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Switchable Complexation between (*O*-Methyl)$_6$-2,6-helic[6]arene and Protonated Pyridinium Salts Controlled by Acid/Base and Photoacid

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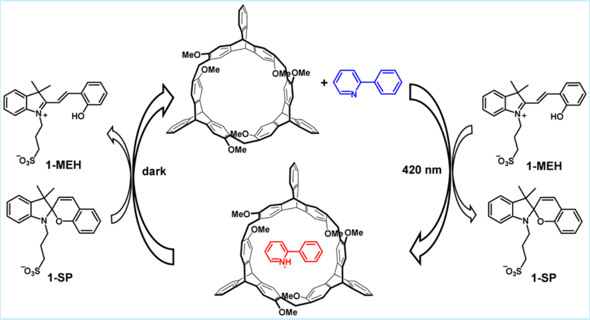
Supporting Information

ABSTRACT: Complexation between (*O*-methyl)$_6$-2,6-helic[6]arene and protonated pyridinium salts was investigated by ^{1}H NMR, ESI-MS, and calculations. It was found that the host and the tested guests could form stable complexes and the binding and release process of the guests in the complexes could be reversibly controlled by acid–base stimulus. Notably, the switchable complexation could also be efficiently controlled by light stimulus in the presence of protonated merocyanine **1-MEH**.



Switchable complexation is a very important and useful process in host–guest systems for its wide applications in the construction of molecular machines,[1] self-healing materials,[2] and responsive supramolecular polymers.[3] In the past decades, various switchable host–guest complexation systems controlled by acid–base,[4] ions,[5] solvents,[6] redox,[7] light,[8] and other stimuli[9] have been reported. Among these stimuli, light response is gaining more and more attention because it is a clean and convenient switchable process. There are three general ways to realize light-responsive behavior: photoisomerization,[10] photochemical reaction,[11] and photoinduced electron transfer.[12] However, these methods all require the host or guest molecules to have special functional groups that are capable of chemical reactions or isomerization under inducement of light or find suitable electron-transfer reactions. These requirements undoubtedly limit their practical applications to some extent. Light-induced proton transfer is a new strategy to realize light-controlled behavior in some host–guest systems that could be responsive to acid and base. Photoacid is a class of chemical species that could release and absorb protons under irradiation of light and dark or heat.[13] It could be used in the field of responsive materials.[14] However, to our knowledge, only one example on the application of photoacid in switchable host–guest complexation was hitherto reported.[15]

Recently, we[16] reported a new kind of macrocyclic arene, 2,6-helic[6]arene, which could form stable complexes with different kinds of quaternary ammonium salts, *N*-heterocyclic salts, and even tropylium cation.[17] Since the helicarene has an electron-rich cavity, we envisaged that its derivatives could also complex with protonated pyridinium salts, and the protonated guests could further provide us an opportunity to investigate the acid–base controlled host–guest complexation.[18] Herein, we report the complexation between (*O*-methyl)$_6$-2,6-helic[6]arene **H** and protonated pyridinium salts **G1**–**G3** (Figure 1). It was found that the binding and release process of the guests in the complexes could be efficiently controlled not only by acid–base stimulus but also by light stimulus in the presence of photoacid **1-MEH**.[19]

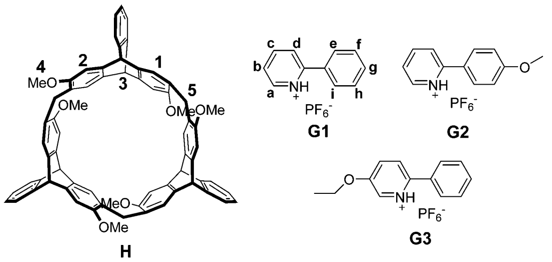


Figure 1. Structures and proton designations of (*O*-methyl)$_6$-2,6-helic[6]arene **H** and guests **G1**–**G3**.

