JOC The Journal of Organic Chemistry

Article

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Selectivity and Cooperativity in the Binding of Multiple Guests to a Pillar[5]arene−Crown Ether Fused Tricyclic Host

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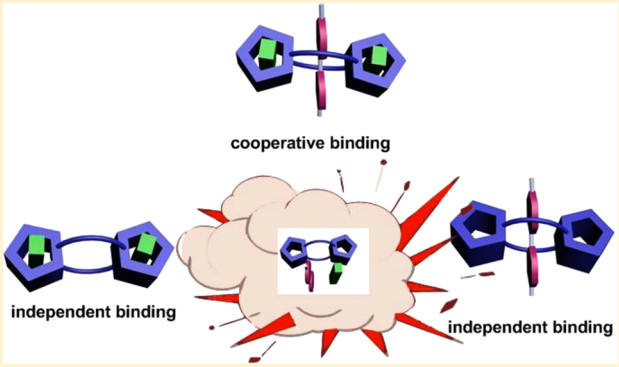
Supporting Information

ABSTRACT: A novel tricylic host molecule **1** that consists of two pillar[5]arene units and a crown ether ring was found to selectively bind two kinds of guest molecules with different shapes, sizes, and electronic constitutions, namely 1,4-dicyanobutane **G1** and paraquat **G2**, with its two macrocyclic subunits, to form a four-component complex **2G1⊂1⊃G2**. An ^{1}H NMR study of stepwise bindings of **G1** and **G2** to host **1** in $CDCl_3$/DMSO-d_6 revealed that the strength of the association between complex **2G1⊂1** and guest **G2** was only one-fourth of that between free **1** and **G2**, demonstrating a negative heterotropic cooperativity of **G1** in the binding of **G2** to host **1**.



INTRODUCTION

Cooperative interactions play a vital role in many natural processes, such as the formation of tobacco mosaic virus (TMV), the allosteric oxygenation of hemoglobin, the regulation of gene expression, as well as protein folding.[1] Mimicking cooperativity chemically would advance our understanding of the cooperative interactions in nature's microscopic events. Therefore, the design and synthesis of artificial receptors that are capable of binding multiple guests in a cooperative manner have been of great interest in the field of supramolecular chemistry.[2] Many macrocyclic receptors of that type have thus been reported. Rowan, Nolte, and co-workers described a double-cavity porphyrin host that displayed negative homotropic allosteric behavior toward viologen ions.[3] A cyclic dimer of a fused porphyrin zinc complex, developed by Aida and co-workers, bound two guest molecules in a cooperative way.[4] Calix[4]pyrrole-based multitopic receptors, recently reported by Sessler and co-workers, showed anion-modulated cation-binding behaviors.[5] However, host molecules composed of topologically different macrocyclic binding sites remain less exploited,[6] possibly due to the difficulties encountered in integrating macrocyclic structures of different geometry and rigidity in an appropriate arrangement. We recently developed a pillar[5]arene−crown ether fused bicyclic host molecule which can discriminatively recognize a 1,4-dicyanobutane molecule by its pillar[5]arene unit and a viologen ion by its crown ether cavity or take up the two guest molecules simultaneously,[7] but no clear cooperativity was displayed by the two guest molecules in their binding to the bidentate host. Herein, we report the formation of a four-component host−guest complex and negative cooperativity displayed by guest molecules in their binding to the tricyclic host molecule **1**, which consists of two pillar[5]arene units and a crown ether ring.

