JOC The Journal of Organic Chemistry

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A1/A2-Diamino-Substituted Pillar[5]arene-Based Acid–Base-Responsive Host–Guest System

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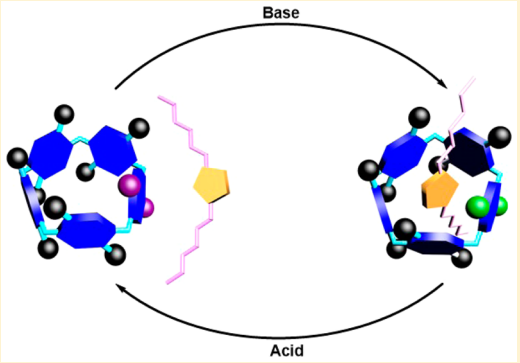
Supporting Information

ABSTRACT: An acid–base-responsive supramolecular host–guest system based on a planarly chiral A1/A2-diamino-substituted pillar[5]arene (**1**)/imidazolium ion recognition motif was created. The pillar[4]arene[1]-diaminobenzene **1** can bring an electron-deficient imidazolium cation into its cylindrically shaped cavity under neutral or basic conditions and release it under acidic conditions.



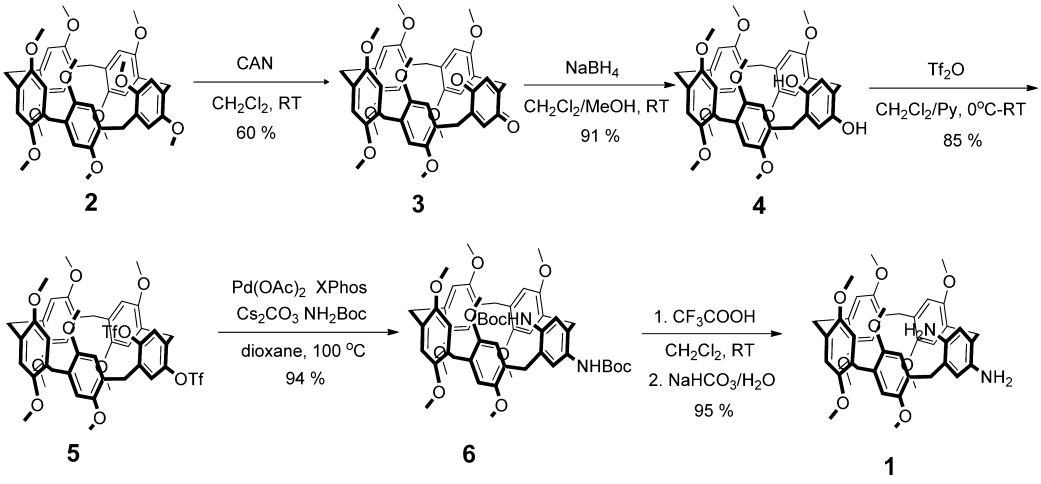
INTRODUCTION

Stimuli-responsive host–guest systems, which exhibit controlled host–guest association/dissociation triggered by external stimuli, such as pH, light, and redox state, are one of the major research focuses of supramolecular chemistry.[1] Building up novel host–guest molecular recognition motifs with high fidelity and responsiveness will certainly contribute to the development of molecular electronics,[1b,2] molecular muscles,[3] organocatalysts,[4] and organogels.[5] Synthetic macrocycles, such as crown ethers,[6] cyclodextrins,[7] calixarenes,[8] cucurbiturils,[9] and cyclophanenes,[10] have long been used as host components in stimuli-responsive host–guest systems. Among them, pillar[*n*]-arenes are a relatively new class of such host molecules, which are usually composed of 5–10 hydroquinone units linked by methylene bridges at *para*-positions.[11] Owing to the tubular-shaped electron-rich cavity structures of pillar[*n*]arenes, numerous host–guest systems consisting of pillar[*n*]arenes and electron-deficient or neutral guest species have been reported,[12] and some of them have already found applications in sensing,[13] separations,[14] artificial transmembrane channels,[15] and drug delivery.[16] Pillar[*n*]arene-based stimuli-responsive host–guest molecular recognition motifs, with the binding/releasing of guest species controlled by light, pH, or redox state, have been developed through mounting various functional groups on the rims of pillar[*n*]arene hosts and selecting guest species with appropriate sizes and functionalities.[17] Among the reported pillar[*n*]arene-based stimuli-responsive host–guest molecular recognition motifs, most of the functional substituents are connected to the aromatic units of pillar[*n*]arenes through C–O, but the examples of connecting functional groups to the aromatic units of pillar[*n*]arenes through linkages other than C–O bonds are rare.[18] We envisioned that mounting amino groups directly to the aromatic units of pillar[*n*]arene through C–N bond formation could provide unique synergistic advantages to pillar[*n*]arene functionalization, as well as novel pillar[*n*]arene-based stimuli-responsive host–guest molecular recognition motifs. However, direct installation of amino functionalities on the aromatic units of pillar[*n*]arenes has been proven quite challenging thus far. The only reported success was Stoddart and co-workers' introduction of two primary amino functions at the positions *ortho* to the hydroxyl groups of an A1/A2-dihydroxypillar[5]arene,[19] but there are no reports on direct replacement of any alkoxy groups at the rims of pillar[*n*]arenes by amino functionalities. What we are reporting herein is a successful synthesis of A1/A2-diamino-substituted pillar[5]arene (**1**), which was achieved through replacement of two A1/A2-alkoxy groups of pillar[5]-arene **2** by primary amino functions, and, more importantly, development of an acid–base stimuli-responsive host–guest system based on this diamino-substituted pillar[5]arene **1** and an imidazolium ion, 1,3-dihexyl-1*H*-imidazol-3-ium (**G**). In this stimuli-responsive host–guest system, modulation of the electronic constitution of the aromatic units of the *para*-

