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Cyclo[4]carbazole, an Iodide Anion Macrocyclic Receptor

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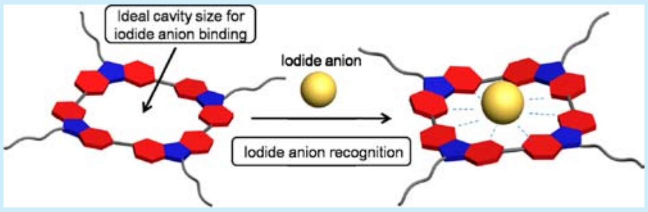
S *Supporting Information*

ABSTRACT: A novel preorganized and rigid iodide anion macrocyclic receptor, cyclo[4]carbazole (**Cy[4]C**), is reported here. The structure of **Cy[4]C** was confirmed by single-crystal X-ray analysis. The binding affinity of **Cy[4]C** for iodide anion was investigated by UV−vis and ^{1}H NMR spectroscopic techniques. The crystal structure of the complex between **Cy[4]C** and chloroform also provided evidence for the recognition ability of **Cy[4]C** toward iodide anion. Furthermore, the 1:1 complexation stoichiometry between **Cy[4]C** and iodide anion was confirmed by high-resolution mass spectrometry and molecular modeling.



Anions play indispensable roles in various fields.[1−5] Specifically, iodide anion is vital for many biochemical activities and exists in many biostructures. For example, the Na$^+$/I$^-$ symporter (NIS), an important plasma membrane glycoprotein, mediates active iodide anion transport for thyroid hormone biogenesis,[6] and thyroid hormones participate in several metabolic processes.[7] Hence, iodide content in foods and drinks is often required nutritional information, and a dose of 80−150 μg of dietary iodine per day is recommended.[8] Consequently, the search for new iodide anion receptors is essential in terms of nutritional studies and biological relevance.[9]

In the past several decades, many anion receptors have been reported,[10] and the main factors that influence the interactions between receptors and anions have been explored, such as preorganization and complementary stereoelectronic arrangement of the receptors.[11] A substantial number of these anions receptors are macrocycle-based. Good examples are fluorinated macrocyclic ethers reported by Farnham that bind fluoride anion,[12] Anslyn's bicyclic cyclophane that combines planar oxyacid anions such as nitrate anion,[13] a calixpyrrole reported by Sessler that complexes fluoride anion,[14] and macrocycles containing triazoles reported by Flood that perform as hosts for various anions.[15] These macrocycles commonly have symmetric structures and preorganized binding sites that enable strong binding affinity toward specific anionic guests. However, most of these macrocycles are receptors for fluoride, chloride, or oxyacid anions; few show recognition toward iodide anion.[16] Due to its large diameter and low electron density,[17] the iodide anion hardly forms hydrogen bonds and anion−π interactions, resulting in the lack of recognition by conventional macrocycles. Therefore, the discovery of new iodide anion receptors is very important but is still a challenge for chemists.

Enlightened by the concept proposed by Cram and co-workers that preorganized macrocycles with preorganized binding site might show stronger binding affinity toward specific guests,[18,19] we rationally designed and synthesized a preorganized, rigid macrocycle cyclo[4]carbazole (**Cy[4]C**) which can perform as a new iodide anion receptor. It was made in one pot via intermolecular coupling reaction of *N*-butyl-3,6-dibromocarbazole using bis[1,5-cyclooctanediene]nickel(0) (Ni[COD]$_2$) (Scheme 1).[20] Considering that aryl C−H groups form stronger hydrogen bonds with anions than alkyl C−H groups,[21] it was anticipated that this macrocycle should be able to bind anions owing to its π-conjugated system and proper cavity size. Interestingly, we found that **Cy[4]C** recognizes iodide anion in chloroform, resulting in a distinct color change visible to the naked eye. Our further studies ascribe this recognition to the preorganization of the macrocycle, its suitable cavity size, and the cooperative effect of multiple hydrogen bonds. The innovative application of this preorganized macrocycle offers us a new way to detect iodide anion or design new anion receptors.