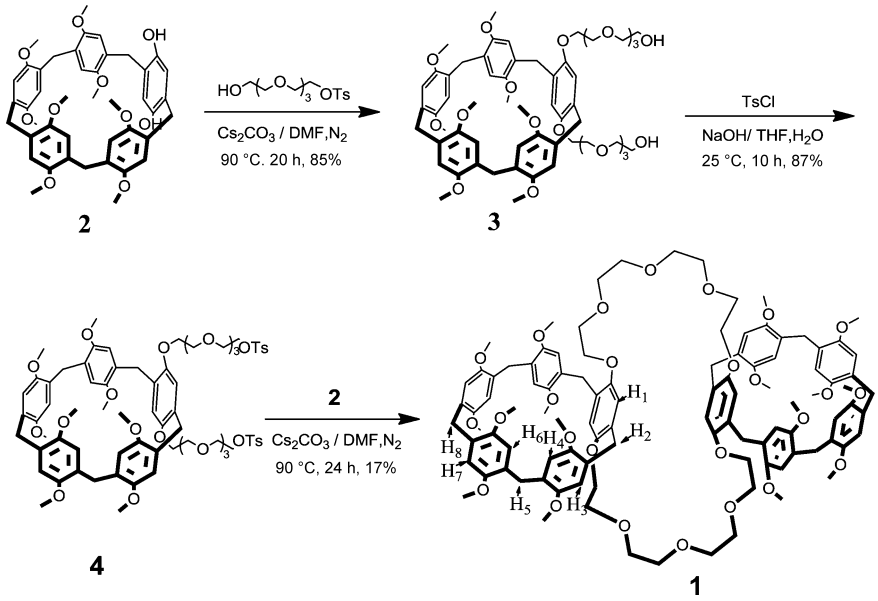
RESULTS AND DISCUSSION

Synthesis of Pillar[5]arene−Crown Ether Fused Tricyclic Host. Synthesis of the pillar[5]arene−crown ether fused tricyclic host **1** is shown in Scheme 1. Dihydroxylated pillar[5]arene **2**, prepared by following a modified literature procedure,[8] was alkylated with tetraethylene glycol monotosylate under basic conditions to give the diol **3**, which was then reacted with tosyl chloride to generate the corresponding

Received: May 11, 2015
Published: July 28, 2015

DOI: 10.1021/acs.joc.5b01038
J. Org. Chem. 2015, 80, 7994−8000

Scheme 1. Synthesis of the Pillar[5]arene–Crown Ether Fused Tricyclic Host 1



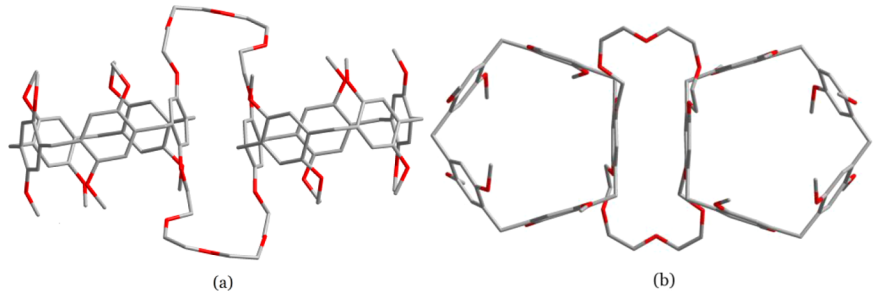


Figure 1. Single crystal structure of **1**: (a) side view, (b) top view. Color code: C (gray), O (red). Hydrogen atoms have been omitted for clarity.

bistosylate **4**. The [1 + 1] macrocyclization reaction of **4** with **2** afforded the desired tricyclic host **1**, which was characterized by ^{1}H NMR, ^{13}C NMR, HR-MS spectrometry, and single-crystal X-ray diffraction analysis. The crystal structure of **1** (Figure 1) clearly revealed its two independent pillar[5]arene moieties and crown ether macrocyclic binding domain.

Host–Guest Interaction between 1 and G1. Since crown ethers[9] and pillararenes[10] are macrocycles with different shapes, rigidities, and guest-binding behaviors, guest-binding behavior of pillar[5]arene and crown ether macrocyclic subunits of **1** was investigated using two different guest molecules, 1,4-dicyanobutane **G1**[11] and paraquat ($\mathbf{MV^{2+}}$) **G2** (Figure 2),[12] respectively. The host–guest interaction between

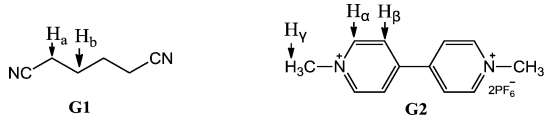


Figure 2. Guest molecules of **G1** and **G2**.

1 and **G1** was thus examined in $CDCl_3$ by an ^{1}H NMR spectroscopic method. As shown in Figure 3, upon mixing **1** and **G1** in 1:2 or 1:4 molar ratios in $CDCl_3$, a significant upfield shift of H_a and H_b of **G1** ($\Delta\delta$ = −2.74 and −3.27 ppm, respectively) caused by the strong shielding effect of the tubular cyclophane was observed, suggesting the formation of a threaded host–guest complex between the pillar[5]arene cavities of **1** and **G1**. A 1:2 stoichiometry between host **1** and guest **G1** (**2G1⊂1**) was confirmed by integration of the proton peaks in the ^{1}H NMR spectrum, which means each of the two pillar[5]arene cavities in **1** hosted one guest molecule of **G1**. The broadening of the **G1** methylene proton peaks indicated slow guest exchange on the NMR time scale. Moreover, a downfield shift ($\Delta\delta$ = 0.590 and 0.440 ppm for H2, the two H2 protons were positioned in different magnetic environments) for the proton signals of the bridging methylene groups pillar[5]arene in **1** was observed, possibly resulted from dipole interactions between the pillar[5]arene subunits of **1** and guest **G1**. In the 2D NMR NOESY spectrum of the 1:2 mixture of **1** and **G1** in $CDCl_3$ (Figure S1), the strong NOE effect between the entrapped **G1** methylene (H_a and H_b) and the pillar[5]arene aromatic protons of **1**, as well as correlation between the protons of **G1** methylene (H_a and H_b) and the protons of pillar[5]arene bridging methylene, were observed, which further supported the assignment of a threaded structure of the three-component complex (**2G1⊂1**). The absence of an NOE effect between the **G1** methylene protons and the protons of ethylene glycol chains of **1** suggested no existence of host–guest interaction between the crown ether unit of **1** and **G1**. No free guest was observed in the ^{1}H NMR spectrum of the 1:2 mixture of **1** and **G1**, implying very strong binding affinities between the tubular pillar[5]arene cavities of **1** and **G1** in $CDCl_3$. Thus, it is not feasible to calculate the binding constant between **1** and **G1** in $CDCl_3$.[11] Single crystals of the

