

**Preparation and structural characterisation of tetrabutylammonium salt of  
mono-ruthenium(III)-substituted  $\alpha$ -Keggin-type silicotungstates with  
4,4'-bipyridine ligand and its electrochemical behaviour in organic solvents.**

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## Instrumentation

Room-temperature Ru L<sub>3</sub>-edge XANES spectra were measured at the BL11 beamline of the Hiroshima Synchrotron Research Center (HSRC).<sup>1</sup> The storage ring was operated at 700 MeV, and the synchrotron radiation from a bending magnet was monochromatized with a Si-(111) double-crystal monochromator. The sample chamber was filled with He, and a sample was mounted on a copper holder connected to a current amplifier. The angle between the incident X-rays and the sample surface was 20°. The X-ray fluorescence yield (XFY) from the sample was measured with a commercial Silicon drift detector (Amptek, XR-100SDD). XANES spectra were recorded from 2825 to 2855 eV with an energy step of 0.25 eV. The sample holder was a copper plate 0.2 mm thick, and it had a hole in the center that was 15 mm in diameter. Powder of the sample was supported on a piece of adhesive tape attached to the hole in the holder.

Electron spin resonance (ESR) spectra were recorded at 77 K on a JEOL JES-RE1X and Bruker ESP300E spectrometers (X-band). Spectra simulation was done by Bruker SimFonia software package. The sample was dissolved in solvent (ca. 0.5 mM) and a proper amount of the solution was placed into a Suprasil quartz tube ( $\phi = 5$  mm). The quartz tube was sealed after several degassed-and-thaw cycles on a vacuum

line.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in aqueous solution were performed on a BAS 50W system at ambient temperature. A glassy carbon working electrode (diameter, 3 mm), a platinum wire counter electrode and an Ag/AgCl reference electrode (203 mV vs NHE at 25 °C) (3M NaCl, Bioanalytical Systems, Inc.) were used. The voltage scan rate was set at 25 mV s<sup>-1</sup>. Approximate formal potential values  $E_{1/2}$  were calculated from the cyclic voltammograms as the average of cathodic and anodic peak potentials for corresponding oxidation and reduction waves.

**Table S1** Experimental ESR parameters of **1**

Solvents <sup>a</sup>	$g_1$	$g_2$	$g_3$	$g_{iso}$
Acetone	2.590	2.366	1.560	2.172
DMF	2.587	2.368	1.560	2.172
DMSO	2.605	2.370	1.520	2.165
Acetonitrile	2.585	2.370	1.560	2.172

<sup>a</sup> DMF: *N,N*-dimethylformamide and DMSO: dimethylsulfoxide.

**Table S2** Experimental ESR parameters in acetonitrile solution at 77 K

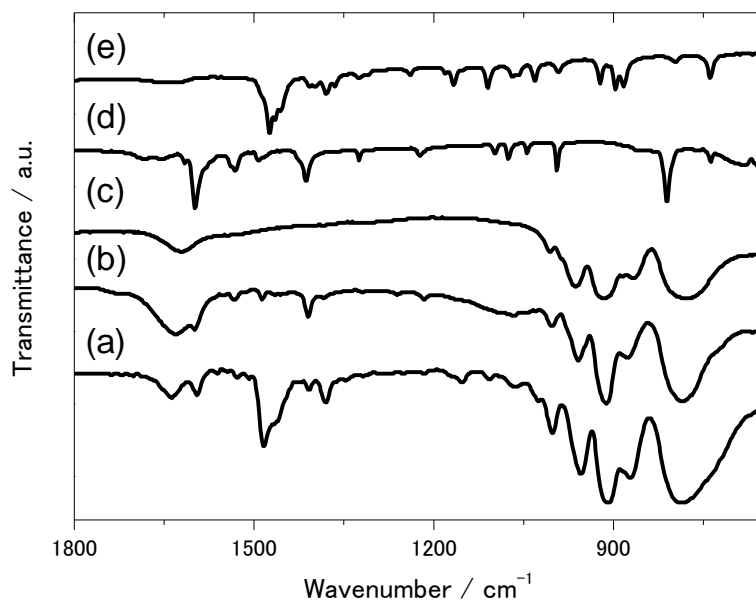
Sample <sup>a</sup>	$g_1$	$g_2$	$g_3$	$g_{iso}$	Ref.
[SiW <sub>11</sub> O <sub>39</sub> Ru <sup>III</sup> (bipy)] <sup>5-</sup> ( <b>1</b> )	2.585	2.370	1.560	2.172	This work
[PW <sub>11</sub> O <sub>39</sub> Ru <sup>III</sup> (py)] <sup>4-</sup>	2.579	2.338	1.603	2.173	[2]
[PW <sub>11</sub> O <sub>39</sub> Ru <sup>III</sup> (DMSO)] <sup>4-</sup>	2.296	2.192	1.877	2.122	[2]

<sup>a</sup> bipy: 4,4'-bipyridine, py: pyridine and DMSO: dimethylsulfoxide.