Received: March 23, 2016
Published: April 18, 2016

DOI: 10.1021/acs.joc.6b00617
J. Org. Chem. 2016, 81, 3877–3881

Scheme 1. Synthesis of Pillar[4]arene[1]diaminobenzene 1



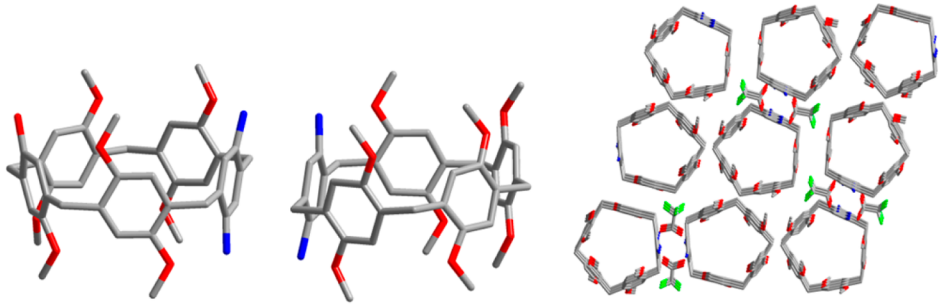


Figure 1. (a) Crystal structures of the two planar enantiomers of pillar[4]arene[1]diaminobenzene **1**, hydrogen atoms are omitted; and (b) chiral one-dimensional channels formed by the two planar enantiomers (**1**). Color code: O (red), N (blue), F (green), and C (gray).

pentacyclophanene **1** was realized through protonation/deprotonation of the amino functionalities, giving the motif acid–base stimuli-responsive host–guest property.

RESULTS AND DISCUSSION

Our work started from the synthesis of A1/A2-diamino-substituted pillar[5]arene **1** (Scheme 1). The synthesis began with a highly selective and efficient partial oxidation of 1,4-dimethoxypillar[5]arene **2** which yielded pillar[4]arene[1]-quinone (**3**).[20] The quinone unit in **3**, obtained through the selective oxidation of the two A1/A2-alkoxy groups, was reduced to *para*-diphenol which was then treated with triflic anhydride to form a bistriflate unit in pillar[4]arene[1]bistriflate **5**.[18,21] The coupling of **5** and *tert*-butyl carbamate by means of a Buchwald-Hartwig reaction gave a Boc-protected pillar[4]-arene[1]diaminobenzene (**6**) in excellent yield.[22] Removing the Boc protective groups of **6** with CF_3COOH resulted in trifluoroacetic salt of pillar[4]arene[1]-diaminobenzene (**1**) which was characterized by ^1H and ^{13}C NMR spectroscopy and HR-ESI mass spectrometry (Supporting Information). The whole synthesis started from pillar[5]arene and **2** was achieved in 40% overall yield. Single crystals of partially protonated **1** were obtained in a mixed solvent of dichloromethane and isopropyl ether, and the structure of the protonated **1**, established by X-ray diffraction analysis, indicated that the A1/A2 methoxy groups at one hydroquinone unit in pillar[5]-arene **2** have been replaced by protonated amino functionalities, and protonated pillar[4]arene[1]diaminobenzene **1** exists as a pair of conformational enantiomers, (*p*R, *p*S, *p*S, *p*S, *p*S) and (*p*S, *p*R, *p*R, *p*R, *p*R), due to the molecule's planar chirality (Figure 1).[23] In the solid state, pillar[5]arene molecules (**1**) are packed by formation of chiral one-dimensional channels (Figure 1), which are completely different from those in **2**.[11a] Pillar[5]arene **1** in free base form is stable in $CHCl_3$ for a few hours, but could be easily oxidized in the air, while the protonated pillar[5]arene **1** is stable both in the air and in solution. The interconversion of the two enantiomers of **1** is at a rate faster than ^1H NMR time scale at room temperature in CD_2Cl_2, as only one set of sharp proton signals was observed in the ^1H NMR spectrum of **1** at room temperature (Supporting Information).

