COPPER MAKES THE DIFFERENCE: DEVELOPING SUSTAINABLE PHOTOREDOX CATALYZED TRANSFORMATIONS

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Abstract:

Synthetic organic chemistry undertakes great efforts to develop new catalytic transformations that utilize greener reagents and avoid stoichiometric additives. In this regard, visible-light photoredox catalysis offers a unique activation mode of molecules, which is serving as an alternative to many thermal transition-metals catalyzed reactions. The vast majority of photoredox catalyzed processes capitalizes on heavy metals namely, Ru(II) or Ir(III)-complexes which can serve as single electron oxidant or reductant in their photoexcited states.

As a low cost-alternative, organic dves are also frequently used photocatalysts but suffer in general from lower photostability. Copper based photocatalysts are rapidly offering emerging, not only economic and ecologic advantages, but in addition are able to interact with substrates beyond electron transfer via inner sphere mechanisms, which has been successfully utilized to achieve challenging transformations. Moreover, the combination of conventional photocatalysts with copper(I) or copper(II) salts allows a most efficient merger of photoredox and transition metal based catalysis. Selected synthetic applications from our laboratory, highlighting the complementary opportunities of copper and iridium based photocatalysts, will be discussed



Photoinduced Cu^{II}XY electron transfer Substrate photoactivation Cu^IX + S1-S Cu Cu^{II}X) Cu'Y S² Ligand R-X transfer 3d¹⁰ 4s [Cu¹-S¹] 29 Cu Cu"XY 63.546 Reductive Cu elimination Ř R¹Cu[⊪]R R¹-R² (R)Cu^{III}XY XCu^{II}-Nu Cu^IX Radical capture Photoinduced homolysis asymmetric induction flexible ligand architecture sustainable affordable

Leading references: S. Engl, O. Reiser, ACS Catal. 2020, 10, 9899; R. Fayad, S. Engl, E. O. Danilov, C.E. Hauke, O. Reiser, F.N. Castellano, J. Phys. Chem. Lett. 2020, 11, 5345; A. Hossain, A. Bhattacharyya, O. Reiser, Science 2019, 364, eaav9713; A. Hossain, S. Engl, E. Lutsker, O. Reiser, ACS Catal. 2019, 9, 1103; T. Rawner, E. Lutsker, C. A. Kaiser, O. Reiser, ACS Catal. 2018, 8, 3950; A. Hossain, A. Vidyasagar, C. Eichinger, C. Lankes, J. Phan, J. Rehbein, O. Reiser, Angew. Chem. Int. Ed. Engl. 2018, 57, 8288.