Directed Phase Transfer of a Coordination Cage and Encapsulated Cargo

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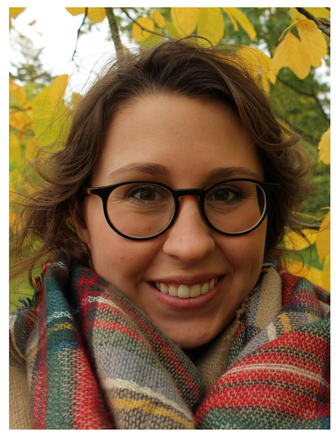


1. Introduction

To successfully address practical separations problems, a guest cannot simply be isolated from its environment; the molecular cargo must be removed to a separate physical space. Here we demonstrate that a $Fe^{II}_4L_4$ coordination cage **1**[1] can transport a cargo from water across a phase boundary and into an ionic liquid layer. This process is triggered by an anion exchange from **1**[SO_4] to **1**[BF_4]. Upon undergoing a second anion exchange, from **1**[BF_4] to **1**[SO_4], the cage – together with its encapsulated guest – can then be manipulated back into a water layer. We envisage that supramolecular technologies based upon these concepts could ultimately be employed to carry out separations of industrially relevant compounds.

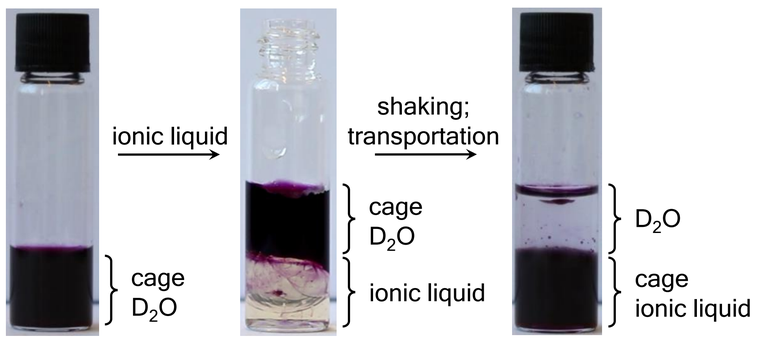


Figure 1: Directed phase transfer of a $Fe^{II}_4L_4$ cage and encapsulated cargo from water to an ionic liquid layer.

2. Transport of cargo by the cage

Having previously demonstrated that coordination cages can be soluble and stable in ionic liquids,[2] we now utilize the hydrophobic ionic liquid 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]) as both a salt to supply BF_4^- anions and a solvent to act as a receiving phase for **1**[BF_4]. By exchanging the BF_4^- counterion for SO_4^{2-}, we can ultimately manipulate cage **1** back into its original aqueous environment.