In order to investigate the host–guest behavior of **1** using a ^1H NMR spectroscopic method, 1,3-dihexyl-1*H*-imidazol-3-ium **G** (Figure 2), an imidazolium ion, a good guest species of pillar[5]arenes reported previously,[24] was selected as a model guest to study its interaction with **1**. As shown in Figure 3, the

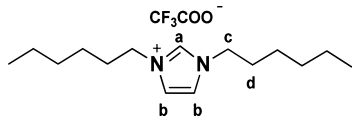


Figure 2. Molecular structure of the imidazolium guest, 1,3-dihexyl-1*H*-imidazol-3-ium G.

DOI: 10.1021/acs.joc.6b00617
J. Org. Chem. 2016, 81, 3877–3881

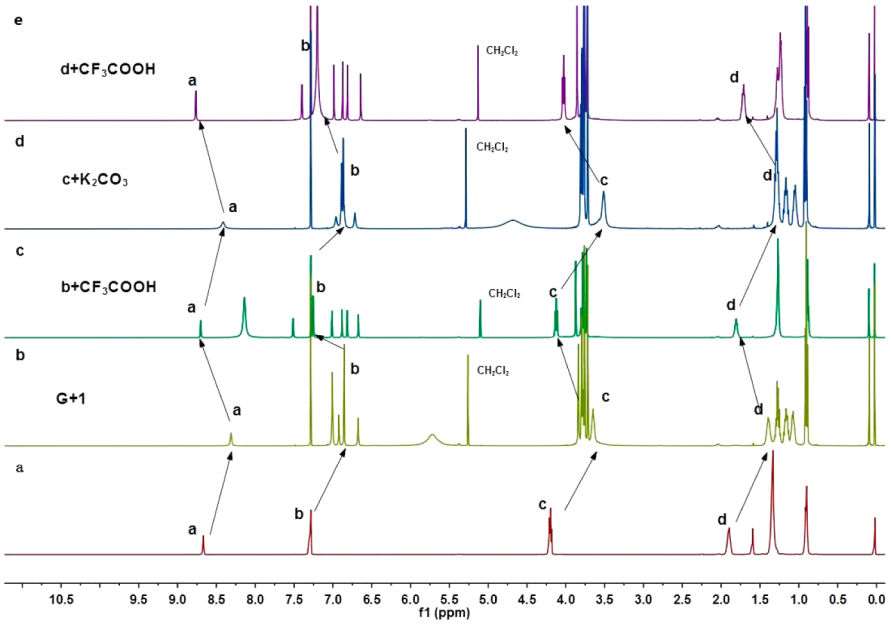
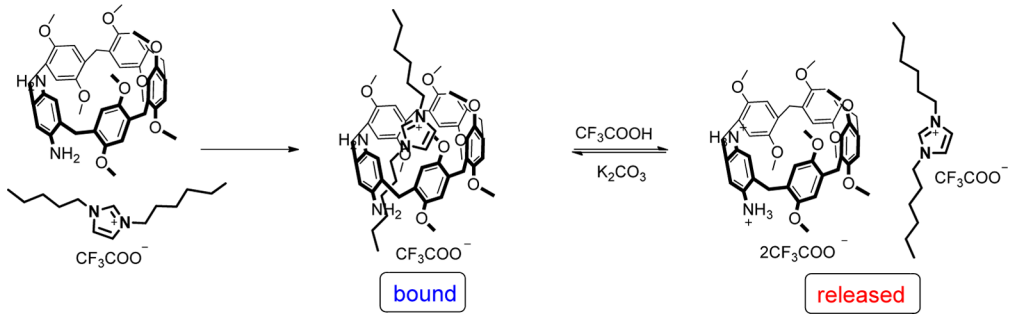


Figure 3. ^{1}H NMR spectra (500 MHz, $CDCl_3$): (a) 10 mM **G**; (b) 10 mM **G** and 10 mM **H**; (c) addition of excessive CF_3COOH in b; (d) addition of excessive K_2CO_3 in c; and (e) addition of excessive CF_3COOH in d.

