Host–Guest Systems

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A Triphasic Sorting System: Coordination Cages in Ionic Liquids

*Angela B. Grommet, Jeanne L. Bolliger, Colm Browne, and Jonathan R. Nitschke**

Abstract: *Host–guest chemistry is usually carried out in either water or organic solvents. To investigate the utility of alternative solvents, three different coordination cages were dissolved in neat ionic liquids. By using ^{19}F NMR spectroscopy to monitor the presence of free and bound guest molecules, all three cages were demonstrated to be stable and capable of encapsulating guests in ionic solution. Different cages were found to preferentially dissolve in different phases, allowing for the design of a triphasic sorting system. Within this system, three coordination cages, namely Fe_4L_6* ***2****, Fe_8L_{12}* ***3****, and Fe_4L_4* ***4****, each segregated into a distinct layer. Upon the addition of a mixture of three different guests, each cage (in each separate layer) selectively bound its preferred guest.*

Designing new functionality into supramolecular cage systems can be accomplished via two different routes: by building a cage with a cavity of specific size,[1] shape,[2] or chemical functionality;[3] or by changing the environmental conditions that govern guest binding.[4] The first method may require considerable synthetic effort,[5] whereas the second requires only variation of the reaction temperature or solvent. Guest binding is enhanced, for example, in a solvent in which the guest is poorly solvated.[6] Although extensive solution-based host–guest investigations have been carried out either in water[7] or in organic solvents,[8] far fewer studies have involved a third class of solvents—ionic liquids (ILs). These salts, which are molten below 100 °C, are good solvents for the encapsulation of guests into organic capsules, such as cucurbiturils[9] and calixarenes.[10] Similarly, Daguenet and Dyson have demonstrated that a Ni metallacage binds chloride in a range of ionic liquids.[11]

Here we introduce the concept of using different coordination cages in multiple IL phases simultaneously. Three cages are shown to be stable and capable of encapsulating guests in imidazolium and phosphonium ILs, allowing us to selectively dissolve cages in specific phases and bind specific guests within hosts. We present a triphasic system (consisting of water and two mutually immiscible, hydrophobic ILs)[12] in which each of three different cages is soluble in only one layer. Upon the addition of three different guests, each cage selectively encapsulates the guest to which it binds most favorably, influencing the composition of each layer.

Nondeuterated ILs were used in this study, precluding the use of ^{1}H NMR techniques. ESI-MS also did not give meaningful results because high-intensity peaks from the charged solvent obscure solute peaks (see Section S2 in the Supporting Information). The use of ^{19}F NMR spectroscopy, however, proved to be a fruitful method for the characterization of host–guest complexes of cages in IL solutions, with fluorinated guests reporting the presence of the cage.

When a fluorinated prospective guest molecule was dissolved in an IL, its characteristic spectrum was recorded using ^{19}F NMR spectroscopy. If this spectrum remained unchanged after the addition of a cage, we inferred that no complexation had occurred. In this case, the cage might not be stable in the IL. Alternatively the cage could be intact, but there may be no driving force for encapsulation: for example, the prospective guest might be too large.

A significant change in the chemical shifts of the resonance signals in the ^{19}F NMR spectrum of the guest, however, would be consistent with guest encapsulation in fast exchange on the NMR timescale, allowing us to conclude that the cage is intact and functional.[13] The detection of an additional set of ^{19}F NMR resonance signals for a guest molecule would indicate the presence of both free and encapsulated guests in slow exchange, also confirming guest binding within a stable cage.[14]

To probe the stability of coordination cages in ionic liquids, a solution of cage **1**[15] (3.3 mM) in 1-ethyl-3-methylimidazolium ethylsulfate ([emim][$EtOSO_3$]) was prepared (Scheme 1 a). After 1,3,5-trifluorobenzene (guest **A**; 5 equiv) was added to a solution of **1** in [emim][$EtOSO_3$] and the mixture stirred for one week at 296 K (Scheme 1 b), three resonances were observed by ^{19}F NMR spectroscopy (Figure S8 b in the Supporting Information). Signals corresponding to trifluoromethanesulfonate (triflate or TfO^-, the counterion for cage **1**) and free 1,3,5-trifluorobenzene were detected at the same chemical shift values in the presence and absence of the cage. We attribute the new signal to 1,3,5-trifluorobenzene within **1**, in slow exchange with free 1,3,5-trifluorobenzene on the NMR timescale.

