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Reversibly Tunable Lower Critical Solution Temperature Behavior Induced by H-Bonded Aromatic Amide Macrocycle and Imidazolium Host–Guest Complexation

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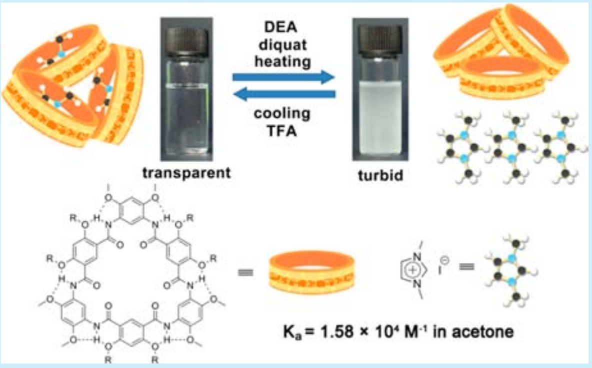
Ⓢ *Supporting Information*

ABSTRACT: A new supramolecular host–guest motif comprising an H-bonded aromatic amide macrocycle and imidazolium cation based ionic liquids was developed, which allows tunable binding affinity via altering N-substitution or counterions. This host–guest system exhibits lower critical solution temperature behavior that can be precisely controlled by adjusting concentration, competitive guest, and acid/base. The demonstrated separation of two organic dyes with the supramolecular complex holds promising applications in separation science.



Host–guest (H–G) chemistry has made its way in recent years into a wide spectrum of applications such as creation of mechanically interlocked molecules (MIMs),[1] generation of responsive MOF (COF) materials,[2] and functionality-tunable nanomaterials for separation science.[3] The advances in these aspects depend significantly on emerging recognition motifs that ensure the implementation of functions. Central to the development of recognition motifs is the complementary interplay between host and guest, for example, the appropriate binding affinity that justifies responsiveness of the recognition system[4] and molecular topology that allows functionality to interact efficiently.[5] In this regard, the combination of macrocyclic molecules and imidazolium (Im) cations features extensively in recognition modules,[6] which mainly stems from the importance of Im-based ionic liquids in versatile applications.[7] In particular, 1*N*,3*N*-dialkylimidazolium salts constitute an important class of room-temperature ionic liquids (RTIL) that can interact with various kinds of macrocycles[8] such as crown ethers, cyclodextrins, calixarenes, cucurbiturils, and pillararenes. However, few documented recognition motifs involving Im-based ionic liquid show lower critical solution temperature (LCST) behavior,[9] which is associated with well-known thermoresponsiveness often observed in polymers. A polymer solution undergoes phase transition from a soluble to an insoluble state above LCST.[10] Furthermore, nonpolymeric LCST materials[11] are still rather rare compared to polymeric LCST systems.

Hydrogen-bonded (H-bonded) aromatic amide macrocycles represent a class of recently emerged 2D cyclic host molecules featuring full amide linkages with backbones enforced by intramolecular hydrogen bonds.[12] Among them, cyclo[6]-aramides have demonstrated their unique ability to serve as receptors for selective recognition with a variety of guests that include guanidinium ions,[12a] metal ions,[13a] organometallic species,[13b] dialkylammonium ions,[13c] diquat salts,[13d] and amino acids.[13e] Interestingly, H–G complexation could be utilized to tune the mesogenic properties of these H-bonded macrocycles for fabricating liquid-crystal materials.[14] Herein, we report on a novel recognition motif comprising cyclo[6]-aramide (**1**) and imidazolium (**4a–g**, Figure 1) that functions as an LCST material with multiple-responsive control of LCST behavior typically exemplified by 1,3-dimethylimidazolium iodide (**4g**). Intriguingly, a demonstrated experiment based on this H–G system shows the possibility of separating two dyes. This is the first observation of a LCST-type phase transition induced by H-bonded aromatic amide macrocycles based on H–G recognition.

