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A Shape-Persistent Cryptand for Capturing Polycyclic Aromatic Hydrocarbons (PAHs)

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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 pentaethyleneoxide loop, is created for capturing polycyclic aromatic hydrocarbons (PAHs). Cryptand 1 formed 1:1 complexes with PAH guest molecules, such as phenanthrene (6), anthracene (7), pyrene (8), triphenylene (9) and tetraphene (10). Single-crystal structure of complex $6\subset 1$ 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 picking up anthracene from the toluene solution 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 combustion processes of fossil fuel.² PAHs are now believed to be one of the main pollutants and harmful chemical species known on the earth³ because some of 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 PAHs-containing particulates suspended in air. On the other hand, PAHs are among the most beautiful and fascinating classes of organic compounds.^{5,1} Due to their outstanding optical and electronic properties, many members of PAHs have been widely investigated in potential applications in organic field-effect transistors (OFETs), organic solar cells (OSCs), fluorescence probes, as well as 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 metallocycles¹¹ have been explored as host molecules for PAHs of various shapes and sizes. Whitlock and co-workers¹² 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 π - π interactions between an aromatic guest molecule and each of the two walls of the receptor cavity. Based on 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. Due to the well-defined spatial shapes and cavity sizes, cryptands have shown much higher binding strength towards guest molecules compared to their analogous crown

ethers.¹⁴ Since 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 described a new cryptand **1** which contains two face-to-face oriented electron-deficient 2,4,6-triphenyl-1,3,5-triazine aromatic walls separated by a distance of approximately 7 Å, and linked by two rigid 1,8-naphthyridine bridges and a flexible pentaethyleneoxide 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.

RESULTS AND DISCUSSION

Our investigation began from the synthesis of 1.8-naphthyridine-bridged cryptand 1 which is outlined in Scheme 1 (details in Supporting Information). Protection 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 bistosylate under basic conditions glycol) 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 which was characterized by ¹H NMR, ¹³C NMR, HR-MS spectrometry and single crystal X-ray diffraction analysis. The crystal structure of 1 (Figure 1) clearly revealed that its sandwich-like structure with the two face-to-face oriented electron-deficient 2,4,6-triphenyl-1,3,5-triazine aromatic units were separated by a distance of approximately 7 Å, which is 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 CHCl₃) by appropriate aligning 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.



Scheme 1. Synthesis of cryptand host 1



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

With synthesized cryptand 1 in hand, the interaction between the cryptand 1 and five electron-rich PAH guests, phenanthrene 6, anthracene 7, pyrene 8, triphenylene 9 and tetraphene 10 (Figure 2), was investigated with 1D and 2D 1 H NMR spectroscopies. The 1 H NMR spectrum of an equimolar mixture of 1 and 6 (10 mM)

in CDCl₃ (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) of cryptand **1**, and α -, β - and γ -phenanthrene proton signals (-0.179, -0.138 and -0.165 ppm) 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 interactions 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**.



Figure 2. The structures of the five PAH guests.



Figure 3. ¹H NMR spectra (400 MHz, CDCl₃, 298 K, c = 10 mM): (a) 6, (b) 1 + 6, (c) 1.

The 2D NOESY spectrum of an equimolar mixture of 1 and 6 (10 mM) in $CDCl_3$ (Supporting Information, Figure S17) clearly showed the correlations between the guest phenanthrene protons (α , β and γ) and the aromatic protons (H_a, H_b, H_c and H_d) of host 1, providing additional evidence for the formation of a sandwich type complex ⊂1. A Job plot (Supporting Information, Figure S18) based on ¹H NMR data indicated that 1 and 6 formed a 1:1 complex. The association constant (K_a) of complex $6 \subset 1$ in CDCl₃ was determined to be $(3.9\pm0.3) \times 10^1$ M⁻¹ by ¹H NMR titration (Supporting Information, Figure S19-S20). Similarly, the 1D and 2D ¹H NMR spectra of equimolar mixtures of host 1 with the PAH guests 7, 8, 9 or 10 in $CDCl_3$ (10 mM) displayed the host-guest interactions between host 1 and each of these guests (Supporting Information, Figure S21, S22, S26, S27, S31, 32, S37, S38), and the formation of 1:1 complexes of host 1 and each of the PAH guests was evidenced by Job plots (Supporting Information, Figure S23, S28, S33, S37). The association constants (K_a) of the complexes between 1 and 7, 8, 9, or 10 in CDCl₃ obtained by ¹H NMR titration, are listed in Table 1 (Supporting Information, Figure S24, S25, S29, S30, S34, S35, S40, S41). The PAH⊂1 complexes 9⊂1 and 10⊂1 were detected by HR ESI-MS spectrometry (1397.4886 and 1397.4881, assigned to $[9 \subset 1 + H]^+$ and $[10 \subset 1 + H]^+$, respectively. (Supporting Information, Figure S36, S42), but the other complexes, $6 \subset 1$, $7 \subset 1$, and $8 \subset 1$, with lower association constants, were not detected by HR ESI-MS experimentally, possibly due to dissociation of the