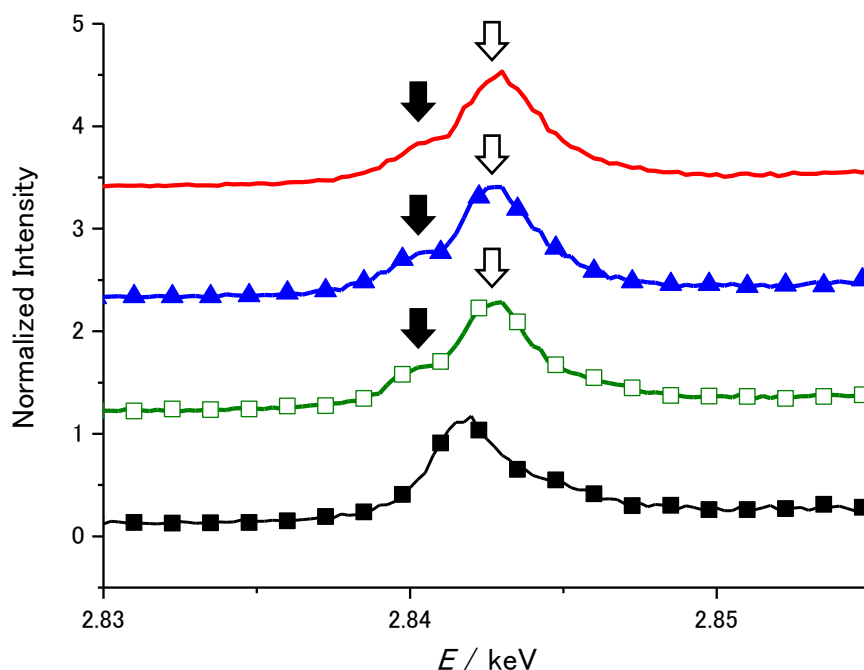
### Stability of **1** in organic solvents

TBA salt of **1** was purified from acetonitrile solution. Single crystal structural analysis indicated that bipyridine was coordinated to Ru in SiW<sub>11</sub>O<sub>39</sub>Ru (Fig. 1). IR spectrum shows that the **1** contained bipyridine ligand and TBA cations (Fig. S1). It was confirmed that the valence of the ruthenium ion in **1** was +3 by using the Ru-L<sub>3</sub>-edge XANES technique (Fig. S2). <sup>1</sup>H-NMR spectrum suggested that the presences of bipyridine ligand coordinating to paramagnetic Ru<sup>III</sup> and TBA cations with molar ratio of 1:5 (Fig. S4). Moreover, ESR spectrum and the  $g_{iso}$  value (2.172) of **1** in acetonitrile

solution were almost the same as those of  $\text{TBA}_4[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{py})]$  ( $g_{\text{iso}} = 2.173$ ) (Fig. S5 and Table S2).<sup>2</sup> These results indicated that the compound **1** was stable in acetonitrile. In addition, ESR spectra and  $g_{\text{iso}}$  values in acetone, DMF and DMSO were almost the same as those in acetonitrile (Fig. S5 and Table S1). It was reported that  $g_{\text{iso}}$  values for  $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{py})]^{4-}$  and  $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{DMSO})]^{4-}$  were different (Table S2).<sup>2</sup> This result indicated that the compound **1** was also stable in these organic solvents. The UV-Vis spectra were almost same after storing six months, indicating **1** was stable in these solvents (Fig. S9).



**Fig. S1.** FT-IR spectra of (a) **1**, (b)  $\text{Cs}_5[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{bipy})]$ , (c)  $\text{Cs}_5[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]$ , (d) 4,4'-bipyridine and (e) tetrabutylammonium bromide.



