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A Shape-Persistent Cryptand for Capturing Polycyclic Aromatic Hydrocarbons

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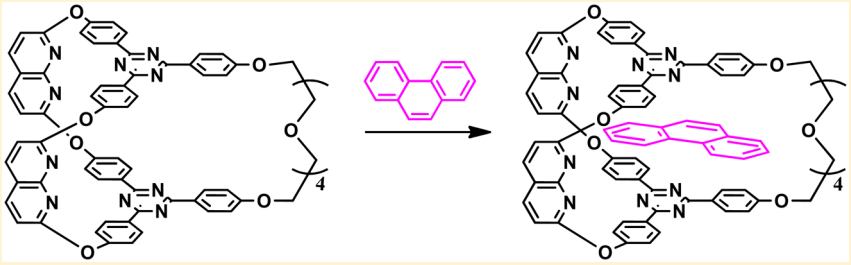
Supporting Information



ABSTRACT: A shape-persistent cryptand **1**, containing two face-to-face oriented electron-deficient 2,4,6-triphenyl-1,3,5-triazine units separated by approximately 7 Å, and bridged by two rigid 1,8-naphthyridine linkers and a pentaethylene oxide loop, is created for capturing polycyclic aromatic hydrocarbons. Cryptand **1** formed 1:1 complexes with PAH guest molecules, such as phenanthrene (**6**), anthracene (**7**), pyrene (**8**), triphenylene (**9**), and tetraphene (**10**). The single-crystal structure of complex **6**⊂**1** revealed that **6** was included in the cavity of **1** via face-to-face $\pi\cdots\pi$ stacking interactions. Soaking crystalline **1** in a toluene solution of anthracene resulted in anthracene from the toluene solution being picked up by the crystalline solid of **1**.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs),[1] consisting of fused aromatic rings that do not contain heteroatoms or carry substituents, are found naturally in oil, coal, and tar or produced as byproducts in fossil fuel combustion processes.[2] PAHs are now believed to be one of the main pollutants and harmful chemical species known on the earth[3] because some smaller PAHs have been found to be carcinogenic, mutagenic, and teratogenic.[4] Human exposure to PAHs is primarily from consumption of contaminated food and water or PAH-containing particulates suspended in air. On the other hand, PAHs are among the most beautiful and fascinating classes of organic compounds.[5,1] Because of their outstanding optical and electronic properties, many PAHs have been widely investigated in potential applications in organic field-effect transistors (OFETs), organic solar cells (OSCs), fluorescence probes, and other optoelectronic devices.[6] Therefore, there is great interest in developing host molecules for PAH binding and detection. Cyclodextrins (CDs),[7] calix[n]arene derivatives,[8] cholic acid,[9] ExBox,[10] and metallocycles[11] have been explored as host molecules for PAHs of various shapes and sizes. Whitlock and co-workers[12] outlined design criteria for the hosts specifically suited for aromatic guests. Such host molecules would contain two aromatic walls separated by a rigid spacer at a distance of approximately 7 Å, permitting favorable $\pi-\pi$ interactions between an aromatic guest molecule and each of the two walls of the receptor cavity. On the basis of this model, many tweezers-like molecules with appropriate geometries and functionalities, capable of binding aromatic guests, have been developed.[13]

As an important class of compounds in host−guest chemistry, cryptands are used to encapsulate large organic guests, such as paraquat derivatives and ammonium salts. Because of the well-defined spatial shapes and cavity sizes, cryptands have shown much higher binding strength toward guest molecules compared to their analogous crown ethers.[14] Because most of the existing cryptand hosts were designed to bind electron-deficient guests, cryptands that could be used to selectively bind electron-rich guests, such as PAHs, are rare.[14a] In this report, we describe a new cryptand **1** that contains two face-to-face oriented electron-deficient 2,4,6-triphenyl-1,3,5-triazine aromatic walls separated by approximately 7 Å, and linked by two rigid 1,8-naphthyridine bridges and a flexible pentaethylene oxide loop, which was intentionally introduced to increase the solubility of **1** in organic solvents. Also described are the complexation between the cryptand **1** and five electron-rich PAHs and soaking the as-synthesized crystalline solid **1** in a toluene solution of anthracene for **1** to pick up anthracene from the solution.

