Photocatalysis Utilizing Photoinduced Electron Transfer Coupled Phase Migration

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Keywords: *Photocatalysis; Phase migration; Photoinduced electron transfer; Ferrocene; Backward electron transfer*

The natural photosynthesis adopts multistep electron and proton transport crossing the interface of Thylakoid membrane for extremely efficient photogenerated charge transport, giving a considerable yield of light-to-chemical conversion.[1] Such redox-directed phase migration can be a rational tool to suppress the backward electron transfer in photocatalysis. We have aimed to construct "photoinduced coupled-electron transfer and phase migration" in two-separatable solvent system, where the oxidized form of an electron donor, generated by the photoinduced electron transfer to a photosensitizer in a liquid phase, migrates to another liquid phase. It is expected to suppress the backward electron transfer between charge separated pair due to their spatial separation.

Herein, we report a reductive coupling of benzyl bromide driven by visible-light-induced coupled electron transfer and phase migration of ferrocene in biphasic solutions composed of water and halogenated solvent (Figure).[2] Visible-light irradiation to the 1,2-dichloroethane/water biphasic solution, where Fc, Ru(II) or Ir(III) complex photosensitizer, and benzyl bromide (Bn-Br) were initially distributed in the DCE phase, facilitated reductive coupling of Bn-Br to dibenzyl (Bn_2) using Fc as an electron donor to form Fc^+. The key finding is that Fc^+, generated by photooxidation of Fc in DCE phase, migrated to the aqueous phase following the driving force due to drastic change of partition coefficient compared with Fc. On the other hand, the same photolysis in the absence of aqueous phase failed to afford any product. Thus, the liquid-liquid phase migration is essential for facilitating reduction of Bn-Br in the DCE phase by spatial separation of Fc^+ to the aqueous phase, suppressing backward charge recombination.

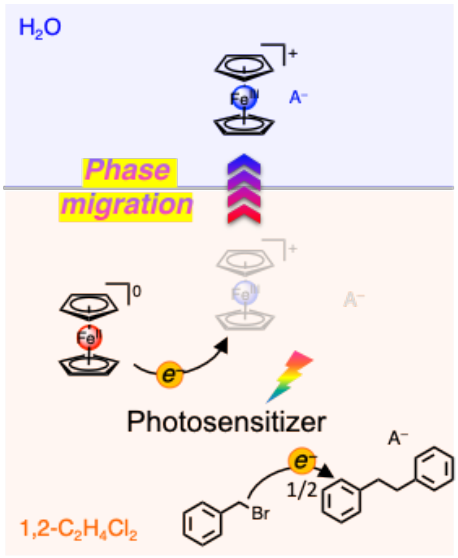

Figure. Photoinduced coupled electron transfer and phase migration developed in this study.

1) A. Thilagam, *J. Math. Chem.* **2014**, *53*, 466.
2) R. Itagaki, S.-Y. Takizawa, H.-C. Chang, A. Nakada, *To be submitted*.