Motivated by the high affinity of cyclo[6]aramide **1** toward dialkyl ammonium,[13c] we reasoned that **1** might form a tight H–G complex with the Im cation because the size of the Im cation (ca. 4.5 Å, Figure S68) is the right fit for the cavity of the cycle (8.17 Å).[14] Indeed, stepwise addition of Im **4a** to a solution of **1** in acetone-d_6 leads to the downfield shifts of protons H^1, H^2, and H^3 of Im along with the concomitant chemical shift changes of internal aromatic protons H^a and H^b of the cycle, indicating the strong H–G interaction (Figure 2). In addition, the observation of only one set of peaks suggests fast-exchange complexation between **1** and **4a** on the ^{1}H NMR

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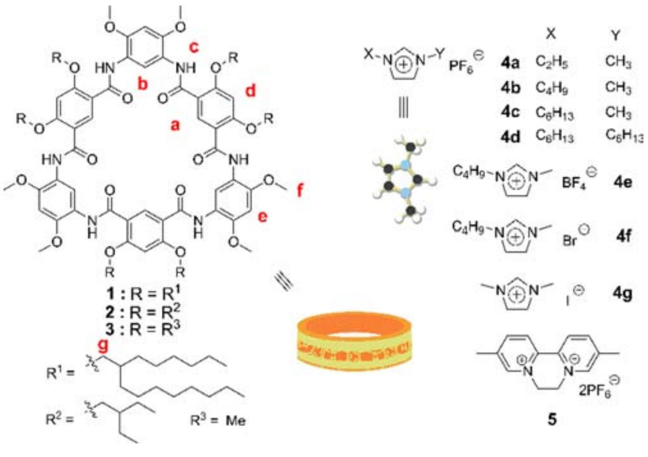

Figure 1. Chemical structures and proton designations of cyclo[6]-aramides **1**−**3**, a series of imidazolium based ionic liquids **4a**−**g**, and diquat derivative **5**.

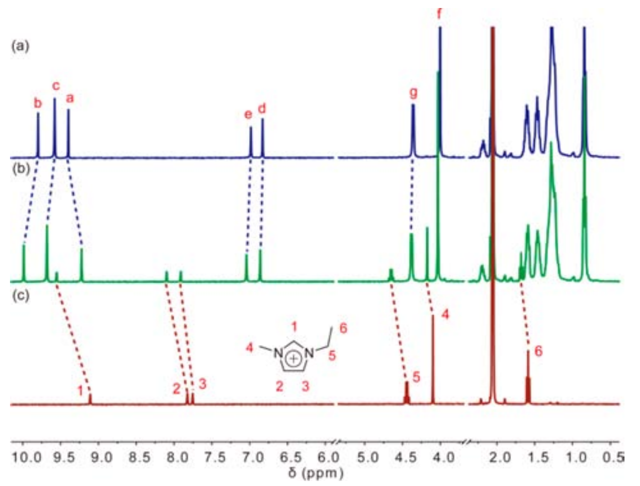

Figure 2. Partial ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 298 K) of solutions of (a) 1 mM **1**; (b) 1 mM **1** and **4a**; and (c) 1 mM **4a**.

time scale at 298 K (Figure S3). The mole ratio and Job's plot experiments indicate a 1:1 stoichiometry for the H−G complex in solution (Figures S5 and S6). In line with the above results is the observation of a peak of the highest intensity at m/z = 2494.29, corresponding to $[\mathbf{1} + \mathbf{4a} + \mathrm{EtOH} - \mathrm{PF_6}^-]^+$, from the high-resolution electrospray ionization mass spectrometry, which also reveals a 1:1 molar ratio for the complex (Figure S7). ^{1}H NMR titration experiments provide a binding constant of $(1.55 \pm 0.57) \times 10^3$ M^{-1} in acetone-d_6 by fitting the concentration-dependent chemical shift changes of H^b on **1** (Figure S4). However, a very high binding affinity ($>10^5$ M^{-1}) in chloroform prevented us from acquiring an accurate K_a value with the same method.