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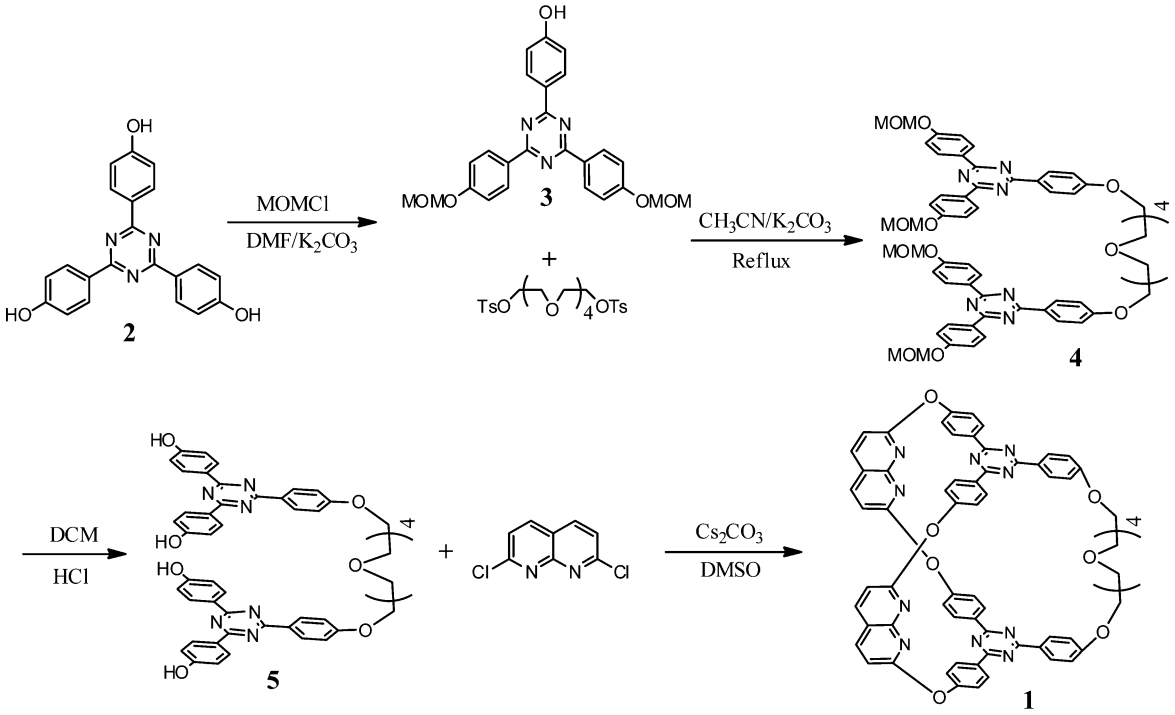
Scheme 1. Synthesis of Cryptand Host 1



RESULTS AND DISCUSSION

Our investigation began from the synthesis of 1,8-naphthyridine-bridged cryptand **1**, which is outlined in Scheme 1 (details in the Supporting Information). Protection of two of the three hydroxyl groups of 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)triphenol (**2**) by chloro(methoxy)methane resulted in phenol **3**, which was reacted with penta(ethylene glycol) bistosylate under basic conditions to generate quadruple methoxymethyl-protected compound **4**. Deprotection of the four methoxymethyl protecting groups of **4** afforded the corresponding tetraphenol **5**. The [1+2] macrocyclization reaction of **5** with 2,7-dichloro-1,8-naphthyridine yielded the desired cryptand **1** that 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 sandwichlike structure with the two face-to-face oriented electron-deficient 2,4,6-triphenyl-1,3,5-triazine aromatic units separated by approximately 7 Å, which is a distance longer than those of previously reported trigonal prismatic bicyclocalixaromatics,[15] and the triazine-walled cavity was filled by two molecules of chloroform, the solvent in which the crystals were harvested. In the solid state, cryptand **1** molecules were packed in layered fashion and formed one-dimensional channels (filled by $CHCl_3$) by appropriate alignment of the windows of the cavity of **1** within each layer (Figure 1). The spaces formed between molecules of **1** within each layer were occupied by solvent molecules (cyclohexane).

