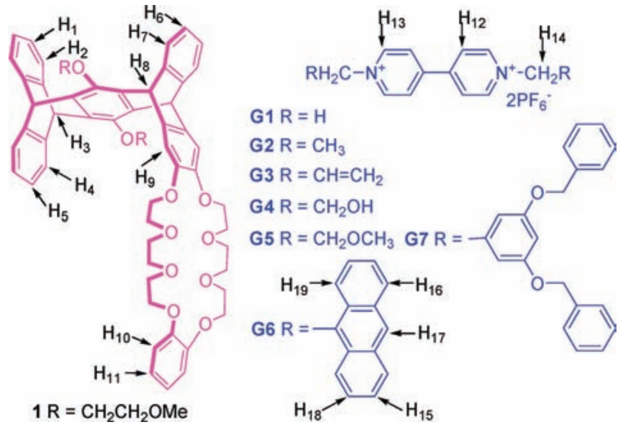
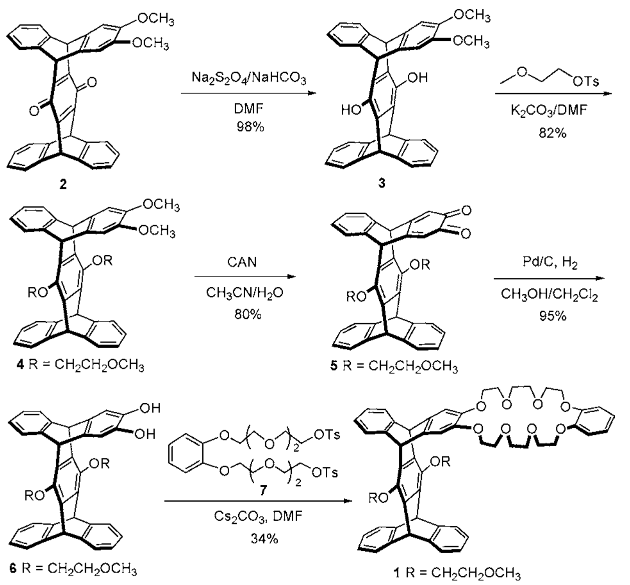


Figure 1. Structure and proton designations of receptor **1** and guests **G1**−**G7**.

Synthesis of receptor **1** is depicted in Scheme 1. Reduction of **2** with $Na_2S_2O_4$ produced **3** in 98% yield, which was then reacted with 2-methoxy-ethyl 4-methyl-benzenesulfonate to give **4** in 82% yield. Compound **4** was further oxidized by cerium ammonium nitrate (CAN) in aqueous CH_3CN, followed by reduction of the *o*-quinone moiety with catalytic hydrogenation to give **6** as a white solid. Finally, the target molecule **1** was obtained in 34% yield by the reaction of **6** with bistosylate **7** in DMF under high dilution conditions in the presence of Cs_2CO_3. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR MALDI-TOF MS, and elemental analysis.[9]

Scheme 1. Synthesis of Receptor **1**



We first investigated the complex ability of **1** toward the paraquat derivatives in solution. When mixing **1** and guest **G1** (4 mM each) in chloroform and acetonitrile (1:1, v/v), a color change from colorless to pale-orange could be found, which was due to the charge transfer interaction between the electron-rich aromatic rings of **1** and the electron-poor bipyridinium rings of guest **G1**. Similar phenomenon could also be observed for other guests. As shown in Figure 2, the ^{1}H NMR spectrum of a 1:1 mixture of **1** and **G1** in $CDCl_3$ and CD_3CN (1:1, v/v) showed a great difference from those for **1** and **G1**. The protons H_{13}, especially, and H_{12} of the pyridium ring shifted significantly upfield, which might be due to the strong shielding affect of the aromatic ring of **1**. Similarly, the H_8−H_{11} proton signals of **1** also shifted upfield, which is attributed to their positions in the shielding region of the bipyridium moiety of **G1**. These observations suggested that a stable complex between **1** and **G1** was formed. Furthermore, ^{1}H NMR spectroscopic titrations afforded a