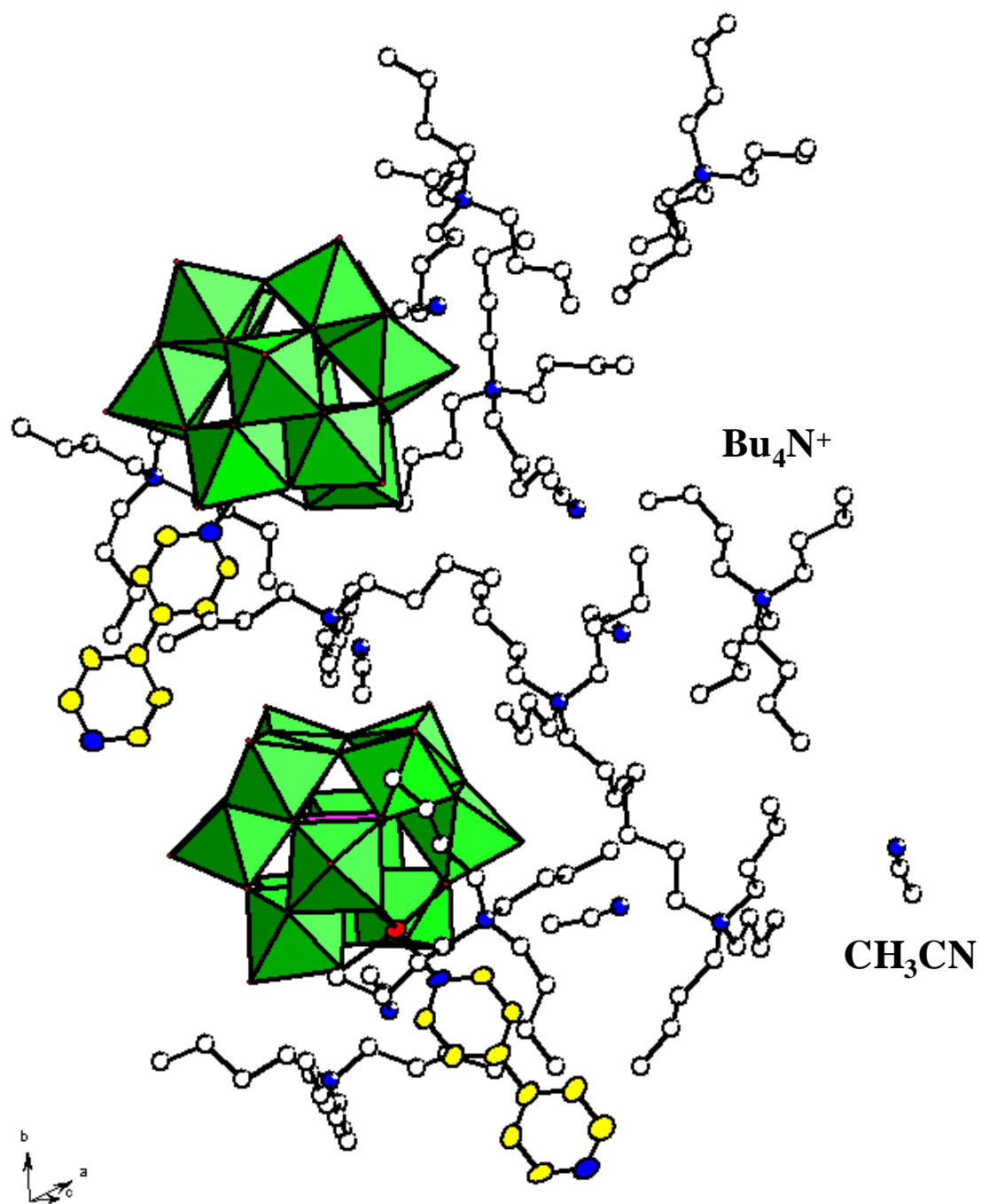
**Fig. S2.** Normalised XANES spectra at the Ru-L<sub>3</sub>-edge. (red line) **1**, (blue line with closed triangles)  $\text{Cs}_5[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{pyridine})]$ , (green line with open squares)  $\text{Cs}_4[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{dms})]$  and (black line with closed squares)  $\text{Cs}_5[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{II}}(\text{dms})]$ . The white and black arrows indicate the peak correspond to  $e_g$  and  $t_{2g}$ , respectively.

