An allosteric photoredox catalyst inspired by photosynthetic machinery

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1. Introduction

1.1. Light-harvesting antenna

• In natural photosynthetic systems, light-harvesting antenna is used to absorb the light efficiently and transfer the energy to reaction center.

1.2. Controling of light harvesting

• In artifical photosynthetic system, it is also important to control the light harvesting and regulate photocatalyst catalytic activitiy between active and inactive states to apply this system.

1.3. Challenge : Creation of ON/OFF switch of light harvesting

• The change of chemical conformation can be used as a switch, but the method for the changing chemical conformation is limited.

• One example is a change via pH change. However, because the pH change affects the nature of the redox reactions, this method prevents the application of this approach in catalyst.[1]

1.4. Author's strategy (Previous work)

• The metal with weakly coordinating ligand system has been developed (Figure 1).[2]

• The author envisioned that this system can be used as an ON/OFF switch in artificial light-harvesting system.

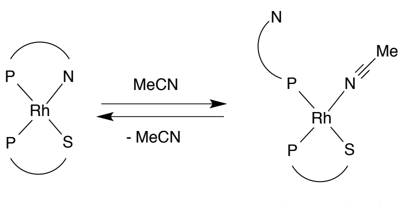

Figure 1. An example of the metal with weakly coordinating ligand system.

1.5. This work

• The light-harvesting system with ON/OFF switch and the light-harvesting/reaction canter mimic that can be regulated in situ and reversibly were reported for the first time.

2. Results and Discussion

2.1. Design of the compound

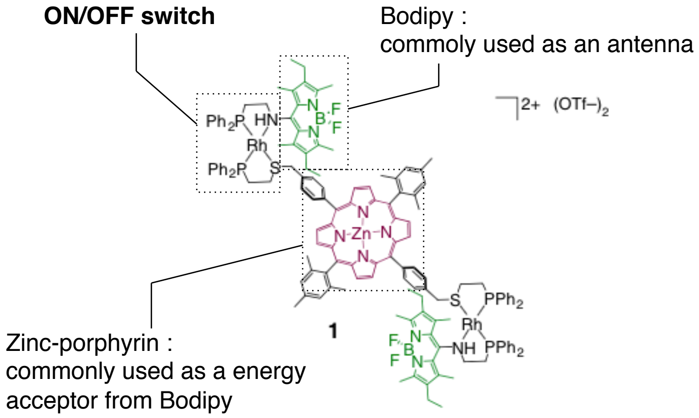

Figure 2. Design of the compound with the ON/OFF switch.

2.2. Effects of allosteric effector binding

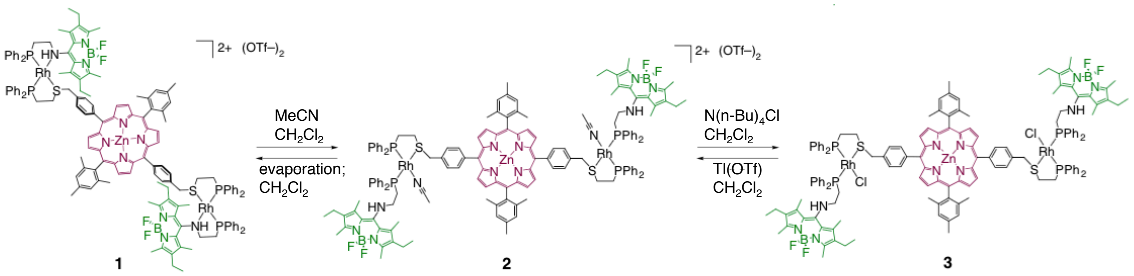

Figure 3. The switching between coordination states with acetonitrile and chloride.

- Three complexes can be converted reversibly (Figure 3).
- To investigate the change of the coordination state can be acted as a switch, fluorescence spectra and cyclic voltammetry were measured (Figure 4, Table 1).
- Coordination of acetonitrile (**2**) increased the energy transfer efficiency to the porphyrin (Figure 4).
- The coordination of hemilabile ligand on the bidentate type (**1**) highered the Bodipy oxidation potential and enhanced photoinduced electron transfer from Rh(I)

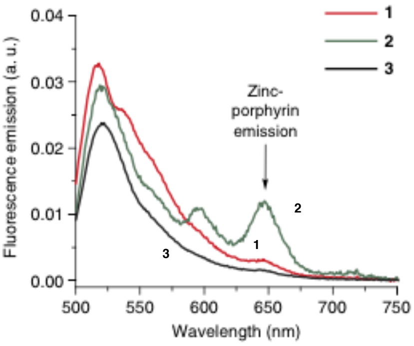

Figure 4. Fluorescence emission spectra ($\lambda_{ex} = 480$ nm).

Table 1. **Oxidation potential.**

Complex	$E_{ox.\,an.}$ Bodipy (V)	$E_{ox.\,an.}$ Rh(I) (V)
1	0.186	0.062
2	0.005	0.098
3	0.032	-0.455

to Bodipy to decrease the energy transfer efficiency to the porphyrin (Table 1).

- Chloride (**3**) lowered the Rh(I) oxidation potential and enhanced photoinduced electron transfer from Rh(I) to Bodipy to decrease the energy transfer efficiency to the porphyrin (Table 1).

=> The change of the coordination state could regulate the light-harvesting switch.

