Supplementary Information

Characterization of a Trinuclear Ruthenium Species in Catalytic Water Oxidation by Ru(bda)(pic)$_2$ in Neutral Media

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Experimental section

Materials. High purity Milli-Q water was used in all experiments. $[Co(NH_3)_5Cl]Cl_2$, $Ce(NH_4)_2(NO_3)_6$ was purchased from Aladdin chemical Co. Ldt. $Ru(bda)(pic)_2$ (**1**),[1] $[Ru(bda)(pic)_2]PF_6$[1, 2] and $Ru(bpy)_3Cl_2$[3] were prepared according to the known procedures. All other chemicals are commercially available and all solvents are reagent grade.

Physical methods. UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer. The electrospray ionization mass (ESI-MS) and high resolution mass spectra (HR-ESI-MS) were recorded on LTQ-Orbitrap XL (Thermo Fisher Scientific, America) and Z-spray ionization source equipped Q-Tof Micro (Micromass Inc., Manchester, England). Elemental analyses were performed on an Elementar VarioELIII elemental analyzer.

Time-Resolved UV-Vis Spectroscopy under Irradiation. Time-resolved UV-Vis spectra during photochemical oxygen evolution was investigated in a quartz cuvette (path length, 10 mm) filled with 3 mL 1% CH_3CN-phosphate buffer solutions (at different pH values, 0.1 M) containing complex **1** (53 μM), $[Ru(bpy)_3]^{2+}$ (13 μM), $[Co(NH_3)_5Cl]^{2+}$ (1 mM). The reaction solution was irradiated from the top of the quartz cuvette using a 300 W xenon arc lamp equipped with a 400 nm cut-off filter. Due to the low solubility of **1** in water, 1% CH_3CN was added into the reaction solution. To facilitate UV-Vis measurement, $[Ru(bpy)_3]^{2+}$ and complex **1** were employed in a ratio of 1:4.

Electrochemical Analysis. The electrochemical measurements were recorded on a CHI 660D electrochemical potentiostat. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disk (diameter, 3 mm) successively polished with 3 and 1 μm diamond pastes and sonicated in ion-free water before use. Potentials versus NHE were calibrated by using $[Ru(bpy)_3]Cl_2$ as a reference with E ($Ru^{II/III}$) = 1.26 V vs. NHE.

Thin-layer spectroelectrochemical Studies. The thin-layer spectroelectrochemistry of complex **1** was carried out in a Y-shaped quartz cuvette equipped with Pt mesh as working electrode, a Pt wire as counter electrode and an Ag/AgCl reference electrode. The quartz cuvette was filled with 2 mL 8×10^{-4} M complex **1** in 1% CH_3CN-phosphate buffer solution (0.1 M)**.** The path length of the Y-shaped quartz cuvette is 1 mm.

Preparation and Isolation of Complex 2. Complex **1** (40 mg, 0.075 mmol) was dissolved in 6 mL H_2O and CH_3CN mixed solvent (*v*/*v* 10:1), to which was slowly added an aqueous solution (0.5 mL) of $NaIO_4$ (10.7 mg, 0.05 mmol). The color of the reaction solution changed from dark red to green. The solution was then treated with excess NH_4PF_6. The resulted green solid was collected, washed with water and dried in vacuum. Vapor diffusion of diethyl ether into the CH_3CN solution of this precipitate yielded purple crystals suitable for X-ray diffraction (yield 32%, 13.8 mg). ^1H NMR (500 MHz, CD_3CN): δ 1.95 (s, 3H), 2.15 (s, 6H), 2.17 (s, 12H), 6.5 (d, 4H, J = 10 Hz), 6.73 (d, 8H, J = 5 Hz), 7.70 (m, 9H), 8.00 (m, 2H), 8.11 (m, 6H), 8.33 (m, 2H), 8.48 (d, 4H, J = 10 Hz). HRMS (ESI): m/z = 719.5777 ($[M-2PF_6]^{2+}$, calcd: m/z = 719.5768). Anal. calcd for $C_{62}H_{59}F_{12}N_{11}O_{11}P_2Ru_3$: C 43.11, H 3.44, N 8.92, found: C 43.06, H 3.51, N 8.84. UV-Vis (1% CH_3CN-phosphate buffer, 0.1 M, pH 7): λ_{max} = 300 nm (4.0×10^4 $M^{-1}cm^{-1}$), 445 nm (1.3×10^4 $M^{-1}cm^{-1}$), 500 nm (1.1×10^4 $M^{-1}cm^{-1}$), 690 nm (5×10^4 $M^{-1}cm^{-1}$).