As previously reported, iron(II) tetrahedral cages can be "unlocked" by adding *p*-toluenesulfonic acid, resulting in guest release.[16] We inferred that cage **1** should also be unlockable in an IL. Since a cage must first be locked in order to be unlocked, success would further confirm that the cage remains intact and functional in the IL (Scheme 1 c). *p*-Toluenesulfonic acid (10 equiv) was thus added to a solution of 1,3,5-trifluorobenzene$\subset$**1** in [emim][$EtOSO_3$]. After stirring at room temperature overnight, the purple solution was observed to turn brown, and the ^{19}F NMR resonance signal assigned to encapsulated 1,3,5-trifluorobenzene disappeared

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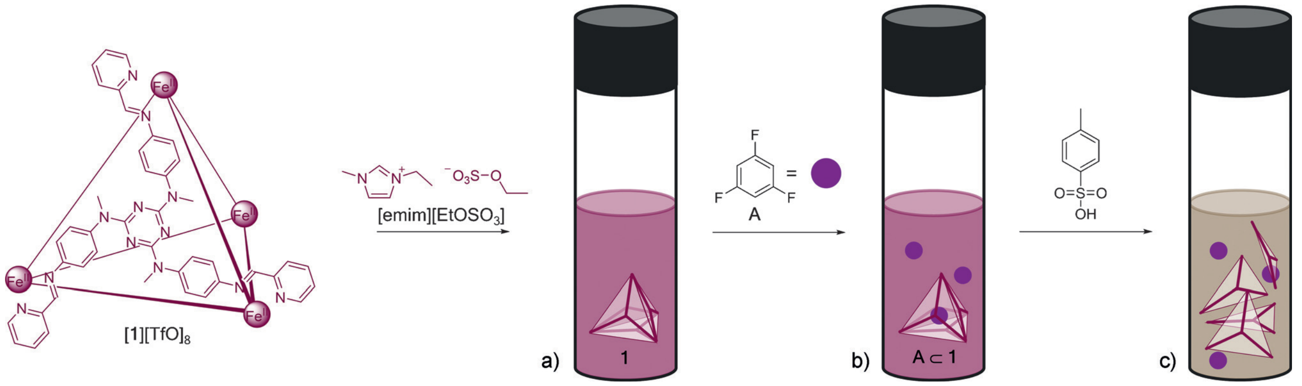
[*] A. B. Grommet, Dr. J. L. Bolliger, Dr. C. Browne, Prof. J. R. Nitschke
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge, CB2 1EW (UK)
E-mail: jrn34@cam.ac.uk
Homepage: http://www-jrn.ch.cam.ac.uk

Dr. C. Browne
Current Address: School of Chemistry, University of Manchester
Oxford Road, Manchester, M13 9PL (UK)

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201505774.

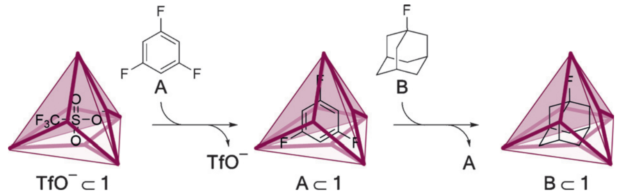


Scheme 1. a) Cage **1** dissolved in the IL [emim][EtOSO$_3$]. b) ^{19}F NMR spectroscopy was used to show that guest **A** was bound within **1**. c) Guest **A** was released from "unlocked" **1** following the addition of *p*-toluenesulfonic acid.

(Figure S8c). The signals from triflate and free 1,3,5-trifluorobenzene, however, remained unchanged. The disappearance of the ^{19}F resonance signal at $\delta = -105.85$ ppm suggested that cage **1** had indeed unlocked to release encapsulated 1,3,5-trifluorobenzene. The ^{1}H NMR spectrum of the sample after the color change confirmed that the IL had not decomposed.