Scheme 2. Schematic Representation of Reversible Binding/Releasing of G Controlled by Protonation/Deprotonation of the Two Primary Amino Functions of 1



^{1}H NMR spectrum of an equimolar mixture of **G** and freshly prepared host **1** (in $CDCl_3$) showed obvious upfield shifts (−0.35, −0.45, −0.54, and −0.50 ppm) for proton signals of H_a, H_b, H_c, and H_d of G, suggesting formation of a threaded [2]pseudorotaxane structure **G⊂1**. The ^{1}H NMR NOESY spectrum of the complex (**G⊂1**) showed NOE correlations between protons H_a, H_b, H_c, and H_d of G and the methoxyl protons of **1** (Supporting Information, Figure S10), supporting the assignment of a threaded structure (**G⊂1**). A Job plot (Supporting Information, Figure S11) based on ^{1}H NMR data also provided evidence of the formation of a 1:1 complex between **1** and **G** in $CDCl_3$, which was further confirmed by ESI-HRMS spectrometry of *m*/*z*: 957.5738, assigned to $[\mathbf{G}\subset\mathbf{1} - CF_3COO^-]^+$ (calcd. for $C_{58}H_{77}N_4O_8$ 957.5736) (Supporting Information, Figure S12). The association constant (*K*a) of **G⊂1** in $CDCl_3$ was determined to be 205.0 ± 20.0 M^{-1} with a ^{1}H NMR titration method (Supporting Information, Figures S13 and S14), so the binding strength is considered a weak one when compared to that of an imidazolium cation to **2** in $CHCl_3$ (1.04 (±0.15) × 10^3 M^{-1}).[24c]

Since amino groups can be easily protonated, substituting the alkoxy groups by amino functions should be able to change the electronic properties as well as the host−guest behaviors of pillar[5]arene cavities through protonating the amino groups. For example, protonation of the amino groups of **1** would change the electron-rich cavity of **1** to an electron-deficient (positively charged) one. As a result, the host−guest property of the protonated **1** would be completely different from that of the neutral **1**. Since protonation and deprotonation of the amino functions can be reversibly controlled by alternate addition of an acid and a base, the controlled binding and release of the guest **G** should therefore be able to be reversibly manipulated. In order to prove this assumption, CF_3COOH was added to the host−guest complex **G⊂1** solution in $CDCl_3$. ^{1}H NMR analysis indicated that the signals of protons H_a, H_b, H_c, and H_d of **G** were shifted back to the positions of free **G** (Figure 3C), showing dissociation of guest **G** from the cavity of protonated **1**. Upon neutralization of the acidic solution of **1** by addition of K_2CO_3, the proton signals of **G** (H_a, H_b, H_c, and H_d) shifted back to the positions corresponding to complex **G⊂1**, a clear evidence of rebinding of **G** by the deprotonated **1** (Figure 3D). It was found in the study that addition of CF_3COOH again into the **G⊂1** solution resulted in the signals shifting back to the positions of free **G**. This result indicated that the releasing and binding of guest **G** by **1** were able to be reversibly controlled by the addition of TFA and K_2CO_3 alternately. Although the proton signals of **1** in ^{1}H NMR

DOI: 10.1021/acs.joc.6b00617
J. Org. Chem. 2016, 81, 3877−3881

spectra became unclear after two cycles of controlled guest binding and releasing due to instability of the diamino-substituted pillar[5]arene **1**, the base-acid regulated binding-releasing of **G** was well verified experimentally (Scheme 2).

CONCLUSION

In conclusion, we have developed an acid−base-responsive supramolecular host−guest system based on an A1/A2-diamino-substituted pillar[5]arene (**1**)/1,3-dihexyl-1*H*-imidazol-3-ium (**G**) molecular recognition motif, in which imidazolium ion **G**, threaded in the tubular cavity of **1** under basic or neutral conditions, was able to be released from the positively charged cavity in an acidic environment. The novel and efficient synthesis of **1** described in this report is the first reported direct replacement of the two A1/A2-alkoxy groups of pillar[5]arene **2** by primary amino functions, which would facilitate the development of new supramolecular systems and functional materials.

EXPERIMENTAL SECTION

General. Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at 400 or 500 MHz spectrometers with TMS as the reference. HRMS spectra were recorded on a micrOTOF-Q spectrometer (ESI). Single crystal X-ray diffraction data were collected on a X-ray diffractometer equipped with a normal focus Mo-target X-ray tube (λ = 0.71073 Å). Data reduction included absorption corrections by the multiscan method. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically.