Photocatalytic Water Oxidation. Oxygen evolution monitored by oxygen electrode: In a typical experiment, $[Co(NH_3)_5Cl]^{2+}$ (2.9×10^{-2} M), $[Ru(bpy)_3]^{2+}$ (6.7×10^{-5} M), **1** (5×10^{-6} M) were dissolved in 2 mL 1 % CH_3CN-phosphate buffer solution (different pHs, 0.1 M) at room temperature. After degassing, the above solution was irradiated by an Xe lamp (300 W) with a cut-off filter (λ > 400 nm) and the evolved oxygen was recorded by a Clark-type oxygen electrode (Hansatech Instruments DW2/2 unit with an S1 electrode).

Oxygen evolution monitored by GC: In a typical experiment, $[Co(NH_3)_5Cl]^{2+}$ (2.9×10^{-2} M), $[Ru(bpy)_3]^{2+}$ (10^{-4} M) and **1** (10^{-5} M) in 5 mL 1% CH_3CN-phosphate buffer solution (different pHs, 0.1 M) were added to a Schlenk bottle with the total volume (including the gas phase and the solution) of 51 mL. The solution was degassed for 20 min prior to irradiation. The photocatalytic water oxidation reaction was started by light irradiation at room temperature using an Xe lamp (300 W) with a cut-off filter (λ> 400 nm). The gas sample was taken by syringe from the headspace of the bottle and analyzed on a Techcomp GC 7890T instrument.

Preparation of $[Ru^{III}(bda)(pic)_2]PF_6$. $[Ru(bda)(pic)_2]PF_6$ was prepared according to the literature method.[1, 2] Complex **1** (53 mg, 0.1 mmol) was dissolved in a 3 mL triflic acid aqueous solution (pH = 1.0) containing 0.2 mL acetonitrile. 1 mL aqueous solution of ammonium cerium nitrate (54.8 mg, 0.1 mmol) was gradually added to the above solution with vigorous stirring. The color of the solution changed to light yellow accompanied by the evolution of oxygen. After adding excess NH_4PF_6 aqueous solution, the resulting mixture was kept stationary to obtain a light yellow precipitate. The precipitate was filtered, washed with diethyl ether and dried in vacuum to give a yellow solid of $[Ru(bda)(pic)_2]PF_6$. HRMS (ESI): m/z = 530.0540 ($[Ru^{III}(bda)(pic)_2]^+$, calcd: m/z = 530.0534). Anal. calcd for $C_{24}H_{20}F_6N_4O_4PRu$: C 42.74, H 2.99, N 8.31, found: C 42.68, H 2.87, N 8.40.

X-Ray Crystallographic Characterization of Complex 2. The single-crystal X-ray diffraction data were collected with a Bruker Smart Apex II CCD diffractometer with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296 K using the ω-2θ scan mode. The absorption corrections were performed by SADABS program. All structures were solved by direct methods and refined on F^2 against full-matrix least-squares methods by using the SHELXTL-97 program package. Hydrogen atoms were located by geometrical calculation. Details of crystal data, data collections and structure refinements are summarized in Table S1. CCDC-1061590 contains the supplementary crystallographic data of **2** for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Disproportion of $[Ru^{III}(bda)(pic)_2]PF_6$. The disproportionation of $[Ru^{III}(bda)(pic)_2]PF_6$ was performed by standing 60 μM $[Ru^{III}(bda)(pic)_2]PF_6$ in a quartz cuvette filled with 3 mL 1% CH_3CN-phosphate buffer solution (0.1 M). The formation of **2** was in situ monitored by UV-Vis in a quartz cuvette filled with 3 mL 1% CH_3CN-phosphate buffer solution (0.1 M). In order to carry out MS spectrometry during disproportionation, a 1 mM phosphate buffer solution was used as solvent to lower the ionization effect of the phosphate and potassium ion.