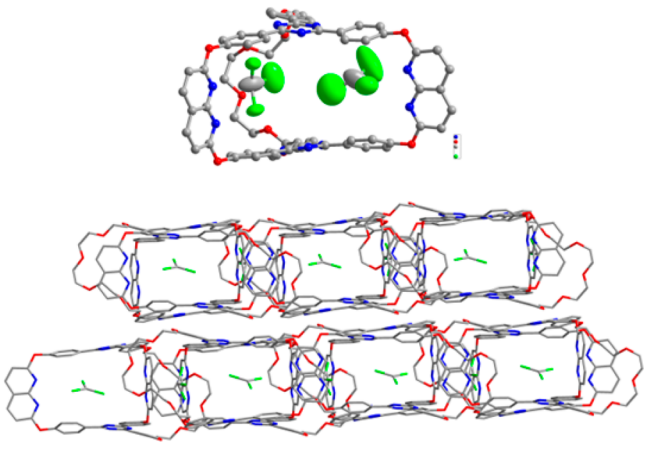


Figure 1. Crystal structure of cryptand **1** (top) and one-dimensional channels formed by appropriately aligning the cavities of **1** in the solid state (bottom). Color code: gray for C, blue for N, red for O, and green for Cl. Hydrogen atoms have been omitted for the sake of clarity.

With synthesized cryptand **1** in hand, the interaction between cryptand **1** and five electron-rich PAH guests, phenanthrene (**6**), anthracene (**7**), pyrene (**8**), triphenylene (**9**), and tetraphene (**10**) (Figure 2), was investigated via one-dimensional (1D) and

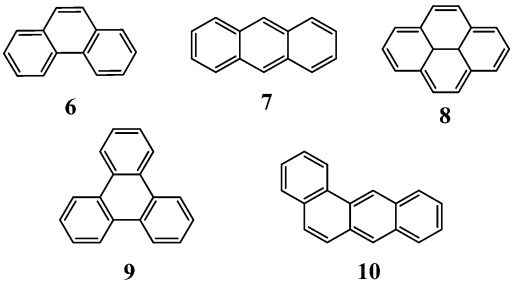


Figure 2. Structures of the five PAH guests.

two-dimensional (2D) ^{1}H NMR spectroscopies. The ^{1}H NMR spectrum of an equimolar mixture of **1** and **6** (10 mM) in $CDCl_3$ (Figure 3) revealed obvious upfield shifts for H_a, H_b, H_c, and H_d (−0.144, −0.035, −0.071, and 0.007 ppm, respectively) of cryptand **1** and *α*-, *β*-, and *γ*-phenanthrene proton signals (−0.179, −0.138, and −0.165 ppm, respectively) of guest **6**. The *ω*1 and *ω*2 proton signals of **6** also shifted upfield but became indistinguishable, resulting from *π*-donor−*π*-acceptor interac-

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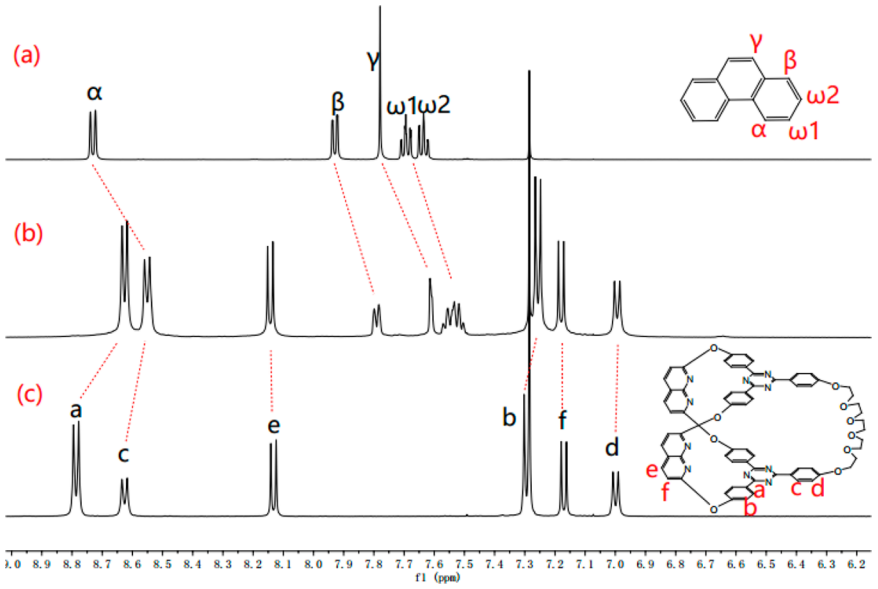
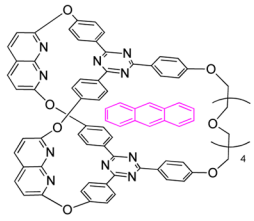
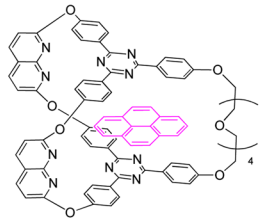
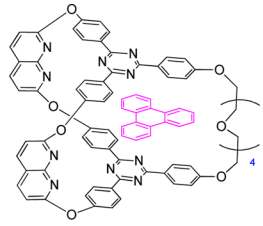
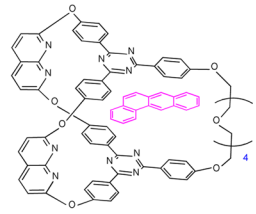


