

# Covalent bonding photosensitizer-catalyst dyads of ruthenium-based complexes designed for enhanced visible-light-driven water oxidation performance

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#### Abstract

We have successfully prepared two ruthenium-based covalent bonding photosensitizer–catalyst dyads through a simple procedure. <sup>1</sup>H NMR spectra of both dyads show that only a single stereoisomer was formed for each dyad. The spectroscopic and electrochemical properties and photocatalytic water oxidation activities of both dyads were investigated in detail. The results indicate that there is negligible electron communication between the photosensitizer and catalyst centers, and each component maintains the desired photophysical and electrochemical properties, which would diminish excited-state electron recombination by facilitating the intramolecular electron transfer. In the presence of excess sacrificial electron acceptor, the dyad with iodide ligand shows a 5.5-fold increase in catalytic performance as compared to its chloro analogue, indicating that the iodide ligand plays an important role during the catalytic cycle. Moreover, compared with the multi-component system, the dyad with iodide ligand exhibits a fourfold increase in catalytic turnover number.

## Introduction

A combination of growing energy requirements and increasingly grave environmental pollution has stimulated a considerable interest in the development of new energy sources [1]. Hydrogen energy is an ideal energy alternative because it possesses a high calorific value and the formation of water as its sole combustion product. Photoinduced water splitting to produce hydrogen and oxygen provides a most straightforward and environmentally benign approach in the conversion of solar energy into chemical fuels [2]. However, as one of the two half reactions, water oxidation is deemed as the main obstacle for water splitting because of its sluggish

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<sup>1</sup> Research Center of Applied Solid State Chemistry, Chemistry Institute for Synthesis and Green Application, Ningbo University, 818 Fenghua Road, Ningbo 315211, Zhejiang Province, People's Republic of China four-electron transfer process [3–5]. Hence, the design of efficient and durable catalysts for catalytic oxygen evolution reaction (OER) is highly demanded. In this context, considerable efforts have been made to the fabrication of three-component systems for photocatalytic water oxidation [6–8]. Molecular water oxidation catalysts (WOCs) based on transition-metal complexes have shown great potential for catalyzing water oxidation due to their facile ligand modification to tune the electronic structures and their amenability to mechanistic and kinetic studies [9–11]. However, these multi-component systems still suffer from diffusion-limited intermolecular electron transfer, which would lead to the excited-state electron–hole recombination, and thus significantly lower the catalytic efficiency.

One promising approach is the development of supramolecular photosensitizer–catalyst dyads by covalently linking a photosensitizer and a catalyst, such that each component retains their original function. Various dimetallic or trimetallic supramolecular complexes have been reported by the groups of Sun [12, 13], Meyer [14, 15] and Thummel [16–18], and these complexes showed superior photocatalytic water oxidation performance compared with the non-covalently linked references. In 2012, Thummel and coworkers reported that the complex  $[Ru^{II}(tpy)(pic)_2I]I$ (tpy = 2,2';6,2''-terpyridine, pic = 4-picoline) functions as an active catalyst for photoinduced water oxidation when irradiated by a blue LED light source. They then incorporated this complex with the photosensitizer into one molecule by using 2,6-di-(1',8'-naphthyrid-2'-yl) pyrazine bridging ligand [16], but the synthetic route to the preparation of bridging ligand is complicated, and the resulting dyad has two stereoisomers, which are extremely difficult to separate. Recently, we reported the synthesis and photocatalytic sulfide oxidation properties of a photosensitizer–catalyst dyad, and the compound tpy–bpy (bpy = 2,2'-bipyridine) was used as the bridging ligand [19]. We have come up with the idea that the tpy–bpy bridging ligand would react with one equivalent of [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] to give a [Ru(bpy)<sub>3</sub>–tpy]<sup>2+</sup> moiety, and the remaining tpy with meridional tridentate ( $\eta^3$ ) chelation provides an open coordination site to afford bimetallic molecular architecture.