The advantage of using 1*N*,3*N*-dialkylimidazolium salts is its flexibility in tuning the properties of ionic liquids by varying either substituents X and Y at two nitrogen atoms or counteranions.[15] Thus, a series of imidazolium derivatives **4a**−**g** were prepared to probe substitution effects upon the binding process and affinity. In all cases, a 1:1 stoichiometry for the H−G complexation between **1** and **4a**−**g** was obtained as indicated by the results from the mole ratio method, Job's plot, and MS experiments (see the Supporting Information). Interestingly, extension of 1N-substitution while keeping 3N unchanged increases the binding association in the order of **4c** > **4b** > **4a** (Table 1). In stark contrast, introduction of an additional longer alkyl group at the 3N atom as in **4d** considerably enhances the association constant up to $(3.40 \pm 0.74) \times 10^4$ M^{-1}, a 6-fold increase with respect to **4c**. This could be rationalized by the likelihood that extending two attaching groups as in **4d** could effectively prevent the guest from sliding. On the other hand, counterions also exert appreciable influence upon the H−G complexation. Specifically, for guests **4b**, **4e**, and **4f** having the same cationic species with different counterions, the H−G pairs show increasing K_a values from PF_6^- to BF_4^- to Br^-. Loose ion pairs involving PF_6^- and BF_4^- usually promote H−G complexation more efficiently than intimate ion pairs associated with halide anions.[16] The reversal observed here, i.e., $Br^- > BF_4^- > PF_6^-$, may suggest that several factors including ion dipole interactions, hydrogen-bond-accepting ability[17] and the size of anions work together in combination to result in the difference of binding affinity.

Table 1. Association Constants and Gibbs Free Energies of Complexes in CD_3COCD_3 at 298 K

complex	K_a[a] (M^{-1})	ΔG[b] (kJ/mol)
$\mathbf{1}\supset\mathbf{4a}$	$(1.55 \pm 0.57) \times 10^3$	−18.2
$\mathbf{1}\supset\mathbf{4b}$	$(3.06 \pm 0.61) \times 10^3$	−19.9
$\mathbf{1}\supset\mathbf{4c}$	$(5.66 \pm 0.57) \times 10^3$	−21.4
$\mathbf{1}\supset\mathbf{4d}$	$(3.40 \pm 0.74) \times 10^4$	−25.9
$\mathbf{1}\supset\mathbf{4e}$	$(9.18 \pm 0.47) \times 10^3$	−22.6
$\mathbf{1}\supset\mathbf{4f}$	$(1.23 \pm 0.62) \times 10^4$	−23.3
$\mathbf{1}\supset\mathbf{4g}$	$(1.58 \pm 0.81) \times 10^4$	−24.0

[a] The association constant K_a values were obtained by proton NMR titration. [b] The Gibbs free energies (ΔG) of complexation were calculated from the K_a values using the equation $\Delta G = -RT \ln K_a$.

To probe the binding site, NOESY experiments revealed through-space NOEs between Im protons (H^1 and H^3) and the internal aromatic proton H^b of **4g** (Figures S52 and S53). Such through-space NOE contacts can occur only if the imidazolium ion threads through the cavity of the macrocycle. The threading of the guest is corroborated by the opposite variation of chemical shift along the alkyl chains. For example, the methylene protons (H^3 and H^4) of **4d** experiences a downfield shift with respect to other alkyl protons (H^5−H^8) on the chain (Figure S24), indicating that H^3 and H^4 are located in a deshielding environment. On the opposite, proton H^5−H^8 show an upfield shift, suggesting the shielding effect due to the location of the Im on the upper above the phenyl ring of **1**.