### Ru L<sub>3</sub>-edge XANES spectra

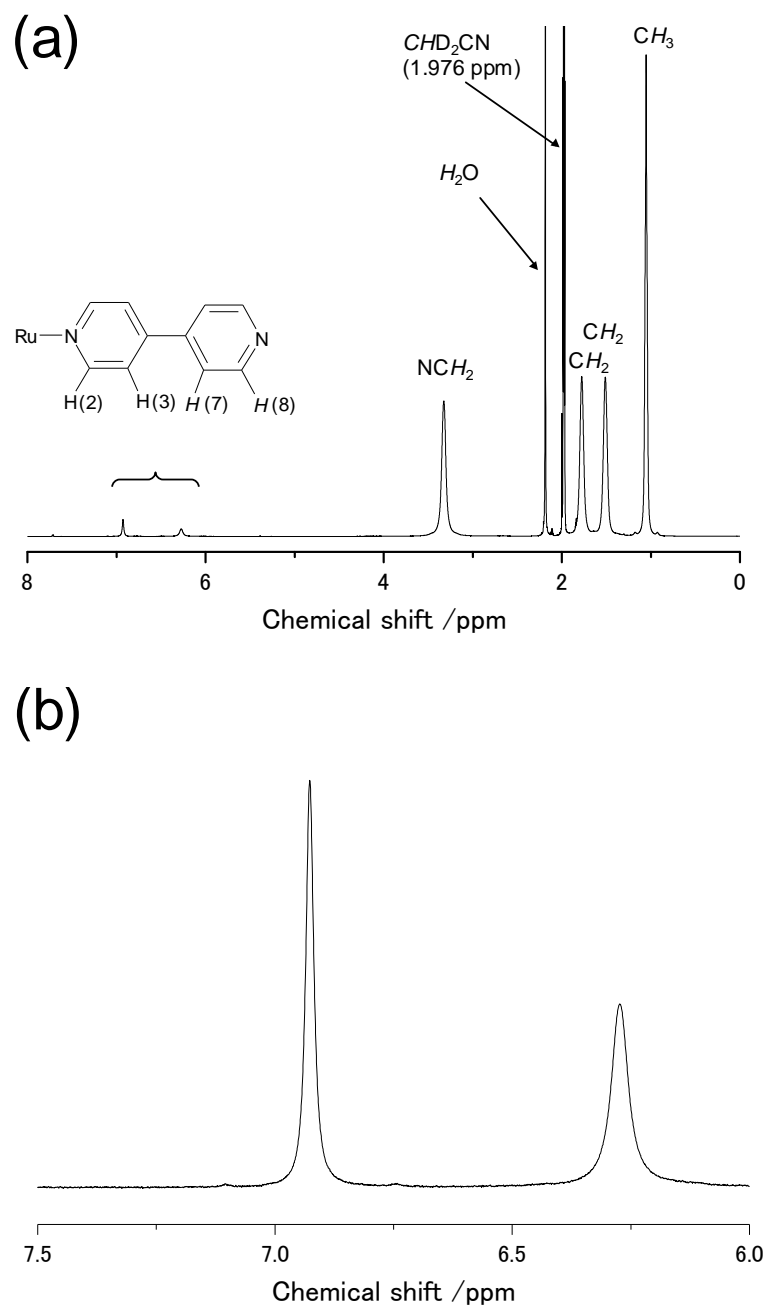
We confirmed the valence of ruthenium in **1** using the X-ray absorption near edge spectra (XANES) technique. It is widely known that chemical shift of the absorption edge shows a simple relation as a function of the oxidation state of the element of interest. We previously reported Ru K-edge and L-edge XANES of  $\text{Cs}_5[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{pyridine})]$ ,<sup>3</sup>  $\text{Cs}_4[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{dms})]$  (dms = dimethyl sulfoxide) and  $\text{Cs}_5[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{II}}(\text{dms})]$ .<sup>4</sup>

The L<sub>3</sub>-edge absorption corresponds to transitions from 2p<sub>3/2</sub> (L<sub>3</sub>) to an unoccupied d states, and a Ru L<sub>3</sub>-edge spectrum reflects the local coordination of Ru and the number of 4d electrons. All investigated Ru compounds have octahedral coordination with low-spin, and two peaks in the spectra correspond to e<sub>g</sub> (white arrows) and t<sub>2g</sub> (black arrows). The peak separation is related to the crystal field strength, and the relative intensity of the t<sub>2g</sub> peak indicates the number of 4d electrons.<sup>5-7</sup> The peak shape of **1** is similar to the peak shapes of Cs<sub>5</sub>[SiW<sub>11</sub>O<sub>39</sub>Ru<sup>III</sup>(pyridine)] and Cs<sub>4</sub>[PW<sub>11</sub>O<sub>39</sub>Ru<sup>III</sup>(dmsO)] in full agreement with a +3 valence of ruthenium in **1**.

