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Cyclo[6]aramide-Tropylium Charge Transfer Complex as a Colorimetric Chemosensor for Differentiation of Intimate and Loose Ion Pairs

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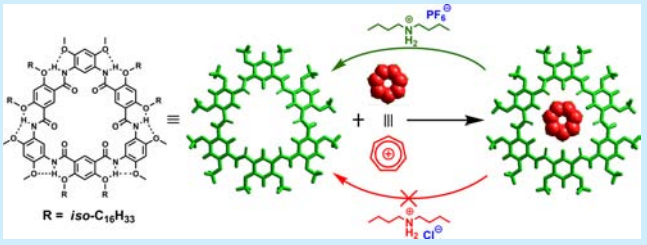
Supporting Information

ABSTRACT: Shape-persistent iso-C_{16}-cyclo[6]aramide (**1**) was found to form a charge-transfer (CT) complex with aromatic carbonium tropylium ($\mathbf{Tr}^+$). The resulting CT complex was evidenced by both experimental results and theoretical calculations. Particularly, dibutylammonium salt with PF_6^- as the counterion can extrude $\mathbf{Tr}^+$ from the CT complex, but it cannot do so with Cl^-, thereby offering a visual approach to identify organic intimate ion pairs and loose ion pairs.



Macrocycle-based host–guest interactions are currently recognized as one of the important tools to implement functions of varying types, such as selective ion binding,[1] gel formation,[2] and catalysis.[3] Among diversified macrocyclic compounds, hydrogen-bonded (H-bonded) macrocycles, which are formed by conformation-directed macrocyclization via folded precursors stabilized by internal hydrogen bonds, are particularly intriguing.[4] Cyclo[6]aramides, as one of these macrocyclic hosts with a shape-persistent[5] backbone, have demonstrated their unique ability to serve as receptors for selective recognition with a variety of guests that include guanidinium ions, metal ions, dialkylammonium ions, diquat salts, and amino acids.[6] A larger cyclo[16]aramide could accommodate even a depsipeptide antibiotic valinomycin.[7] These results provide opportunities for use in such applications as construction of pseudorotaxanes, extractive separation of lanthanides, and specific discrimination of L-arginine. Our very recent study revealed the importance of host–guest (H–G) interactions in manipulating liquid crystal properties with cyclo[6]aramides as macrocyclic mesogens.[8] Given the large electron-rich π-surface of the molecular backbone, cyclo[6]-aramides are expected to bind well to electron-deficient cationic aromatic species. However, the host–guest chemistry in this aspect has been rarely explored. Specifically, all organic guests involved in these studies are nitrogen-containing cations.[6d,e]

Tropylium ($\mathbf{Tr}^+$),[9] as a large aromatic carbonium, has been a subject of interest in host–guest chemistry involving many different classes of macrocycles, such as resorcinarenes,[10] acetylene macrocycles,[11] crown ethers,[12] cryptands,[13] and pillararenes.[14] In no cases is the complexation of $\mathbf{Tr}^+$ concerned with the use of 2D shape-persistent H-bonded macrocycles. Herein we report the charge-transfer complexation of tropylium tetrafluoroborate by iso-C_{16}-cyclo[6]aramide (**1**) (Figure 1) and the serendipitous discovery of its ability to differentiate loose and intimate dibutylammonium (DBuA, **4** and **5**) ion pairs with the naked eye. Theoretical calculations using the density functional theory (DFT) method with a model compound (**2**) were performed to provide the optimized geometry of the CT complex. To our knowledge, ion pairs are traditionally identified by conductivity, potentiometry, and ESR techniques;[15] however, this work offers the first example as a visual approach to detect intimate organic ion pairs and loose ion pairs.

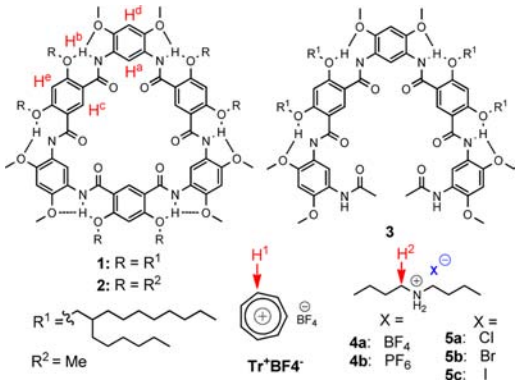


Figure 1. Chemical structures and proton designations of cyclo[6]-aramides **1** and **2**, pentamer **3**, tropylium tetrafluoroborate ($\mathbf{Tr}^+\mathbf{BF}_4^-$), and secondary ammonium salts as the ion pairs.

