

H₂ Evolution Photocatalyzed by a Pt(II) complex Cycling Between Singly and Triply Reduced Species

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Recently, photocatalytic hydrogen evolution (PHE) from water has attracted much attention toward the achievement of carbon-neutral energy

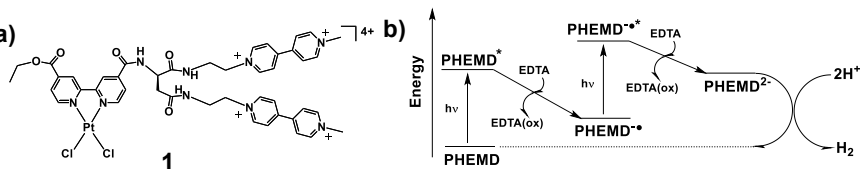


Fig. 1 a) Structure of a PHEMD in the previous work, b) Scheme of PHE catalyzed by 1.

society. In this research area, catalysts are classified into two types; homogeneous and heterogeneous catalysts. Homogeneous catalysts, such as Pt(II) complexes, have the advantage in the point that the catalytic activity and selectivity are finely controlled based on the modification of the molecular structure. In this context, our group has made great efforts to develop photo-hydrogen-evolving molecular devices (PHEMDs), which can promote PHE as a single molecular photocatalyst in the presence of sacrificial electron donors.^{1,2)} During the course of these studies, our group has recently reported a mononuclear Pt(II) photocatalyst tethered to methylviologen (MV²⁺) moieties (**1** in Figure 1), which promotes PHE via two consecutive photo-driven electron transfer steps leading to the formation of a two-electron-reduced species (PHEMD^{2•-}) which can thermally drive H₂ evolution reaction (Figure 1b).³⁾

Here, we report on a new Pt(II) complex which promotes PHE as a PHEMD (**2** in Figure 2).⁴⁾ In its molecular structure, two MV²⁺ moieties are located closer to the Pt(II) chromophore than the previous systems. Results of spectral changes by photolysis of **2** in the catalytic solution indicate the quantitative formation of PHEMD^{2•-} during catalytic reaction in this system. Furthermore, **2** showed quite clear response for PHE upon turn ON and OFF of the light irradiation (Figure 3a). This indicates the thermal hydrogen evolution with PHEMD^{2•-} does not proceed, and the formation of three-electron-reduced species (PHEMD^{3••-}) by further photoexcitation of PHEMD^{2•-} is necessary for PHE in this system (Figure 3b). We assume that the modification of the molecular structure results in the difference on the catalytic mechanism between present and previous studies.⁴⁾

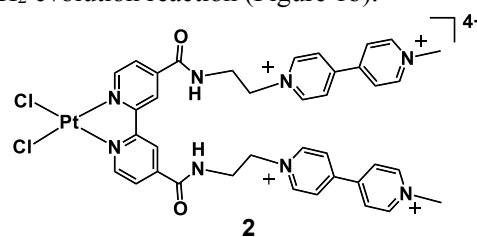


Fig. 2 Structure of a PHEMD in this work.

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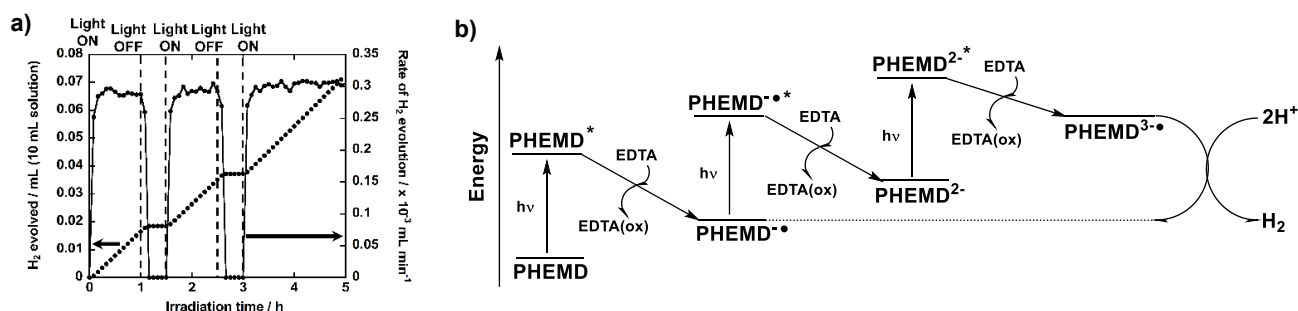


Fig. 3 a) Photochemical H₂ production from an aqueous acetate buffer solution (pH 5.0, 10 mL; at 20 °C under Ar) containing 0.1 mM **2**, 0.1 M

NaCl, and 30 mM EDTA, b) Scheme of PHE promoted by **2**.

1) H. Ozawa and K. Sakai, *Chem. Commun.*, **2011**, 47, 2227; 2) M. Kobayashi, S. Masaoka and K. Sakai, *Angew. Chem. Int. Ed.*, **2012**, 51, 7431; 3) K. Kitamoto and K. Sakai, *Angew. Chem. Int. Ed.*, **2014**, 53, 4618; 4) K. Yamamoto, K. Kitamoto, K. Yamauchi and K. Sakai, *Chem. Commun.*, **2015**, 51, 14516.