Durable Photocatalytic Reduction of Carbon Dioxide Using Ionic Liquids

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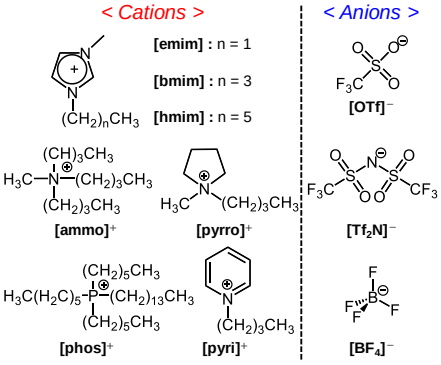
Metal complexes have attracted global attention since *fac*-Re(N^N)(CO)$_3$X-type complexes (N^N = diimine ligand, X = Cl^-, Br^-) were reported as a visible-light-driven photocatalyst in *N,N*-dimethylformamide (DMF) containing amines firstly by Lehn and co-workers, because of their high reaction selectivity and efficiency.[1] A large variety of photosensitizers, catalysts, and electron donors have been synthesized to improve turnover numbers and quantum yields.[2] The solvents, in contrast, have barely been changed from the first system; the best durability and efficiencies of the photocatalytic reactions were recorded when using DMF or *N,N*-dimethylacetamide (DMA) as a main solvent and triethanolamine (TEOA) as an additive for promoting photocatalysis. Aiming to diversify photocatalytic systems for CO_2 reduction using metal complexes, this study investigated the use of various ionic liquids as reaction solvents (Figure 1).[3] The photophysical properties of a photosensitizer complex and the photocatalytic ability of mixed systems consisting of the photosensitizer and a Re(I) catalyst in twelve kinds of ionic liquids were systematically investigated by comparison with those in DMA. Even though the photophysical properties of the photosensitizer complex in ionic-liquid solutions were quite similar to those in DMA, both the photosensitizing ability and the photocatalytic abilities of the systems strongly depended on the structures of the ionic liquids. Several ionic liquids were successfully used as new solvents for the photocatalytic systems showing durability similar to or higher than DMA solutions. Moreover, we found that some of the ionic liquids are also useful as an additive to increase the durability of photocatalytic systems because of decrease in the overpotential for the catalytic reaction on the Re(I) complexes. When using a Ru(II) diimine complex as a photosensitizer and a Re(I) complex as a catalyst in a mixture of DMA and [bmim][Tf_2N] (3:1 v/v), the turnover number of CO formation became 1.5 times that in DMA-TEOA mixed solution.



Ionic liquids used in this study	
1	[emim][OTf]
2	[bmim][OTf]
3	[hmim][OTf]
4	[emim][Tf_2N]
5	[bmim][Tf_2N]
6	[hmim][Tf_2N]
7	[emim][BF_4]
8	[bmim][BF_4]
9	[ammo][Tf_2N]
10	[phos][Tf_2N]
11	[pyrro][Tf_2N]
12	[pyri][Tf_2N]

Figure 1. Structures and abbreviations of the ionic liquids used in this study.

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