

# Electronic Supplementary Information

## Dimers of Delocalized Ru<sub>3</sub>O Clusters Linked by Ortho-metallated 2,2'-Bipyrimidine in $\mu_4-\eta^1(\text{C}), \eta^1(\text{C}), \eta^2(\text{N,N}), \eta^2(\text{N,N})$ Mode

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## Experimental Section

**[2](PF<sub>6</sub>)**. To a dichloromethane (20 mL) solution of 2,2'-bipyrimidine (24 mg, 0.15 mmol) was added dropwise a dichloromethane (30 mL) solution of **[1](PF<sub>6</sub>)** (101 mg, 0.10 mmol). After being stirred at room temperature for 2 d, the solution was concentrated in vacuo and purified by alumina column (neutral, 200-300 mesh) chromatography. The second main band was collected using dichloromethane-methanol (80 : 1) as an eluent. Crystallization by layering petroleum ether onto the solution gave 62 mg of blue product. Yield: 58%. Anal. Calcd. for C<sub>28</sub>H<sub>30</sub>F<sub>6</sub>N<sub>6</sub>O<sub>11</sub>PRu<sub>3</sub>: C, 31.29; H, 2.81; N, 7.82. Found: C, 31.54; H, 2.70; N, 7.70. ES-MS (CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub>): 931 [M-(PF<sub>6</sub>)]<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1608 (COO), 1547 (COO), 1418 (COO), 843 (PF<sub>6</sub>).

**2a**. To a dichloromethane (25 mL) solution of **[2](PF<sub>6</sub>)** (54 mg, 0.05 mmol) kept at 0°C was dropwise added an excess aqueous solution of hydrazine (ca. 20%) with stirring until the color became green from pale blue. The solution was stirred for 15 min, then to which 30 mL of cold water was added. After the stirring continued for ten minutes, the dichloromethane layer was separated on an extraction funnel. The product was crystallized twice by layering n-hexane onto the dichloromethane solution and dried in vacuo to give 39 mg of green microcrystals. Yield: 84%. Anal. Calcd. for C<sub>28</sub>H<sub>30</sub>N<sub>6</sub>O<sub>11</sub>Ru<sub>3</sub>: C, 36.17; H, 3.25; N, 9.04. Found: C, 36.54; H, 3.40; N, 9.12. ES-MS (CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub>): 931 [M]<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1535 (s, COO), 1412 (s, COO).

**[3](PF<sub>6</sub>)<sub>2</sub> and [3a](PF<sub>6</sub>)**. 2,2'-Bipyrimidine (16 mg, 0.10 mmol) was added to a dichloromethane (50 mL) solution of **[1](PF<sub>6</sub>)** (242 mg, 0.24 mmol). After being stirred at room temperature for three days, the solution was filtered, concentrated in vacuo, and chromatographed on an alumina column (neutral, 200-300 mesh). The first band was eluted with dichloromethane to give a blue product which was identified as [Ru<sub>3</sub>O(OAc)<sub>6</sub>(py)<sub>3</sub>](PF<sub>6</sub>). Compound **[3a](PF<sub>6</sub>)** was

separated as the second band using dichloromethane-methanol (v/v 200 : 1) as an eluent. Crystallization by layering diethyl ether onto the acetone solution gave 40 mg (yield 22%) of green block crystals. Compound [3](PF<sub>6</sub>)<sub>2</sub> was eluted with dichloromethane-methanol (v/v 150 : 1) as the third band. Layering petroleum ether onto the dichloromethane solution afforded 40 mg (yield 20%) of black blue crystals. For [3](PF<sub>6</sub>)<sub>2</sub>: Anal. Calcd. for C<sub>48</sub>H<sub>54</sub>F<sub>12</sub>N<sub>8</sub>O<sub>22</sub>P<sub>2</sub>Ru<sub>6</sub>: C, 28.95; H, 2.73; N, 5.63. Found: C, 29.32; H, 3.49; N, 5.30. ES-MS (CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub>): 851 [M-(PF<sub>6</sub>)<sub>2</sub>]<sup>2+</sup>. IR (KBr, cm<sup>-1</sup>): 1608 (m, COO), 1548 (s, COO), 1417 (s, COO), 843 cm<sup>-1</sup> (s, PF<sub>6</sub>). For [3a](PF<sub>6</sub>): Anal. Calcd. for C<sub>48</sub>H<sub>54</sub>F<sub>6</sub>N<sub>8</sub>O<sub>22</sub>PRu<sub>6</sub>·Et<sub>2</sub>O·H<sub>2</sub>O: C, 32.22; H, 3.43; N, 5.78. Found: C, 32.74; H, 3.70; N, 5.70. ES-MS (CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub>): 1702 [M-(PF<sub>6</sub>)]<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1607 (m, COO), 1535 (s, COO), 1416 (s, COO), 843 (s, PF<sub>6</sub>).

**3b.** To an acetonitrile solution of [3](PF<sub>6</sub>)<sub>2</sub> or [3a](PF<sub>6</sub>) kept in ice water was added dropwise an excess aqueous solution of hydrazine (ca. 20%) with the color turning to green. Cold water was added to the solution to afford green precipitate which was filtered, washed with cold water, and then dried in vacuo. Yield: 70%. Anal. Calcd. for C<sub>48</sub>H<sub>54</sub>N<sub>8</sub>O<sub>22</sub>Ru<sub>6</sub>: C, 33.89; H, 3.20; N, 6.59. Found: C, 33.72; H, 3.55; N, 6.22. ES-MS (CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub>): 1702 [M]<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1629 (m, COO), 1534 (s, COO), 1416 (s, COO).