(*O*-Methyl)$_6$-2,6-helic[6]arene **H**[16] and guests **G1**–**G2**[18] were synthesized according to the previously reported methods. **G3** was obtained by treatment of 5-ethoxy-2-phenylpyridine with concentrated HCl in methanol followed by counterion exchange with ammonium hexafluorophosphate in aqueous acetone. The ^{1}H NMR experiments were first carried out to test the complexation between **H** and guests **G1**–**G3**. As shown in Figure 2, when equivalent host **H** and guest **G1** were mixed in $CDCl_3$ and CD_3CN (2:1 v/v), the ^{1}H NMR spectrum showed one new set of proton signals, which was a distinctive

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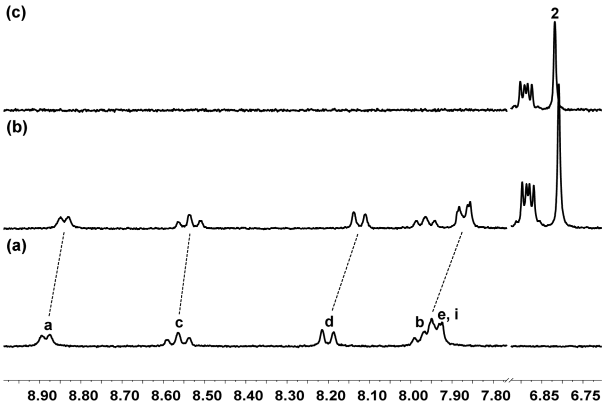

Figure 2. Partial ^{1}H NMR spectra (300 MHz $CDCl_3/CD_3CN$ = 2:1 v/v 298 K) of (a) free guest **G1**, (b) host **H** with 1.0 equiv guest **G1**, and (c) free host **H**. $[\mathbf{H}]_0 = [\mathbf{G1}]_0$ = 1.0 mM.

difference from those of free host **H** and free guest **G1**. These results suggested that the complex **H·G1** could be formed, and the complexation between host **H** and guest **G1** was a fast exchange process on the NMR time scale. Moreover, it was also found that the protons H_a and H_d of guest **G1** showed upfield shifts ($\Delta\delta$ = 0.05 and 0.10 ppm, respectively), while the H_2 signal of host **H** showed a slightly upfield shift ($\Delta\delta$ = 0.01 ppm), which implied that the pyridine part of **G1** might be located in the cavity of host **H**, and the benzene ring of **G1** was located outside the cavity. The ^{1}H NMR spectroscopic titrations further afforded a quantitative estimate for the complexation between host **H** and guest **G1**. Consequently, the stoichiometry of this complex was determined to be 1:1 by a Job plot (Figure S18), and the association constant K_a for the complex **H·G1** was calculated to be $(1.06 \pm 0.09) \times 10^2$ M^{-1}. Similar to the case of **G1**, macrocycle **H** could also form 1:1 complexes with guests **G2**−**G3** in solution (Figures S21 and S24), and the association constants were calculated to be $(3.35 \pm 0.26) \times 10^2$ M^{-1} and 80.02 ± 9.94 M^{-1}, respectively.

The electrospray ionization (ESI) mass spectra could provide more evidence for the formation of the complexes. As a result, the strongest peak at m/z 1134.4724 for $[\mathbf{H{\cdot}G1}]^+$ was found by using the solution of **H** and **G1** in 2:1 (v/v) $CHCl_3$ and CH_3CN (Figure S13), which indicated the formation of a 1:1 stable complex between host **H** and guest **G1**. Similarly, formation of the 1:1 complexes between host **H** and **G2**−**G3** were evidenced by the ESI mass spectra, in which the strong peaks at m/z 1164.4832 and 1178.4970 for $[\mathbf{H{\cdot}G2}]^+$ and $[\mathbf{H{\cdot}G3}]^+$ were found (Figures S14 and S15), respectively.

To explore the complexation mode and gain further insights into the structural characteristics of these complexes, DFT calculations of the complexes at the B3LYP/6-31G level were also carried out. As shown in Figure 3, the pyridine ring of the guest was surrounded by **H**, and the benzene ring of the guest was outside of the ring of the host. The calculated results were consistent with those of the ^{1}H NMR experiments (Figure 2). ESPs of the free host and the free guests provided further evidence for the complexation mode (Figure S39). It was found that the cavity of **H** was electron-rich, and the pyridine rings of the guests were electron-poor. Therefore, it could be inferred that there might exist electrostatic interaction between the two components of the complexes. Meanwhile, the cation···π interaction, N−H···π and C−H···π interactions between the protons on the pyridine ring of **G1** and the benzene rings surrounding the cavity of the host, and C−H···O hydrogen-bonding interaction between the protons of benzene ring of **G1** and the oxygen atom of **H** with the distances ranged from 2.31 to 2.93 Å could also be observed. In the case of **G2**−**G3**, they showed a complexation mode with host **H** similar to that of **G1** (Figures S37 and S38).