Figure 3. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K, c = 10 mM) of (a) **6**, (b) a **1**/**6** mixture, (c) **1**.

Table 1. Host−Guest Complexes between 1 and PAH 7, 8, 9, or 10 and Their Corresponding Association Constants (M^{-1}) Determined by ^{1}H NMR Titration

			
$(4.2 \pm 0.4) \times 10^1$	$(1.2 \pm 0.1) \times 10^2$	$(2.2 \pm 0.2) \times 10^2$	$(2.4 \pm 0.2) \times 10^2$

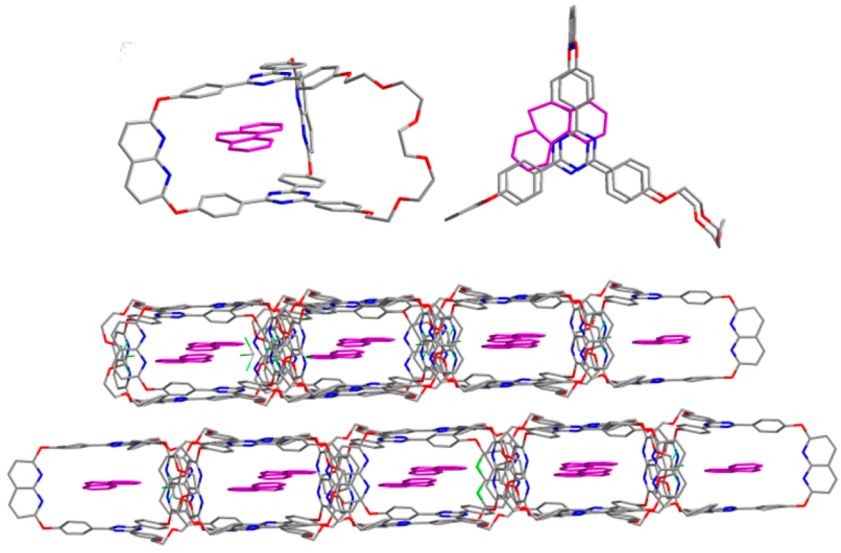


Figure 4. Crystal structure of the host−guest complex between cryptand **1** and phenanthrene (**6**): side view (top left), top view (top right), and one-dimensional channels in the crystal packing filled by **6** (bottom).

tions between the electron-rich phenanthrene plane and the electron-deficient 2,4,6-triphenyl-1,3,5-triazine aromatic walls of the host. The proton signals (H_e and H_f) of the 1,8-naphthyridine units and oxyethylene loop in host **1** experienced no obvious change upon complexation, implying no interaction existed between the outer edges of the 1,8-naphthyridine bridges or oxyethylene loop of host **1** and guest **6**.

The 2D NOESY spectrum of an equimolar mixture of **1** and **6** (10 mM) in $CDCl_3$ (Figure S17) clearly showed the correlations between the guest phenanthrene protons (α, β, and γ) and the