2.3. Antenna-reaction center mimic assembly

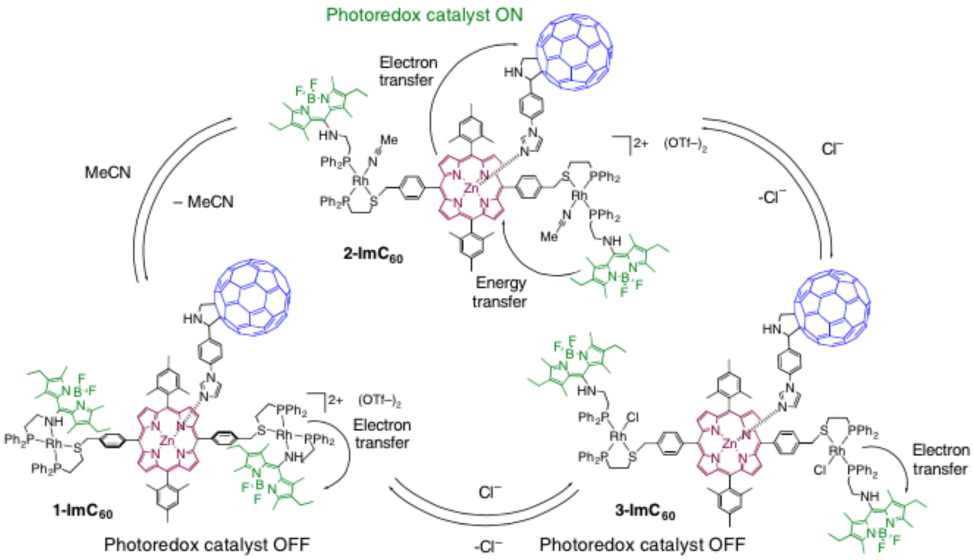

Figure 5. Allosteric regulation of a light-harvesting antenna/reaction center mimic.

- To make the charge separation state, fullerene was utilized as an electron acceptor.
- Axial coordination to the porphyrin's Zn(II) in **1**–**3** was exploited to incorporate an imidazole-modified fullerene moiety (**ImC$_{60}$**), thus giving **(1–3)-ImC$_{60}$** (Figure 5).[3]

2.4. Regulation of charge separation in the reaction center mimic

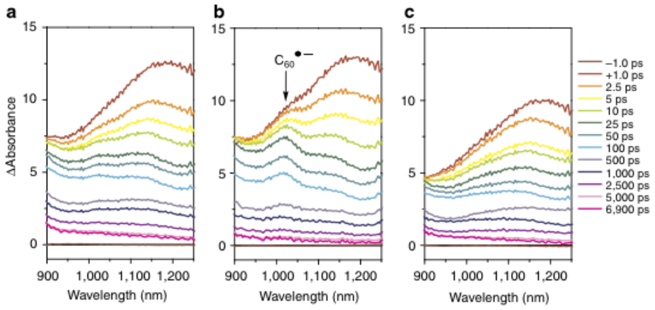

Figure 6. NIR-TA spectra of **(1-3)-ImC$_{60}$**. Excitation of 3μM solutions of **1**(a), **2**(b), and **3**(c) with 1.1-μJ laser pulses in the presence of 10 equiv. of **ImC$_{60}$** in CH_2Cl_2 (λ_{em} = 477 nm).

- To investigate whether the switch system can regulate charge separation in the reaction center mimic, the NIR-TA spectra were measured (Figure 6).
- Absorption at 1,010 nm, charactaristic of the fullerene radical anion, was markedly larger in the case of **2-ImC$_{60}$** (Figure 4b) relative to both **1-ImC$_{60}$** and **3-ImC$_{60}$** (Figure 6a,c).

=> The photoinduced electron transfer switch could regulate charge separation within the central reaction center mimic.

2.5. Allosteric control of photoredox catalytic activity

- The allosteric regulation of the photoredox activity of **(1–3)-ImC$_{60}$** in situ was studied in the presence of methyl viologen as an electron acceptor and 1-benzyl-1,4-dihydronicotinamide as a sacrificial reductant (Figure 7).
- The addition of a single drop of acetonitrile enhanced photoredox activity to form **2-ImC$_{60}$** as evidenced by absorbance changes at 630nm, characteristic of the reduced methyl viologen.[4]

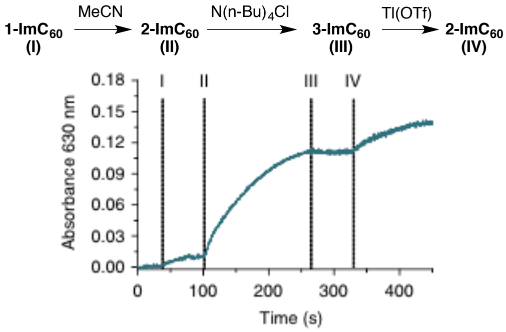

Figure 7. Catalytic reduction of methyl viologen. Changes in the absorbance at 630 nm in the presence of 5 mM CH_2Cl_2 solution of **1** with 10 equiv. of **ImC$_{60}$**.

- The catalyst can be deactivated and reactivated *in situ* via the addition and abstraction of chloride.

=> The light-harvesting framework could be regenerated into its active state reversibly without significant loss in catalytic activity.

3. Conclusion

- The light-harvesting system with the ON/OFF switch has been developed.
- The metal with weakly coordinating ligand system enabled this switch.
- Photoredox catalytic activity was regulated *in situ* and reversibly.

4. References

(1) a) Moore, T. A.: Flleming, G. R.; Gust, D. *et al. J. Am. Chem. Soc.* **2011**, *133*, 2916. b) Baitalik, S. *et al. Inorg. Chem.* **2013**, *52*, 7933. (2) Mirkin, C. A. *et al. Acc. Chem. Res.* **2005**, *38*, 825. (3) D'Souza, F.; Ito, O. *et al. J. Phys. Chem. A* **2002**, *106*, 3243. (4) Watanabe, T. *et al. J. Phys. Chem.* **1982**, *86*, 2617.