In water and acetonitrile, strongly binding guests have been shown to displace weakly binding guests within coordination cages.[17] Competition experiments carried out using a cage in IL solution were undertaken to further probe whether guest encapsulation proceeds similarly in ILs as in water and organic solvents. Two fluorinated guests, 1,3,5-trifluorobenzene (**A**) and 1-fluoroadamantane (**B**), were added to separate solutions of cage **1** dissolved in [emim][EtOSO$_3$]. After one week, the binding constants (K_a) of the two guests were determined by integrating the ^{19}F resonance signals from the free and encapsulated species (Section S6 in the Supporting Information). 1-Fluoroadamantane ($K_a = 150\,\text{M}^{-1}$) was found to bind more strongly than 1,3,5-trifluorobenzene ($K_a = 80\,\text{M}^{-1}$), which in turn bound more strongly than triflate ($K_a = 4.4\,\text{M}^{-1}$), the counter-ion for **1**. No significant change to the ^{19}F NMR spectrum was detected after an additional week, indicating that equilibrium had been attained (see Section S6 for a short discussion on the kinetics and thermodynamics of this system).

Based on these differences in guest-binding affinity, we designed a sequence of guest exchanges involving **1** dissolved in [emim][EtOSO$_3$] (Scheme 2). Initially, ^{19}F NMR signals for both free and encapsulated triflate were detected (Figure S12a). After the addition of 1,3,5-trifluorobenzene (5 equiv), the signal for encapsulated triflate disappeared and was replaced by signals attributable to free and encapsulated **A** (Figure S12b), indicating that **A** had replaced bound triflate. Following the addition of 1-fluoroadamantane **B** (5 equiv), the signal for encapsulated **A** diminished in intensity and signals assigned to free and encapsulated **B** appeared (Figure S12c). Using the free triflate signal as a reference, the proportion of cage **1** binding 1,3,5-trifluorobenzene was determined to be 58% before and 20% after the addition of 1-fluoroadamantane (see Section S6 for further discussion). The decrease in the proportion of cage-bound 1,3,5-trifluorobenzene indicated that **B** displaced the more weakly binding **A**, as anticipated based upon their binding constants.