Detect the formation of 2 from Ru^{III} by HR-ESI-MS.

The self-transformation of $[Ru^{III}(bda)(pic)_2]^+$ was further described by mass spectrometry (Figure S4). Initially, Ru^{III} as the only species was detected in solution. Subsequently, two new signals at 547.0515 and 569.0161 appeared. They were assigned to $[Ru^{IV}{=}O + H]^+$ and $[Ru^{II} + K]^+$ resulted from disproportionation. The formation of **2** was then evidenced by two growing signals at 719.0787 and 1584.1170 due to the reaction between Ru^{II}-OH_2 with $Ru^{IV}{=}O$. The former signal corresponds to $[Ru^{III}(bda)(pic)_2\text{-}O\text{-}Ru^{IV}(pic)_2(OH_2)(CH_3CN)\text{-}O\text{-}Ru^{III}(bda)(pic)_2]^{2+}$ and the latter corresponds to $\{[Ru^{III}(bda)(pic)_2\text{-}O\text{-}Ru^{IV}(pic)_2(OH_2)(CH_3CN)\text{-}O\text{-}Ru^{III}(bda)(pic)_2] + (PF_6)^-\}^+$

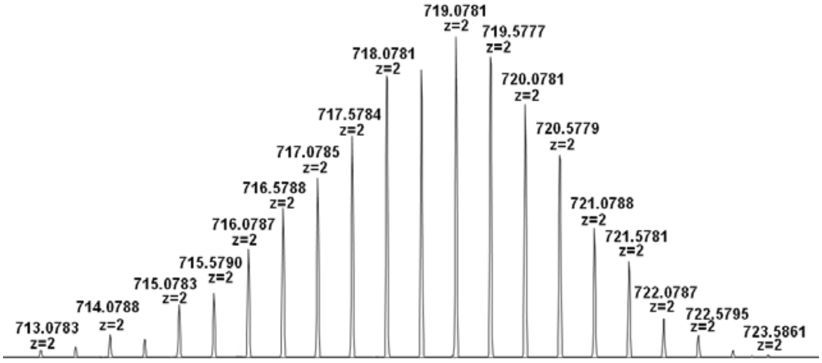

Figure S1 HR-ESI-MS spectrum of the green species generated from photochemical reaction.

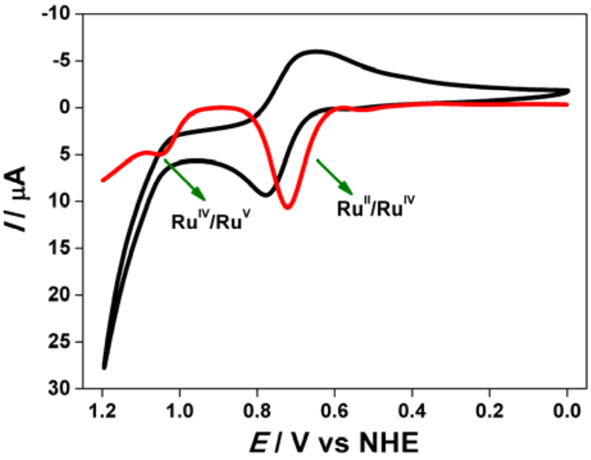

Figure S2 CV and DPV of complex **1** (1 mM) in 1% CH_3CN-phosphate buffer solution (0.1 M, pH 7).

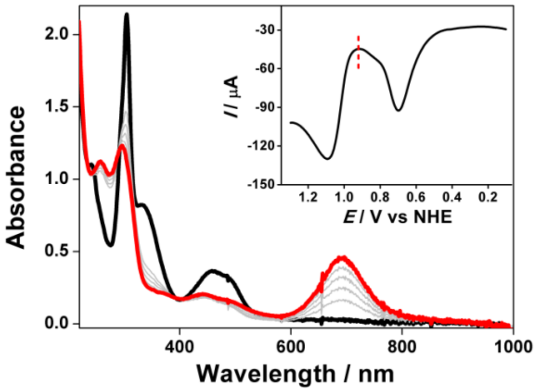

Figure S3 UV-Vis spectral changes of 8×10^{-4} M complex **1** in phosphate buffer solution (pH 7, 0.1 M, 1% CH_3CN) at a constantly applied potential of 0.9 V. The spectra before and after electrolysis are shown in black and red, respectively. The inset shows DPV of 8×10^{-4} M complex **1** in the same solution. The path length of the quartz cuvette is 1 mm.

