# **Electronic Supplementary Material (ESI)**

# Visible light-driven water oxidation by a highly efficient dinuclear ruthenium complex

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#### **General Methods and Experimental Details**

**Chemicals**. All chemicals were purchased from Sigma-Aldrich and used as received. All solvents were dried by standard methods when needed. Complexes **1**, **P1**, **P2** and **P3** were prepared according to the reported procedures in references 1-4, respectively.

**UV/Vis absorption spectroscopy**. The UV/Vis absorption spectra were measured on a LAMBDA 750 UV-Visible spectrophotometer (PerkinElmer Ltd).

**ESI-MS**. ESI-MS spectra were measured on a FINNIGAN LCQ ADVANTAGE MAX mass spectrometer (Thermo Fisher Scientific).

- <sup>10</sup> **Electrochemistry**. Cyclic voltammetry and differential pulse voltammetry were performed in phosphate buffer solution, with an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie), using a glassy carbon disk (diameter 3 mm, freshly polished) as the working electrode, a platinum wire in a compartment separated from the bulk solution by a fritted disk as counter-electrode. The electrolyte used was 8.3 mM phosphate buffer solution, and the reference electrode was Ag/AgCl
- <sup>15</sup> in 3 M KCl in water. Potentials are versus NHE by using Ru(bpy)<sub>3</sub>Cl<sub>2</sub> as a reference with  $E(Ru^{2+/3+}) = 1.26 V.^{5}$

**Oxygen Evolution Measurements**. The evolved oxygen was analyzed by means of Clark-type oxygen electrode in liquid phase and gas chromatography (GC) in gas phase.

- (a) By oxygen electrode in the liquid phase. A Clark-type oxygen electrode (Hansatech Instruments, <sup>20</sup> Oxygraph OXYG1 and DW2/2 unit) equipped with 4 optical windows for photosynthesis was employed to measure the produced oxygen in liquid phase. In a typical run, a mixture of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 mM), catalyst **1** (1.49  $\mu$ M) and photosensitizer (0.13 mM) in pH 7.2 phosphate buffer (20 mM, 1.5 mL) / acetonitrile (30  $\mu$ L), was purged with nitrogen for 20 min. The reaction mixture was then illuminated with a Xe-lamp (500W; intensity where irradiated: ~ 0.3 W/cm<sup>2</sup>; cut-off filter,  $\lambda$  > 400 nm) <sup>25</sup> for 80-120 s. Temperature was kept at 11 °C by a circulating water bath. The generated O<sub>2</sub> was
- measured and recorded vs time by this system. In the case of  $[Co(NH_3)_5Cl]Cl_2$  as acceptor, the mixture contains  $[Co(NH_3)_5Cl]Cl_2$  (29 mM), catalyst **1** (1.14  $\mu$ M) and photosensitizer (10  $\mu$ M) in pH 7.0 phosphate buffer (40 mM, 2.0 mL) / acetonitrile (40  $\mu$ L), and the illumination time was 25 min

(b) By GC in the gas phase. Evolved oxygen in gas phase was analyzed with a 3000A Micro GC  $_{30}$  (Agilent Technologies) equipped with a thermal conductive detector and a 5Å Molecular sieve column (12 $\mu$ m/320 $\mu$ m/10m) allowing auto sampling and analysis. Helium was used as carrier gas. In a typical measurement, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 mM), catalyst **1** (10.8  $\mu$ M) and photosensitizer (0.5 mM) in pH 7.2

phosphate buffer (20 mM, 10 mL) / acetonitrile (550  $\mu$ L), were mixed in the reaction flask which was connected to the GC through a septum via a 1/16 in. gas sampling tubing. The reaction mixture was deaerated with helium for more than 30 min and then illuminated with visible light for 60 min. The temperature of the flask was kept at 17 °C by a circulating water bath. The generated O<sub>2</sub> was measured <sup>5</sup> by GC every 5 min and the sample was pumped for 10s before injection. The system is tightened and no O<sub>2</sub> leaked from air could be detected by analysis the change of nitrogen content in the system.

**Turnover Number Determination**. The turnover number (TN) of oxygen evolution in the head space of the reaction flask was determined by GC. After illumination for 30 min, the lamp was turned off. After 30 min, GC analysis was performed, and the amount of oxygen formed and the turnover number <sup>10</sup> were calculated.

In the case of  $Na_2S_2O_8$  as acceptor, the reaction mixture was neutralized with 0.2 M aqueous NaOH solution to pH 7.2, and more acceptor (23 mg) and/or sensitizer (3 µmol in 0.3 mL ACN) were added, and the mixture was irradiated again for 30 min and the GC measurement was done once again after 30 min. This process could be repeated 3 times. The oxygen produced was combined and the total <sup>15</sup> turnover number was calculated.