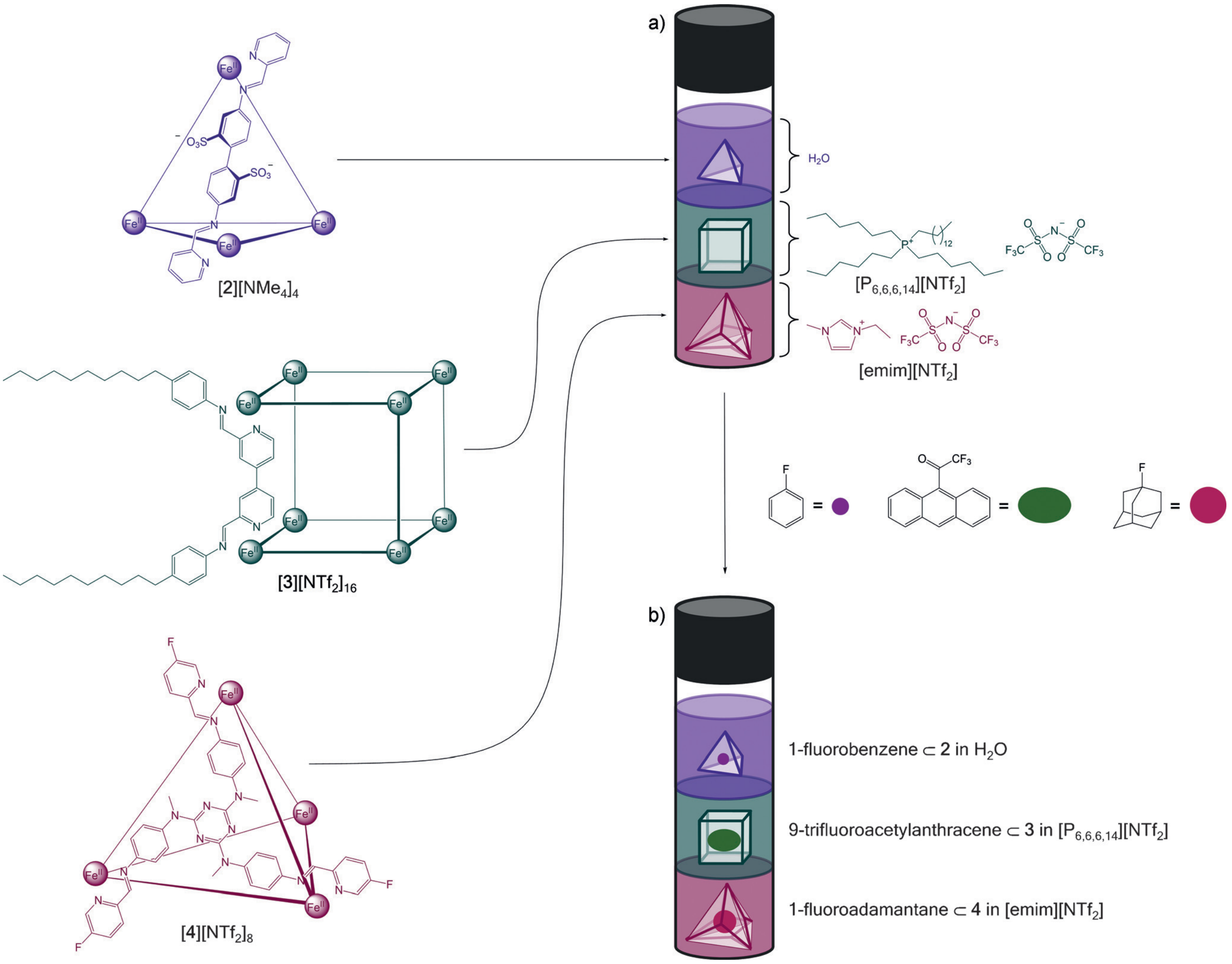


Scheme 2. Selective guest exchange within **1** dissolved in in the IL [emim][EtOSO$_3$], based upon differences in guest-binding affinity.

The properties of ILs, such as their polarity and hydrophobicity, can be tuned through the choice of the cation and anion, each of which contribute different characteristics to the bulk liquid.[12] ILs can thus be designed to dissolve different solutes selectively and be rendered mutually miscible or immiscible. In combination with coordination cages, complex phase-sorting behavior may thus be engineered, as shown in Scheme 3. The triflimide anions (NTf_2^-) of [$P_{6,6,6,14}$][NTf_2] and [emim][NTf_2] render these ILs hydrophobic. The large, lipophilic [$P_{6,6,6,14}$]$^+$ ion and small, more polar [emim]$^+$ ions do not associate strongly with each other, making the two ILs mutually immiscible. Together with water, these two ILs form a triphasic system.

Cage **2**[16] (Scheme 3) bears twelve sulfonate groups, rendering this cage highly soluble in water and insoluble in the two hydrophobic IL layers. Cage **3**[18] (Scheme 3) is decorated with 24 decyl chains, making it lipophilic and insoluble in water. Although [emim][NTf_2] is hydrophobic, it is also highly polar: a combination of properties unique to ILs.[19] Therefore, only [$P_{6,6,6,14}$][NTf_2] offers a suitably lipophilic solvent for cage **3**.

Selecting a cage that dissolves readily in [emim][NTf_2] required a nuanced approach. Cage **1** is only sparingly soluble in [emim][NTf_2], despite having good solubility in the similar IL, [emim][EtOSO$_3$]. Since the only difference between these two ILs is their anion, we hypothesized that the more fluorous environment in [emim][NTf_2] contributed to the poor solubility of cage **1**. We therefore incorporated twelve fluorine atoms into the periphery of cage **4** by employing 5-fluoro-2-



Scheme 3. Within a triphasic system, cages **2**, **3**, and **4** were observed to partition selectively into H_2O, $[P_{6,6,6,14}][NTf_2]$, and $[emim][NTf_2]$, and to bind selectively 1-fluorobenzene, 9-trifluoroacetylanthracene, and 1-fluoroadamantane, respectively.

formylpyridine as a subcomponent instead of the parent 2-formylpyridine used in the preparation of **1** (Section S3). This change resulted in a marked increase in the solubility of **4** in $[emim][NTf_2]$, and cage **4** was therefore used in the sorting system of Scheme 3. As seen in Figure 1, the affinity of each cage (**2**–**4**) for its designated layer was visually conspicuous. Each of three vials were filled with 0.5 mL of each phase (water (top layer), $[P_{6,6,6,14}][NTf_2]$ (middle layer), and $[emim][NTf_2]$ (bottom layer)). Solid samples of cage **2**, cage **3**, and cage **4** were added to the first, second, and third vials, respectively. After the addition of the cage, all vials were shaken vigorously and the phases were allowed to settle. Cage **2** was thus observed to be soluble only in water (Figure 1 a), whereas cage **3** dissolved only in $[P_{6,6,6,14}][NTf_2]$ (Figure 1 b), and cage **4** only in $[emim][NTf_2]$ (Figure 1 c).