Pillar[5]arenes **2**, **3**, and **4** (Scheme 1) were prepared according to the reported procedures.[11a,18,20,21]

Pillar[4]arene[1]bistriflate (5).[18b] To a solution of **4** (600.0 mg, 0.83 mmol) and pyridine (0.28 mL, 275.0 mg, 3.48 mmol) in CH_2Cl_2 (200 mL) was added triflic anhydride (0.28 mL, 469.6 mg, 1.66 mmol) at 0 °C, resulting in a mixture which was stirred at room temperature for 24 h, washed with aqueous HCl solution (1.0 M, 3 × 50 mL), and concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1 (v/v)) to afford **5** as white solid (671.2 mg, 82%); mp 106.6−107.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (s, 2H), 6.88 (s, 2H), 6.85 (s, 2H), 6.84 (s, 2H), 6.76 (s, 2H), 3.96−3.80 (m, 10H), 3.78 (s, 6H), 3.75 (s, 6H), 3.73 (s, 6H), 3.68 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.9, 150.7, 150.7, 150.5, 146.2, 133.9, 129.7, 128.4, 127.9, 124.5, 124.1, 122.4, 119.8, 117.3, 114.8, 113.9, 113.8, 113.6, 55.7, 55.7, 55.7, 55.1, 52.6, 30.5, 29.5, 29.4, 29.2. HRMS (ESI): calcd for $C_{45}H_{45}F_6O_{14}S_2$ $[M + H]^+$ 987.2149, found 987.2150; calcd for $C_{45}H_{48}F_6NO_{14}S_2$ $[M + NH_4]^+$ 1004.2415, found 1004.2415.

Boc-Protected Pillar[4]arene[1]diaminobenzene (6). A mixture of compound **5** (652.0 mg, 0.66 mol), Cs_2CO_3 (861.0 mg, 2.64 mmol), XPhos (95.2 mg, 0.20 mmol), $Pd(OAc)_2$ (15.0 mg, 0.066 mmol), and NH_2Boc (295.6 mg, 2.64 mmol) in dioxane (200 mL) was heated to 100 °C under nitrogen for 4 h, filtered, and concentrated to result in a residue which was subjected to column chromatography (EtOAc/petroleum ether =1/20 (v/v)) to afford **6** as white solid (570.7 mg, 94%); decomposed at 177 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (s, 2H), 7.73 (s, 2H), 6.90 (s, 2H), 6.86 (s, 2H), 6.83 (s, 2H), 6.71 (s, 2H), 4.02 (m, 2H), 3.86 (s, 6H), 3.84−3.68 (m, 24H), 3.47 (m, 2H), 1.73−1.43 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.6, 151.7, 150.7, 150.7, 148.5, 131.3, 129.6, 128.9, 128.3, 127.6, 126.9, 122.4, 114.2, 114.1, 114.0, 113.7, 79.3, 56.1, 55.9, 55.9, 55.8, 30.9, 30.1, 29.3, 28.6. HRMS (ESI): calcd for $C_{53}H_{68}N_3O_{12}$ $[M + NH_4]^+$ 938.4798, found 938.4798.

Pillar[4]arene[1]diaminobenzene (1). To a solution of **6** (460.0 mg, 0.50 mmol) in CH_2Cl_2 (50 mL) was added CF_3COOH (2.0 mL) resulting in a mixture which was stirred at room temperature for 24 h, washed with 10% $NaHCO_3$ solution (2 × 10 mL) and brine (2 × 5 mL), and then concentrated to afford a crude product. Recrystallization of the crude product in CH_2Cl_2 and PE afforded **1** as colorless solid (342.2 mg, 95%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.15 (s, 2H), 7.02 (s, 2H), 6.93 (s, 2H), 6.90 (s, 2H), 6.63 (s, 2H), 4.20−3.89 (m, 2H), 3.89−3.67 (m, 30H), 3.32 (s, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 151.8, 150.3, 150.3, 148.2, 129.9, 128.3, 127.8, 125.1, 114.5, 113.2, 113.2, 112.3, 56.5, 55.5, 55.4, 31.6, 30.7, 29.4, 29.2. HRMS (ESI): calcd for $C_{43}H_{49}N_2O_8$ $[M + H]^+$ 721.3489, found 721.3492.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00617.

Spectroscopic data for new compounds and complexes, titration protocol, Job plots, and determination of the association constants (PDF)

X-ray crystallographic data of **1** (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (21371177) and the "Strategic Priority Research Program" of the Chinese Academy of Sciences (XDA01020304).

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DOI: 10.1021/acs.joc.6b00617
J. Org. Chem. 2016, 81, 3877−3881