Our prior study showed that cyclo[6]aramides bearing linear alkyl chains are prone to aggregate severely in both polar and nonpolar solvents.[6c] This greatly impedes accurate determination of the binding affinity of the macrocycles toward guest molecules. However, those that are incorporated with branched

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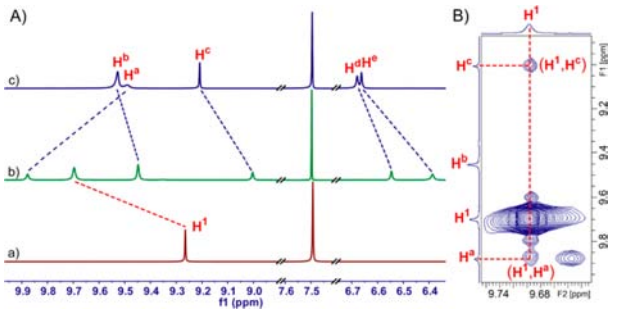

Figure 2. (A) Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, 1/1, v/v) of (a) $\mathbf{Tr}^+$ (2.0 mM), (b) $\mathbf{1} \supset \mathbf{Tr}^+$ (2.0 mM for each), and (c) **1** (2.0 mM). (B) Expanded 2D NOESY spectrum (600 MHz, $CDCl_3/CD_3CN$, 1/1, v/v) of $\mathbf{1} \supset \mathbf{Tr}^+$ (20 mM for each).

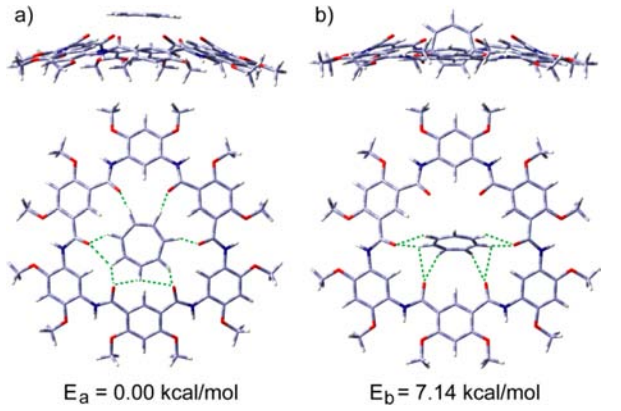

Figure 3. Side (up) and top (down) views of optimized geometry of $\mathbf{2} \supset \mathbf{Tr}^+$ at the RB3PW91/6-31G(d,p) level: (a) parallel conformation; (b) perpendicular conformation. The green dashed lines indicate intermolecular H-bonds. All side chains are replaced by methyl groups for simplicity (gray = C, white = H, red = O, and blue = N).

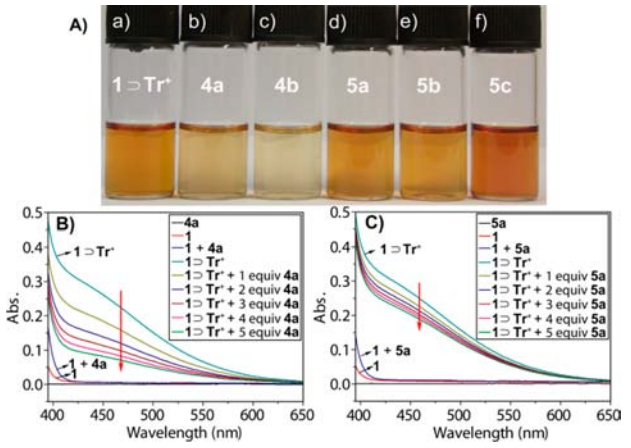

Figure 4. (A) Visible color changes of 5 mM $\mathbf{1} \supset \mathbf{Tr}^+$ (a) and after addition of various DBuA: **4a** (b), **4b** (c), **5a** (d), **5b** (e), and **5c** (f), each one for 8 equiv. (B) UV−vis spectra of $\mathbf{1} \supset \mathbf{Tr}^+$ (1 mM) after addition of 1−5 equiv of **4a** and (C) 1−5 equiv of **5a**.