DOI: 10.1021/acs.joc.5b01038
J. Org. Chem. 2015, 80, 7994–8000

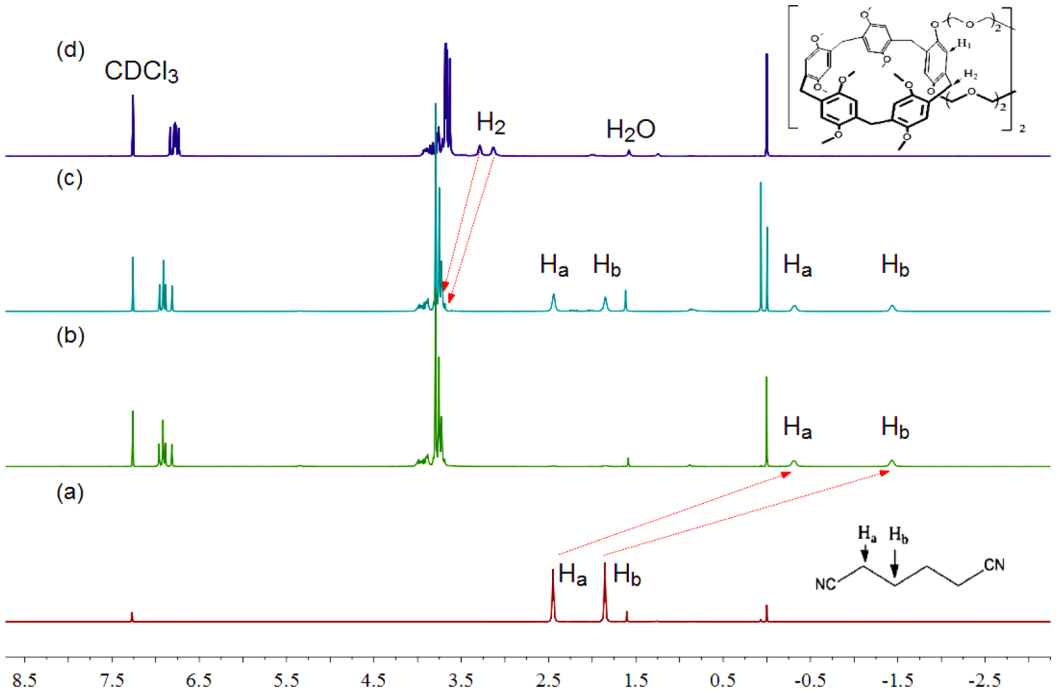


Figure 3. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) free **G1** (16.0 mM), (b) **1** (4.0 mM) + **G1** (8.0 mM), (c) **1** (4.0 mM) + **G1** (16.0 mM), (d) free **1** (4.0 mM).

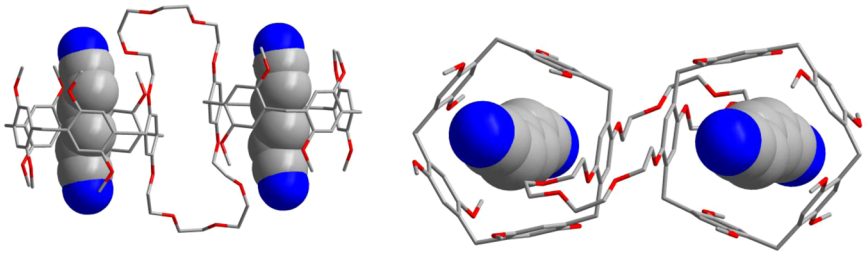


Figure 4. Single crystal structure of **2G1⊂1**: (a) side view, (b) top view. Color code: C (gray), O (red), N (blue). Hydrogen atoms have been omitted for clarity.

1:2 host–guest complex **2G1⊂1** were obtained by slow diffusion of *n*-hexane into a $CHCl_3$ solution of a 1:2 host–guest mixture of **1** and **G1**. An X-ray diffraction study performed on the single crystals unambiguously established the threaded [3]pseudorotaxane structure of **2G1⊂1** (Figure 4). The host–guest complex **2G1⊂1** was stabilized by multiple supramolecular interactions including hydrogen bonding and C–H···π interactions between **1** and **G1**.