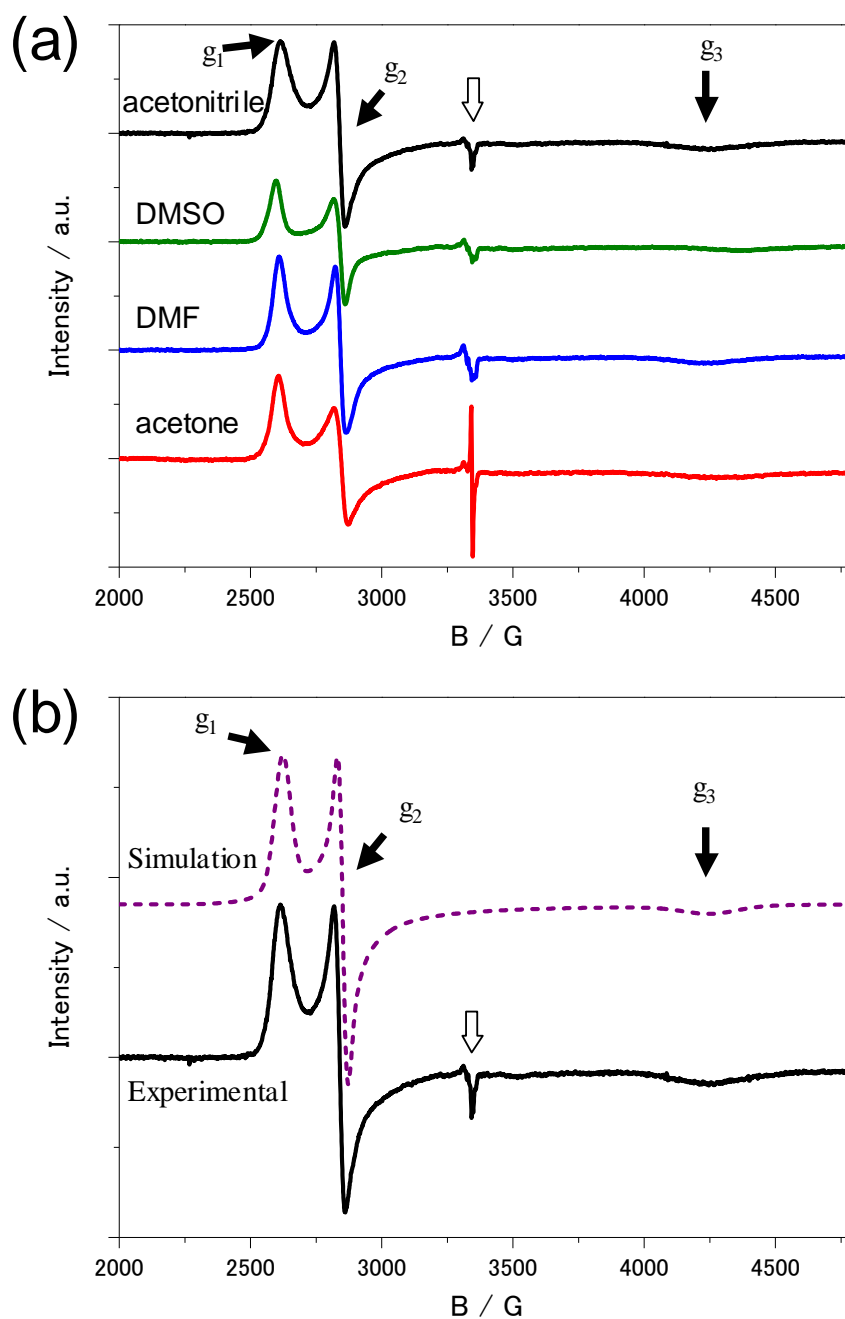




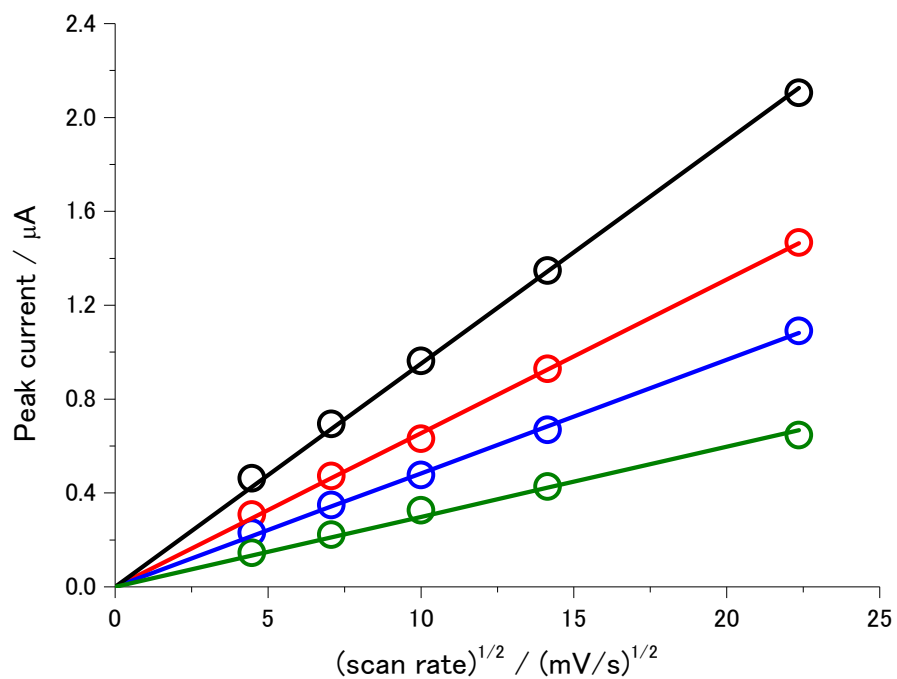
**Fig. S3.** Crystal packing of 1. Colour code: C white (C of bipyridine-ring yellow), N blue and Ru red balls,  $\text{SiO}_4$  blue tetrahedral and  $\text{WO}_6$  green octahedral.