alkyl groups on the macrocyclic periphery were found to display a nonaggregational behavior, which renders it possible to acquire the binding constants for appraising the affinity ability of cyclo[6]aramides toward secondary ammonium[6d] or diquat salts.[6e] Thus, the complexation with tropylium cation was explored based on cyclo[6]aramide **1** with branched alkyl side chains. Compound **3**, which bears the same number of carbonyl oxygen atoms, serves as a control to see if there is presence of the macrocyclic effect in binding of $\mathbf{Tr}^+$.

The formation of charge-transfer complex interaction between cyclo[6]aramide and tropylium was first indicated by the pronounced color change upon mixing the macrocyclic host **1** and the guest in a mixed solvent of chloroform and acetonitrile. At the same time, the charge transfer band was also observed in UV−vis spectra (Figure S4, Supporting Information). ^{1}H NMR spectra clearly show the marked downfield shift of tropylium protons by 0.44 ppm in $CDCl_3/CD_3CN$ (1/1, v/v) (Figure 2A). Concomitant with the change of proton chemical shifts on the guest molecule, aromatic protons of the macrocycle also experience a change of both downfield and upfield shifts of protons H^a and H^c, indicating the complexation of $\mathbf{Tr}^+$ by the host **1**.

To explore the binding site, two-dimensional NOESY experiments were performed in $CDCl_3/CD_3CN$ with the macrocycle **1** and $\mathbf{Tr}^+$ (Figure 2B). Correlations between the signals attributable to the interior aromatic protons of **1** (denoted as a and c) and protons of $\mathbf{Tr}^+$ (denoted as 1) are observed. In contrast, no cross-peaks associated with the interaction of peripheral alkyl protons and protons 1 appear (Figure S5, SI), strongly suggesting that the complexation may most likely occur with the cation residing in a region within close reach of the macrocyclic cavity. The results from Job's plot and mole ratio plot experiments indicated a 1:1 stoichiometry for the CT complex in solution (Figures S7 and S12, SI). In line with the above results, matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectrometry of an equimolar mixture of **1** and $\mathbf{Tr}^+$ also showed the formation of the complex. A peak of the highest intensity at $m/z = 2427.558$, corresponding to $[\mathbf{1} \supset \mathbf{Tr}]^+$, is observed, indicating a 1:1 molar ratio for the complex (Figure S6, SI). The identity of the 1:1 complex is supported by matching the isotope distribution with the computer simulated one (right inset in Figure S6).

To examine the macrocyclic effect on the complexation toward $\mathbf{Tr}^+$, compound **3** containing the same number of carbonyl groups was compared to the macrocycle **1** for their affinity toward the cation. UV−vis titration experiments in $CHCl_3/CH_3CN$ (1/1, v/v) offered a binding affinity of 1.49×10^4 M^{-1} for $\mathbf{Tr}^+$ by cyclo[6]aramide **1** (Figure S11, SI). This value is almost an order of magnitude larger than the K_a value of 2.85×10^3 M^{-1} for the acyclic analogue **3** (Figure S18, SI). The enhanced binding affinity is attributed to the well-preorganized carbonyl groups on the macrocyclic platform, which favors the intermolecular H-bonding with $\mathbf{Tr}^+$ as compared to those carbonyl groups on the pentameric **3** with helical conformation.[6d]

Computational simulations based on DFT method were performed for the complex system at the RB3PW91/6-31G(d,p) level. The molecular model disclosed the optimized structure of the charge-transfer complex $\mathbf{2} \supset \mathbf{Tr}^+$ of cyclo[6]aramide **2** and $\mathbf{Tr}^+$ in parallel conformation (Figure 3a). The parent framework of cyclo[6]aramides adopts a shallow or almost planar geometry according to previous theoretical calculations.[7] The interior cavity (8.17 Å in diameter) as revealed by our recent X-ray crystal structure[8] seems to match well for accommodating an electron-deficient $\mathbf{Tr}^+$ (5.12 Å in diameter).[12b] However, careful inspection of the conformation of a supposed "concentric circles" model showed that the inter-H bonding distance for each potential H-bond is less than 1.53 Å, which is too close to be accepted as reasonable hydrogen bonds. Therefore, $\mathbf{Tr}^+$ cannot