UV-vis Analysis of the Sensitizer after Illumination. A small amount of the solution (100  $\mu$ L) was taken from the reaction mixture containing the sensitizer (1 mM) and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 mM) in the absence or presence of complex 1 (38  $\mu$ M), and added to 0.1% EtOH in water (3 mL) and the absorption spectrum was measured. After the reaction mixture was illuminated for 10 min, the same amount (100  $\mu$ L) of the reaction mixture was added to 0.1% EtOH aqueous solution (3 mL), and UV-vis absorption

was measured again. The decomposition of the sensitizer after illumination was estimated by analysis the absorption at  $\sim$  360 nm.

<sup>25</sup> Table S1. Electrochemical and Absorption Data of **P1–P3** 

		P1	P2	P3
$E_{ox}^{a}$	рН 7.0	1.37	1.45	1.50
	pH 7.2	1.40	1.49	1.54
$\lambda_{max,MLCT}$		$430 (1.0 \times 10^4),$	440 $(1.2 \times 10^4)$ ,	440 ( $1.26 \times 10^4$ ),
$(\varepsilon, \mathrm{M}^{-1}\mathrm{cm}^{-1})^b$		$479(1.19 \times 10^4)$	$486 (1.70 \times 10^4)$	$479(1.68 \times 10^{4})$

<sup>*a*</sup> in phosphate buffer solution; DPV value, V vs NHE. <sup>*b*</sup> in acetonitrile.

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<sup>10</sup> Figure S1. Cyclic Voltammograms of **1** in (a) pH 7.0 and (b) pH 7.2 buffer solution.



Figure S2. Kinetics of O<sub>2</sub> evolution in liquid phase measured by the Clark-type oxygen electrode in the <sup>20</sup> presence of different photosensitizers. Conditions: Xe lamp, 500 W,  $\lambda$ > 400 nm, 9.8 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.13 mM photosensitizer and 1.49  $\mu$ M complex **1** in a reaction mixture (1.53 mL) (1.5 mL pH 7.2 phosphate buffer solution + 0.03 mL acetonitrile).



Figure S3. Kinetics of  $O_2$  evolution in liquid phase measured by the Clark-type oxygen electrode in a reaction mixture (1.5 mL) containing Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 mM) and **1** (1.52  $\mu$ M) in the presence of **P1** ((A) 0.032 mM; (B) 0.047 mM; (C) 0.062 mM and (D) 0.090 mM).

### Stability of complex 1 under acidic conditions

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The stability of complex 1 in acidic environment was studied by means of UV-vis and ESI-MS.

Figure S4a shows the UV-vis spectra of **1** in a phosphate (8.3 mM) buffer solution (pH 7.2) and in a 10 mM  $H_3PO_4$  solution (pH 2.6). Figure S4b gives the UV-vis spectra of **1** when its pH was adjusted <sup>5</sup> from 2.6 (in 10 mM  $H_3PO_4$ ) to 7.2 with aqueous NaOH solution (2 M). The results show that (1) UV-vis spectra of **1** at pH 2.6 and 7.2 are identical; (2) the UV-vis spectrum of **1** remains unchanged when it was neutralized with NaOH from an acidic solution.



Figure S4. (a) UV-vis spectra of complex **1** (10  $\mu$ M) at pH 2.6 in 10 mM H<sub>3</sub>PO<sub>4</sub> solution (black curve) and at pH 7.2 in a phosphate (8.3 mM) buffer (red curve); (b) UV-vis spectra changes of complex **1** (10  $\mu$ M) upon pH-adjusting with 2M NaOH from pH 2.6 (initial 10 mM H<sub>3</sub>PO<sub>4</sub> solution, black curve) to pH 3.2 (red curve) and pH 7.2 (blue curve).

Figure S5 gives the ESI-MS spectra of complex **1** at various pH values, which shows that the structure of complex **1** under acidic and basic conditions is the same.



s Figure S5. ESI-MS spectra of complex  $1 (10 \ \mu\text{M})$  (a) at pH 4.2 in 0.1 mM H<sub>3</sub>PO<sub>4</sub> solution; (b) at pH 6.6 in 0.08 mM phosphate buffer solution; (c) at pH 9.4 in 0.08 mM phosphate solution.

The results from UV-vis and MS measurements give a clear conclusion that complex **1** is very stable in both acidic and basic environments.

### References

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