Highly Recyclable MOF-Based Photoredox Catalytic Systems Containing Ru(II) Polypyridyl Complexes

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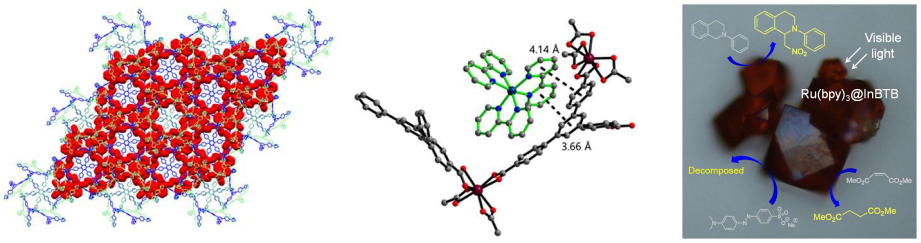
The chemical transformation of organic compounds by photoredox catalytic systems is an important research theme in modern chemical world. In this regard, we have been exploring the heterogenized photoredox catalytic systems with high stability for repeated use. A series of cationic Ru(II) polypyridyl photoredox catalysts were successfully immobilized into the large mesoscale channels of isostructural InBTB[1] or InTATB[2] metal-organic frameworks (MOFs, H_3BTB = 1,3,5-benzenetribenzoic acid, and H_3TATB = 4,4',4''-*s*-triazine-2,4,6-triyltribenzoic acid) to give RuL_3@InBTB and RuL_3@InTATB, respectively. The 3D frameworks of InBTB and InTATB are negatively charged and ammonium-based counter-cations are located near the In(III) ions. The $[RuL_3]^{2+}$ photoredox catalysts with a strong metal-ligand charge transfer (MLCT) under visible light irradiation are $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine), $[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline), and $[Ru(bpz)_3]^{2+}$ (bpz = 2,2'-bipyrazine). Thus, this method was proven to be very effective for the immobilization of large $[RuL_3]^{2+}$ ions through a simple cation exchange.

The luminescence lifetimes of these RuL_3@InBTB and RuL_3@InTATB were compared with free $[RuL_3]^{2+}$ catalysts in the solid state. Interestingly, most of the captured $[RuL_3]^{2+}$ catalysts showed enhanced excited state lifetimes. Thus, several representative photoredox catalytic reactions such as the aza-Henry reaction, hydrogenation of dimethyl maleate, and decomposition of methyl orange were investigated by using RuL_3@InBTB and RuL_3@InTATB under visible light irradiation. The heterogenized catalytic systems exhibited good catalytic activities. Additionally, high recyclability of these heterogenized photoredox catalytic systems was demonstrated.[3]



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