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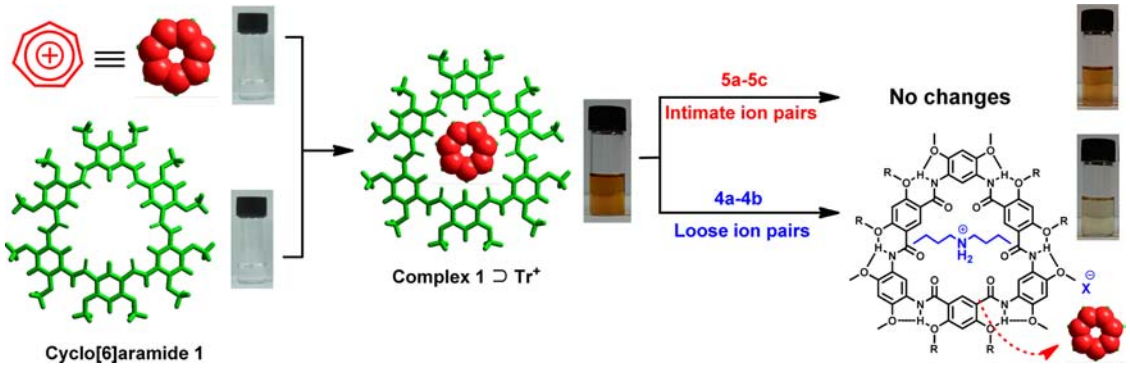

Figure 5. Schematic representation of the formation of CT complex **1** ⊃ Tr^+ and its use for megascopic detection of intimate ion pairs and loose ion pairs.

Table 1. Apparent Binding Constants K_a (M^{-1}) of 1 with Dibutylammonium Salts at 298 K

complex	ion pair[a]	K_a (M^{-1})[b]
1·4a	loose	$(1.15 \pm 0.15) \times 10^4$
1·4b	loose	$(9.55 \pm 1.15) \times 10^3$
1·5a	intimate	$(2.63 \pm 0.39) \times 10^3$
1·5b	intimate	$(6.50 \pm 0.37) \times 10^3$
1·5c	intimate	$(1.42 \pm 0.10) \times 10^4$

[a]The type of ion pairs before complexation was established by related references.[17] [b]The apparent binding constant K_a values were obtained by proton NMR titration.

locate inside the cavity of **2**. Subsequent simulations offer an optimized parallel structure in which the Tr^+ sits above the shallow bowl-shaped macrocycle with the stabilization energy of 7.14 kcal/mol being smaller compared to the perpendicular model (Figure 3b). Moreover, the charge of Tr^+ decreases to +0.938 in the parallel conformation (Table S3, SI), suggesting the charge transfer from **1** to Tr^+.

Interestingly, nine inter-H bonds exist between tropylium hydrogens and carbonyl oxygens in this parallel conformation. The presence of H-bonds is consistent with the results from dilution experiments where tropylium hydrogen in the complex **1** ⊃ Tr^+ experiences a small downfield shift with decreasing the concentration of the complex (Figure S9, SI). In addition, the shift to a lower wavenumber of carbonyl group of the charge-transfer complex in IR spectra also indicates the H-bonding interaction between Tr^+ and the macrocycle (Figure S8, SI).