Host–Guest Interaction between 1 and G2. Due to the poor solubility of paraquat ($MV^{2+}\cdot 2PF_6^-$) **G2** in $CDCl_3$, the host–guest interaction between **1** and **G2** was examined in a mixed solvent of $CDCl_3$ and DMSO-d_6 (v/v, 3:1). A red solution immediately resulted from mixing the colorless solutions of **1** and **G2**, implying the formation of a charge-transfer complex. The complexation behavior was further studied by ^{1}H NMR spectroscopy in $CDCl_3$/DMSO-d_6 (v/v, 3:1). As shown in Figure 5, upfield shifts for α- and β-pyridinium and *N*-methyl proton signals (−0.27, −0.37, and −0.08 ppm) of **G2** were observed in the ^{1}H NMR spectrum of an equimolar mixture of **1** and **G2**, indicating the existence of π-donor/π-acceptor interactions between the hydroquinone planes of the crown ether unit in **1** and the pyridinium rings of **G2**. Moreover, upfield shifts for proton signals of the hydroquinone units (−0.17 ppm) and the pillar[5]arene bridging methylene groups connected to the two hydroquinone units (−0.22 ppm) of the crown ether ring were observed, possibly due to the face-to-face π-stacking and charge-transfer interactions between the two electron-rich hydroquinone rings in the crown ether subunit of **1** and the electron-poor pyridinium planes of **G1**. The splitting of the pillar[5]arene bridging methylene protons (H2) indicated the change of magnetic environment caused by rotational restriction of the hydroquinone units upon formation of the host–guest complex **G2⊂1**. A 2D ^{1}H NMR NOESY spectrum of an equimolar mixture of **1** and **G2** in $CDCl_3$/DMSO-d_6 (v/v, 3:1) also supported the formation of a threaded complex (**G2⊂1**) with the bipyridinium cation of **G2** threading into the crown ether cavity of **1** (Figure S2). Correlation signals between the α- and β-pyridinium and *N*-methyl protons of **G2** and those of the oligoethylene glycol protons of the crown ether of **1**, the β-pyridinium protons of **G2**, and the crown ether hydroquinone protons of **1** were clearly seen in the spectrum. The above data are consistent with a molar ratio plot of the β-pyridinium protons of **G2** with the formation of a 1:1 complex between

DOI: 10.1021/acs.joc.5b01038
J. Org. Chem. 2015, 80, 7994–8000

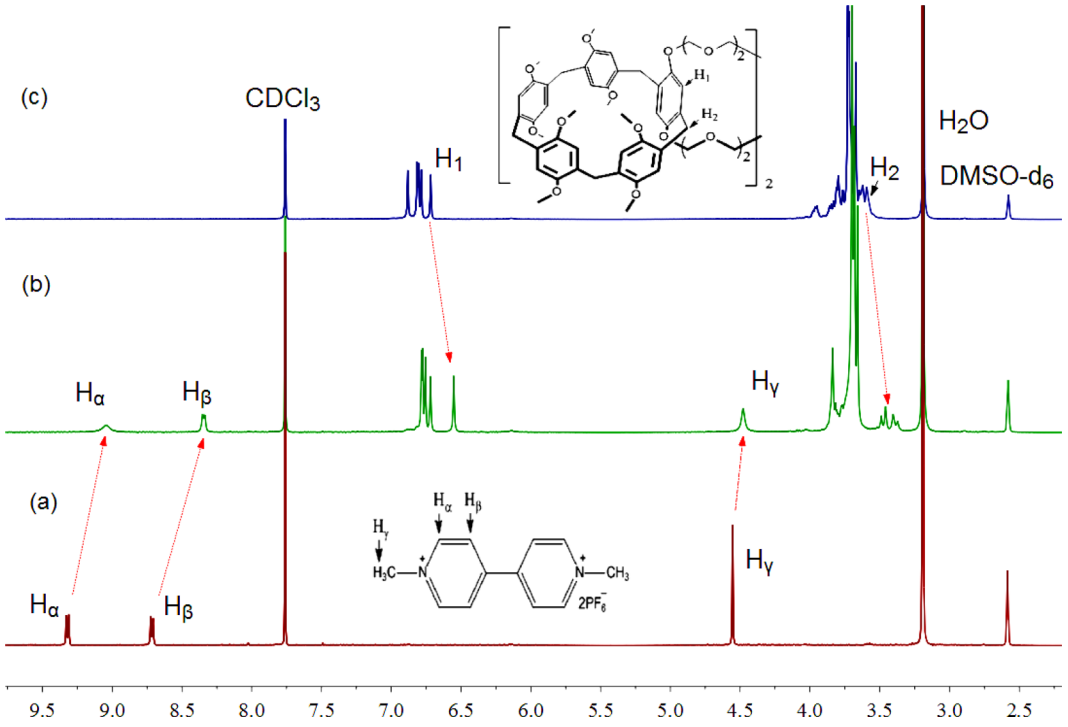


Figure 5. ^{1}H NMR spectra (400 MHz, $CDCl_3$/DMSO-d_6 (v/v, 3:1)) of (a) free **G2** (6.7 mM), (b) **1** (6.7 mM) + **G2** (6.7 mM), (c) free **1** (6.7 mM).