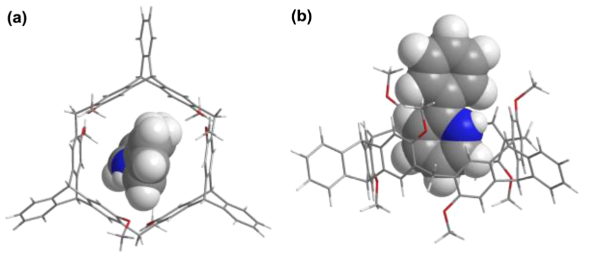

Figure 3. Calculated structure of the complex **H·G1** at the B3LYP/6-31G level. (a) Top view and (b) side view of the complex.

Since pyridine is easily protonated to a pyridinium salt, and vice versa, we envisaged that the association and dissociation of the complexes between macrocycle **H** and guests **G1**−**G3** could be controlled by acid and base reversibly. As shown in Figure 4, it was found that when 1.5 equiv of DBU was added into the solution of complex **H·G1** in CD_3CN, all proton signals of the complexed guest disappeared, and only the proton signals of **H** and the deprotonated **G1** were found (Figure 4c), indicating that the complex was dissociated. When 1.5 equiv of TfOH was added into the above solution, the complex reformed (Figure 4d). Thus, the switchable process between **H** and **G1** could be efficiently controlled by the addition and removal of the acid and base. Similarly, the binding and release process of **G2** and **G3** in their complexes with **H** could also be controlled by acid and base (Figures S25 and S26).

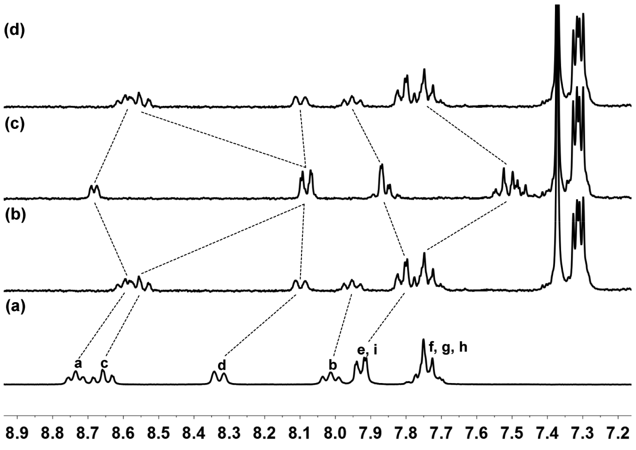

Figure 4. Partial ^{1}H NMR spectra (300 MHz, CD_3CN, 298 K) of (a) **G1**, (b) **G1** + **H** (1.0 equiv), (c) solution of b 1.5 equiv of DBU added, and (d) solution of c 1.5 equiv of TfOH added. $[\mathbf{H}]_0$ = 3.0 mM.

It was known that the photoacid **1-MEH**[19] could undergo a light-induced ring-closing reaction to form the spiropyran **1-SP** and release a proton to the environment. Conversely, **1-SP** could absorb a proton to transform into **1-MEH** in the dark (Figure 5a). Considering that pyridine can be protonated and deprotonated by acid and base, we deduced that if **1-MEH** was used to control formation and deformation of the complexes between host **H** and the protonated pyridinium salt, a switchable host−guest complexation could be efficiently achieved (Figure 5b). Consequently, we further carried out

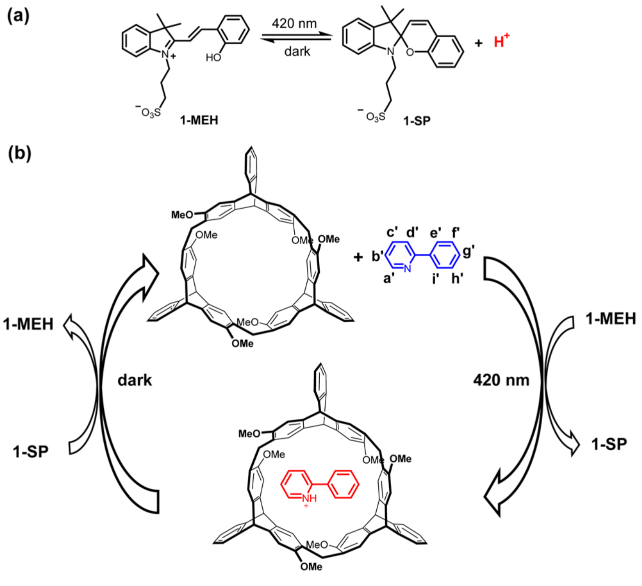

Figure 5. (a) Conversion between **1-MEH** and **1-SP**. (b) Schematic representation of photoacid controlled association and dissociation process.