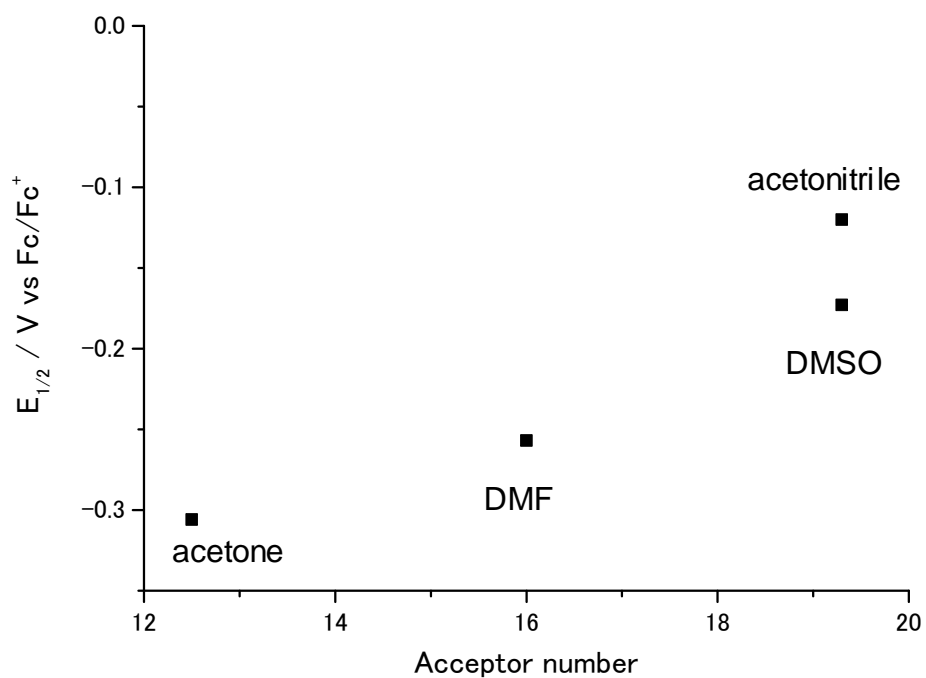
**Fig. S4.** (a)  $^1\text{H}$ -NMR spectrum of **1** and (b) its expanded spectrum.



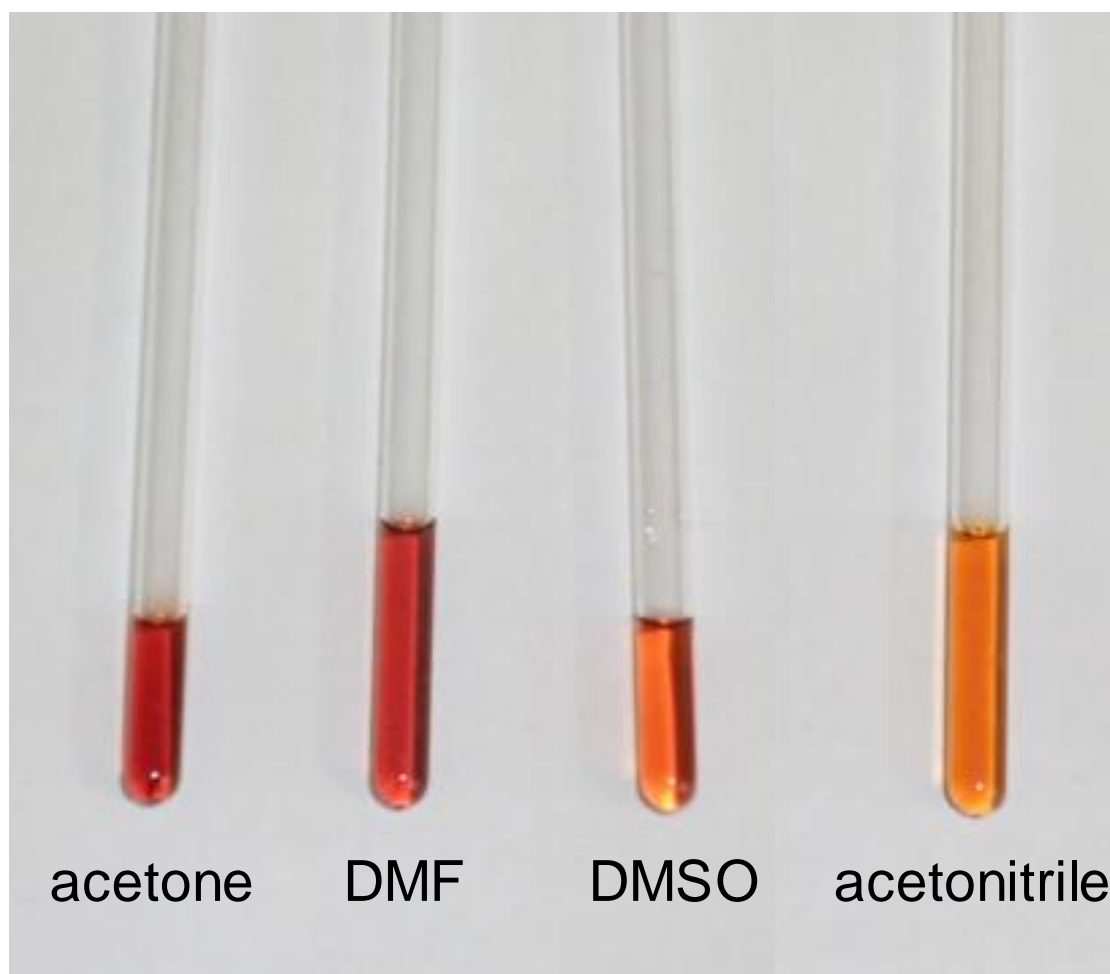
**Fig. S5.** (a) ESR spectra of **1** in the organic solvents at 77 K. (b) Experimental and simulated ESR spectra of **1** in acetonitrile at 77 K. DMF is *N,N*-dimethylformamide and DMSO is dimethylsulfoxide. White arrow indicates unknown peak.