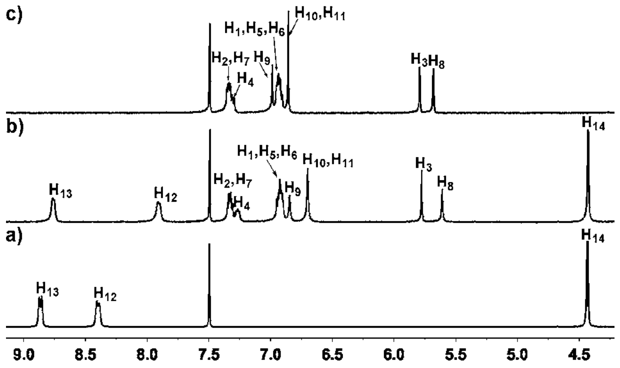


Figure 2. Partial ^{1}H NMR spectra (300 MHz, 1:1 v/v $CDCl_3$/CD_3CN, 298 K) of (a) free guest **G1**, (b) **1** and 1.0 equiv of **G1**, and (c) free host **1**. $[\mathbf{1}]_0 = 4.0$ mM.

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(9) See Supporting Information.

quantitative estimate between **1** and **G1** by monitoring the changes of the chemical shift of the proton H_{12}. The results showed that the 1:1 complex **1·G1** was formed by a mole ratio plot.[9] Accordingly, the apparent association constant $K_{a,exp,\mathbf{1\cdot G1}}$ was calculated to be 450 (±10.2) M^{-1} by the Scatchard plot,[10] which is bigger than that of the complex between dibenzo^{24}crown-8 (DB24C8) and the paraquat.[11]

Similarly, we found that paraquat derivatives **G2**−**G7** could also form 1:1 complex with receptor **1**. According to the Scatchard plots, the association constants between **1** and the guests were further calculated,[9] and the results (Table 1) showed that stronger complexation between **1** and **G5** was observed, whereas for the guests containing terminal hydroxyl, anthracyl, and the first generation Frechet-type dendron group, slightly weak complexation with **1** was shown.

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

	$bpy^{2+} \rightarrow bpy^{+}$	$bpy^{+} \rightarrow bpy$	K_a $[M^{-1}]$[b]
$[\mathbf{G1}]^{2+}$	−0.789	−1.214	
$\mathbf{1}\cdot[\mathbf{G1}]^{2+}$	−0.767	−1.180	450.0 ± 10.2
$[\mathbf{G2}]^{2+}$	−0.721	−1.158	
$\mathbf{1}\cdot[\mathbf{G2}]^{2+}$	−0.703	−1.141	545.9 ± 25.1
$[\mathbf{G3}]^{2+}$	−0.673	−1.095	
$\mathbf{1}\cdot[\mathbf{G3}]^{2+}$	−0.635	−1.059	559.7 ± 47.9
$[\mathbf{G4}]^{2+}$	*c*	*c*	
$\mathbf{1}\cdot[\mathbf{G4}]^{2+}$			250.1 ± 4.2
$[\mathbf{G5}]^{2+}$	−0.679	−1.111	
$\mathbf{1}\cdot[\mathbf{G5}]^{2+}$	−0.648	−1.089	715.5 ± 36.1
$[\mathbf{G6}]^{2+}$	−0.624	−1.053	
$\mathbf{1}\cdot[\mathbf{G6}]^{2+}$	−0.632	−1.063	285.3 ± 2.7
$[\mathbf{G7}]^{2+}$	−0.707	−1.137	
$\mathbf{1}\cdot[\mathbf{G7}]^{2+}$	−0.642	−1.070	284.2 ± 3.8

[a] Solvent: CH_3CN, $[NBu_4]PF_6$ 0.1 M, [**G**]/[**1**] = 1:3, [**G**] = 1.0 × 10^{-3} M. Working electrode: Pt. Scan rate: 0.1 V s^{-1}. [b] From the ^1H NMR titration experiments. Solvent: $CDCl_3/CD_3CN$ (1:1, v/v). [c] Adsorption on the electrode surface.