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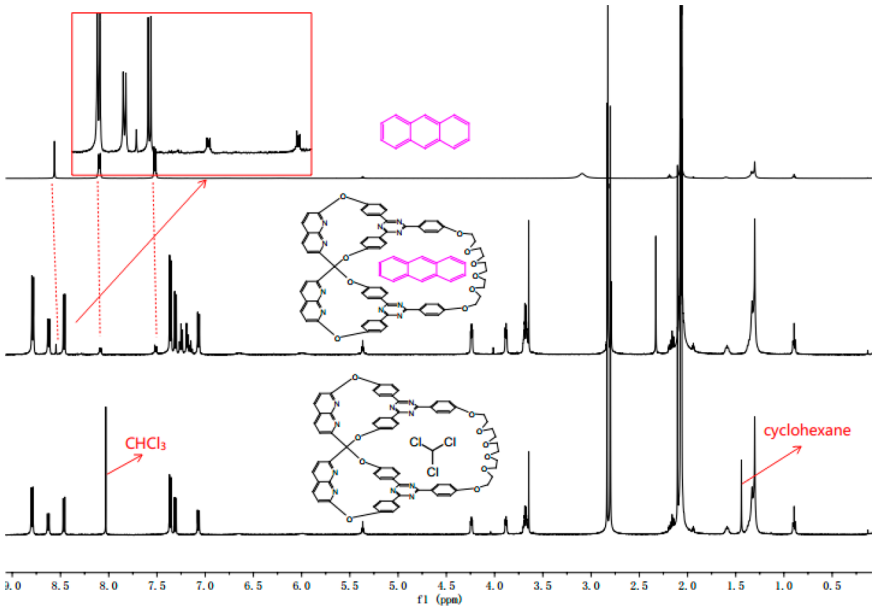

Figure 5. ^{1}H NMR spectra (400 MHz, acetone-d_6) of the crystalline solid of cryptand **1** with $CHCl_3$ and cyclohexane (bottom), the solid of cryptand **1** after soaking in a 1.0 mM solution of **7** in toluene for 1 day (middle), and **7** (top).

aromatic protons (H_a, H_b, H_c, and H_d) of host **1**, providing additional evidence of the formation of a **6**⊂**1** sandwich type complex. A Job plot (Figure S18) based on ^{1}H NMR data indicated that **1** and **6** formed a 1:1 complex. The association constant (K_a) of complex **6**⊂**1** in $CDCl_3$ was determined to be $(3.9 \pm 0.3) \times 10\ M^{-1}$ by ^{1}H NMR titration (Figures S19 and S20). Similarly, the 1D and 2D ^{1}H NMR spectra of equimolar mixtures of host **1** with PAH guest **7**, **8**, **9**, or **10** in $CDCl_3$ (10 mM) displayed host−guest interactions between host **1** and each of these guests (Figures S21, S22, S26, S27, S31, S32, S37, and S38), and the formation of 1:1 complexes of host **1** and each of the PAH guests was evidenced by Job plots (Figures S23, S28, S33, and S37). The association constants (K_a) of the complexes between **1** and **7**, **8**, **9**, or **10** in $CDCl_3$ obtained by ^{1}H NMR titration are listed in Table 1 (Figures S24, S25, S29, S30, S34, S35, S40, and S41). PAH⊂**1** complexes **9**⊂**1** and **10**⊂**1** were detected by HR ESI-MS spectrometry (1397.4886 and 1397.4881, assigned to $[\mathbf{9}\subset\mathbf{1} + H]^+$ and $[\mathbf{10}\subset\mathbf{1} + H]^+$, respectively) (Figures S36 and S42), but the other complexes, **6**⊂**1**, **7**⊂**1**, and **8**⊂**1**, with lower association constants, were not detected by HR ESI-MS experimentally, possibly because of dissociation of the complexes in the gas phase. Fortunately, single crystals of complex **6**⊂**1** suitable for X-ray diffraction analysis were harvested by slow evaporation of the complex solution in a mixed solvent of chloroform and cyclohexane. Although the low-quality X-ray diffraction data set, possibly due to the involvement of highly disordered solvent molecules, failed to allow us to perform high-quality refinement, it provided enough evidence to confirm the structural skeleton, showing **6** is intercalated between the two electron-deficient 2,4,6-triphenyl-1,3,5-triazine aromatic walls of **1** (Figure 4). The complex is stabilized mainly by π-donor−π-acceptor interaction between **1** and **6**, consistent with the ^{1}H NMR data. In the solid state, the complexes were packed in layers, and one-dimensional channels were formed within each layer by the inherent cavities of **1** that were filled by guest molecules of **6**. The trapped solvent molecules ($CHCl_3$ and cyclohexane) were squeezed out during the structural refinement, and the crystals were determined to have a **1**:**6**:$CHCl_3$:cyclohexane ratio of 1:1:2:0.5 by ^{1}H NMR analysis of the crystalline solid (Figure S43).

