



Synthesis, structure, and host-guest properties of an anthracene-based macrocyclic arene

Liping Bao^{a,b}, Xiaoyan Shu^{a,*}, Ma Yu^a, Dabin Hou^{a,*}, Lei Cui^b, Chunju Li^{b,*}

^a School of Life Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, Sichuan, PR China

^b College of Science, Shanghai University, Shanghai 200444, PR China

ARTICLE INFO

Article history:

Received 3 December 2017

Revised 2 January 2018

Accepted 5 January 2018

Available online 6 January 2018

Keywords:

Molecular recognition

New macrocycles

New hosts

Macrocyclic arenes

Host-guest properties

ABSTRACT

A new anthracene-based macrocyclic host (**H**) was designed and synthesized. **H** has a molecular box-type structure with a flexible cavity. It exhibits highly strong binding affinities towards selected cationic model guests, butyl viologen (**BV**), dibutylammonium (**DBA**), and octyltrimethylammonium (**OTMA**). For example, the association constant of **H** and **BV** is up to $(2.2 \pm 0.3) \times 10^7 \text{ M}^{-1}$; it is interesting to observe host-guest charge-transfer band (and color change) and fluorescence quenching of **H**'s anthracene unit due to the formation of inclusion complex.

© 2018 Elsevier Ltd. All rights reserved.

As an important part of supramolecular chemistry, macrocyclic arenes have shown interesting recognition properties and functional applications.^{1–3} They are made up of aromatic rings linked by the bridges of methylene ($-\text{CH}_2-$) and/or heteroatoms such as O, S, and N, including calixarenes, calixpyrroles, resorcinarenes, cyclotrimeratrylenes, calixnaphthalenes, pillar[n]arenes,^{4,5} corona [n]arenes,⁶ oxatub[4]arene,⁷ calix[n]imidazole,⁸ helic[6]arenes⁹ and biphen[n]arenes.^{10,11} These synthetic receptors have been widely used to construct attractive and functional molecules and molecular assemblies.

On the other hand, anthracene is a particularly significant supramolecular synthon because of its flat, panel-like shape,¹² large π -surface area, and intrinsic photophysical and photochemical properties.¹³ Moreover, anthracenes display a well-known proclivity to establish ordered aromatic interactions in solution and in the solid state. Although the supramolecular hosts containing benzene, heterocycle, and naphthalene monomers have been well documented, the macrocyclic arenes based on anthracene scaffolds have been relatively rarely reported. The introduction of anthracenes to supramolecular macrocycles could provide not only peculiar recognition behaviors, but also interesting fluorescence properties.

Herein, we demonstrate the synthesis, structure, and host-guest properties of a new anthracene-based supramolecular host

* Corresponding authors.

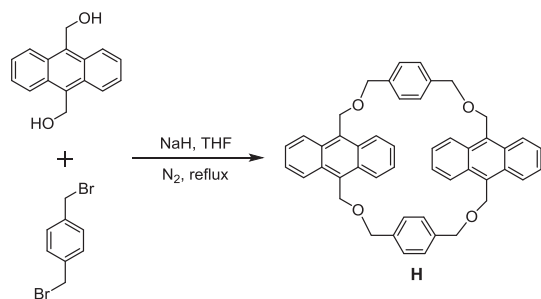
E-mail addresses: sxy713@163.com (X. Shu), dbhou@126.com (D. Hou), cjli@shu.edu.cn (C. Li).

(**H**, Scheme 1), which is made up of 9, 10-anthracene and 1, 4-benzene units connected by $-\text{CH}_2\text{OCH}_2-$ linkers. This new macrocyclic arene can be conveniently prepared by a one-pot Williamson etherification reaction, and shows a box-shaped topology and good recognition properties.

The synthetic route of host **H** was shown in Scheme 1. Williamson etherification reaction proceeded smoothly when using α , α' -dibromo-*p*-xylene and 9, 10-bis(hydroxymethyl)anthracene as reactants in the presence of NaH in anhydrous THF. Macrocyclic **H** was isolated by silica gel column chromatography with 15% yield. Larger macrocycles such as “3 + 3” and “4 + 4” types were not observed in the reaction mixture by high resolution mass spectrometry (HR-MS) analysis.