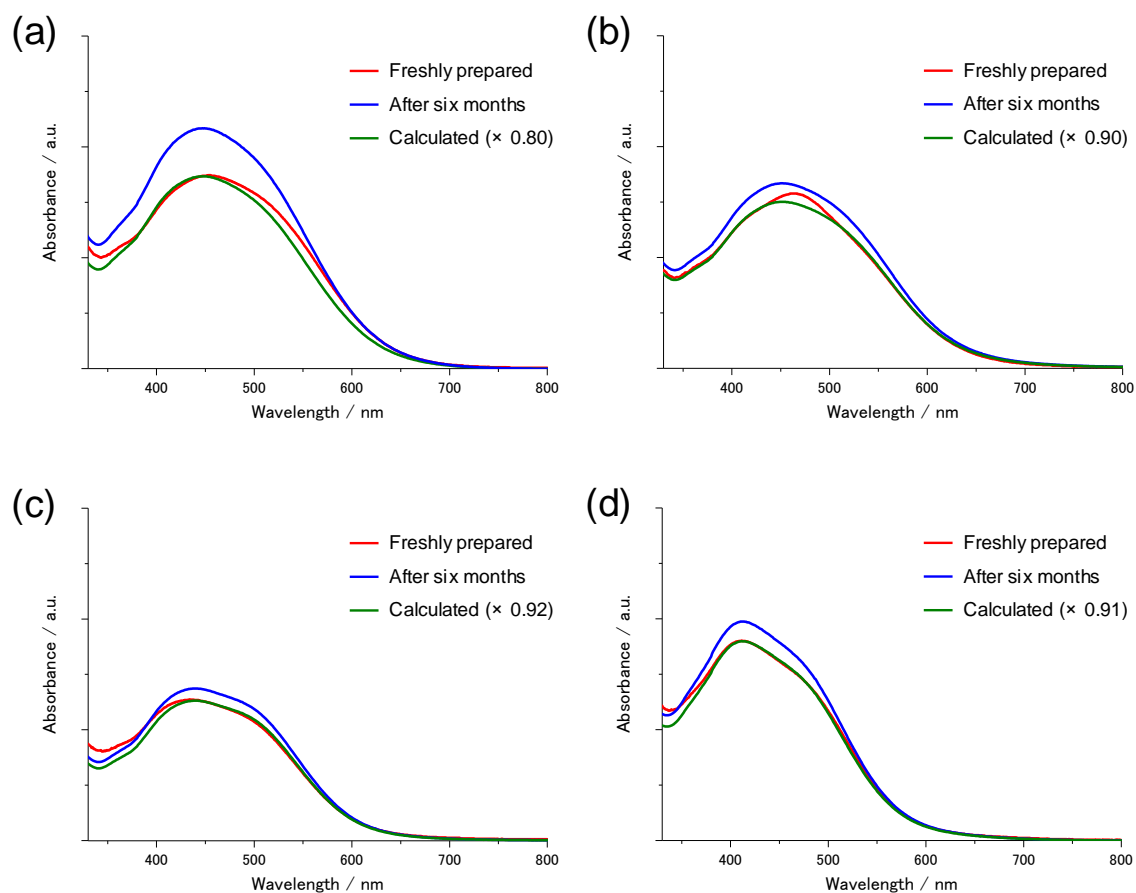
**Fig. S6.** Oxidation peak currents of  $\text{Ru}^{\text{IV/III}}$ -bipy in various organic solvents plotted against  $(\text{scan rate})^{1/2}$ . (red) acetone, (blue) *N,N*-dimethylformamide (DMF), (green) dimethylsulfoxide (DMSO) and (black) acetonitrile.



**Fig. S7.** Relationship between the redox potential of Ru<sup>IV/III</sup> and the acceptor number of solvents studied. DMF is *N,N*-dimethylformamide and DMSO is dimethylsulfoxide.



**Fig. S8.** Photograph of **1** dissolved in various organic solvents. DMF is *N,N*-dimethylformamide and DMSO is dimethylsulfoxide.