As human exposure to PAHs is primarily from polluted environments, we are interested in using cryptand **1** to absorb PAHs to develop potential materials that can be used to remove environmental PAH pollutants. We envisioned that crystalline solids of **1** might be used to absorb PAHs via the displacement of the chloroform molecules that occupy the one-dimensional channels. To our delight, the replacement of chloroform molecules in the one-dimensional channels of the crystalline solids of **1** with anthracene (**7**) was achieved by soaking crystalline **1** in a solution of **7** (1.0 mM) in toluene for 1 day. The crystalline solid of **1** was characterized by ^{1}H NMR spectroscopy before and after soaking (the soaked solid **1** was thoroughly washed with toluene). The ^{1}H NMR spectrum of the soaked crystalline solids of **1** in acetone-d_6 indicated that **7** was indeed sequestered by crystalline **1**, chloroform was no longer in the soaked crystalline solids, and the **1**:**7** ratio was determined to be 5:2 by integration of corresponding peaks in NMR, with the remaining cavities filled by toluene molecules (Figure 5). Unfortunately, the soaked solid of **1** was no longer in decent crystalline form and thus was unsuitable for X-ray diffraction analysis.

■ CONCLUSION

In conclusion, we have created a new cryptand **1** that was found to be able to encapsulate PAHs, such as phenanthrene (**6**), anthracene (**7**), pyrene (**8**), triphenylene (**9**), and tetraphene (**10**), by forming 1:1 complexes through face-to-face $\pi\cdots\pi$ stacking interactions. Crystalline **1** was able to sequester anthracene (**7**) once **1** was soaked in a solution of **7** in toluene. Further research of complexation of PAHs and potential applications is ongoing.

■ 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 with 400 MHz (for 2D NMR) or 500 MHz spectrometers with TMS as the reference. HRMS spectra were

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recorded on a micrOTOF-Q spectrometer (ESI). Single-crystal X-ray diffraction data were collected on an 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 determined 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.

4,4′,4″-(1,3,5-Triazine-2,4,6-triyl)triphenol (2). 4-Hydroxybenzonitrile (1.19 g, 10.0 mol) was added to trifluoromethanesulfonic acid (8 mL) portionwise over 4 h at 0−5 °C under nitrogen, resulting in a mixture that was stirred at 0−5 °C for 1 h and kept at room temperature overnight. Water (10 mL) was added, and the resulting mixture was neutralized with an aqueous NH_3H_2O solution (28%). The precipitate was filtered and washed with water to afford **2** (1.0 g, 84%): mp >300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.28 (s, 3H), 8.56 (d, J = 8.5 Hz, 6H), 6.98 (d, J = 8.5 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.5, 162.3, 131.1, 127.0, 116.1; HR-MS calcd for $C_{21}H_{15}N_3O_3H^+$ $[M + H]^+$ 358.1186, found 358.1193.

4-{4,6-Bis[*p*-(methoxymethoxy)phenyl]-1,3,5-triazin-2-yl}-phenol (3). To a solution of **2** (1.02 g, 2.86 mmol) in DMF (40 mL) was added K_2CO_3 (787.7 mg, 5.7 mmol), followed by dropwise addition of a solution of chloromethyl methyl ether (458.9 mg, 5.7 mmol) in DMF (5 mL). The reaction mixture was stirred at room temperature for 2 h, poured into water (200 mL), and extracted with EtOAc (3 × 100 mL). The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4, and concentrated, resulting in a residue that was subjected to column chromatography (0.6:100 CH_3OH/CH_2Cl_2) to afford **3** as a white solid (200.0 mg, 16%): mp 167.6−168.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (m, 12H), 7.20 (d, J = 9.0 Hz, 8H), 6.98 (d, J = 9.0 Hz, 2H), 5.31 (s, 4H), 3.56 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.8, 170.5, 162.5, 161.0, 131.2, 130.9, 129.5, 126.9, 116.5, 116.1, 94.2, 56.3; HR-MS calcd for $C_{25}H_{23}N_3O_5H^+$ $[M + H]^+$ 446.1710, found 446.1731.