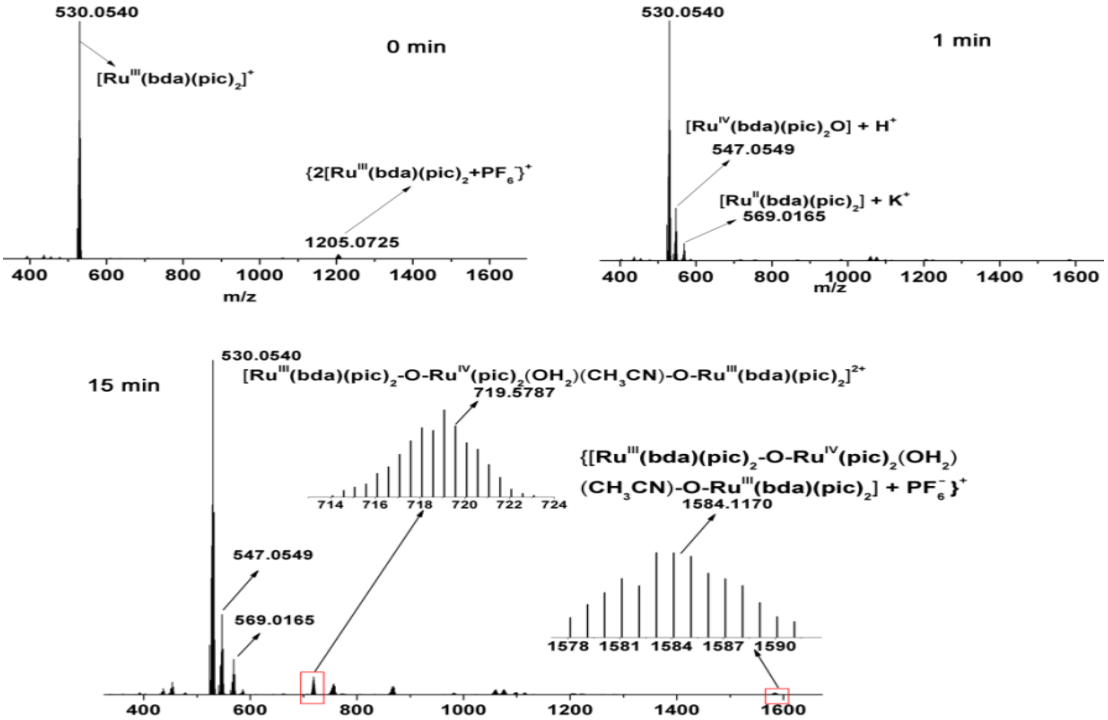

Figure S4 ESI-HRMS spectral changes of [Ru^{III}(bda)(pic)$_2$]PF$_6$ in 1% CH$_3$CN-phosphate buffer solution (pH 7, 1 mM) during a period of 15 min. Initially, Ru^{III} as the only species was detected in solution. Subsequently, two new signals at 547.0515 and 569.0161 appeared. They were assigned to [Ru^{IV}=O + H]$^+$ and [Ru^{II} + K]$^+$ resulted from disproportionation. The formation of **2** was then evidenced by two growing signals at 719.0787 and 1584.1170 due to the reaction between Ru^{II}-OH$_2$ with Ru^{IV}=O. The former signal corresponds to [Ru^{III}(bda)(pic)$_2$-O-Ru^{IV}(pic)$_2$(OH$_2$)(CH$_3$CN)-O-Ru^{III}(bda)(pic)$_2$]$^{2+}$ and the latter corresponds to {[Ru^{III}(bda)(pic)$_2$-O-Ru^{IV}(pic)$_2$(OH$_2$)(CH$_3$CN)-O-Ru^{III}(bda)(pic)$_2$] + (PF$_6$)$^-$}$^+$.