Initially, in order to enhance its solubility, the NH group of 3,6-dibromocarbazole was substituted by an alkyl group. Enlightened by cyclization reactions using Ni[COD]$_2$,[20,22] the synthetic conditions for **Cy[4]C** were optimized. MALDI-TOF mass spectrometry is a valuable tool for structure detection and distinction. Actually, peaks of cyclo[*n*]carbazole (**Cy[*n*]C**) (n = 4, 5, 6, 7) macrocycles with various sizes, including an intense peak at 885 corresponding to **Cy[4]C**, were found in the MALDI-TOF spectrum (Figure S3). Moreover, this MALDI-TOF spectrum demonstrated that *N*-butyl-3,6-dibromocarbazole preferred to form cyclic structures instead of linear oligomers because peaks related to linear oligomers could be hardly found.[23] Pure **Cy[4]C** was obtained by column

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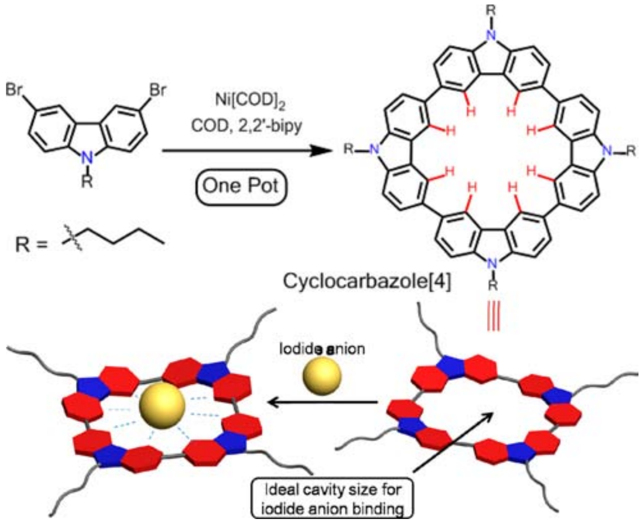
Scheme 1. Synthesis and Chemical Structure of Cy[4]C and Cartoon Representation of Iodide Anion Recognition by Cy[4]C[a]



[a]COD: *cis*-1,5-cyclooctanediene.

chromatography and characterized by NMR spectroscopy (Figures S4 and S5).

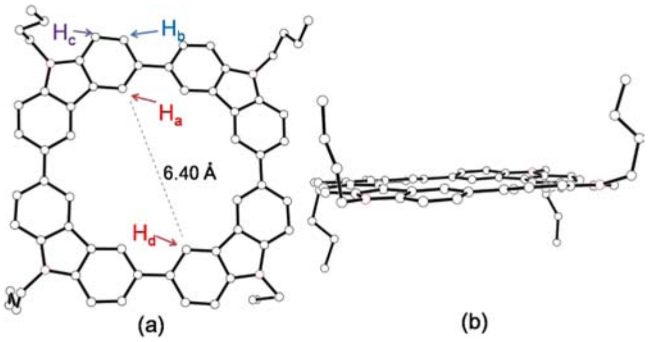


Figure 1. Ball-and-stick view of the X-ray crystal structure of **Cy[4]C**: (a) top view; (b) side view. Nitrogens are red. Hydrogens were omitted for clarity.

The structure of **Cy[4]C** was proven by single-crystal X-ray analysis (Figure 1). The single crystal of **Cy[4]C** was obtained by slow evaporation of a solution of **Cy[4]C** in a 1:1 chloroform/*n*-pentane mixture. In the top view (Figure 1a), all nitrogen atoms are located external to the cavity, and the average distance between nuclei of two *para*-positioned hydrogens, such as H_a and H_d, is 6.40 Å, meaning that **Cy[4]C** has a cavity with a diameter of 4.00 Å since the van der Waals radius of the hydrogen atom is 1.20 Å.[24a] This cavity diameter is smaller than the diameter of iodide anion (4.40 Å) and larger than the diameters of fluoride anion, chloride anion, and bromide anion (2.57, 3.62, and 3.92 Å, respectively).[24b] In the side view (Figure 1b), the ring is almost planar with a small twist because of its π-conjugated system. This crystal structure indicates that the cavity of **Cy[4]C** is preorganized to bind iodide anion.