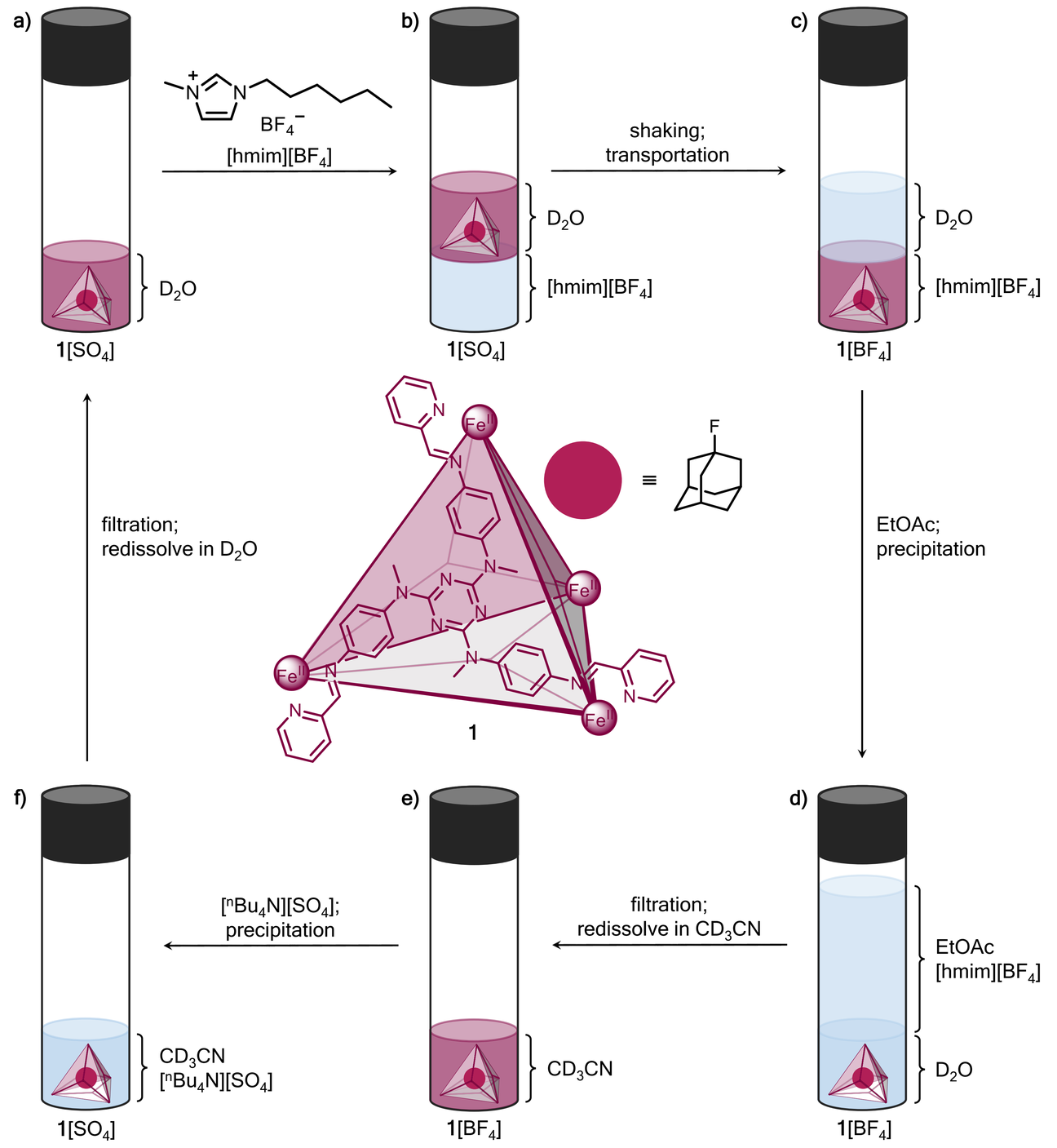
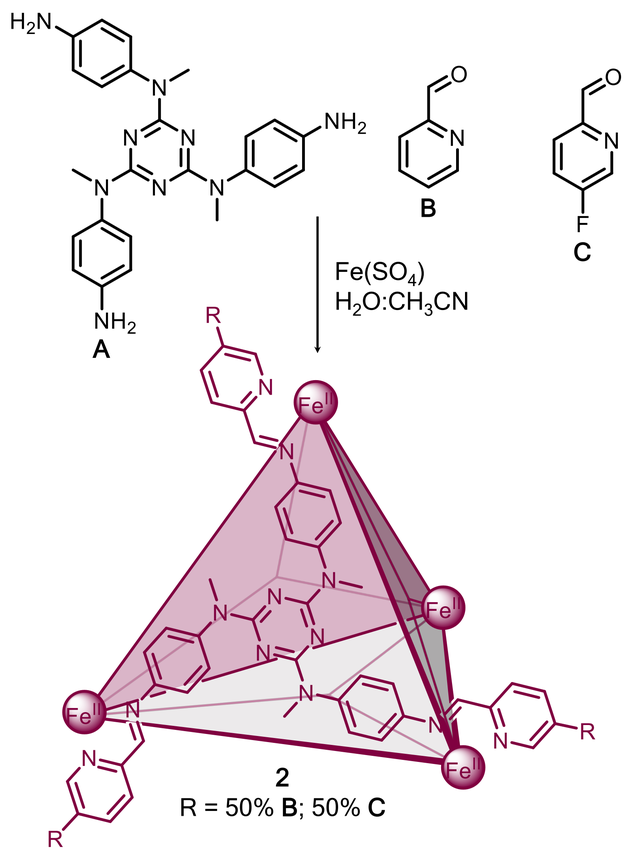


Figure 2: 1-Fluoroadamantane ⊂ **1**[SO_4] dissolved in water. b) Addition of [hmim][BF_4]. c) Upon shaking, 1-fluoroadamantane ⊂ **1** transferred from the water to the ionic liquid layer. d) Upon addition of EtOAc, 1-fluoroadamantane ⊂ **1**[BF_4] was filtered off and redissolved in CD_3CN. e) Upon addition of [^{n}Bu$_4$N][SO_4], 1-fluoroadamantane ⊂ **1**[SO_4] precipitated. f) Solid 1-fluoroadamantane ⊂ **1**[SO_4] was filtered off and redissolved in water, completing the cycle.