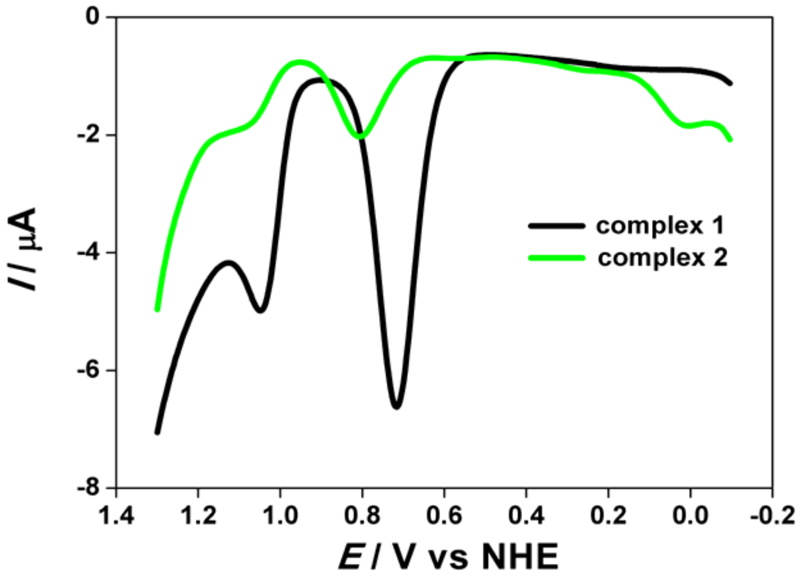

Figure S5 DPVs of complex **1** (1.0 mM, black line) and complex **2** (0.33 mM, green line) in phosphate buffer solution (pH 7, 0.1 M, 1% CH_3CN).

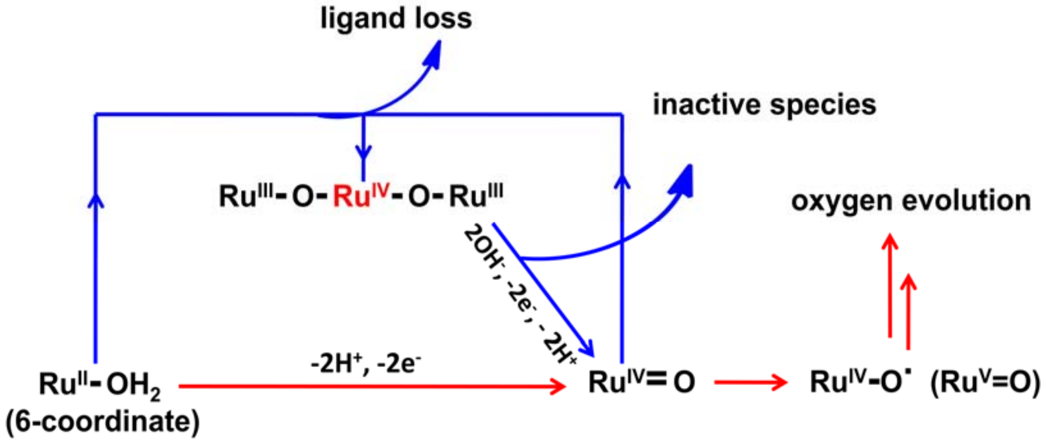

Figure S6 Proposed water oxidation mechanism for complex **1** under neutral conditions.