host **1** and guest **G2** obtained by an NMR technique (Figure S3). Excess **G2** did not lead to further binding of **G2** by the pillar[5]arene subunits of **1**.[13] The association constant (K_a) of **G2⊂1** in $CDCl_3$/DMSO-d_6 (v/v, 3:1) was determined to be (9.06 ± 0.78) × 10^2 M^{-1} with a ^{1}H NMR titration method (Supporting Information, Figures S4 and S5). Single crystals of 1:1 host–guest complex **G2⊂1** were obtained by slow evaporation of the 1:1 host–guest mixture in a mixture of chloroform and acetone (v/v, 1:1), and X-ray diffraction analysis unambiguously established a threaded [2]-pseudorotaxane structure **G2⊂1** (Figure 6), which was stabilized by hydrogen bonding, charge-transfer, and π–π stacking interactions.

Simultaneous Complexation of G1 and G2 by the Tridentate Host 1. The simultaneous binding of the two guest species **G1** and **G2** by the tridentate host **1** was examined in $CDCl_3$/DMSO-d_6 (v/v, 3:1). Mixing the tricyclic host **1** and guests **G1** and **G2** in a 1:2:1 molar ratio in $CDCl_3$/DMSO-d_6 (v/v, 3:1) immediately resulted in a bright red solution,

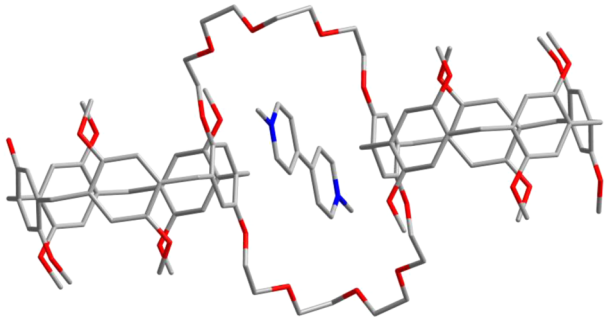


Figure 6. Single crystal structure of [2]pseudorotaxane **G2⊂1**. Color code: C (gray), O (red), N (blue). Hydrogen atoms have been omitted for clarity.

implying the formation of a charge-transfer complex between **1** and **G2**. The complexation behavior between host **1** and guests **G1** and **G2** was further studied with ^{1}H NMR spectroscopy. ^{1}H NMR spectra of host **1**, guests **G1** and **G2**, complexes **2G1⊂1** and **G2⊂1**, and a 1:2:1 molar mixture of **1**, **G1**, and **G2** in $CDCl_3$/DMSO-d_6 (v/v, 3:1) are shown in Figure 7. Significant upfield shift and broadening of signals for H_a and H_b ($\Delta\delta$ = −2.86 and −3.32 ppm, respectively) of **G1** in the mixture of **1**, **G1**, and **G2** are consistent with formation of a threaded host–guest complex between **1** and **G1**, and a 1:2 stoichiometry between **1** and **G1** was confirmed by integration of the proton peaks in the mixture of **1**, **G1**, and **G2**. There were almost no changes for chemical shifts of the protons of **G1** in the mixture of **1**, **G1**, and **G2** compared with those in the mixture of **1** and **G1** (**2G1⊂1**), indicating the presence of **G2** did not affect the binding strength between **1** and **G1**. An upfield shift for the α- and β-pyridinium proton signals of **G2** (−0.18 and −0.39 ppm) was also observed in the mixture of **1**, **G1**, and **G2**, indicating that **G2** also interacted with host **1** in the mixture. In the 2D ^{1}H NMR NOESY spectrum of **1**, **G1**, and **G2** in 1:5:1 molar ratios in $CDCl_3$/DMSO-d_6 (v/v, 3:1) (Figure S6), the methylene protons (H_a and H_b) of **G1** showed strong correlations with those of the pillar[5]arene aromatic protons, the pillar[5]arene bridging methylene protons, and the methoxyl protons of host **1**, which supported the assignment of the threaded structure for the complex **2G1⊂1**. The observed correlations between the signals of the α- and β-pyridinium and *N*-methyl protons of **G2** and those of the protons of oligo-ethylene glycol chains in **1** signified the formation of a threaded complex **G2⊂1**. A Job plot based on ^{1}H NMR data revealed that host **1** and guest **G2** complexed in a 1:1 ratio in the mixture of **1**, **G1**, and **G2** in $CDCl_3$/DMSO-d_6 (v/v, 3:1) (Figure S7). Thus, all of the above data provided strong evidence that the pillar[5]arene and crown ether macrocyclic subunits of the tridentate host **1** can selectively recognize 1,4-dicyanobutane **G1** and paraquat **G2**,