The crystal structure of **Cy[4]C** prompted us to determine whether it is a new receptor for iodide anion. To evaluate this, commercially available tetrabutylammonium salts (TBAX) were taken into consideration owing to their simple composition and good solubility in chloroform. Thus, 50 equiv of tetrabutylammonium salts (TBAX, X = F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, ClO_4^-, NO_3^-) was added into solutions of **Cy[4]C** in chloroform to form colorless transparent mixtures, respectively. Surprisingly, 2 h later, the solution containing **Cy[4]C** and TBAI became light yellow, whereas the other solutions remained colorless; this indicated interactions between **Cy[4]C** and iodide anion. In order to investigate the recognition ability of **Cy[4]C** for iodide anion, we carried out a series of host−guest recognition experiments in chloroform. First, UV−vis experiments were used to verify the binding behavior between **Cy[4]C** and iodide anion (Figure 2). From the UV−vis spectra, the solution of **Cy[4]C** (2.00 μM in $CHCl_3$) exhibited one maximum absorption band at 300 nm. Upon addition of 50.0 equiv of TBAI, the absorption band at 300 nm ascended accompanied by a new absorption band at 360 nm, manifesting that a new moiety formed in solution. However, the addition of 50.0 equiv of other TBAX mentioned above did not interfere with the absorption band of **Cy[4]C**, which indicated that **Cy[4]C** could recognize iodide anion in chloroform. Subsequent fluorescence emission spectra also demonstrated the responsiveness of **Cy[4]C** toward iodide anion. As shown in Figure S6, the fluorescence emission intensity of **Cy[4]C** decreased after the addition of TBAI to the solution of **Cy[4]C**.

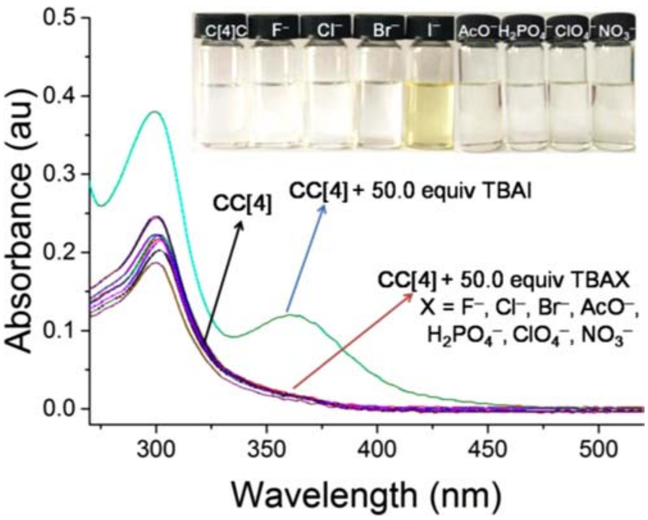


Figure 2. UV−vis spectra of **Cy[4]C** (2.00×10^{-3} mM) in $CHCl_3$ and mixed solutions of **Cy[4]C** and TBAX (X = F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, ClO_4^-, NO_3^-) (50.0 equiv). Inset: photograph showing the colors of these mixed solutions.

As previously mentioned, the association process of **Cy[4]C** and iodide anion is not accomplished rapidly. Time-dependent absorption measurements for a 1:50 mixture of **Cy[4]C** and TBAI in chloroform showed that the absorption band changed gradually with time (Figure S7a). We plotted the absorbance intensity at 360 nm versus the complexation time (Figure S7b). According to the plot, the complexation was completed in approximately 2 h. Therefore, the data about the investigation of the complexation between **Cy[4]C** and TBAI were recorded 2 h after TBAI addition to the solution of **Cy[4]C**.