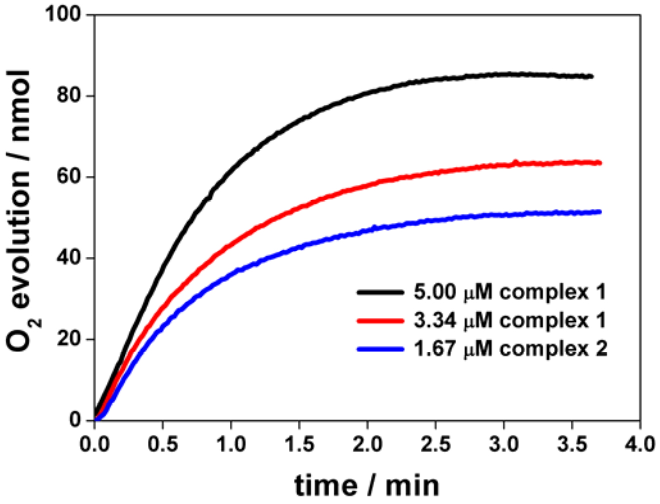

Figure S7 Photocatalytic oxygen evolution detected by Clark-type electrode in 2 mL 1 % CH_3CN-phosphate buffer solution (pH 7.0) containing $[Co(NH_3)_5Cl]^{2+}$ (29 mM), $[Ru(bpy)_3]^{2+}$ (6.7×10^{-5} M) and complex **1** (5×10^{-6} M, black line), complex **1** (3.34×10^{-6} M, red line) and complex **2** (1.67×10^{-6} M, blue line).

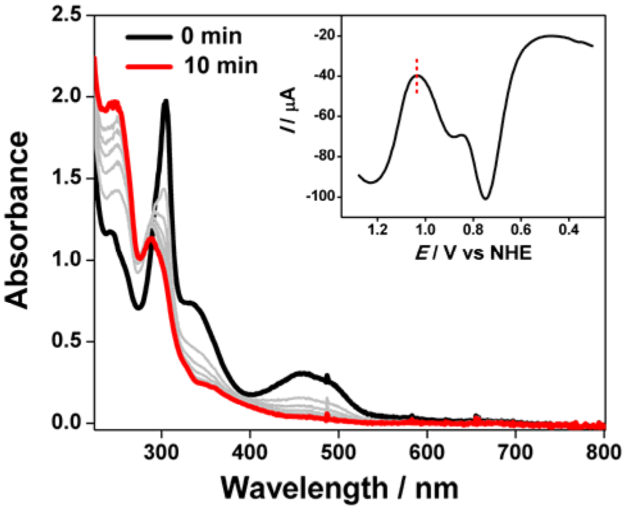

Figure S8 UV-Vis spectral changes of 8×10^{-4} M complex **1** in 1% CH_3CN-phosphate buffer solution (pH 4, 0.1 M) at a constant potential of 1.0 V for 10 min. The inset shows the DPV of complex **1** at pH 4. The path length of the quartz cuvette is 1 mm.

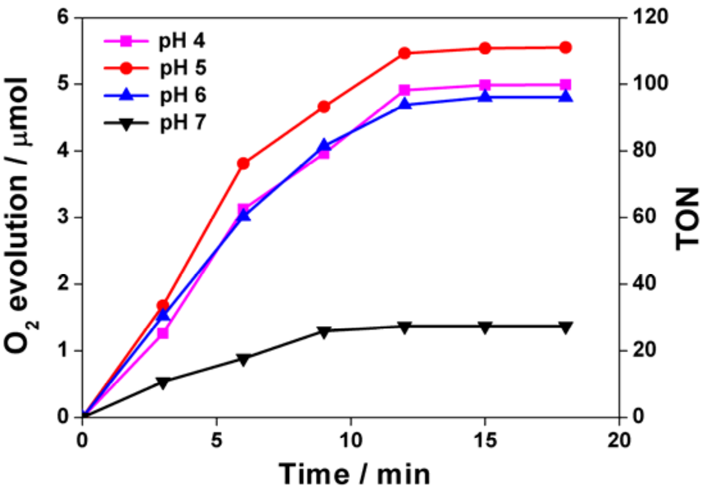

Figure S9 Photocatalytic oxygen evolution in 5 mL 1 % CH_3CN-phosphate buffer solution containing $[Co(NH_3)_5Cl]^{2+}$ (29 mM), $[Ru(bpy)_3]^{2+}$, and complex 1 (1×10^{-5} M) at different pHs. The data were recorded by GC.