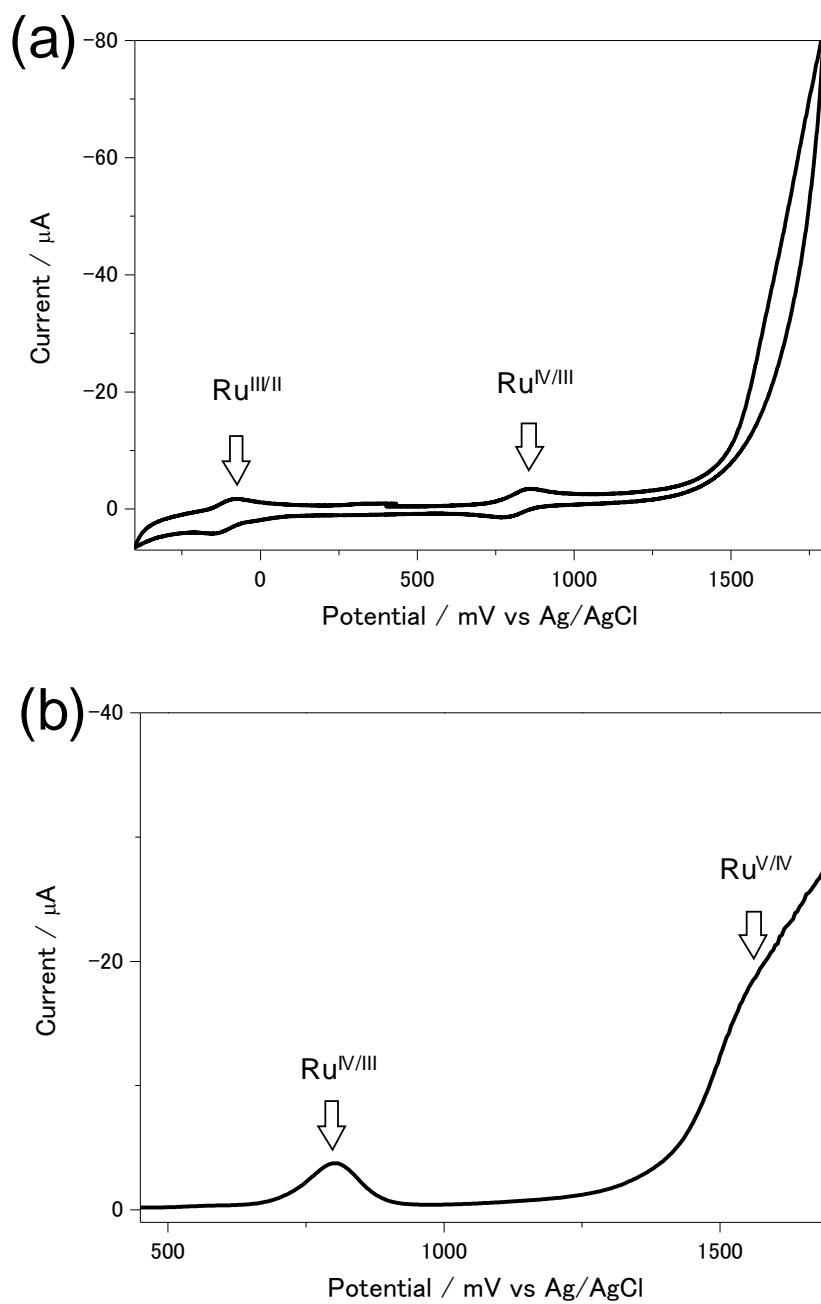
**Fig. S9.** UV-Vis spectra of **1** in (a) acetone, (b) DMF, (c) DMSO and (d) acetonitrile. UV-Vis spectra of (red) freshly prepared solution and (blue) the solution after storing six months, and (green) calculated UV-Vis spectra. DMF is *N,N*-dimethylformamide and DMSO is dimethylsulfoxide.

#### UV-Vis spectra of **1** in the organic solvents after storing six months

In order to prove stability of **1** in the organic solvents, UV-Vis spectra of **1** dissolved in the organic solvents and UV-Vis spectra of **1** in the solution which was stored six months were compared. In all solvents, UV-Vis absorbance of the stored solution was higher than the freshly prepared solution due to evaporation of solvents. The calculated

spectra, which were estimated by considering evaporation, gave close agreement with the spectra of freshly prepared solution within the range of 400-800 nm, except for the DMF solution, in which the absorption band at around 480 nm was slightly decreased. Although **1** might be slightly decomposed in DMF, **1** was stable in the organic solvents.





**Fig. S10.** (a) CV and (b) DPV curves of  $\text{Cs}_5[\text{SiW}_{11}\text{O}_{39}\text{Ru}(\text{bipy})]$  in 0.5 M  $\text{KH}_2\text{PO}_4$  aqueous solution (pH 6.54).

## References

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