An Effect of Structural Modification in the Photo-hydrogen-evolving Ru^{II}Pt^{II} Dimers

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The second example of a photo-hydrogen-evolving (PHE) molecular device consisting of a Ru(bpy)$_3{}^{2+}$ (bpy = 2,2′-bipyridine) derivative and a *cis*-PtCl$_2$ unit has been successfully prepared and characterized to reveal that the PHE activity is quite sensitive to the structural modification at the bridging spacer unit connecting the Ru^{II} and Pt^{II} centers.

The studies on the visible-light-induced splitting of H_2O into H_2 and $\frac{1}{2}O_2$ have attracted considerable attention in recent years due to the environmental problems as well as the world's energy needs. Extensive efforts have also been made to fabricate molecular devices which possess multiple functionalities.[1] In this context, we recently reported the first example of a "photo-hydrogen-evolving" molecular device (**1**) (Chart 1), which does evolve H_2 from an aqueous acetate buffer solution (pH 5) in the presence of a sacrificial electron donor (EDTA; ethylenediaminetetraacetic acid) under visible light illumination.[2] This compound was designed based on our original finding in the H_2-evolving activities of amidate-bridged *cis*-diammineplatinum(II) dimers ([Pt$_2$(NH$_3$)$_4$(μ-amidato)$_2$]$^{2+}$) in a photosystem made up of EDTA, Ru(bpy)$_3{}^{2+}$, and methylviologen (*N*,*N*′-dimethyl-4,4′-bipyridinium).[3] We also reported on several related Ru^{II}Pt^{II} analogs (e.g., **2** and **3** shown in Chart 1), which do not exhibit such PHE activities at all.[4] Common structural features of these Ru^{II}Pt^{II} analogs, having a composition of [(bpy)$_2$Ru(SL)PtCl$_2$]$^{2+}$, are that they are all well emissive and possess a *cis*-PtCl$_2$ unit at the H_2-evolving center, where SL denotes a tetradentate spacer ligand which connects two metal centers. Since the spacer units used in these inactive analogs **2** and **3** are partly made up of aliphatic linkages by use of alkyl chains, the aromaticity preserved in the spacer unit of **1** was suggested to play a key role in the exceptional PHE activity of **1**.[4b] In order to further investigate the important factors affecting the PHE activity, various Ru^{II}Pt^{II} analogs have been prepared and their PHE activities have been evaluated in our group. Here, we communicate the synthesis and the PHE activity of compound **7** (Chart 2). Note that the binding direction of the same spacer unit is reversed in replacing **1** with **7**.

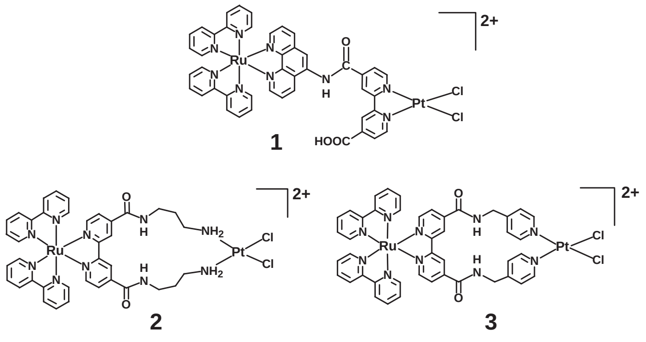

Chart 1.

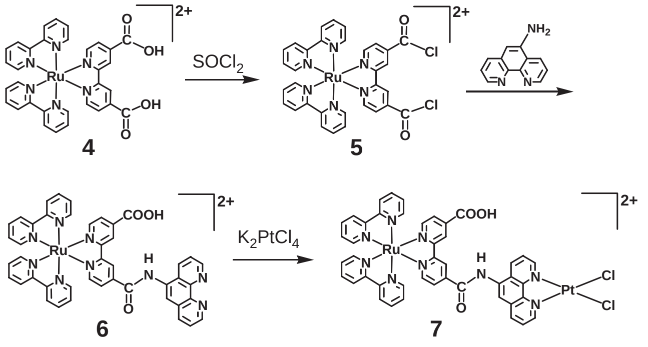

Chart 2.

