Electrochemically Switchable Molecular-Tweezers
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Abstract: Synthetic receptors possessing two complexing chromophores connected by a single spacer are referred to as molecular tweezers. We report an electrochemically triggered molecular tweezers, which is a calix[4]arene-bis-porphyrin conjugate, that acts as a proof-of-concept demonstration system showing an electro-statically induced approach to guest release. The electrochemical behavior represents that 1,4-diazabicyclo[2.2.2]octane (DABCO) is released from the complex formed between calix[4]arene-bis-porphyrin conjugate and DABCO, just after cooperative two-oxidation occurs at 0.41 V.

Key words: supramolecular chemistry, porphyrinoids, calixarenes, molecular recognition

1 INTRODUCTION
Considerable effort within the molecular machines modeling community continues to focus on building machines on the molecular scale. Synthetic receptors possessing two complexing chromophores connected by a single spacer are referred to as molecular tweezers. Somewhat related to the movements displayed by some tweezers systems are some of the first molecular-level machine reported in the literature, wherein breathing motions play a key role. The success of these early examples has inspired the development of new tweezers systems. Of particular interest are those that can be controlled by external stimuli. In this regard, porphyrins are attractive as building blocks. It is well-known that porphyrin oligomers play an important role in biological systems and their coordination properties permit the construction of various supramolecular structures. We previously reported bis-porphyrin, which is a calix[4]arene-porphyrin conjugate, that acts as a molecular tweezers. Specifically, we found that this system forms an inclusion complex with 1,4-diazabicyclo[2.2.2]octane (DABCO) that involves coordination to the porphyrin zinc center. Unfortunately, as initially developed this system could not easily be controlled by external stimuli. However, we appreciated that if molecular tweezers have two well-defined specific states, a guest binding "on" state and an "off" state in which the guest is not bound, switching is possible. For instance, the binding and release of a guest by an external trigger, such as light, pH, and ions, becomes possible. Electrochemical switching is also attractive, and examples of systems

Scheme 1  Schematic representation of the complex formed between 1 and 2.

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wherein redox processes involving molecular tweezers induce, for example, chewing motion and conformational switching are known. In this work, we report an electrochemically triggered molecular tweezers, system 1, that acts as a proof-of-concept demonstration system showing an electro-statically induced approach to guest release. To the best our knowledge such an approach is without precedent in the literature.

2 EXPERIMENTAL PROCEDURES

Calix[4]arene-bis-porphyrin conjugate 1 was prepared as reported previously. Experimental details for the UV-visible, cyclic and linear sweep voltammetric studies were included in the supporting information.

3 RESULTS AND DISCUSSION

The electrochemical behavior of bis-porphyrin 1 was studied by cyclic voltammetry and linear sweep voltammetry. The host 1 gives rise to three reversible redox waves, as can be seen from an inspection of Fig. 1. Two one-electron oxidation steps corresponding to the Por/Por⁻ redox couple at $E_{1/2} = +0.27 \ (\Delta E_p = 0.10 \ V)$ and $+0.49 \ (\Delta E_p = 0.08 \ V)$ vs. Ag/AgNO₃ are assigned as the first redox of each porphyrin. A one-electron oxidation step corresponding to the Por⁻/Por²⁺ system at $E_{1/2} = +0.76 \ V (\Delta E_p = 0.10 \ V)$ vs. Ag/AgNO₃ is assigned to the second redox feature of one porphyrin present in 1. It is considered likely that the second redox wave of the other porphyrin appears at around +1.05 V and is thus buried in the base current. Richer et al. reported similar electrochemical behavior for a Ni-porphyrin dimer, which is closely bonded on planar through the metal complex. On this basis we suggest that two redox waves based on Por/Por⁻ system result from the effect of the close intramolecular through-space interaction between the two porphyrins.

As noted above, we have previously reported that the co-facial bis-porphyrin 1 can form an ensemble with 2, affording a 1:1 complex or 1:2 complex, as inferred from UV-visible and ¹H-NMR spectroscopic analyses. The stoichiometry of 1 and 2 in the complex depends on the concentration of 2. Figure 2 shows the anodic linear sweeping potential curves of 1 as determined in the presence of various concentrations of 2 ([2]/[1] = 0, 0.4, 0.8, 1.2, 1.6, 2.0, 3.0, 5.0). The first oxidation peaks of the two porphyrins at $E_p = 0.32$ and 0.53 V vs. Ag/AgNO₃ (Fig. 2a) correspond to the formation of Por⁻ in 1. The addition of 2 gives rise to a new, reversible oxidation peak between 0.32 and 0.53 V (Fig. 2a-d). A new, broad oxidation feature