6,6′-({[Oxybis(ethane-2,1-diyl)]bis(oxy)}bis(4,1-phenylene))-bis{2,4-bis[4-(methoxymethoxy)phenyl]-1,3,5-triazine} (4). A mixture of **3** (1.00 g, 2.25 mmol), penta(ethylene glycol) bistosylate (620.0 mg, 1.13 mmol), and Cs_2CO_3 (1.24 g, 8.98 mmol) in acetonitrile (200 mL) was refluxed for 10 h, poured into water (200 mL), and extracted with EtOAc (3 × 100 mL). The organic extracts were washed with brine, dried with anhydrous Na_2SO_4, and concentrated, resulting in a residue that was subjected to column chromatography (1:100 CH_3OH/CH_2Cl_2) to afford **4** as faint yellow oil (1.10 g, 90%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (m, 12H), 7.19 (d, J = 8.5 Hz, 8H), 7.06 (d, J = 9.0 Hz, 4H), 5.29 (s, 8H), 4.24 (t, J = 4.5 Hz, 4H), 3.92 (t, J = 4.5 Hz, 4H), 3.81−3.67 (m, 12H), 3.54 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 170.6, 162.3, 160.7, 130.7, 130.6, 130.1, 129.1, 115.9, 114.4, 94.2, 70.9, 70.7, 69.7, 67.5, 56.2; HR-MS calcd for $C_{60}H_{64}N_6O_{14}H^+$ $[M + H]^+$ 1093.4553, found 1093.4581.

4,4′,4″,4‴-({[(Oxybis(ethane-2,1-diyl)]bis(oxy)}bis(4,1-phenylene))bis(1,3,5-triazine-6,2,4-triyl)tetraphenol (5). To a solution of **4** (262.1 mg, 0.24 mmol) in a mixed solvent of CH_3OH and CH_2Cl_2 (5 mL, 4:1, v/v) was added concentrated hydrochloric acid (5 mL, 37%), resulting in a mixture that was heated at 50 °C for 5 h. The reaction mixture was concentrated, and the residue was subjected to column chromatography (5:100 CH_3OH/CH_2Cl_2) to afford **5** as a yellow solid (210.0 mg, 96%): mp 134.7−137.2 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.28 (s, 4H), 8.61 (d, J = 9.0 Hz, 4H), 8.55 (d, J = 8.5 Hz, 8H), 7.15 (d, J = 9.0 Hz, 4H), 6.98 (d, J = 8.5 Hz, 8H), 4.22 (t, J = 4.5 Hz, 4H), 3.80 (t, J = 4.5 Hz, 4H), 3.67−3.49 (m, 12H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.6, 170.3, 162.7, 162.4, 131.1, 130.8, 128.6, 126.9, 116.1, 115.1, 70.4, 70.3, 69.3, 67.9, 49.1; HR-MS calcd for $C_{52}H_{48}N_6O_{10}H^+$ $[M + H]^+$ 917.3505, found 917.3512.

Cryptand 1. A mixture of **5** (100.0 mg, 0.11 mmol), 2,7-dichloro-1,8-naphthyridine (43.6 mg, 0.22 mmol),[16] and Cs_2CO_3 (179.2 mg, 0.55 mmol) in DMSO (16 mL) was heated at 120 °C for 2 h, poured into water (80 mL), and extracted with CH_2Cl_2 (3 × 60 mL). The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated, resulting in a residue that was purified by column chromatography (1:100 CH_3OH/CH_2Cl_2) to afford **1** as a white solid (26.0 mg, 20%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, J = 8.5 Hz, 8H), 8.61 (d, J = 8.5 Hz, 4H), 8.13 (d, J = 8.5 Hz, 4H), 7.30 (d, J = 9.0 Hz, 8H), 7.17 (d, J = 8.5 Hz, 4H), 7.00 (d, J = 8.5 Hz, 4H), 4.22 (t, J = 4.0 Hz, 4H), 3.91 (t, J = 4.5 Hz, 4H), 3.78−3.68 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 170.6, 164.9, 162.4, 156.6, 153.9, 139.6, 133.2, 130.7, 130.6, 128.7, 122.7, 116.8, 114.4, 111.3, 71.1, 70.9, 70.8, 69.6, 67.6; HR-MS calcd for $C_{68}H_{52}N_{10}O_{10}H^+$ $[M + H]^+$ 1169.3941, found 1169.3960.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01115.

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

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

X-ray crystallographic data of the **6⊂1** complex (CIF)

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Notes

The authors declare no competing financial interest.

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