DOI: 10.1021/acs.joc.5b01038
J. Org. Chem. 2015, 80, 7994–8000

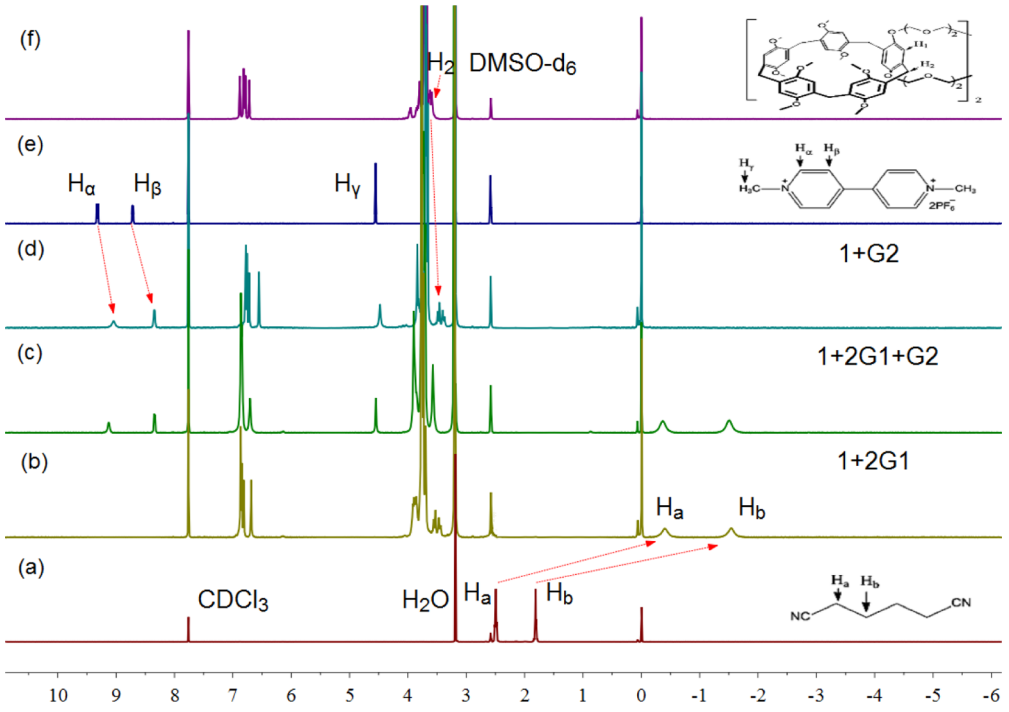


Figure 7. ^{1}H NMR spectra (400 MHz, $CDCl_3$/DMSO-d_6 (v/v, 3:1)) of (a) free **G1** (4.0 mM), (b) **G1** (8.0 mM) + **1** (4.0 mM), (c) **1** (4.0 mM) + **G1** (8.0 mM) + **G2** (4.0 mM), (d) **1** (4.0 mM) + **G2** (4.0 mM), (e) **G2** (4.0 mM), (f) free **1** (4.0 mM).

respectively, or take up the two kinds of guest species (**G1** and **G2**) simultaneously by forming a four component host−guest complex **2G1⊂1⊃G2**. Nevertheless, growing single crystals of complex **2G1⊂1⊃G2** was attempted without success.

The associate constant (K_a) between host **1** and guest **G2** in $CDCl_3$/DMSO-d_6 (v/v, 3:1) was determined to be (2.26 ± 0.17) × 10^2 M^{-1} in the presence of **G1** by a ^{1}H NMR titration method (Figures S8 and S9), which was found to be only one-fourth of that without the presence of **G1**. The decrease of the binding strength between host **1** and guest **G2** in the presence of **G1** suggested the existence of a negative cooperative effect displayed by **G1** in the binding of **G2** to host **1**, which was possibly resulted from the decrease of the strength of π-donor/π-acceptor interactions between the electron-rich hydroquinone planes of the crown ether unit of host **1** and the electron-deficient bipyridinium plane of guest **G2**. Such a decrease was possibly caused by an electron-withdrawing effect exerted on the electron-rich hydroquinone planes of the crown ether ring of host **1** by the electron-deficient cyano groups of **G1**.

CONCLUSION

In summary, we have successfully constructed tricyclic host molecule **1** consisting of two pillar[5]arene subunits and a crown ether macrocycle. 1D and 2D ^{1}H NMR spectroscopic analysis in $CDCl_3$/DMSO-d_6 (v/v, 3:1) indicated that the two pillar[5]arene subunits in **1** could selectively form a double-threaded complex (**2G1⊂1**) with 1,4-dicyanobutane **G1**, while the crown ether ring in **1** could complex with paraquat **G2** to form a stable charge-transfer complex (**G2⊂1**). Moreover, the tricyclic host **1** was capable of simultaneously taking up two **G1** and one **G2**, resulting in the formation of a four-component supramolecular complex **2G1⊂1⊃G2**. Shape and size match between the macrocyclic host motifs and guest species played an essential role in such selectivity. ^{1}H NMR results also showed a negative cooperative binding effect of **G1** toward the binding of **G2** to **1**, possibly caused by the decrease of the π-donor/π-acceptor interaction strength between the electron-deficient bipyridinium plane of guest **G2** and the electron-rich hydroquinone planes of the crown ether ring of host **1**. Taken together, this work demonstrated the usefulness of pillar[5]-arene-based multidentate macrocyclic host molecules in developing multicomponent host−guest systems for studying cooperative interactions. Such systems also hold potential in many applications, such as construction of complex mechanically interlocked molecules, development of sensors for detection of multiple substrates, and fabrication of sophisticated supramolecular polymers.

EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all commercial reagents and solvents were used without purification. Separation by flash column chromatography was performed on silica gel (230−400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer with TMS as the reference. Mass spectra (ESI analysis) were recorded on a spectrometer (LC/MS). 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), and 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, while hydrogen atoms were added at their geometrically ideal positions and refined isotropically.

Synthesis of Compound 3 (Scheme 1). A mixture of **2** (0.722 g, 1.0 mmol), Cs_2CO_3 (3.250 g, 10.0 mmol), and 2-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]ethyl 4-methylbenzenesulfonate (3.480 g, 10.0 mmol) in 150 mL of DMF was heated to 90 °C under nitrogen for 20 h. The reaction mixture was

DOI: 10.1021/acs.joc.5b01038
J. Org. Chem. 2015, 80, 7994−8000

poured into 1 M HCl (300 mL) and extracted with ethyl acetate (3 × 100 mL). The organic phase was combined, washed with brine, and dried over anhydrous sodium sulfate. The solvent was removed, and the residue was purified by silica gel column chromatography using ethyl acetate and petroleum ether (EA/PE = 50/1) as eluent to afford **3** as a white solid (0.914g, yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 2H), 6.81 (s, 8H), 4.02−4.05 (t, 4H), 3.83−3.85 (m, 4H), 3.77(s, 10H), 3.68−3.71 (m, 28H), 3.53−3.55 (m, 4H), 3.43−3.45 (t, 4H), 3.18−3.21 (t, 4H), 3.05−3.06 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.7, 150.6, 150.5, 149.7, 128.5, 128.3, 128.2, 128.1, 128.1, 114.9, 114.2, 113.9, 113.7, 113.6, 71.8, 70.8, 70.6, 70.2, 70.0, 69.5, 67.8, 61.5, 55.9, 55.7, 55.6, 55.5, 29.17, 29.5, 29.4. HR-MS: m/z calcd [M + Na^+] for $C_{59}H_{78}O_{18}$ Na^+ 1097.5057, found 1097.5080.

Synthesis of Compound 4. A solution of sodium hydroxide (0.400 g, 10.0 mmol) in water (10 mL) was added to a mixture of **3** (2.150 g, 2.0 mmol) and *p*-toluenesulfonyl chloride (1.900 g, 10.0 mmol) in THF (70 mL). After the reaction mixture has been stirred at 25 °C for 10 h, it was poured into water (250 mL) and extracted with ethyl acetate (3 × 100 mL). The organic phase was combined, washed with water (2 × 50 mL), and dried over anhydrous sodium sulfate. The solvent was removed, and the residue was purified by silica gel column chromatography using ethyl acetate and petroleum ether (EA/PE = 1/1) as eluent to afford **4** as a white solid (2.40 g, yield 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73−7.75 (d, 4H), 7.07−7.09 (d, 4H), 6.82 (s, 2H), 6.75−6.76 (t, 8H), 4.10−4.12 (t, 4H), 3.61−4.01 (m, 46H), 3.55−3.58 (m, 8H), 3.34−3.36 (d, 8H), 1.98 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.7, 150.6, 150.5, 150.5, 149.8, 145.0, 132.6, 129.9, 128.7, 128.3, 128.2, 128.1, 128.1, 127.6, 115.1, 114.0, 113.9, 113.9, 113.7, 70.8, 70.7, 70.4, 70.2, 70.1, 69.1, 68.5, 68.0, 55.9, 55.7, 55.6, 29.6, 29.4, 29.3, 20.9. HR-MS: m/z calcd [M + Na^+] for $C_{73}H_{90}O_{22}S_2Na^+$ 1405.5261, found 1405.5257.