Herein, we designed and prepared a Ru-based photosensitizer-catalyst dyad and its corresponding iodo analogue.  $[Ru(bpy)_3]^{2+}$  unit is used as the photosensitizer (denoted as  $Ru_{phot}$ ),  $[Ru(tpy)(pic)_2Cl]^+$  (denoted as  $Ru_{cat}$ -Cl) or  $[Ru(tpy)(pic)_2I]^+$  ( $Ru_{cat}$ -I) unit acts as the catalyst, photosensitizer and catalyst unit are covalently linked by a single bond to form  $Ru_{phot}$ - $Ru_{cat}$ -Cl and  $Ru_{phot}$ - $Ru_{cat}$ -I, respectively. In the presence of excess  $Na_2S_2O_8$  as the sacrificial oxidant, both dyads were investigated as the catalysts for photocatalytic water oxidation,  $Ru_{phot}$ - $Ru_{cat}$ -Cl requires an induction period prior to the commencement of oxygen evolution and  $Ru_{phot}$ - $Ru_{cat}$ -I achieves a higher turnover number (TON) than the non-covalently linked reference under the same conditions.

# **Experimental section**

## Materials

4,4'-Dimethyl-2,2'-bipyridine, SeO<sub>2</sub>, RuCl<sub>3</sub>.3H<sub>2</sub>O, 4-picoline, KI, 2-acetylpyridine, NH<sub>4</sub>PF<sub>6</sub>, and other chemicals were purchased from commercial sources, unless otherwise noted. 4-Methyl-2,2'-bipyridine-4'-carbaldehyde, ligands tpy–bpy, Ru<sub>phot</sub>–tpy, and Ru(bpy)<sub>2</sub>Cl<sub>2</sub> were prepared according to published procedures [19–22], and the purity of each compound was ensured by <sup>1</sup>H NMR spectra based on the reported data. All solvents used in synthetic procedures and measurements were analytical grade and used without further purification. Standard phosphate buffer (0.1 M, pH 7.0) was prepared from mixing NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> aqueous solutions, and the final pH value was confirmed by a pH meter (Mettler Co. FE20 K).

#### **Characterizations and measurements**

<sup>1</sup>H NMR spectra were recorded on a Bruker Avance II 400 spectrometer operating at 400 MHz, and the proton chemical shifts ( $\delta$ , ppm) were calibrated relative to tetramethylsilane. Matrix-assisted laser desorption/ionization time-of-light (MALDI-TOF) mass spectra were obtained on a Bruker BIFLEX III mass spectrometer. Elemental analyses were obtained on a Vario EL III instrument. Electronic absorption spectra were obtained on a Shimadzu UV-2501PC spectrophotometer. The photoluminescence properties were measured at room temperature by using a Hitachi F-4600 Molecular fluorescence spectrometer. Cyclic voltammetry measurements were performed on a CHI 660E electrochemical potentiostat equipped with a glassy carbon (GC) working electrode, a saturated calomel reference electrode (SCE), and a platinum slice as the counter electrode. All potentials recorded were converted to normal hydrogen electrode (NHE) scale according to the equation:  $E_{\rm NHE} = E_{\rm SCE} + 0.245$  V. Prior to each experiment, the glassy carbon (GC) electrode was successively polished with 3.0 and 1.0 um aluminum oxide powder and then sonicated in ion-free water, and then the solution was degassed by bubbling with high-purity nitrogen for 30 min.