The electrospray ionization mass spectrum (ESI-MS) provided more evidence for formation of the complexes between **1** and guests **G1**−**G7**. As a result, the strong peaks at *m*/*z* 567.58, 581.62, 593.48, 597.71, 611.62, 743.75, and 865.05 for $[\mathbf{1\cdot G1}\text{-}2PF_6^{-}]^{2+}$, $[\mathbf{1\cdot G2}\text{-}2PF_6^{-}]^{2+}$, $[\mathbf{1\cdot G3}\text{-}2PF_6^{-}]^{2+}$, $[\mathbf{1\cdot G4}\text{-}2PF_6^{-}]^{2+}$, $[\mathbf{1\cdot G5}\text{-}2PF_6^{-}]^{2+}$, $[\mathbf{1\cdot G6}\text{-}2PF_6^{-}]^{2+}$, and $[\mathbf{1\cdot G7}\text{-}2PF_6^{-}]^{2+}$, respectively, were all observed,[9] which indicated that the stable complexes between **1** and the guests formed.

Formation of the 1:1 complex between **1** and **G6** was further confirmed by its X-ray crystal structure.[12,13] As shown in Figure 3, the guest positioned in the cavity of tweezer-like pentiptycene mono(crown ether) and was adjacent to the DB24C8 moiety. It was found that the bipyridinium unit in the complex was distorted by a −18.76° dihedral angle between the bipyridinium rings. A couple of $\pi-\pi$ stacking interactions between the paraquat ring and the aromatic ring of the host with distances of 3.28 (A) and 3.32 Å (B) were observed. Moreover, there existed not only multiple hydrogen bonds ($d_{H\cdots O}$ = 2.679 Å for a, 2.38 Å for b, 2.58 Å for c, 2.68 Å for d, 2.64 Å for e) between the protons of the bipyridinium ring and ether oxygen atoms of the host, but also $C-H\cdots\pi$ interactions ($d_{H\cdots\pi}$ = 2.85 Å for C, 2.82 Å for D, 2.70 Å for E, 2.64 Å for F, 2.77 Å for G, 2.74 Å for H, and 2.69 Å for I) between the methylene protons and aromatic protons of the DB24C8 moiety of the host and anthrance ring of the guest and also between the bipyridinium proton and central ring of the pentiptycene scaffold. These multiple noncovalent interactions between the host and guest play an important role in the stability of the complex **1·G6**.

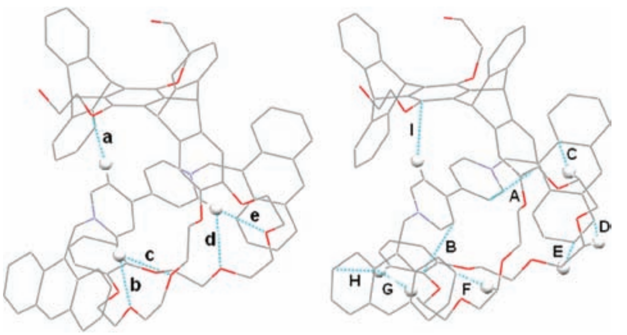

Figure 3. Views of the crystal structure of the complex **1·G6**. Blue lines denote the noncovalent interactions between the host and the guest. Solvent molecules, PF_6^{-} counterions, and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

Since the paraquat derivatives are well-known organic redox-active molecules, their electrochemical behaviors in the presence and absence of receptor **1** were also studied, and the half-wave potential values are summarized in Table 1. As expected, the guests except **G4** all showed two reversible one-electron reduction processes that correspond to the successive reduction of the 4,4′-bipyridinium core.[3a,14] The CV patterns for reduction of the paraquat derivatives were remarkably affected in the presence of **1**. In particular, as for guests **G1**−**G3**, **G5**, and **G7**, both the cathodic and anodic peaks of the first and second one-electron reduction processes moved to the less negative values upon the addition of **1**, whereas with guest **G6**, both peaks moved very slightly to the more negatives values. Such behaviors suggested that the complexes between **1** and the paraquat derivatives formed, which were caused by the charge transfer interactions, and the complexes dissociated upon two one-electron reduction of the bipyridinium ring.