Single crystals of **H** were obtained by slow evaporation of its CH_2Cl_2 and *n*-hexane solution. X-ray crystallographic analysis clearly determined the production of macrocyclic arene **H** and its structure in the solid state (Fig. 1). This new macrocycle exhibits a “molecular box” structure. The centroid-centroid distance between two benzenes is 10.05 Å; while that for two anthracene units is as near as 3.67 Å, indicating strong π - π stacking interactions between them. According to the crystal structure, **H** does not have enough cavity in the solid state. We surmise the cavity size of **H** in solution is not fixed on account of its relatively flexible $-\text{CH}_2\text{OCH}_2-$ bridges, i.e., it could swell to fit suitable guests in solution.

The host-guest properties of **H** were then examined. Due to its π -rich cavity, three cationic molecules, butyl viologen (**BV**), dibuty-



Scheme 1. Synthesis of the anthracene-based macrocyclic host **H**.

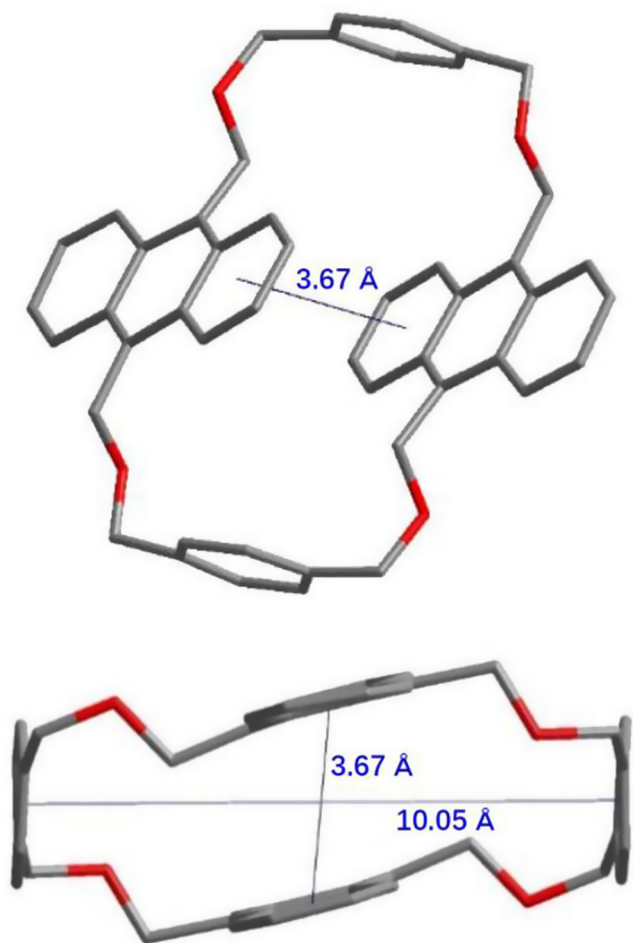
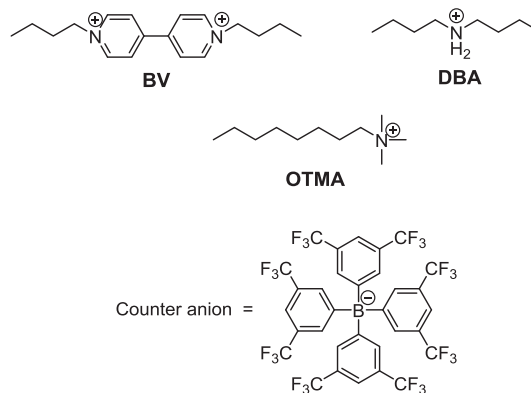


Fig. 1. Two views of crystal structure of **H**.