Additionally, in order to further investigate the binding behavior between **Cy[4]C** and iodide anion, ^{1}H NMR experiments were carried out to observe chemical shift changes of aryl hydrogens on **Cy[4]C** (Figure S8). Upon gradual addition of 0.1−50.0 equiv of TBAI to a solution of **Cy[4]C**, the peak of H_a (Figure 1) shifted downfield. A possible explanation for this

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phenomenon could be the formation of hydrogen bonds between the encapsulated electron-withdrawing iodide anion and internal hydrogen atoms of **Cy**[**4**]**C**. The hydrogen bonds reduced the internal aryl electron density resulting in a downfield shift of the H_a peak.[25] Simultaneously, the peaks related to H_b and H_c shifted upfield, respectively, after the addition of TBAI to the solution of **Cy**[**4**]**C**, which also confirmed the host−guest recognition.[26]

In order to further verify the host−guest complexation between **Cy**[**4**]**C** and iodide anion, we attempted to obtain the single crystal of the complex between **Cy**[**4**]**C** and I^- but unfortunately failed. However, a single crystal of a 1:1 complex of **Cy**[**4**]**C** and chloroform was obtained by the solvent diffusion method (Figure 3). In the top view (Figure 3a), one chlorine atom is located at the center of **Cy**[**4**]**C**, and two distances (A and B in Figure 3) between the chlorine atom and two internal aryl hydrogen atoms on the ring are marked. The interactions between the chlorine atom and these two hydrogen atoms can be considered as hydrogen bonds according to a previously reported criterion, 2.000 Å < d(H···Cl) < 3.300 Å and C−H···Cl angle >90°.[27] The distances between the chlorine atom and the other six internal aryl hydrogen atoms vary from 3.325 to 3.375 Å, and their interactions can be regarded as van der Waals interactions.[28] Hydrogen bonds and van der Waals interactions are the main forces to fix the chlorine atom at the center of **Cy**[**4**]**C**. The other two chlorine atoms of the chloroform molecule form C−Cl···π interactions (C and D in Figure 3) with **Cy**[**4**]**C**.[29] This also helps to stabilize the **Cy**[**4**]**C**/chloroform complex. In the side view (Figure 3b), the **Cy**[**4**]**C** macrocycle in the complex is obviously twisted compared with the structure of **Cy**[**4**]**C** alone (Figure 1). This twisted conformation is conducive to the formation of hydrogen bonds and can provide a suitable binding geometry for chloroform. These results indicate that the long complexation complete time of iodide anion by **Cy**[**4**]**C** is possibly because of the competitive complexation of iodide anion and chloroform toward **Cy**[**4**]**C**. In addition, the preorganization compensates the lower intrinsic affinity of aryl C−H donor,[19] and hence, this π-conjugated, rigid macrocycle has the ability to form hydrogen bonds and complex with a halide anion guest. The **Cy**[**4**]**C**/chloroform complex crystal structure implies that the binding ratio between **Cy**[**4**]**C** and halide anion is 1:1. Actually, the high-resolution mass spectrum (HRMS) of a solution of **Cy**[**4**]**C** and TBAI also indicated 1:1 complexation stoichiometry between **Cy**[**4**]**C** and iodide anion (Figure S9).

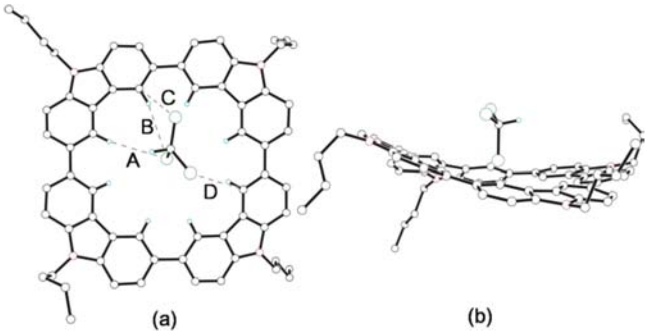

Figure 3. Ball-and-stick views of the crystal structure of the **Cy**[**4**]**C**/chloroform complex: (a) top view; (b) side view. Hydrogens are blue, nitrogens are red, and chlorines are green. Hydrogens except those involved in interactions between **Cy**[**4**]**C** and chloroform were omitted for clarity. H···Cl distances (Å) and C−H···Cl angles (deg) of hydrogen bonds: A, 3.15, 170; B, 3.23, 167. Cl···C distances (Å) of C−Cl···π interactions: C, 3.75; D, 4.06.