Slow vapor diffusion of CH_3OH into a $CHCl_3$ solution containing **2** and **4a** afforded single crystals suitable for X-ray diffraction. However, the crystals were weakly diffracting, and the data could be refined to a resolution of 1.30 Å (Figures S66 and S67) possibly due to the properties of Im-based ionic liquids, which are known to be very difficult to crystallize in H−G complexes.[8i] From the partially resolved structure, it is possible to tell that **4a** does thread through the cavity of cyclo[6]aramide **2**. In addition, there are two PF_6^- anions in the asymmetric unit, one of which is located closely from the center of imidazolium cation. To retrieve detailed structural information, molecular mechanics simulations were performed to gain a better understanding of the noncovalent interactions that govern the binding affinity. The simulated structure of the complex $[\mathbf{3}\supset\mathbf{4a}]^+$ (Figure 3 and Figure S61) reveals that the cavity of **3** could well accommodate Im cation. With six

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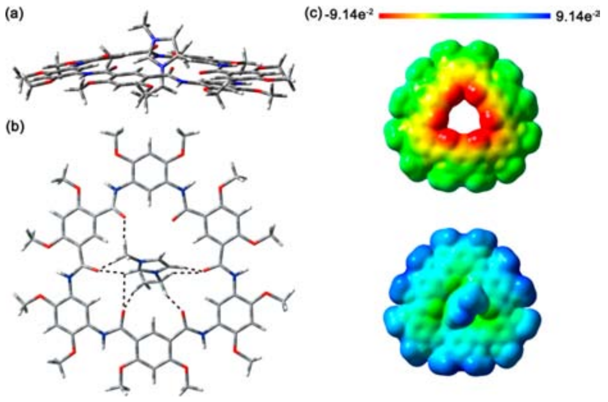

Figure 3. Side view (a) and top view (b) of optimized geometry of **3**⊃**4a** at the RB3LYP/6-31G (d, p) level. The dark dashed lines indicate intermolecular H-bonds (gray = C, white = H, red = O, and blue = N). (c) Mapped surface of **3** (upper) and **3**⊃**4a** (down).

introverted electron-rich amide oxygen atoms (Figure 3c), the inclusion complex is stabilized by C–H(sp^3)···O and C–H(Ar)···O hydrogen bonds (H···O 2.03–3.07 Å) (Figure 3b and Figure S61) and thus is suitable for the development of an ion–dipole interaction via electron transfer from electron-rich **3** to **4a** (Figure 3c). Therefore, the optimized geometry of **3** with included **4a** closely matches the structure suggested by X-ray crystallographic analysis. On the other hand, the shift (ca. 8 cm^{-1}) to a lower wavenumber of carbonyl groups of the complex **1**⊃**4a** in the IR spectra also suggests H-bonding interactions between the Im cation and the macrocycle (Figure S8). The above evidence indicates that the imidazolium ring of the guest threads into the cavity of the macrocycle, pointing to the formation of [2]pseudorotaxane-type complex.

Since neither **1** nor **4g** exhibited any LCST behavior individually, the possibility of inducing LCST or phase behavior by utilizing H–G complexation was explored. Different from ionic liquids **4a–f**, compound **4g** is sparsely soluble in chloroform,[9] and so a mixture of **4g** and chloroform actually consists of two layers at ambient temperature (Figure S54a). Upon addition of 0.2 equiv of **1** to the mixture, a noticeable transition from two immiscible phases to a homogeneous solution was observed (Figure S54b), indicating that H–G interaction occurred between **1** and **4g**. When the temperature is varied, this H–G system shows tunable thermoresponsive properties; i.e., the solution gradually turns turbid (Figure S54c) with increasing temperature and becomes transparent again upon cooling. Therefore, a mixture containing both **1** and **4g** in chloroform constitutes a novel nonpolymeric LCST system that operates following a mechanism of H–G complexation-induced LCST-type phase change. Manipulation of the clouding point (T_{cloud}) is most important in evaluating the LCST behavior. Fortunately, three approaches were found to allow adjusting T_{cloud}. First, it is possible to control the T_{cloud} simply by varying the concentration of either the guest or the host. When the molar ratio of **1** to **4g** changed from 0.18 to 0.24 equiv while maintaining the concentration of **4g** at 0.25 M, T_{cloud} gradually increased from 36.5 to 53.4 °C (Figure S56), showing a molar-ratio-dependent T_{cloud}. If the molar ratio was kept constant at 0.20, then T_{cloud} rose from 42.0 to 47.4 °C (Figure S55) with an increase in concentration of **4g** from 0.25 to 0.45 M. These data indicate that increasing the concentration of either of the species in the H–G system results in the enhanced T_{cloud}. These observations are quite different from most LCST-type systems where a decrease in T_{cloud} is usually observed as the concentration of the solute increases.[18] Second, diquat derivative **5** (Figure 1) was selected as a competitive guest and added to the solution of **1**⊃**4g**. The T_{cloud} was found to change in a different trend as above due to the strong binding capability of **5** by **1** (Figures S57 and S58).[13d] Third, to our surprise, the addition of DEA followed by treatment with TFA led to a reversible change of the T_{cloud} between 42.2 and 25.2 °C (Figures S59 and S60). This process is reproducible at least three times at 0.01 M EDA and 0.01 M TFA ($[\mathbf{1}]_0$ = 0.05 M, $[\mathbf{4g}]_0$ = 0.25 M).

