PhD Thesis Proposal (09.2022-09.2025)

Photoactive molecular materials based on 1,10-phenanthrolines for dual photoredox/transition metal catalysis

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Recently it was demonstrated that intriguing synergy can emerged when visible light is combined with transition metal catalytic (redox) catalysis. Unprecedent efficiency and unusual reactivity were reported under these conditions for the reactions performed by using photoredox catalysts (PC) in tandem with transition metal catalysts (TMC) (metallaphoto-catalyzed reactions) (Fig. 1A).[1] These dual catalyzed reactions allow to expand the classical scope of substrates in transition-metal-catalyzed transformations or completely change many vital strategies for C–H functionalization, C(sp^3)–C(sp^2) and C(sp^3)–C(sp^3) bond forming reactions, olefin difunctionalization and so forth.

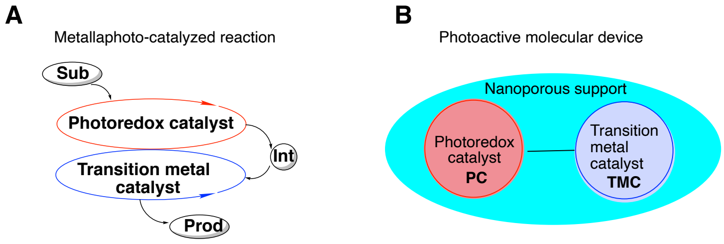

Fig. 1. Schematic representation of a metallaphoto-catalyzed (PTM-catalyzed) reaction (A) and a photoactive molecular device for dual catalized photoreactions (B).

The objectives of this project are 1) to explore the synthesis and catalytic properties of bimetallic complexes combining photoredox and redox catalytic sites in one molecular entity and 2) to investigate the immobilization of these complexes into porous solid matrices to prepare reusable photoactive molecular materials (PMMs) in which catalytic activity of bimetallic complexes will be increased by positive effects of the support.

PMMs for metallaphoto-catalyzed reactions should consist of three sub-units 1) photoredox sites (PC); 2) redox sites (TMC) and 3) a porous support (Fig. 1B). Our strategy for their preparation relies on the synthesis of soluble bimetallic catalysts for metallaphoto-catalyzed reactions followed by their immobilization in solid supports. We expect to develop a general and simple synthetic approach to *reusable, multi-process* and *multi-functional catalysts* combining a rational design on the molecular level with efficient methodologies of material chemistry.

We propose to develop PMMs based on bimetallic complexes with 1,10-phenanththroline chelators. First, close arrangement of two catalytic sites will be achieved at the molecular level by the preparation bimetallic catalytic systems **1** and **2** (R = H) shown in Fig. 2. Next, Ru^{II}/M^{II} (M^{II} = Ni^{II}, Cu^{II}) complexes thus obtained will be used as catalysts in homogeneous metallaphoto-catalyzed reactions. To complete the development of PMMs, we will incorporate these bimetallic complexes into solid supports allowing the reusability and the increase of their activity due to a close arrangement of several PC around the M^{II} catalytic site. Our particular attention will be paid to the preparation of nanoporous materials providing a rapid diffusion of the substrate to the catalytic sites. To obtain stable materials and avoid catalyst leaching, the complexes will be immobilized through phosphonate anchoring groups (Fig. 2, R = PO_3H_2) forming strong bonds with metal oxides (Fig. 3).[2] Finally, the catalytic properties of porous molecular materials thus obtained will be explored in metallaphoto-catalyzed reactions. Recovery and reuse of the catalysts will be also investigated

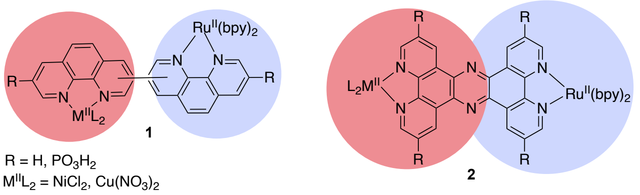

Fig. 2. Structure of bimetallic complexes with 1,10-phenanthroline-based ligands.

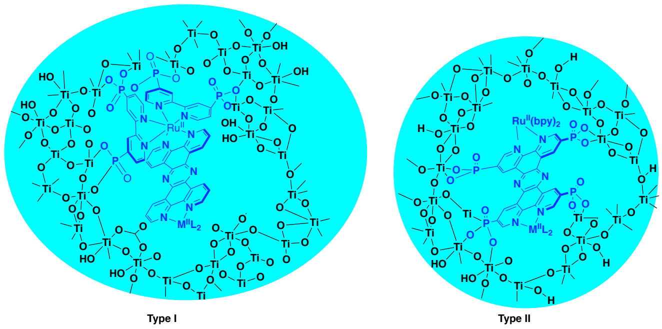

Fig. 3. Representative examples of mesoporous titania xerogels functionalized by PC and TMC.

References

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2.(a) E. Ranyuk, C. M. Douaihy, A. Bessmertnykh-Lemeune, R. Guilard, *New J. Chem.* 2011, *35,* 1189–1193. (b) 3. A. Mitrofanov, S. Brandes, F. Herbst, S. Rigolet, A. Bessmertnykh-Lemeune and I. Beletskaya, *J. Mater. Chem. A*, 2017, *5*, 12216-12235.