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(12) Crystal data for $(\mathbf{1\cdot G1})_4$: $C_{392}H_{360}F_{48}N_8O_{48}P_8$; M_r = 7110.64; monoclinic; space group *P21/n*; *a* = 16.000(3) Å, *b* = 24.700(5) Å, *c* = 24.300(5) Å; *β* = 103.40(3)°; *V* = 9342(3) Å^3; *Z* = 1; *T* = 173(2) K; 13414 reflections collected, 9663 independent, giving R_1 = 0.1456, wR_2 = 0.3937 for observed unique reflection ($I > 2\sigma(I)$) and R_1 = 0.1706, wR_2 = 0.4149 for all data.

(13) Because of the lack of heavy atoms in the complex and the presence of disordered PF_6^{-}, the quality of the X-ray diffraction data was low. However, the overall geometry of the complex was clealy established.

Since host **1** contains a DB24C8 moiety and paraquat derivatives are cationic molecules, we tried to investigate the potassium ion controlled binding and release of the guest molecules in the above complexes.[15] Consequently, a series of ^{1}H NMR experiments were carried out. As shown in Figure 4c, the ^{1}H NMR spectrum of a 1:1 mixture of **1** and guest **G6** showed formation of the 1:1 complex **1·G6**. When excess KPF_6 salts were added to the above solution, it was found that the proton signals of the complex **1·G6** were totally disappeared, while the proton signals of guest **G6** shifted downfield almost to the original positions (Figure 4d). Moreover, the aromatic proton signals of host molecule shifted nearly to the original positions while the peak shape of the crown ether region had a big change. These observations indicated that the potassium ion bound to the crown ether moiety, which resulted in the release of the guest **G6** from the cavity of the host molecule probably as a result of the extra electrostatic repellent force. When 18-crown-6 was added into the above system, it was further found that the proton signals of complex **1·G6** recovered (Figure 4e), which suggested that complex **1·G6** formed again. Thus, the ion-controlled binding and release of the guest **G6** could be easily performed by addition and removal of the potassium ion. Similarly, it was found that the binding and release of the guests **G1** and **G5** in the complexes **1·G1** and **1·G5** could also be efficiently controlled by the potassium ion.[9]

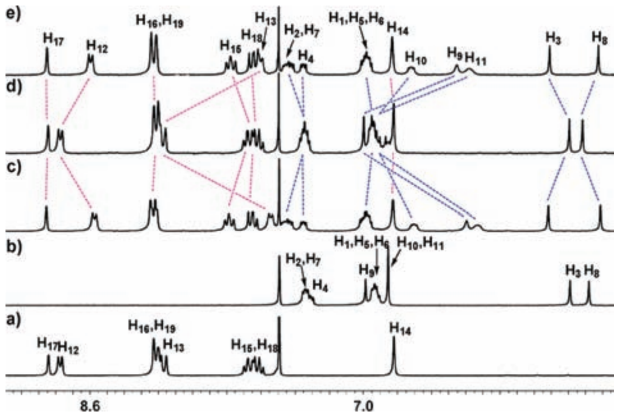

Figure 4. Partial ^{1}H NMR spectra (300 MHz, 1:1 v/v $CD_3CN/CDCl_3$, 298K) of (a) free guest **G6**, (b) free host **1**, (c) **1** and 1.0 equiv of **G6**, (d) the mixture obtained after adding KPF_6 (2 equiv) to solution (c), (e) the mixture obtained after adding 18-crown-6 (3 equiv) to (d). $[\mathbf{1}]_0 = 4$ mM.

In summary, we have synthesized a novel tweezer-like receptor containing a pentiptycene moiety and a benzene unit linked by two crown ether chains and proven that it could form stable complexes with paraquat derivatives with different functional groups in solution and in the solid state. Moreover, we found that formation of the complexes were caused by the charge transfer interactions and the complexes dissociated upon two one-electron reductions of the bipyridinium ring. It was also found that binding and release of the guest molecules could be easily controlled by the addition and removal of potassium ion. More applications of the pentiptycene based receptor in supramolecular chemistry are underway in our laboratory.

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Supporting Information Available: Synthesis and characterization data, and copies of ^{1}H and ^{13}C NMR spectra for new compounds. Copies of ESI-MS and ^{1}H−^{1}H COSY spectra for the complexes. Determination of the association constants. Cyclic voltammetry curves. X-ray crystallographic files in CIF format for complexes **1·G6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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