

## Electrochemical atomic force microscopy of two-dimensional trinuclear ruthenium molecular assembly and dynamics under redox state control

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## Experimental

**Materials.** The chemical reagents and solvents used in this study were purchased from commercial sources and used as received. All chemical syntheses were performed in air. The  $[\text{Ru}_3\text{O}(\text{CHCl}_2\text{CO}_2)_6(\text{CH}_3\text{OH})_3]\text{CHCl}_2\text{CO}_2$  complex was prepared as previously reported.<sup>1</sup>

**Methods.** Fourier-transform infrared (FT-IR) spectra were obtained using a JASCO FT/IR-4000 instrument and the attenuated total reflectance (ATR) method. UV-vis spectra were recorded on a Shimadzu UV-3600 plus UV-vis-NIR spectrometer using  $\text{CH}_3\text{CN}$  as the solvent.  $^1\text{H}$  NMR spectra were obtained at 600 MHz on a JEOL ECZ-600R/S1 spectrometer using  $\text{CDCl}_3$  as the solvent and TMS as an internal standard. Elemental analysis was performed at the Laboratory for Organic Elemental Microanalysis, Kyoto University.

**Synthesis of  $[\text{Ru}_3\text{O}(\text{CHCl}_2\text{CO}_2)_6(\text{bpy})_3]$  (bpy = 4,4'-bipyridine) (Complex 2).** In a two-necked round-bottom flask, the precursor  $[\text{Ru}_3\text{O}(\text{CHCl}_2\text{CO}_2)_6(\text{CH}_3\text{OH})_3]\text{CHCl}_2\text{CO}_2$  (0.112 g, 0.085 mmol) and bpy (0.374 g, 2.395 mmol) were dissolved in MeOH (100 mL), and the solution was refluxed with stirring for 2 h, during which the initial dark green color of the solution changed to reddish brown. After cooling, the resulting solution was evaporated to dryness. The solid residue was dissolved in a minimal amount of MeOH, separated by size-exclusion column chromatography with Sephadex LH-20, and eluted with MeOH. A reddish-brown main band was collected and evaporated to dryness to give a crude solid that contained a small amount of bpy (based on  $^1\text{H}$  NMR spectroscopy,  $\text{CDCl}_3$ ). Recrystallization of the crude solid twice from  $\text{CHCl}_3/n$ -pentane yielded a pure compound. Yield: 59.2 mg (44.8%). Anal. Calcd. for  $[\text{Ru}_3\text{O}(\text{CHCl}_2\text{COO})_6(\text{bpy})_3]$  ( $\text{C}_{42}\text{H}_{30}\text{Cl}_{12}\text{N}_6\text{O}_{13}\text{Ru}_3$ ): C, 32.43; H, 1.94; N = 5.40%. Found: C, 32.19; H, 1.86; N, 5.42%. FT-IR (ATR,  $\text{cm}^{-1}$ ): 1594 (m,  $\nu_{\text{asym}}(\text{COO})$ ) and 1389 (s,  $\nu_{\text{sym}}(\text{COO})$ ) (m = medium, s = strong).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 293 K)  $\delta$ 9.28 (d,  $J = 6.9$  Hz, 6H, 2,6-H of external pyridyl ring in bpy), 8.89 (d,  $J = 5.5$  Hz, 6H, 2,6-H of coordinated pyridyl ring in bpy), 8.11 (d,  $J = 6.2$  Hz, 6H, 3,5-H of

external pyridyl ring in bpy), 7.80 (d,  $J = 4.8$  Hz, 6H, 3,5-H of coordinated pyridyl ring in bpy), 5.76 (s, 6H,  $\text{CHCl}_2\text{CO}_2^-$ ). UV-vis ( $\text{CH}_3\text{CN}$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ ): 935 (3,300), 400 (5,500), 243 (18,000).

**Chemicals.** Perchloric acid, sulfuric acid (ultrapure grade), and methanol (pure grade) were purchased from Cica Merck. All the chemicals were used without further purification. Complex **2**-modified HOPG substrate was prepared by casting 10  $\mu\text{L}$  of 2.3  $\mu\text{M}$  Complex **2** methanolic solution onto a clean HOPG surface. After drying in air, the modified HOPG substrate was placed in an electrochemical glass cell through an O-ring (fluoro-power, P-6). The diameter of the O-ring was 0.6 cm, meaning that the electrode area was 0.283  $\text{cm}^2$ .

**Measurements.** Electrochemical measurements were performed in 0.1 M  $\text{HClO}_4$  and/or  $\text{H}_2\text{SO}_4$  under an Ar atmosphere at 20–25  $^\circ\text{C}$  using an ALS/HCH model 650CY electrochemical analyzer (BAS Japan). For cyclic voltammetry, HOPG (Bruker, ZYB grade) substrates were used as the working electrodes after cleavage by scotch tape before each experiment. A reversible hydrogen electrode (RHE) and coiled Pt wire were used as the reference and counter electrodes, respectively.

AFM measurements were conducted a multimode AFM equipped with a Nanoscope V controller (Bruker, Billerica, MA, USA) under ambient and/or electrochemical conditions with the ScanAsyst (PeakForceTapping) mode. EC-AFM measurements were performed in either 0.1 M  $\text{HClO}_4$  or 0.1 M  $\text{H}_2\text{SO}_4$  using an Electrochemistry TappingMode fluid cell (Bruker, MMTMEC) with SNL-10 and/or SCANASYST Fluid+ cantilever (Bruker, tip radius 2 nm). AFM images were obtained at scanning rates of 1 and/or 2 Hz. All potential values were referenced to an RHE.

## References

- 1) A. Inatomi, M. Abe, and Y. Hisaeda, *Aust. J. Chem.*, 2012, **65**, 1599–1607.