3. Tuning cage solubility

The specific transport cycle outlined in Figure **2** is not the only possible manifestation of this concept; both the ionic liquid and the cage can be systematically modified. The following figure illustrates how cage solubility can be tuned by incorporating **B** and **C**.



R	Soluble in H_2O	Soluble in [emim][NTf_2]
100% **B**	Yes	No
100% **C**	No	Yes
50% **B**; 50% **C**	Yes	Yes

Figure 3: Cage **1** composed of 12 equivalents of **B** is soluble in water but insoluble in [emim][NTf_2]; an analogous cage composed of 12 equivalents of **C** is soluble in [emim][NTf_2] but insoluble in water; mixed cages **2**, prepared from 6 equivalents of **B** and 6 equivalents of **C** is soluble in both [emim][NTf_2] and water.

4. Separating a mixture of cages and their cargos

The transport in Figure **2** is enabled by counteranion exchange of a cationic cage. [Me_4N]**3** is anionic, however:[3] no transition of this cage from water to the ionic liquid is observed. This feature allowed the separation of a mixture of two different cages and thus two different encapsulated guests.

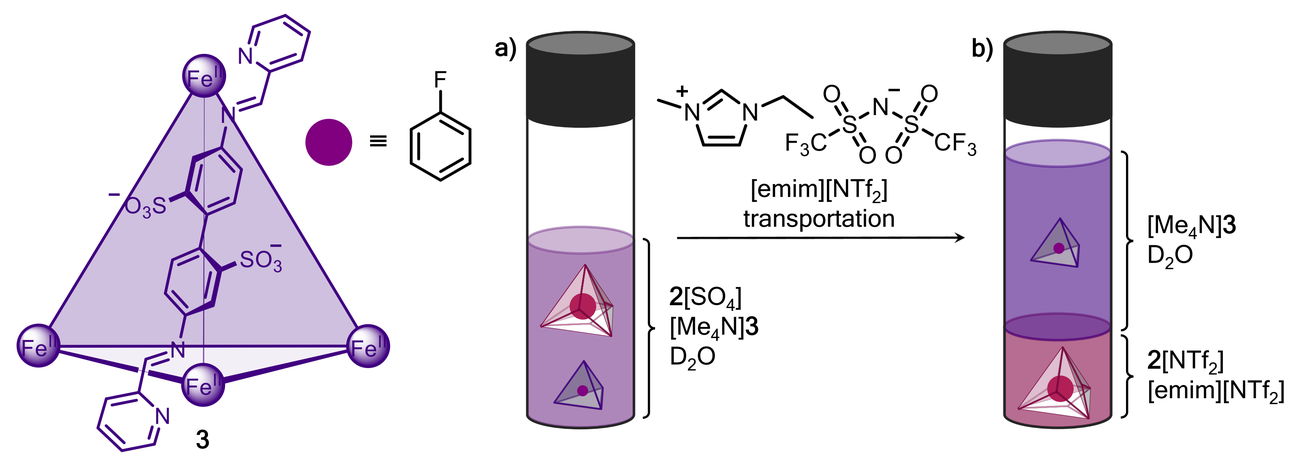


Figure 4: a) 1-Fluoroadamantane ⊂ **2**[SO_4] and 1-fluorobenzene ⊂ [Me_4N]**3** dissolved in water. b) Upon the addition of [emim][NTf_2], 1-fluoroadamantane ⊂ **2** transferred from the water to the ionic liquid layer, whereas 1-fluorobenzene ⊂ [Me_4N]**3** remained dissolved in water.

References

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[2] Grommet, A. B.; Bolliger, J. L.; Browne, C.; Nitschke, J. R. *Angew. Chem. Int. Ed.* **2015**, *54*, 15100-15104.
[3] Mal, P.; Schultz, D.; Beyeh, K,; Rissanen, K.; Nitschke, J. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 8297-8301.

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