In the synthesis of **7**, a bis(chlorocarbonyl) complex **5** was first prepared by treating **4**[4b,5] with thionyl chloride in dry acetonitrile. Complex **5** was then reacted with 5-amino-phen (phen = 1,10-phenanthroline) to give an Ru(bpy)$_3{}^{2+}$ derivative tethered to an uncoordinated phen moiety (**6**)[6] followed by platination of **6** to give the final product **7**.[7,8]

Compounds [**4**]Cl$_2$, [**6**](PF$_6$)$_2$·4H$_2$O, and [**7**]Cl$_2$·9H$_2$O display very similar absorption properties at the metal-to-ligand charge-transfer (MLCT) band domain (Figure S3),[10] indicating that **6** and **7** preserve the absorption properties characteristic of the starting complex **4**. The luminescence wavelength is slightly red-shifted upon introduction of a 5-amino-phen unit (Figures 1a and 1b), implying that the lowest excited state is stabilized by the extended hybridization in the bridging spacer unit, which is also supported by the results of DFT calculations (Figure S5;[10] see the [LUMO+2]). The luminescence intensity is further diminished upon platination of a free phen moiety in **6** in giving

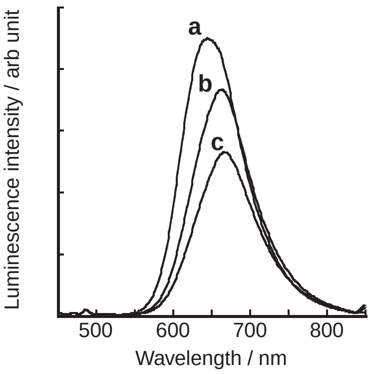

Figure 1. The uncorrected luminescence spectra in water (in air, 20 °C) of [**4**]Cl$_2$ (a), [**6**](PF$_6$)$_2$·4H$_2$O (b), and [**7**]Cl$_2$·9H$_2$O (c), where the excitation wavelength was fixed at 425 ± 2.5 nm and all the solutions had an equal absorbance (0.1) at 425 nm.

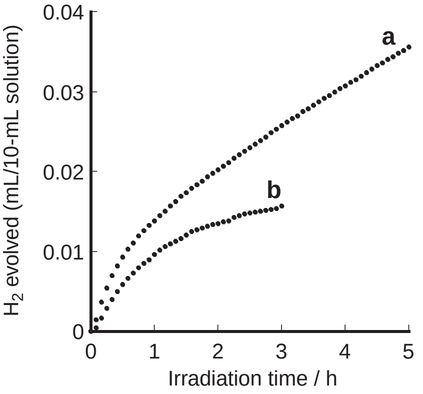

Figure 2. Photochemical hydrogen production from aqueous acetate buffer solutions (0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na; pH 5.0, 10 mL) containing 30 mM EDTA (disodium salt) in the presence of additional photocatalysts: (a) 0.1 mM [**1**]$Cl_2 \cdot 3H_2O$ (taken from Ref. 2), and (b) 0.1 mM [**7**]$Cl_2 \cdot 9H_2O$. The irradiation was carried out using a 350-W Xe lamp with a Pyrex-glass filter ($\lambda >$ ca. 350 nm), under the continuous flow of Ar (10.0 mL/min), where the vent gas was automatically analyzed by gas chromatography every 5 min. The photolysis solutions were immersed in a water bath thermostated at 20 °C.

7, suggesting that the intramolecular electron or energy transfer is enhanced in this new $Ru^{II}Pt^{II}$ dimer **7**. The luminescence intensity ratio of the platinated product and the non-platinated precursor compound (i.e., a Pt-induced quenching ratio) is ca. 28% for the present **7**/**6** couple. The Pt-induced quenching ratio for **1** was reported as ca. 70%.[2,4b] On the other hand, the extent of quenching was relatively small in **2**[4a] and **3**;[4b] the Pt-induced quenching ratio was reported to be ca. 25% for **3**. In this context, we recently pointed out that the Pt-induced quenching ratio seems intimately correlated with the PHE activity of the molecular device.[4b] The observed lower PHE activity of **7** in comparison with that of **1** (vide infra) is consistent with such a tendency.