Synthesis of Compound 1. A mixture of **2** (0.722 g, 1.0 mmol), Cs_2CO_3 (1.300 g, 4.0 mmol), and **4** (1.382 g, 1.0 mmol) in DMF (300 mL) was heated to 90 °C under nitrogen for 24 h. The reaction mixture was poured into 1 M HCl (100 mL) and extracted with dichloromethane (3 × 100 mL). The organic phase was combined, washed with brine, and dried over anhydrous sodium sulfate. The solvent was removed, and the residue was purified by silica gel column chromatography using ethyl acetate and petroleum ether (EA/PE = 1/2) as eluent to afford compound **1** as a white solid (0.300 g, yield 17%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75−6.84 (m, 20H), 3.64−3.92 (m, 84H), 3.30 (s, 8H), 3.15 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 150.8, 150.7, 150.6, 149.8, 128.6, 128.23, 128.1, 128.0, 115.3, 114.3, 114.1, 114.0, 113.7, 70.3, 69.7, 68.0, 55.9, 55.8, 55.6, 29.7, 29.5, 29.3. HR-MS: m/z calcd [M + Na^+] for $C_{102}H_{120}O_{26}$ Na^+ 1783.7992, found 1783.7960.

Crystallographic data of 1: [$C_{51}H_{60}O_{13}$]; M_r = 880.99; T = 296(2) K; monoclinic; space group $P2(1)/n$; a = 12.3918(4) Å; b = 12.0736(4) Å; c = 34.0914(11) Å; α = 90°; β = 94.2900(10)°; γ = 90; V = 5086.2(3) Å^3; Z = 4; ρ_{calcd} = 1.150 g/cm^3; crystal size = 0.35 × 0.27 × 0.15 mm; μ = 0.082 mm^{-1}; reflections collected 58994; unique reflections 8991; data/restraints/parameters 8991; GOF on F^2 0.912; R_{int} for independent data 0.1123; final R_1 = 0.0713, wR_2 = 0.2031; R indices (all data) R_1 = 0.1581, wR_2 = 0.2326; largest diff peak and hole 0.529 and −0.529 e Å^{-3}.

Crystallographic data of 2G1⊂1 (1): [$C_{58}H_{60}Cl_3N_2O_{13}$]; M_r = 1099.43; T = 173(2) K; triclinic; space group P; a = 10.8366(4) Å; b = 13.7308(5) Å; c = 19.8398(8) Å; α = 98.1920(10)°; β = 94.9950(10)°; γ = 98.2110(10)°; V = 2874.55(19) Å^3; Z = 2; ρ_{calcd} = 1.270 g/cm^3; crystal size = 0.29 × 0.13 × 0.04 mm; μ = 0.223 mm^{-1}; reflections collected 33809; unique reflections 10063; data/restraints/parameters 10063/0/685; GOF on F^2 1.037; R_{int} for independent data 0.0393; final R_1 = 0.0949, wR_2 = 0.2609; R indices (all data) R_1 = 0.1382, wR_2 = 0.3060; largest diff. peak and hole 2.026 and −0.865 e Å^{-3}.

Crystallographic data of 2G1⊂1 (2): [$C_{57}H_{70}N_2O_{14}$]; M_r = 1007.15; T = 213 K; monoclinic; space group $C2/c$; a = 16.259(2) Å; b = 17.706(3) Å; c = 37.855(6) Å; α = 90°; β = 96.191(2)°; γ = 90°; V = 10834(3) Å^3; Z = 8; ρ_{calcd} = 1.235 g/cm^3; crystal size = 0.300 × 0.220 × 0.060 mm; μ = 0.088 mm^{-1}; reflections collected 37548; unique reflections 11795; data/restraints/parameters 11795/72/704; GOF on F^2 1.071; R_{int} for independent data 0.0475; final R_1 = 0.0982, wR_2 = 0.3084; R indices (all data) R_1 = 0.1684, wR_2 = 0.3512; largest diff peak and hole 0.618 and −0.436 e Å^{-3}.

Crystallographic data of G2⊂1: [$C_{114}H_{134}F_{12}N_2O_{26}P_2$]; M_r = 2238.17; T = 173 (2) K; monoclinic; space group $P2(1)/c$; a = 12.6946(8) Å; b = 30.8143(19) Å; c = 18.2906(11) Å; α = 90°; β = 93.275(2)°; γ = 90°; V = 7143.1(8) Å^3; Z = 2; ρ_{calcd} = 1.041 g/cm^3; crystal size = 0.47 × 0.21 × 0.18 mm; μ = 0.104 mm^{-1}; reflections collected 82305; unique reflections 12582; data/restraints/parameters 12582/8/703; GOF on F^2 1.078; R_{int} for independent data 0.1044; final R_1 = 0.0998, wR_2 = 0.2943; R indices (all data) R_1 = 0.1489, wR_2 = 0.3235; largest diff peak and hole: 1.676 and −0.940 e Å^{-3}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01038.

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

Crystallographic data of **1** (CIF)

Crystallographic data of **2G1⊂1** (**1**) (CIF)

Crystallographic data of **2G1⊂1** (**2**) (CIF)

Crystallographic data of **G2⊂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, 21071053, 21002031) and the "Strategic Priority Research Program" of the Chinese Academy of Sciences (XDA01020304).

DOI: 10.1021/acs.joc.5b01038
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DOI: 10.1021/acs.joc.5b01038
J. Org. Chem. 2015, 80, 7994−8000