## Synthesis of Ruphot-Rucat-Cl

A mixture of Ru<sub>phot</sub>-tpy (600 mg, 0.70 mmol) and RuCl<sub>3</sub>.3H<sub>2</sub>O (200 mg, 0.70 mmol) in 20 mL ethanol was heated at reflux for 5 h, and after cooling to room temperature, the solvent was evaporated by rotary evaporation. The residue was then dissolved in 5 mL 4-picoline, followed by addition of 0.2 mL triethylamine, and the resulting solution was further refluxed overnight. After the reaction was cooled to room temperature, excess NH<sub>4</sub>PF<sub>6</sub> was added and brown solid was precipitated; the crude product was filtered off and washed with ethanol and diethyl ether, respectively. The product was purified by chromatography on silica gel, eluting with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (v/v, 50:1), giving a red solid with a yield of 56%. High-resolution electrospray ionization-mass spectrometry (HR-ESI-MS) (m/z): calcd 1428.1332 [M-PF<sub>6</sub>]<sup>+</sup>, found 1428.1260; calcd 641.5795 [M–2PF<sub>6</sub>]<sup>2+</sup>, found 641.5702. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) 9.24 (d, 2H, J=4.8 Hz), 9.00 (d, 1H, J=1.6 Hz), 8.74 (s, 2H), 8.71 (s, 1H), 8.54 (t, 4H, J=8.2 Hz), 8.52 (d, 2H, J = 4.4 Hz, 8.07 (m, 6H), 7.95 (dd, 1H, J = 6.0, 1.9 Hz), 7.90 (d, 1H, J = 6.0 Hz), 7.83 (d, 1H, J = 5.6 Hz), 7.81 (td, 2H, J=6.9, 1.0 Hz), 7.77 (d, 2H, J=5.4 Hz), 7.74 (d, 5H, J = 6.6 Hz), 7.59 (d, 1H, J = 5.8 Hz), 7.42 (m, 4H), 7.31 (d, 1H, J = 5.0 Hz), 6.79 (d, 4H, J = 6.2 Hz), 2.59 (s, 3H), 2.12 (s, 6H). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN): δ (ppm) 158.9, 158.8, 158.5, 158.4, 158.3, 157.0, 156.3, 156.0, 152.5, 152.3, 151.9, 151.8, 151.7, 151.6, 151.0, 150.8, 145.3, 139.8, 138.0, 137.2, 137.0, 136.1, 128.9, 127.1, 126.2, 125.7, 124.9, 124.0, 123.8, 123.7, 123.4, 121.8, 120.2, 24.0, 20.5. Anal. Calcd for C<sub>58</sub>H<sub>49</sub>ClF<sub>18</sub>N<sub>11</sub>P<sub>3</sub>Ru<sub>2</sub>.H<sub>2</sub>O: C, 43.80; H, 3.23; N, 9.69. Found: C, 43.65; H, 3.18; N, 9.55.

## Synthesis of Ruphot-Rucat-I

A mixture of 200 mg Ru<sub>phot</sub>-Ru<sub>cat</sub>-Cl and 50 mg KI in EtOH/CH<sub>2</sub>Cl<sub>2</sub> (20 mL, 1:1, v/v) was refluxed overnight, and after cooling to room temperature, 20 mL hexane was added to the solution, and the precipitate was collected and washed with hexane. The crude product was purified with column chromatography on silica gel, a mixture of CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (v/v, 10:1) was used as the eluent and afforded Ru<sub>phot</sub>-Ru<sub>cat</sub>-I as deep red solid with a yield of 48%. HR-ESI-MS (m/z): calcd 1483.9393 [M-I]<sup>+</sup>, found 1483.9432; calcd 678.5174  $[M-2I]^{2+}$ , found 678.5180; calcd 410.0434  $[M-3I]^{3+}$ , found 410.0430. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ (ppm) 9.76 (d, 2H, J = 4.8 Hz); 9.43 (d, 1H, J = 1.8 Hz); 9.26 (s, 1H); 8.97 (s, 2H); 8.88 (d, 2H, J = 8.0 Hz); 8.58 (t, 4H, J = 9.2 Hz); 8.12 (td, 2H, J=7.9, 1.4 Hz); 8.08 (m, 5H); 7.93 (t, 2H, J = 6.1 Hz); 7.81 (m, 8H); 7.75 (d, 1H, J = 5.0 Hz); 7.59 (d, 1H, J = 5.8 Hz); 6.78 (d, 4H, J = 6.2 Hz); 2.64 (s, 3H); 2.11 (s, 6H). Anal. Calcd for  $C_{58}H_{49}I_4N_{11}Ru_2$ : C, 43.27; H, 3.07; N, 9.57. Found: C, 43.10; H, 2.99; N, 9.43.

#### Photochemical water oxidation

Photochemical water oxidation was performed in a singlenecked flask equipped with a Clark oxygen probe (YSI 5331) under the irradiation of a white LED light source. The Clark probe was calibrated in oxygen-saturated and oxygen-free water, respectively. Prior to experiment, 5 mL phosphate buffer containing 10.0 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added to the flask and the Clark probe was immersed in the buffer, and the buffer was purged with  $N_2$  to remove the dissolved oxygen, and 25 µL aqueous solution of the dyad (1.0 mM) was injected by a syringe through the probe gap. The amount of the evolved oxygen was recorded as a function of time and reported as the average value from three independent measurements.

 $TON = n_{O2}/n_{cat}$ .