![Fig. 1 Cyclic voltammogram of porphyrin dimer 1 (0.2 mmol dm⁻³) on the Pt electrode in 0.5 mol dm⁻³ TBAP-CH₂Cl₂; scan rate, 0.1 V s⁻¹.](image)

![Fig. 2 Linear sweeping potential curves of porphyrin dimer 1 (0.2 mmol dm⁻³) with/without 2 on the Pt electrode in 0.5 mol dm⁻³ TBAP-CH₂Cl₂; [2]/[1] = (a)0, (b)0.4, (c)0.8, (d)1.2, (e)1.6, (f)2.0, (g)3.0, (h)5.0; scan rate, 0.1 V s⁻¹.](image)
at \( E_p = 0.41 \) V vs. Ag/AgNO\(_3\) was observed in the presence of \( \mathbf{2} \), up until the point that 1.2 equiv had been added (Fig. 2a-d). This broadened peak (see in Fig. 2d) is assigned to the cooperative oxidation of two porphyrins in 1 from 2Por to 2(Por\(^+\)). This cooperative double oxidation of 1 is attributed to the fixed sandwich-like conformation of the complex formed between 1 and 2. However, the potential of the second oxidation peak for the porphyrins present in 1 remains unchanged at \( E_p = 0.80 \) in Fig. 2a-d. This electrochemical behavior is reiterated under conditions of multiple potential sweep cycling. Taken in concert, these results provide support for the view that 2 is released from the complex just after cooperative two-oxidation occurs at 0.41 V (Scheme 2). The release of 2 from the complex is ascribed to not only the decrease in the steric constraint imposed by the calix\([4]\)arene conformation but also the weakness of the noncovalent bond between the zinc porphyrin radical cation and 2. In the presence of 5 equivalents of 2 (cf. Fig. 2h), both oxidation peaks at \( E_p = 0.41 \) and 0.80 V vs. Ag/AgNO\(_3\) in Fig. 2d decrease in amplitude, while new two oxidation peaks grow in at \( E_p = 0.36 \) and 0.68 V vs. Ag/AgNO\(_3\). Integration of each of these latter peaks leads to the conclusion that each involves a 2 electron process. On this basis we conclude that each porphyrin in 1 is oxidized independently in forming a 1:2 host-guest external monodentate complex. Unfortunately, the NMR titration study of the oxidized bis-porphyrin in the presence of 2 was not implemented because of employed voltage effect.

In order to detect the absorption spectra of zinc porphyrin cation in 1, the optically transparent thin-layer electrode method was employed, which procedures were precisely shown in the supporting information (page S3, Fig. S4). Figure 3 shows the absorbance change of the porphyrin radical cation at 466 nm upon applied voltage from 0 to 1.3 V (blue line to red line)\(^{20}\). (Supporting Information, Fig. S1, Fig. S2). Of course, in order to be consistent with the cyclic voltammetric data, the potential was determined vs Fe/Fe\(^+\) instead of vs Ag/AgCl. Ag/AgCl system has a difference in the electrical potential about \(-0.9 \) V vs Fe/Fe\(^+\) system\(^{20}\). The potential of 1.3 V vs Ag/AgCl was estimated as \(+0.4 \) V vs Fe/Fe\(^+\). The Soret band at around 420 nm decreased and the porphyrin radical cation peaks at around 466 nm gave rise upon applied voltage from 0 to 1.3 V (blue line to red line). As for the radical cation peak of the porphyrin (red line), the absorbance of free porphyrin 1 (thin red line) is at 466 nm the same as that of sandwich type 1:1 complex involving porphyrin 1 (dotted red line), but the radical cation peak of 1:2 host-guest external monodentate complex (thick red line) shifted to 470 nm (Supporting Information, Fig. S3); again, this provides support for the notion that the sandwich type 1:1 complexed porphyrin 1 releases 2 after being subject to a cooperative two-oxidation processes. Finally, from a plot for increase of 470 nm absorbance vs [2] upon applied voltage of 1.3 V, the binding constant \( K \) within a 1:2 host-guest external monodentate complex was estimated by a Benesi-Hildebrand equation\(^{25}\) to be \(1.3 \times 10^3 \) M\(^{-1}\). It was difficult to determine two \( K \) values for two step complexation upon applied voltage. Examination of CPK molecular models assuming an affinity of two zinc porphyrin radical cations\(^{28}\) suggests that 1 may allow guest 2 to approach from the external side of the porphyrin.
CONCLUSION

The present study underscores the appealing notion that molecular tweezers based on calix[4]arene porphyrin conjugate can be used as electrochemically triggered catch & release receptors. Further characterization of this novel molecular tweezers and generalization of the present finding to other systems is currently ongoing.

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Supporting Information

This material is available free of charge via the Internet at http://dx.doi.org/jos.66.10.5650/jos.ess.17027

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