The PHE activity of **7** was investigated by monitoring the amount of H_2 evolved while photoirradiating a solution of **7** in an aqueous acetate buffer solution (pH 5) containing EDTA under Ar atmosphere. As shown in Figure 2, **7** exhibits a PHE activity, even though the activity is effectively lower than that of the first effective model **1**. The lower PHE activity of **7** might reflect the lower photoinduced electron-transfer efficiency in **7** in comparison with that in **1**. For instance, it seems probable that a possible proton-coupled electron transfer (PCET) reaction leading to formation of a Pt–H intermediate species might be sensitive to the change in the binding direction of the spacer unit as further discussed below. The quantum efficiency for the H_2 formation, estimated from the initial rate of H_2 production, is determined as 0.39% for **7**, which compares with the value of 0.61% reported for **1**.[2]

In order to better understand the lowest ^{3}MLCT excited state of **7**, one of several possible conformers for **7** was fully optimized at the B3LYP level of density functional theory method, where the polarizable continuum model (PCM) was employed to take the solvation effect (H_2O) into consideration. The use of PCM generally gives a reasonable solution, since the three filled t_{2g} orbitals for Ru^{II} and the filled d_{z^2} orbital for Pt^{II} respectively occupy the [HOMO]–[HOMO − 2] and the [HOMO − 3] (Figure S4).[10] Such a reasonable solution could not be given by the optimization of the same structure in vacuo. This is consistent with the results of our DFT calculations carried out for **1**.[9] In the optimized structure of **7**, the phen moiety is inclined by 70.4° with respect to the 4-carboxy-bpy plane, in which carbamoyl unit is roughly coplanar with the phen moiety. Importantly, the LUMO in **7** corresponds to the π^*(ccbpy) bound to Ru^{II} (Figure S5)[10] but that in **1** corresponds to the π^*(ccbpy) bound to Pt^{II} (ccbpy = 4-carboxy-4′-carbamoyl-bpy).[9] The energy level of the π^*(ccbpy) orbital must be greatly stabilized by the electron-withdrawing effects of the carboxylate and carbamoyl groups in the ccbpy moiety. Since the ^{3}MLCT excited state is considered as a resting state for the H_2-forming reaction (e.g., a PCET process), the dramatic difference between **1** and **7** in the location of the photochemically generated reducing equivalent (ccbpy$^{\bullet -}$) could be the major reason for the difference in the PHE activities of **1** and **7**. Indeed, the distance between the ccbpy unit and the Pt^{II} center in **7** is much longer than that in **1**.

In summary, we have succeeded in the development of the second example of a photo-hydrogen-evolving molecular device **7**, revealing that the PHE activity is quite sensitive to the structural change in the spacer unit. Extended studies are still in progress in our laboratory.

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6 Anal. Calcd for $C_{44}H_{39}N_9O_7P_2F_{12}Ru$ ([**6**]$(PF_6)_2 \cdot 4H_2O$): C, 44.16; H, 3.28; N, 10.53%. Found: C, 43.95; H, 3.17; N, 10.46%. ESI-TOF MS: m/z 980.33 for [**6**(PF_6)]$^+$ (Figure S1).[10]

7 Anal. Calcd for $C_{44}H_{41}N_9O_8Cl_2P_2F_{12}RuPt$ ([**7**]$(PF_6)_2 \cdot 5H_2O$): C, 35.69; H, 2.79; N, 8.51%. Found: C, 35.61; H, 2.56; N, 8.41%. ESI-TOF MS: m/z 550.66 for ([**7**$^{2+}$]) (Figure S2).[10]

8 Anal. Calcd for $C_{44}H_{49}N_9O_{12}Cl_4RuPt$ ([**7**]$Cl_2 \cdot 9H_2O$): C, 39.62; H, 3.70; N, 9.45%. Found: C, 39.25; H, 3.38; N, 9.41%.

9 Unpublished results, which will be separately reported elsewhere.

10 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

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