Photocatalytic System Integrated with Water Oxidation by a Liquid-Liquid Phase-Migrating Electron Mediator

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Photocatalytic molecular conversions giving value added product are of great interest. Ideally, it is desirable to utilize water as an electron source for these molecular conversion reactions. Artificial Z-scheme reaction system composed of two-different photocatalysts is a potential strategy to connect various reductive molecular conversions with water oxidation, as demonstrated in overall water splitting.[1] However, it is basically difficult to perform organic molecular conversions integrated with water oxidation due to low solubility of organic reactants in water. In this study, we develop a stepwise Z-scheme photocatalytic system utilizing a water/1,2-dichloroethane (DCE) biphasic solution with a ferrocenium/ferrocene (Fc^+/Fc) phase-migrating electron mediator to connect reductive coupling of benzyl bromide in DCE phase and water oxidation (Figure 1a).

In an aqueous solution, $(Fe,Ru)O_x$-modified Bi_4TaO_8Cl photocatalyzed water oxidation with a Fc^+ electron acceptor, generating O_2 and Fc (Figure 1b). On the other side, Fc can be utilized as an electron donor for photocatalytic reduction of benzyl bromide (Bn-Br) with an $[Ir(C6)_2(dmb)](PF_6)$ photoredox catalyst in a DCE phase (Figure 1c). Importantly, the latter reaction regenerated Fc^+ which is spontaneously going back to aqueous phase.[2] Eventually, the Fc^+/Fc redox couple transports an electron by the photoredox induced liquid-liquid phase migration to achieve photoreduction of Bn-Br coupled with water oxidation.

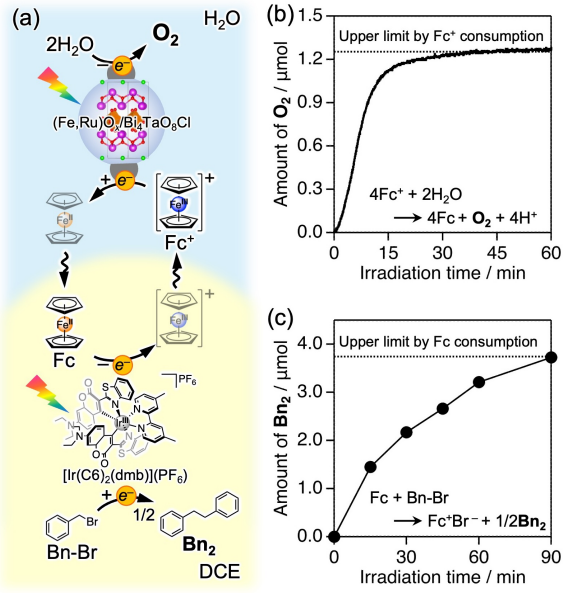

Figure 1. (a) Conceptual scheme of a biphasic photocatalysis. Time course of half reactions of (b) O_2 evolution using $(Fe,Ru)O_x/Bi_4TaO_8Cl$ and Fc^+ electron acceptor and (c) dibenzyl (Bn_2) formation using $[Ir(C6)_2(dmb)](PF_6)$ and Fc electron donor.

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