Photochemical H_2 evolution using a Ru-based Photosensitizer tethered to Six Viologen Acceptors

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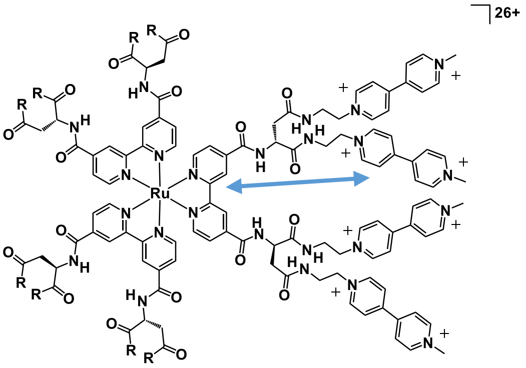
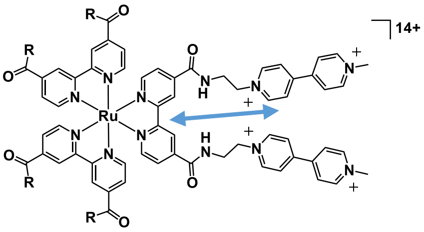
Recently, many efforts have been made to develop photocatalytic systems mimicking the functions of natural photosynthesis in order to achieve solar-to-fuels production. In natural photosynthesis, quinone pool effectively promotes subsequent biochemical processes by storing high-energy electrons which are generated by photodriven processes. Our group has recently succeeded to demonstrate such photodriven multi-electron storage behavior in single-molecular systems consisting of a single $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) pigment tethered to multiple MV^{2+} (methylviologen) electron acceptors (e.g.; **complex 1** in Fig. 1).[1,2] Additionally, H_2 evolution based on these systems was conducted in the presence of an H_2-evolving catalyst.[1,2] Moreover, we previously investigated the correlation of the catalytic behavior and the distance between the chromophore and the MV^{2+} acceptors in Pt(II)-MV^{2+} single-molecular photocatalytic systems.[3] Herein, we present a new single-molecular electron-storage system (**complex 2** in Fig. 1) with a shorter distance between functional sites versus **complex 1**. The effects of structural modification on electron storage and photocatalytic behavior are hence studied.



complex 1 (previous work)



complex 2 (this work)

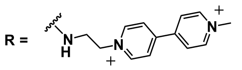


Fig. 1 Structures of **complex 1** (top) and **2** (bottom).

Monitoring of UV-vis-NIR spectral modification upon visible-light irradiation of an aqueous 0.1 M acetate buffer solution (pH 5.0) containing **complex 2** (0.04 mM) and EDTA (ethylenediaminetetraacetic acid disodium salt; 30 mM) showed the appearance of bands in the visible to near infrared region. This indicates the formation of two distinct radical species of MV^{2+}, monomer and π-dimer forms. The number of stored electrons per complex was spectrophotometrically estimated to be 3.32 at saturation stage. The rate of electron storage was also estimated as 91.3 2e h^{-1}, which is much lower than for **complex 1** (630 2e h^{-1}).[1,4] Furthermore, **complex 2** promoted photochemical H_2 evolution from water in the presence of colloidal Pt as an H_2-evolving catalyst, and EDTA as a sacrificial electron donor. It was found that **complex 2** possesses higher stability than **complex 1** during the photocatalytic reaction.[1,4] The detailed photochemical behavior of **complex 2** is presented, and the difference in its catalytic activity versus previous systems is discussed.

1) K. Kitamoto, M. Ogawa, G. Ajayakumar, S. Masaoka, H.-B. Kraatz, and K. Sakai , *Inorg. Chem. Front.*, **2016**, *3*, 671; 2) K. Kitamoto and K. Sakai, *Chem. Eur. J.*, **2016**, *35*, 12381; 3) K. Yamamoto, K. Kitamoto, K. Yamauchi, and K. Sakai, *Chem. Commun.*, **2015**, *51*, 14516; 4) K. Yamamoto and K. Sakai, **2018**, *to be submitted*.