Encapsulation of the Large $[Ru(bpy)_2(dppz)]^{2+}$ Photosensitizer within Anionic Frameworks of Indium-Based MOFs

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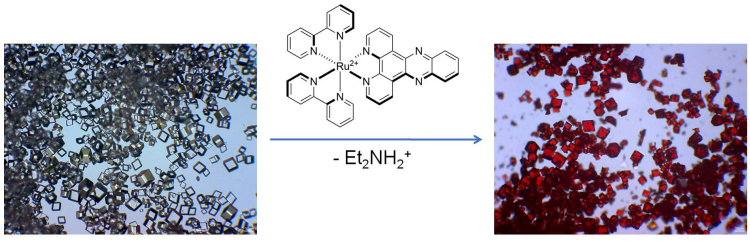
The large cationic complex $[Ru(bpy)_2(dppz)]^{2+}$ (bpy = 2,2′-bipyridine; dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) was successfully encapsulated within the mesoscale channels of two isostructural anionic In-MOFs, InBTB and InTATB,[1,2] which possess distinct pore environments, to yield $Ru(bpy)_2(dppz)$@InBTB and $Ru(bpy)_2(dppz)$@InTATB via a cation-exchange method. While InTATB contains electron-accepting central triazine rings exposed to the channels, InBTB features electron-donating central phenyl rings. Both $Ru(bpy)_2(dppz)$@InBTB and $Ru(bpy)_2(dppz)$@InTATB exhibited greatly enhanced photoluminescence (PL) emission intensity in the solid state compared with free crystalline $[Ru(bpy)_2(dppz)][BF_4]_2$. The encapsulated complexes also showed prolonged excited-state PL lifetimes, attributed to confinement effects within the MOF frameworks. The visible-light photoredox catalytic activities of the two heterogenized systems were evaluated for the aza-Henry reaction of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (THIQ) and for the aerobic oxidation of benzyl halides at room temperature.[3,4] Both catalysts exhibited comparable photoredox catalytic activities in these reactions, with no appreciable differences observed despite the distinct pore environments of the host frameworks. The $Ru(bpy)_2(dppz)$@InTATB catalyst demonstrated excellent recyclability, retaining most of its catalytic activity over six consecutive aza-Henry reaction cycles, with only a slight decrease in reactivity observed in the sixth run.



InBTB $Ru(bpy)_2(dppz)$@InBTB

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