ammonium (**DBA**) and octyltrimethylammonium (**OTMA**), were chosen as model guests (**Scheme 2**). For all ^1H NMR and the following fluorescence experiments, $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ was used as a solvent because guest **BV** had very poor solubility in $\text{CDCl}_3/\text{CHCl}_3$. **Fig. 2** shows the ^1H NMR spectra of **BV** in the absence and in the presence of approximately 1.0 equivalent (eq.) of **H**. Upon addition of **H**, the proton signals of **BV**, except for the end **f**, show remarkable upfield shifts (from -0.32 to -2.35 ppm) and broadening effects as a consequence of inclusion induced shielding effects (**Fig. 2B**). The $\Delta\delta$ values of the guest's protons are in the order of $f < e < d < c < a < b$, i.e., from the tail to the middle. These results reveal that the host and guest form a [2]pseudorotaxane-type complex with **BV**'s viologen nucleus located inside the cavity of **H**. ^1H NMR titration experiments were done; a mole ratio plot for **H** and **BV** proved consistent with the 1:1 host–guest binding stoichiometry (**Fig. S9**).



Scheme 2. Structure of three cationic guests: butyl viologen, **BV**, dibutylammonium, **DBA**, and octyltrimethylammonium, **OTMA**. The counter anions are tetrakis [3,5-bis(trifluoromethyl)phenyl] borate.

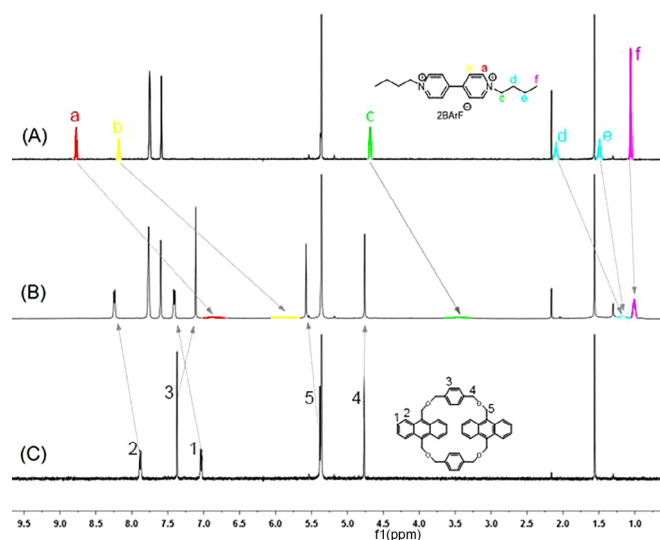


Fig. 2. ^1H NMR spectra (500 MHz, 298 K) of (A) **BV**, (B) **BV** + **H**, (C) **H** in CD_2Cl_2 at 1.0 mM.

For secondary ammonium salt **DBA**, similar NMR changes, such as large upfield shifts and substantial broadening effects, were observed when mixing with macrocycle **H** (**Fig. S10, B**), suggesting the formation of a [2]pseudorotaxane. However, for quaternary ammonium salt **OTMA**, the head protons $\text{H}_{\text{A-C}}$ pronouncedly shift upfield for 0.98 ppm. Meanwhile, small downfield shifts were observed for the tail protons $\text{H}_{\text{C-1}}$ (**Fig. S10, D**), indicating that they were located outside of the cavity of **H**. These results suggest that the binding site of **OTMA** is not its middle linker, but its end ammonium moiety.

H and **BV** alone are colorless in CH_2Cl_2 solution, while their 1:1 mixture yields light red color (**Figs. 3 and 4**). This is due to the charge transfer (CT) interactions between **H**'s π -rich cavity and π -deficient **BV**. As shown in **Fig. 3**, the 1:1 mixture of **BV** and **H** exhibited a strong CT band at 525 nm. No obvious color changes and CT bands were found for **DBA** and **OTMA** since they were not typical electron acceptors.

To quantitatively study the binding strength of **H** towards these guests, fluorescence titration experiments were performed to determine the association constants (K_{a}). From **Fig. 5**, the fluorescence of **H** was dramatically quenched by adding **BV**. This is due

Download English Version:

<https://daneshyari.com/en/article/7830469>

Download Persian Version:

<https://daneshyari.com/article/7830469>

[Daneshyari.com](https://daneshyari.com)