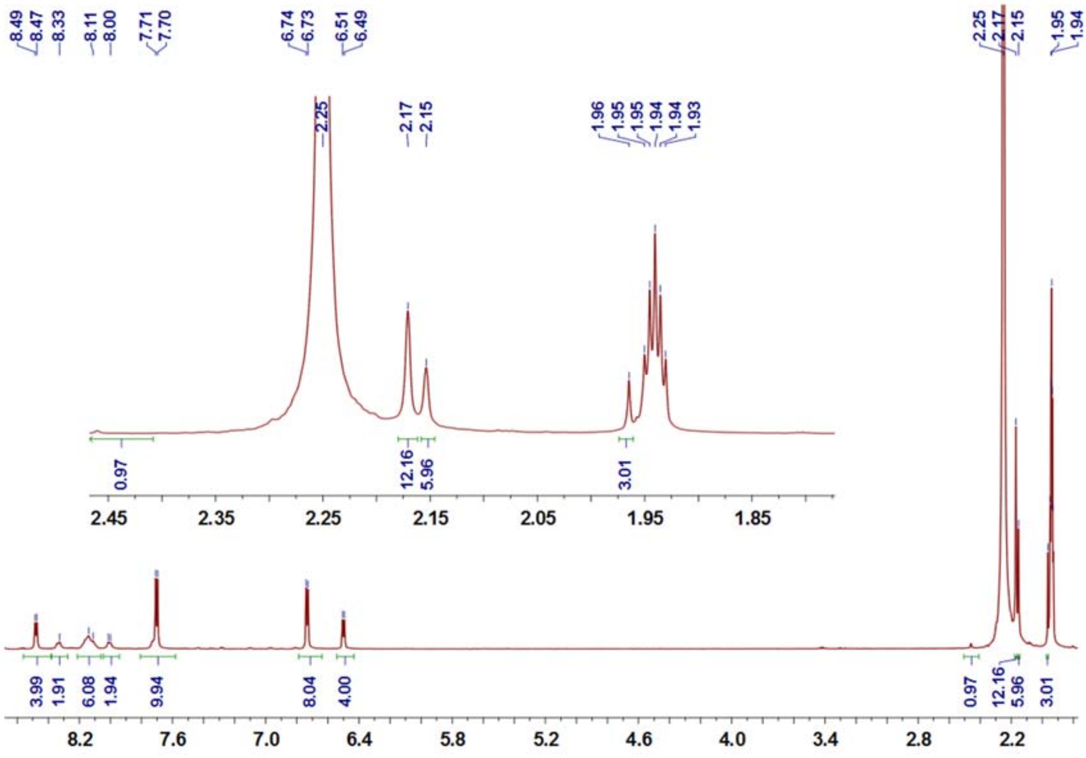

Figure S10 ^1H NMR spectrum of **2** in CD_3CN.

Table S1 Crystallographic data of complex **2**.

Complex	**2**
Formula	$[C_{62}H_{59}N_{11}O_{11}Ru_3](PF_6)_2$
Fw	1727.36
Crystal system	triclinic
Space group	*P -1*
T	296(2) K
a/Å	15.8008(7)
b/Å	16.2412(11)
c/Å	19.6284(11)
α/deg	107.027(4)
β/deg	102.696(3)
γ/deg	109.127(2)
V/Å^3	4263.5(4)
Z	2
D_{calcd}/Mg m^{-3}	1.346
Radiation type	Mo K_α
absorption coefficient μ	0.642
θ Range/°	2.154/27.663
Reflns collected	19085
no. parameters	887
F(000)	1732
GOF on F^2	1.040
R_{int}	0.0521
Final R_1 ($I > 2\sigma(I)$)	0.0706
Final wR_2 ($I > 2\sigma(I)$)	0.2160

References

1. L. Duan, A. Fischer, Y. Xu and L. Sun, *J. Am. Chem. Soc.*, 2009, **131**, 10397-10399.
2. L. Li, L. Duan, Y. Xu, M. Gorlov, A. Hagfeldt and L. Sun, *Chem. Commun.*, 2010, **46**, 7307-7309.
3. M. S. Lowry, W. R. Hudson, J. Pascal, R. A. and S. Bernhard, *J. Am. Chem. Soc.*, 2004, **126**, 14129-14135.