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\textsubscript{3}L\textsubscript{4} coordination cage \textit{t} 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 \( \text{t}[\text{SO}_4^2] \) to \( \text{t}[\text{BF}_4] \). Upon undergoing a second anion exchange, from \( \text{t}[\text{BF}_4] \) to \( \text{t}[\text{SO}_4^2] \), 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.

2. Transport of cargo by the cage
Having previously demonstrated that coordination cages can be soluble and stable in ionic liquids,\textsuperscript{t} we now utilize the hydrophobic ionic liquid 1-benzyl-3-methylimidazolium tetrafluoroborate ([hmim][BF\textsubscript{4}]) as both a salt to supply BF\textsubscript{4}\textsuperscript{-} anions and a solvent to act as a receiving phase for \( \text{t}[\text{BF}_4]\ ). By exchanging the BF\textsubscript{4}\textsuperscript{-} counterion for SO\textsubscript{4}\textsuperscript{2-}, we can ultimately manipulate cage \( \text{t} \) back into its original aqueous environment.

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.

![Figure 3: Tuning cage solubility](image)

4. Separating a mixture of cages and their cargos
The transport in Figure 2 is enabled by counterion exchange of a cationic cage, [Me\textsubscript{N}3] is anionic, however\textsuperscript{2} 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: Separating a mixture of cages and their cargos](image)

References

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