**Crystal Structural Determination.** Crystals of [3a](PF<sub>6</sub>)·Et<sub>2</sub>O·H<sub>2</sub>O suitable for X-ray crystallography were grown by layering diethyl ether onto the dichloromethane solution. A Single crystal sealed in a capillary with mother liquor was measured on a SIEMENS SMART CCD diffractometer by  $\omega$  scan technique at room temperature using graphite-monochromated Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. Absorption corrections by SADABS were applied to the intensity data. The structure was solved by direct method and the heavy atoms were located from E-map. The

remaining non-hydrogen atoms were determined from the successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated geometrically and refined with isotropic thermal parameters. The structures were refined on  $F^2$  by full-matrix least-squares methods using the SHELXTL-97 program package. The crystallographic data are summarized in Table 1.

**Physical Measurements.** Elemental analyses were performed on a Perkin-Elmer Model 240C automatic instrument. The electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. The UV-Vis-NIR spectra were measured on a Perkin-Elmer Lambda 900 UV-vis-NIR spectrometer. The IR spectra were recorded on a Magna 750 FT-IR spectrophotometer using KBr pellets. The cyclic voltammogram (CV) and differential pulse voltammogram (DPV) were made with a potentiostat/galvanostat Model 263A in dichloromethane solutions containing 0.1 M  $(\text{Bu}_4\text{N})(\text{PF}_6)$  as supporting electrolyte. CV was performed at a scan rate of  $100 \text{ mV s}^{-1}$ . DPV was measured at a rate of  $20 \text{ mV s}^{-1}$  with a pulse height of 40 mV. Platinum and glassy graphite were used as counter and working electrodes, respectively, and the potential measured against Ag/AgCl reference electrode. The potential measured was always referenced to the half-wave potentials of the ferrocenium/ferrocene couple ( $E_{1/2} = 0$ ).

**Table S1.** Electrochemical data of compounds [2](PF<sub>6</sub>) and [3](PF<sub>6</sub>)<sub>2</sub><sup>a</sup>

Compound	$E_{1/2}^{(4+/3+)}$ ( $E_{1/2}^A$ )	$E_{1/2}^{(3+/2+)}$ ( $E_{1/2}^{A'}$ )	$\Delta E_{1/2}^A$ ( $K_c$ ) <sup>c</sup>	$E_{1/2}^{(2+/+)}$ ( $E_{1/2}^B$ )	$E_{1/2}^{(+/0)}$ ( $E_{1/2}^{B'}$ )	$\Delta E_{1/2}^B$ ( $K_c$ ) <sup>c</sup>	$E_{1/2}^{(0/-)}$ ( $E_{1/2}^C$ )	$E_{1/2}^{(-2/-)}$ ( $E_{1/2}^{C'}$ )	$\Delta E_{1/2}^C$ ( $K_c$ ) <sup>c</sup>
[2](PF <sub>6</sub> ) <sup>b</sup>	+0.75			-0.39			-1.73		
[3](PF <sub>6</sub> ) <sub>2</sub>	+0.93	+0.83	0.10 (49)	-0.18	-0.41	0.23 (7730)	-1.70	-1.95	0.25 (16840)

<sup>a</sup> Potential data in volts vs Fc/Fc<sup>+</sup> ( $E_{1/2} = 0$ ) are from single scan cyclic voltammograms recorded in dichloromethane solutions containing 0.1 M (Bu<sub>4</sub>N)(PF<sub>6</sub>) as supporting electrolyte at 25°C. CV was performed at a scan rate of 100 mV s<sup>-1</sup>. DPV was measured at a rate of 20 mV s<sup>-1</sup> with a pulse height of 60 mV. Platinum and glassy graphite were used as counter and working electrodes, respectively, and the potentials were measured against Ag/AgCl reference electrode. <sup>b</sup> [2](PF<sub>6</sub>) is monomeric Ru<sub>3</sub>O cluster compound with ortho-metallated bpym. <sup>c</sup> The comproportionation constants,  $K_c$ , were calculated by the formula  $K_c = \exp(\Delta E_{1/2}/25.69)$  at 298 K.

**Table S2.** UV-Vis absorption spectral data for complexes [2](PF<sub>6</sub>)–**3b** in dichloromethane

	$\lambda_{\max}/\text{nm}$ ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )		
	IC <sup>a</sup>	CLCT <sup>b</sup>	Ligand-centered transitions
[2](PF <sub>6</sub> )	704 (7430)	330 (15190)	245 (36230)
<b>2a</b>	778 (7210)	380 (13030)	247 (32080)
[3](PF <sub>6</sub> ) <sub>2</sub>	727 (18790)	350 (28350)	238 (62660)
[3a](PF <sub>6</sub> )	752 (18420)	382 (26750)	246 (54200)
<b>3b</b>	814 (20190)	404 (30120)	248 (52840)

<sup>a</sup> IC is intracluster transitions. <sup>b</sup> CLCT is cluster-to-ligand charge transfer transitions.