By considering the partially overlapping guest-binding preferences of the three cages in Scheme 3, we were able to bring about a situation in which each host bound a single guest selectively in its respective phase. Many of the guests bound by cage **2** can also be encapsulated by cage **4**. In water, benzene binds strongly to **2** and weakly to the fluorine-free

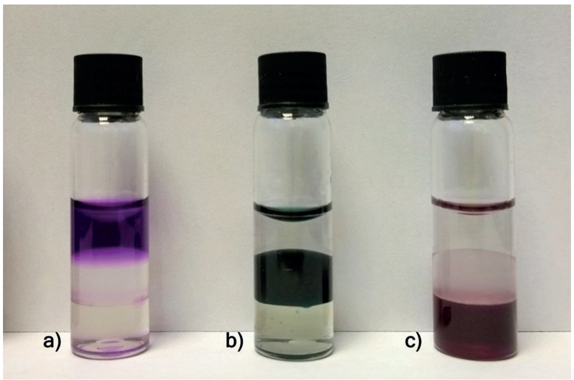


Figure 1. Equal volumes (0.5 mL) of water (top layer), $[P_{6,6,6,14}][NTf_2]$ (middle layer), and $[emim][NTf_2]$ (bottom layer) were added to each vial. A solid sample of cage **2** was added to the first vial, **3** to the second vial, and **4** to the third vial, respectively. Each vial was shaken vigorously for 10 seconds and allowed to settle before the photo was taken. a) Cage **2** is soluble only in water. b) Cage **3** is soluble only in $[P_{6,6,6,14}][NTf_2]$. c) Cage **4** is soluble only in $[emim][NTf_2]$.

analogue of **4** (cage **1**).[15,20] We therefore selected 1-fluorobenzene as a guest for **2**. Cage **3** has been previously shown to encapsulate 9-acetylanthracene in cyclohexane.[18] Since a fluorinated guest is required for this study, 9-trifluoroacetylanthracene was chosen as a guest for cage **3**. This guest is too large to bind inside **2** or **4** and therefore can only be encapsulated by **3**. Cage **1** has been previously shown to encapsulate adamantane with high affinity in acetonitrile.[15] Therefore, 1-fluoroadamantane was selected as a guest for cage **4**.

To a triphasic mixture of **2** in water (5.0 mM), **3** in $[P_{6,6,6,14}][NTf_2]$ (1.5 mM), and **4** in [emim]$[NTf_2]$ (1.5 mM), 30 equivalents each (relative to **2**, **3**, or **4**) of 1-fluorobenzene, 9-trifluoroacetylanthracene, and 1-fluoroadamantane were added. The mixture was stirred for two weeks at room temperature. A control experiment, in which identical amounts of the three phases and guests were present, but no cages, was set up and stirred in parallel. The layers were then allowed to separate and each layer was isolated for analysis by ^{19}F NMR spectroscopy.

In the top layer (**2** in H_2O), a ^{19}F NMR signal was detected for encapsulated 1-fluorobenzene (Figure S15). No signals were detected for any free guests in water because all three guests were preferentially soluble in the IL layers. In the middle layer (**3** in $[P_{6,6,6,14}][NTf_2]$), ^{19}F NMR signals were evident for encapsulated 9-trifluoroacetylanthracene, free 9-trifluoroacetylanthracene, free triflimide, free 1-fluorobenzene, and free 1-fluoroadamantane (Figure S16). In the bottom layer (**4** in [emim]$[NTf_2]$), ^{19}F NMR signals were detected for encapsulated 1-fluoroadamantane, free 9-trifluoroacetylanthracene, free triflimide, free 1-fluorobenzene, and free 1-fluoroadamantane (Figure S17). The cage in each layer thus encapsulated only the guest that it was observed to bind most strongly. Crucially, this system allowed guests to be partitioned into phases that they would have avoided in the absence of the hosts.

This study establishes the use of guest-binding coordination cages in IL phases, which have become an increasingly used alternative to traditional organic solvents,[21] with potential applications in fields as diverse as catalysis,[22] cellulose processing,[23] CO_2 sequestration,[24] and extraction.[25] This work adds to the toolbox of complex self-assembled systems[26] by extending the preparation of such systems into new solvents. The triphasic system described herein appears extensible, for example, to fluorous phases. Given the selective guest binding detected, new applications are envisaged in chemical separations or in phase-transfer catalysis.

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Keywords: coordination cages · encapsulation · host–guest systems · ionic liquid · supramolecular chemistry

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