## **Results and discussion**

The synthetic approach for preparation of the bridging ligand (tpy–bpy) and two dyads  $Ru_{phot}-Ru_{cat}-Cl$  and  $Ru_{phot}-Ru_{cat}-I$  is shown in Scheme 1. Firstly, the assembly of the bridging ligand tpy–bpy with  $Ru(bpy)_2Cl_2$  in 1:1 molar ratio was used to introduce the photosensitizer moiety. Treatment of this monomeric complex  $Ru_{phot}$ -tpy with one equivalent  $RuCl_3.3H_2O$  in excess 4-picoline under refluxing condition, afforded the dyad  $Ru_{phot}$ -Ru<sub>cat</sub>-Cl in 56% yield. To prepare the analogous dyad  $Ru_{phot}$ -Ru<sub>cat</sub>-I, the chloro dyad was treated with excess KI to exchange chloride for iodide.

Both dyads were characterized on the basis of <sup>1</sup>H NMR spectra, HR-ESI–MS and elemental analysis. <sup>1</sup>H

NMR and <sup>1</sup>H–<sup>1</sup>H COSY NMR spectra show that the proton peaks are clearly resolved and only a single stereoisomer was formed for Ru<sub>phot</sub>-Ru<sub>cat</sub>-Cl (Fig. 1, Fig. S3). The distinct doublet at 9.24 ppm for Ru<sub>phot</sub>-Ru<sub>cat</sub>-Cl is assigned to the tpy protons closest to chloro ligand [19, 22]. In the case of Ru<sub>phot</sub>-Ru<sub>cat</sub>-I, the doublet is shifted to downfield region, appearing at 9.76 ppm, this difference reflects the fact that as the halide ligand becomes larger, de-shielding effect gets stronger. The mass spectrum of Ru<sub>phot</sub>-Ru<sub>cat</sub>-I recorded under a positive ion mode shows one single-charge peak at m/z = 1483.9432, ascribed to  $[Ru_{phot}-Ru_{cat}-I-I]^+$ , another two fragments at m/z 678.5180 and 410.0430 corresponding to [Ru<sub>phot</sub>-Ru<sub>cat</sub>-I-2I]<sup>2+</sup> and [Ru<sub>phot</sub>-Ru<sub>cat</sub>-I-3I]<sup>3+</sup> ions, respectively (Figs. S5-S7). As for Ru<sub>phot</sub>-Ru<sub>cat</sub>-Cl, the HR-ESI-MS signals recorded at m/z = 1428.1260 ([Ru<sub>phot</sub>-Ru<sub>cat</sub>-Cl-PF<sub>6</sub>]<sup>+</sup>, z = 1) and 641.5702 ( $[Ru_{phot}-Ru_{cat}-Cl-2PF_6]^{2+}$ , z=2) suggest that the complex exists as a dimetallic form in homogeneous solution (Fig. S8, S9).

The electronic absorption and the redox properties of both dyads were investigated, and the related data are summarized in Table 1. Firstly, the UV–Vis absorption spectra were recorded in CH<sub>3</sub>CN; Ru<sub>phot</sub>-Ru<sub>cat</sub>-Cl exhibits strong absorptions in the ultraviolet and visible regions; the absorption bands in the ultraviolet range centered at 360 and 380 nm are attributed to ligand-dominated  $\pi - \pi^*$  transitions, and the absorption bands centered at 453 and 535 nm are originated from the metal-to-ligand charge transfer (MLCT) absorptions of Ru<sub>phot</sub> and Ru<sub>cat</sub>-Cl moieties, respectively [23]. The large difference between the MLCT absorptions in Ruphot-Rucat-Cl indicates that the photosensitizer and catalytic metal sites are largely electronically uncoupled. Compared to Ru<sub>phot</sub>-Ru<sub>cat</sub>-Cl, the MLCT absorptions of  $Ru_{phot}$ - $Ru_{cat}$ -I are blue-shifted to higher energy ( $\lambda_{max}$  at 447 and 520 nm), due to an increase in  $d_{\pi-\pi^*}$  energy gap caused by Cl<sup>-</sup> to I<sup>-</sup> ligand exchange [24] (Fig. 2). In addition, both dyads are essentially non-emissive at room temperature, while the mononuclear complex Ru<sub>phot</sub>-tpy is a strong emitter with a  $\lambda_{max}$  at 631 nm (Fig. S10), the quenching indicates the presence of either energy or electron transfer between the Ruphot and Rucat-Cl portions.