Ionic liquids (ILs) are known to hold great potential as green solvents in separation science.[19] More importantly, many IL-containing binary systems experience a liquid–liquid phase separation with LCST. This thermoresponsive phase behavior may be utilized for efficient extraction and separation.[20] Among the very limited examples of LCST binary systems comprising macrocyclic hosts and guests, only one report involved the use of imidazolium.[9] To demonstrate the possibility of separation based on H–G interactions, two dyes (methylthionine chloride and carotene) were chosen as model compounds (Figure 4).

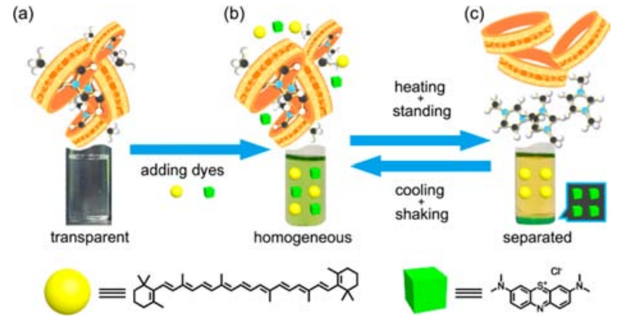

Figure 4. Schematic representation of the **1**⊃**4g** interaction-induced LCST-type phase separation in the mixing and demixing procedure for segregation of two organic dyes.

The strong binding affinity as quantified by K_a values in acetone offers the possibility of showing LCST behavior via sufficiently strong host–guest interaction in an organic solvent ($CHCl_3$) (Figure 4a) for subsequent two-phase extraction. Since a mixture of methylthionine chloride (blue) and carotene (yellow) is soluble in the chloroform solution of **1** and **4g**, the mixture presents a homogeneous solution (Figure 4b).

Upon heating to 50 °C and standing, the solution turned into two stable layers with carotene in the chloroform phase and methylthionine chloride in the ionic liquid phase of **4g** (Figure 4c). Then, upon cooling to 20 °C and shaking, the solution turned into a homogeneous solution again. It should be noted that macrocycle **1** shows little interaction with the two chosen dyes. With controlled reversibility and reproducibility, this H-bonded aromatic amide macrocycle–imdazolium H–G complex system may find applications in product and educt separation based on supramolecular interaction-induced LCST-type phase change.

In summary, we have demonstrated an H-bonded aromatic amide macrocycle/ionic liquid H–G recognition motif that exhibits LCST-type phase transition. This shape-persistent macrocycle is found to efficiently complex a series of imidazolium-based ILs in acetone with binding affinity that is tunable by altering either N-substitution or counterions. This H–G complexation is responsible for the LCST-type solution behavior, which can be conveniently controlled by three approaches and used for the separation of two organic dyes. So far, the use of H-bonded amide macrocycles for LCST behavior has been untapped. Allowing for the controllability of the H−G interactions and the variation of host−guest pairs, this novel host−guest interaction-induced LCST-type phase change holds promise for IL-based applications, such as creating soft matters, intelligent gels, and thermoresponsive extractants for separation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03125.

> Experimental procedures and characterization of compound **4**, titration experiments, and molecular modeling (PDF)

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Notes

The authors declare no competing financial interest.

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