Using the photo-Fries reaction as a photochemical probe to quantify the cage effects of ionic liquids

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The **cage effect** of a solvent or material is a measure of restriction placed on solute molecules by the solvent cage and describes how effectively the species can escape the solvent cage. A large cage effect gives rise to a high yield of in-cage products whereas a high yield of cage escape products is found for systems with a small cage effect. The cartoon in Figure 1 outlines cage escape for a pair of photochemically generated radicals.

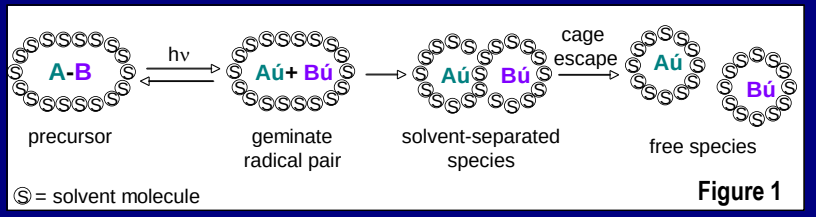


Figure 1

In this work we investigate the cage effect of **ionic liquids** (Figure 2, top right), an interesting class of "green" materials that have found application as solvents for synthesis and catalysis, hosts for molecular electronic devices, and electrolytes in dye-sensitized solar cells. If ionic liquids are found to have a large cage effect, this could dramatically alter the product distribution or catalytic activity in synthetic systems and limit the efficiency of a photovoltaic or electronic device.

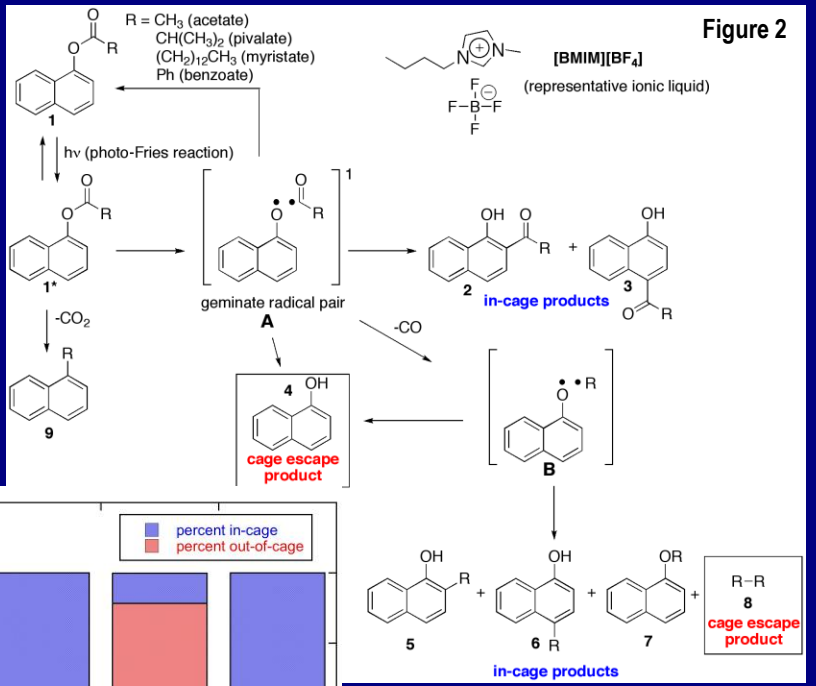
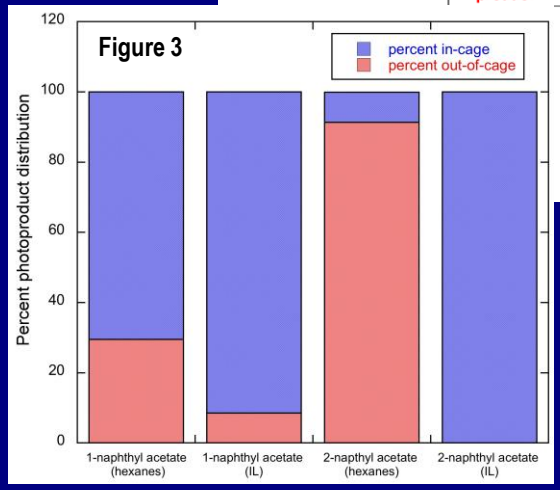


Figure 2

We use the photo-Fries reaction (Figure 2) as a photochemical probe reaction and use gas chromatography-mass spectrometry to quantify the photoproduct distribution, and hence ratio of in-cage to cage-escape products. Our early results (Figure 3) suggest a significant increase in the ratio of in-cage: cage-escape products when the reaction is carried out in ionic liquid media compared to molecular solvent (hexane). This result suggests a significant cage effect for ionic liquid media.



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