Cyclic voltammetry (CV) of both dyads at glassy carbon electrode was recorded in degassed CH<sub>3</sub>CN (Fig. 3). Ru<sub>phot</sub>-Ru<sub>cat</sub>-I shows two separated monoelectronic oxidation waves: the first reversible oxidation couple at  $E_{1/2}^{ox} = 0.98$  V versus NHE corresponding to Ru<sup>III/II</sup> oxidation of the Ru<sub>cat</sub>-I site and the second irreversible oxidation wave at  $E_{ox} = 1.23$  V versus NHE is similar to the Ru<sup>III/II</sup> couple of Ru<sub>phot</sub>-tpy. Reductively, Ru<sub>phot</sub>-Ru<sub>cat</sub>-I possesses a reversible redox couple at -0.80 V versus NHE, which is assigned to the addition of an electron to the lowest unoccupied molecular orbital (LUMO) on the most electronegative polypyridine ligand. In comparison, the CV plot for Ru<sub>phot</sub>-Ru<sub>cat</sub>-Cl is similar to



Scheme 1 Synthetic procedure for the bridging ligand and two dyads



Fig. 1 Downfield regions of the <sup>1</sup>H NMR spectra for  $Ru_{phot}$ - $Ru_{cat}$ -Cl and  $Ru_{phot}$ - $Ru_{cat}$ -I in CD<sub>3</sub>CN

that of Ru<sub>phot</sub>–Ru<sub>cat</sub>–I and exhibits a reversible Ru<sup>III/II</sup><sub>cat</sub> couple at 0.95 V versus NHE and an irreversible Ru<sup>III/II</sup><sub>phot</sub> wave at 1.30 V versus NHE [25]. Based on the above results, there is negligible electron communication between the photosensitizer and catalyst centers, indicating that each individual component maintains the desired photophysical and electrochemical properties, which would diminish excited-state electron recombination by facilitating the intramolecular electron transfer. In the light-driven water oxidation systems catalyzed by molecular photosensitizer–catalyst dyad, the excited-state reduction potential of the photosensitizer part must be larger than the ground station oxidation potential of the dyad [17]. Owing to the luminescent property of the complex  $Ru_{phot}$ –tpy, we can obtain the excited-state redox potential of the photosensitizer. Similar potential differences about +0.24 and +0.18 V are achieved for  $Ru_{phot}$ – $Ru_{cat}$ –Cl and  $Ru_{phot}$ –Ru<sub>cat</sub>–I, respectively, demonstrating both dyads are capable to catalyze water oxidation under visible light irradiation, and they may own similar catalytic performance.

We evaluated the photocatalytic water oxidation performances of both dyads by monitoring the catalytic TON as a function of reaction time in deoxygenated phosphate buffer. As shown in Fig. 4,  $Ru_{phot}$ - $Ru_{cat}$ -I shows superior catalytic activity compared with that of  $Ru_{phot}$ - $Ru_{cat}$ -Cl, a modest TON of 66 was achieved within a period of 130 s while  $Ru_{phot}$ - $Ru_{cat}$ -Cl only gives a low TON of 12. The control experiments show that no water oxidation activity Table 1Electronic absorptionand redox properties of  $Ru_{phot}$ - $Ru_{cat}$ -Cl and  $Ru_{phot}$ -Ru<sub>cat</sub>-I andtheir analogous mononuclearcomplexes in deoxygenatedCH<sub>3</sub>CN solution

Compound Ru <sub>phot</sub> -tpy	$\lambda_{\rm max}/{\rm nm}~(\epsilon/{\rm M}^{-1}~{\rm cm}^{-1})^{\rm a}$		$E_{1/2}^{\mathrm{ox}} \left(\Delta \mathrm{E}\right)^{\mathrm{b}}$	$E_{1/2}^{\rm red}  (\Delta {\rm E})^{\rm b}$	<sup>c</sup> E* <sup>red</sup> <sub>1/2</sub>
	355 (44,000)	465 (17,000)	1.26 (60)	-1.14(73)	
[Ru(tpy)(pic)Cl] <sup>+</sup>	380 (46,000)	540 (8900)	0.95 (85)	-1.18 (85)	
[Ru(tpy)(pic)I] <sup>+</sup>	385 (42,000)	525 (8000)	1.00(80)	-1.22 (80)	
RU <sub>phot</sub> -Ru <sub>Cat</sub> -Cl	360 (41,000)	453 (9800)	0.95 (70)	-0.77 (75)	1.19
	380 (42,000)	535 (10,500)	1.30 (63)	-1.10 (ir)	
RU <sub>phot</sub> -Ru <sub>cat</sub> -I	360 (44,000)	447 (12,000)	0.98 (78)	-0.80 (60)	1.16
	380 (45,000)	520(10,000)	1.23 (ir)	-1.15 (ir)	