To gain insight into the complexation process, a series of secondary ammonium salts **4a**−**4b** and **5a**−**5c** were examined for their competitive interactions with the tropylium complex. These salts were found to bind well with cyclo[6]aramides.[6d] Interestingly, addition of dibutylammonium tetrafluoroborate **4a**, a loose ion pair, to the complex in $CHCl_3/CH_3CN$ causes the color to fade. With PF_6^- as the counteranion in **4b**, the solution turns almost colorless. In sharp contrast, the halide series **5a**−**5c** as the intimate ion pairs are much insusceptible in effecting the color change. The visible color changes are consistent with the results from UV−vis spectra. When adding **4a** or **4b** to **1** ⊃ Tr^+ gradually, the CT band decreases dramatically (Figures 4B, and S20, SI). However, intimate ion pairs **5a** and **5b** only induces a limited drop of the CT band (Figures 4C and S21, SI). These changes in UV−vis spectra indicated that loose ion pairs are much more destructive to the complex **1** ⊃ Tr^+ than intimate ion pairs. Particularly, quantitative analysis was conducted to determine the residual **1** ⊃ Tr^+ after addition of DBuA at 450 nm. For loose ion pairs **4a** and **4b**, the percentage of residual **1** ⊃ Tr^+ was only 31% and 31%, respectively, while there were still 76% and 73% of the CT complex left for **5a** and **5b** with up to 5 equiv of DBuA. When iodide ion is used as the counterion in **5c**, the absorbance cannot be determined accurately due to the interference from tropylium iodide (Figure S22, SI).[16] To rationalize the difference in their ability to decompose the complex, apparent binding constants of the complexation involving these guest salts were determined (Table 1).

In the case of **4a**, an apparent binding constant of 1.15×10^4 M^{-1} in $CDCl_3/CD_3CN$ (1:1, v/v) was obtained by fitting the concentration-dependent change of the chemical shifts[6d] of proton **4a**-H^2 (Figure S25, SI). The other salt **4b** shows the K_a value being close to **4a** (Figure S27, SI). Replacing the counterions of **4** with halide anions led to **5a**−**5c** with K_a values at the order of magnitude 10^3 M^{-1} except for **5c** (Figures S29, S31, and S33, SI), indicative of considerably reduced binding affinity when halide ions are present as the counteranions. For example, with chloride as the counterion of the ion pair, **1·5a** provides a K_a of 2.63×10^3 M^{-1}, showing ca. 4.4-fold decrease with respect to **1·4a** in association affinity. This implicated that the binding of loose ion pair **4a** by the host is more favorable than the binding of intimate ion pair **5a**. In general, the macrocycle has the preferential complexation of **4** over **5**. With this in mind, the color change of the CT complex triggered by addition of ion pairs is well explained by the illustration in Figure 5. Since the K_a of **1·5a** (or **1·5b**) is 1 order of magnitude lower than that of **1** ⊃ Tr^+ complex (1.49×10^4 M^{-1}), **5a** (or **5b**) is unable to compete with Tr^+ when **1** ⊃ Tr^+ is exposed to intimate ion pairs **5**. In the case of **5c**, despite the approximate K_a value for **1·5c** (1.42×10^4 M^{-1}) and the CT complex, the solution becomes dark brown. This is ascribed to the enhanced coloration by the CT interaction between Tr^+ and the iodide in **5c**.[16]

Although the binding affinity between **1** and **4a** (or **4b**) is comparable to that between **1** and Tr^+, the larger percentage of the guest salts (in excess) drives the decomplexation equilibrium of **1** ⊃ Tr^+ and **4a**, for example, toward the forward reaction, leading to the rivaling replacement of Tr^+. In addition, the loose ion pair is easier to dissociate as compared to the intimate ion pair[17] and therefore is more favorable in binding to the macrocycle in the recognition event. Given the conspicuous color change, the observation above suggests a visual methodology of distinguishing intimate ion pairs from loose ion pairs in solution based on cyclo[6]aramide-tropylium complex. So far, differentiations of ion pairs rely on such methods as conductivity, ESR, etc. Our results provide an alternative approach to identify organic intimate ion pairs and loose ion pairs.

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In conclusion, iso-C_{16}-cyclo[6]aramide was found to form a charge-transfer complex with tropylium tetrafluoroborate via the strong CT interaction and H-bonding. This represents the first example of host−guest chemistry between hydrogen bonded macrocycles and carbonium cations. Both experimental evidence and computational analysis support the formation of the complex. More importantly, the CT complex can be used as a colorimetric chemosensor for differentiating intimate and loose DBuA ion pairs via the guest−competitive complexation process. Our results provide a visual and effective approach to distinguish the tightness of ion pairs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02829.

Experimental procedures and characterization of compound **3**, titration experiments, and molecular modeling (PDF)

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Notes

The authors declare no competing financial interest.

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