Table 1. Host-guest complexes between 1 and PAHs 7-10 and their corresponding association constants (M^{-1}) determined by ¹H NMR titration.

complexes in the gas phase. Fortunately, single crystals of the complex $6 \subset 1$ suitable for X-ray diffraction analysis were harvested by slow evaporation of the complex

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solution in a mixed solvent of chloroform and cyclohexane. Although the low quality X-ray diffraction data set, possibly due to 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 ¹H 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** which were filled by guest molecules of **6**. The trapped solvent molecules (CHCl₃ and cyclohexane) were squeezed out during the structural refinement and were determined to have a **1**:6:CHCl₃:cyclohexane ratio of 1:1:2:0.5 by ¹H NMR analysis of the crystalline solid (Supporting Information, Figure S43).



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

As human exposure to PAHs is primarily from polluted environments, we are interested in using cryptand **1** to absorb PAHs in order to develop potential materials which 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 which occupy the one-dimensional channels. To our delight, the replacement of chloroform molecules in the one-dimensional channels of the crystalline solids of **1** by anthracene (**7**) was achieved by soaking crystalline **1** in a solution of **7** (1.0 mM) in toluene for one day. The crystalline solid of **1** was characterized by ¹H NMR spectroscopy before and after soaking (the soaked solid **1** was thoroughly washed with toluene). The ¹H 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 ratio of **1** to **7** 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.



Figure 5. ¹H NMR spectra (400 MHz, acetone- d_6) of: crystalline solid of cryptand 1 with CHCl₃ and cyclohexane (bottom), solid of cryptand 1 after soaking in a 1.0 mM solution of 7 in toluene for 1 day (middle), 7 (top).

CONCLUSION

In conclusion, we have created a new cryptand 1 which was found to be able to encapsulate polycyclic aromatic hydrocarbons (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 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. ¹H and ¹³C NMR spectra were recorded at 400 MHz (for 2D NMR) 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 ($\lambda = 0.71073$ Å). Data reduction included absorption corrections by the multi-scan 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.

(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 which 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 aqueous NH₃H₂O solution (28%). The precipitate was filtered and washed with water to afford **2** (1.0 g, 84%), m. p. > 300 °C. ¹H 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).

¹³C 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 K₂CO₃ (787.7 mg, 5.7 mmol), and 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 and poured into water (200 mL), and extracted with EtOAc (3 ×100 mL). The combined organic extracts were washed with brine, dried with anhydrous Na₂SO₄, and concentrated to result in a residue which was subjected to column chromatography (CH₃OH/CH₂Cl₂ = 0.6 : 100) to afford **3** as a white solid (200.0 mg, 16%), m. p 167.6-168.1°C. ¹H NMR (500 MHz, CDCl₃): 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); ¹³C 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 C₂₅H₂₃N₃O₅H⁺ [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-(methox ymethoxy)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 Cs₂CO₃ (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 Na₂SO₄, and concentrated to result in a residue which was subjected to column chromatography (CH₃OH/CH₂Cl₂ = 1:100) to afford **4** as faint yellow oil (1.10 g, 90%). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (126 MHz, CDCl₃): 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-triazi ne-6,2,4-triyl))tetraphenol (5): To a solution of **4** (262.1 mg, 0.24 mmol) in a mixed solvent of CH₃OH and CH₂Cl₂ (5 mL, 4:1, v/v) was added concentrated hydrochloric acid (5 mL, 37%) resulting in a mixture which was heated at 50 °C for 5 h. The reaction mixture was concentrated, and the residue was subjected to column chromatography (CH₃OH/CH₂Cl₂ = 5 : 100) to afford **5** as a yellow solid (210.0 mg, 96%), m. p. 134.7-137.2°C. ¹H 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). ¹³C 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 C₅₂H₄₈N₆O₁₀H⁺ [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 Cs₂CO₃ (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 CH₂Cl₂ (3 ×60 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated to result in a residue which was purified by column chromatography (CH₃OH/ CH₂Cl₂ =1:100) to afford **1** as a white solid (26.0 mg, 20%), m. p. > 300°C. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (126 MHz, CDCl₃): 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 C₆₈H₅₂N₁₀O₁₀H⁺ [M + H]⁺ 1169.3941, found 1169.3960.

ASSOCIATED CONTENT

Supporting Information

Spectroscopic data for new compounds and complexes, titration protocol, Job plots, determination of the association constants, and X-ray crystallographic data of 1 and $6 \subset 1$ (CIF files). This material is available free of charge via the Internet at <u>http://pubs.acs.org.</u>

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The authors declare no competing financial interest.

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