<sup>a</sup>Measured in CH<sub>3</sub>CN ( $1.0 \times 10^{-5}$  M) at room temperature. <sup>b</sup>The redox properties of these compounds (1.0 mM) in degassed CH<sub>3</sub>CN containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub> as supporting electrolyte were performed on a CHI 660E electrochemical potentiostat,  $E_{1/2} = (E_{ox} + E_{red})/2$  in volts, and  $\Delta E = E_{ox} - E_{red}$  in millivolts, ir = irreversible. <sup>c</sup> $E_{1/2}^{red} = E_{1/2}^{red} + E_{em}$ 



**Fig. 2** UV–Vis spectra of  $Ru_{phot}$ – $Ru_{cat}$ –Cl and  $Ru_{phot}$ – $Ru_{cat}$ –I in deoxygenated CH<sub>3</sub>CN solution ( $1.0 \times 10^{-5}$  M) at room temperature

was detected in the absence of the dyad or  $Na_2S_2O_8$ . In addition, as for  $Ru_{phot}$ - $Ru_{cat}$ -Cl, an induction period of 15 s is required prior to the commencement of oxygen evolution. It seems likely that the chloro and iodo dyads may

undergo a different catalytic step. Thummel's work has revealed that the complex  $[Ru(tpy)(pic)_2Cl]^+$  is the WOC precursor and a H<sub>2</sub>O-chloride ligand exchange process is involved as the initial step. However,  $[Ru(tpy)(pic)_2I]^+$  is not requiring an original H<sub>2</sub>O-halogen exchange process, the iodide ligand would be retained during the catalytic cycle [16, 24]. To make a comparison of intra- and intermolecular catalytic activities toward water oxidation, the efficiency of a three-component system (5 mL) containing  $[Ru(tpy)(pic)_2I]^+$  (0.01 mM),  $[Ru(bpy)_3]^{2+}$  (1.0 mM) and  $Na_2S_2O_8$  (10.0 mM) was investigated. The three-component system shows a considerably slower initial oxygen evolution rate and a lower TON value of 15 compared to those obtained from the supramolecular system (0.01 mM) under identical conditions (with a TON of 60) (Fig. 5). This result indicates that the assembly of photosensitizer and catalyst via covalent bonds results in superior water oxidation activity as it avoids diffusion-limited intermolecular electron transfer and thus enables accelerated intramolecular electron transfer from the catalyst to photosensitizer moiety [26–28].



**Fig.3** Cyclic voltammograms of  $Ru_{phot}$ - $Ru_{cat}$ -I with positive scan (**a**) and negative scan (**b**) in degassed CH<sub>3</sub>CN containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub> as supporting electrolyte. Conditions: the concentration of  $Ru_{phot}$ - $Ru_{cat}$ -I is 1.0 mM, the scan rate is 100 mV s<sup>-1</sup>



**Fig.4** Comparison of the photocatalytic water oxidation activities for  $Ru_{phot}$ - $Ru_{cat}$ -Cl (5.0×10<sup>-6</sup> M) and  $Ru_{phot}$ - $Ru_{cat}$ -I (5.0×10<sup>-6</sup> M) under the same conditions



Fig. 5 Comparison of the photocatalytic water oxidation activities for intra- and intermolecular systems

# Conclusion

In summary, two new molecular dyads have been prepared by anchoring a  $Ru(bpy)_3^{2+}$  photosensitizer with a [Ru(tpy)  $(pic)_2X$ <sup>+</sup> water oxidation catalyst. The redox and spectroscopic measurements indicate little electron coupling between the photosensitizer and catalyst portions, and each fragment maintains the desired photophysical and catalytic properties. The photocatalytic properties toward water oxidation were evaluated, and the iodo dyad exhibits a higher TON value with no induction period required prior to the initiation of oxygen evolution, indicating that Ruphot-Rucat-I is not the catalyst precursor. In addition, Ru<sub>phot</sub>-Ru<sub>cat</sub>-I gives a fourfold increase in the TON value as compared to the three-component system, which highlights the advancement in catalytic efficiency of the photosensitizer-catalyst dyad system. More importantly, this current study is expected to inspire further effort towards using supramolecular catalysts for photoinduced water splitting.

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