An energy-minimized structure of the **Cy**[**4**]**C**/iodide anion complex created via PM6 molecular modeling validated the existence of hydrogen bonds between internal aryl hydrogens and iodide anion. As shown in Figure 4, the iodide anion is located at the center of macrocycle (for the top view, see Figure 4; for the side view, see Figure S10). The average distance between the iodide anion and each surrounding hydrogen is 3.07 Å, smaller than the sum, 3.40 Å, of the van der Waals radii of the hydrogen atom and the iodide anion,[24] indicating the possible existence of hydrogen bonds between all eight internal aryl hydrogens and the iodide anion. The results of molecular modeling are consistent with the aforementioned ^1H NMR spectra (Figure S8), for which the peak related to internal hydrogens in NMR shifts downfield due to the hydrogen bond formation. Besides, compared with the encapsulated chlorine atom, the larger iodide anion has a just suitable size to match and fill the whole cavity of **Cy**[**4**]**C**, resulting in the binding of **Cy**[**4**]**C** to iodide anion.

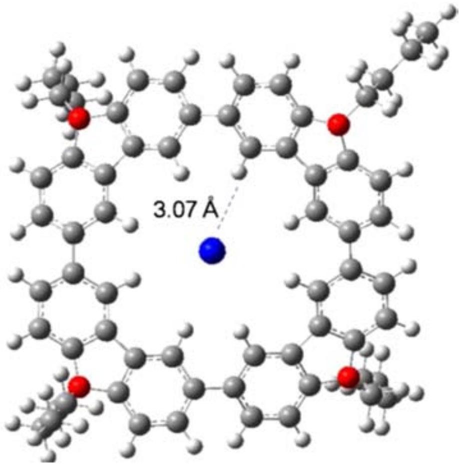

Figure 4. Energy-minimized structure of **Cy**[**4**]**C** and iodide anion complex simulated by Gaussian computer program.

To further study the binding affinity of **Cy**[**4**]**C** toward iodide anion, UV−vis absorption spectral variation of **Cy**[**4**]**C** (4.00×10^{-3} mM) in $CHCl_3$ was monitored during titration with different concentrations of TBAI from 0.0 to 5.00 equiv. We found that with an increasing amount of TBAI the absorption intensity at 360 nm gradually increased (Figure S11). The association constant (K_a) was determined to be 81.8 ± 9.2 M^{-1} for 1:1 complexation by a plot of absorption intensity alternation versus TBAI concentration. Considering **Cy**[**4**]**C** is an electron-rich macrocycle, this association constant is reasonable.[30]

In summary, we synthesized a preorganized, rigid macrocycle, cyclo[4]carbazole, and its structure and host−guest interactions toward halide anions were studied. Cyclo[4]carbazole shows colorimetric and fluorencent recognition for iodide anion in chloroform. The crystal structure of the **Cy**[**4**]**C**/chloroform complex as well as HRMS implied its ability to encapsulate iodide anion to form a 1:1 complex. Moreover, the planar structure of **Cy**[**4**]**C** with an inner cavity diameter of 4.00 Å provides an ideal size for iodide anion complexation. The energy-minimized structure study shows that iodide anion matches the cavity of **Cy**[**4**]**C** exactly and forms multiple hydrogen bonds with the host. As a new receptor for iodide anion, **Cy**[**4**]**C** has potential to play an important role in iodide anion sensing and provide a new perspective to design iodide anion receptors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, NMR spectra, UV−vis spectra, X-ray crystallographic files (CIF) for **Cy[4]C** and its chloroform complex and other materials. These materials are available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02500.

> Experimental details, NMR spectra, UV−vis spectra, X-ray crystallographic data for **Cy[4]C** and its chloroform complex and other materials (PDF)
> X-ray data for **Cy[4]C** (CIF)
> X-ray data for **Cy[4]C** and chloroform (CIF)

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Notes

The authors declare no competing financial interest.

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