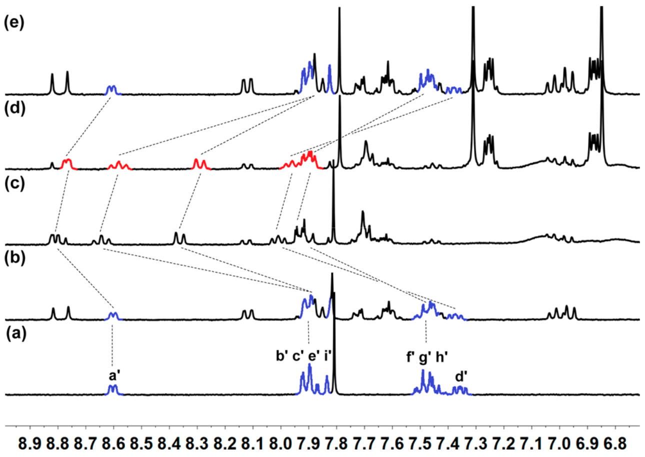

Figure 6. Partial ^1H NMR spectra (300 MHz, MeOD/CDCl$_3$ = 11/1 *v*/*v*, 298 K) of (a) 2-phenylpyridine, (b) 2-phenylpyridine + **1-MEH** (1.2 equiv) before irradiation, (c) solution of b irradiated for 5 min with 420 nm light, (d) solution of c 1.0 equiv of **H** added, and (e) solution of d placed under dark conditions for 120 min. $[\mathbf{H}]_0 = [\mathbf{G1}]_0$ = 3.0 mM.

the ^1H NMR spectral experiments. As shown in Figure 6, when 1.2 equi of **1-MEH** was added into the solution of 2-phenylpyridine, no changes of the proton signals of the neutral guest were found (Figure 6b). But after the solution was irradiated by 420 nm light, the proton signals of 2-phenylpyridine shifted downfield significantly, suggesting that 2-phenylpyridine was protonated by the photoacid to form the protonated salt (Figure 6c). Then, when 1.0 equiv **H** was added into the above solution, the proton signals of the protonated guest all upshifted (Figure 6d), which indicated that the complex between **H** and the guest formed. When the above solution was placed under dark conditions for 120 min, it was found that all proton signals of the guest were back to the original places (Figure 6e), suggesting that the complex dissociated into host **H** and 2-phenylpyridine. These results indicated photoacid **1-MEH** could be used to efficiently control the formation and deformation of the complexes between host **H** and the protonated pyridinium salt. Similarly, the formation and deformation of complexes **H·G2** and **H·G3** could also be controlled by light in the presence of photoacid **1-MEH** (Figures S27 and S28). Moreover, it was further found that this reversible process could be repeated more than 10 times (Figures S29–S31).

In conclusion, we have demonstrated that the (*O*-methyl)$_6$-2,6-helic[6]arene can form stable complexes with the protonated pyridinium salts, which were evidenced by the ^1H NMR, ESI-MS spectra, and calculations. We also found that the binding and release process of the guests in the complexes could be efficiently controlled by acid–base stimuli. In particular, it was found that photoacid **1-MEH** could be used to efficiently control the association and dissociation of the complexes, which represents a new kind of photoacid stimuli-responsive host–guest system and is also the first photoacid controlled host–guest complexation based on protonated pyridinium salts. The results presented herein could provide an opportunity to further construct photoacid-driven molecular machines and responsive supramolecular materials based on the 2,6-helicarene derivatives, which are underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01296.

> Synthetic routes and characterization data of new compounds; ^1H NMR titration studies and theoretical calculations; acid–base and photoacid controlled binding and release process of the guests (PDF)

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Notes

The authors declare no competing financial interest.

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