

Electronic Supplementary Information

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Synthesis and electrochemical properties of bipyrimidine bridged triruthenium complexes

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Syntheses and characterizations of complexes

$[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{CO})(\text{py})(\text{H}_2\text{O})]$ was synthesized according to the recorded method.¹

I. $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_5(\text{CO})(\text{py})(\text{bpym-}N,N',C)](\mathbf{1})$

5 Synthesis

To a 10ml CH_2Cl_2 solution of $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{CO})(\text{py})(\text{H}_2\text{O})]$ (100mg, 0.125mmol) was added *ca.* 2eq bipyrimidine (42mg, 0.214mmol), and the solution was stirred at room temperature for 2~3 days.

The solution was evaporated to dryness using rotary evaporator, and the residue was dissolved in a minimal amount of CH_2Cl_2 . This solution was placed on a column packed with silica gel (Wakogel C-
10 200) and $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CH}_2\text{OH}$ (98.5/1.5) was used as eluent. The second blue-purple fraction was collected and evaporated to dryness. A blue-purple solid was obtained. Yield: 30mg (27%)

$^1\text{H NMR}$ (400MHz, δ vs TMS in CDCl_3) 9.38(dd, 1H, bpym), 9.08(dd, 1H, bpym), 8.95(d, 2H, py-*o*), 8.12(d, 1H, py-*p*), 8.06(t, 2H, py-*m*), 7.97(d, 1H, bpym), 7.87(t, 1H, bpym), 7.69(d, 1H, bpym), 2.30(s, 3H, acetate-methyl), 2.26(s, 3H, acetate-methyl), 2.03(s, 3H, acetate-
15 methyl), 1.86(s, 3H, acetate-
methyl), 1.71(s, 3H, acetate-methyl)

Anal. Calcd. for $\mathbf{1} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 31.94, H, 2.84, N, 7.60%. Found: C, 31.76, H, 2.44, N, 7.51

NMR spectra

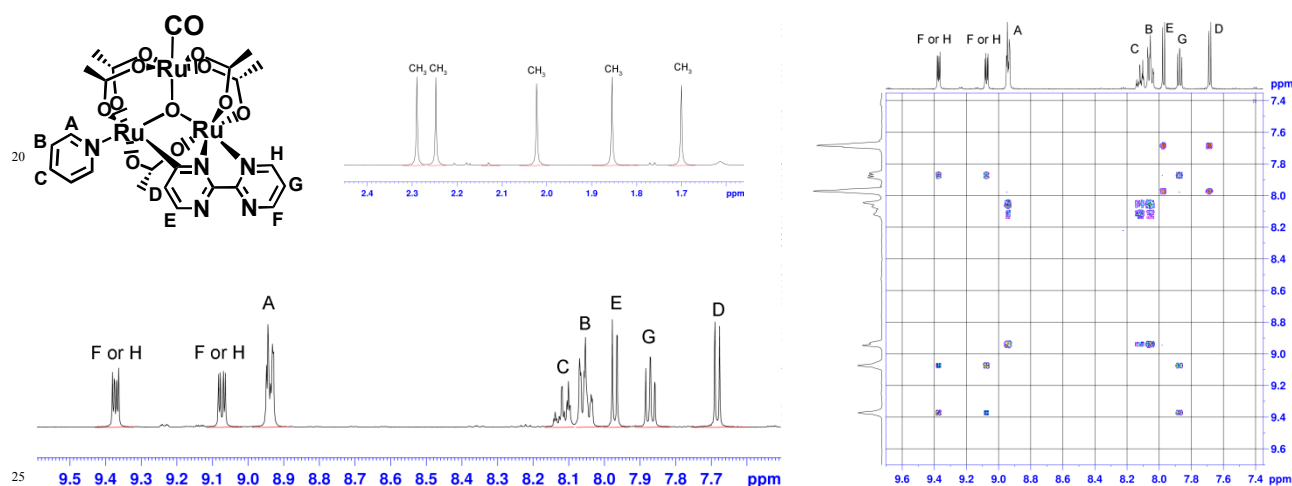


Fig S1. $^1\text{H NMR}$ (400MHz) (left) and COSY (right) spectrum of compound **1** in CDCl_3

II. $[\{\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_5(\text{CO})(\text{py})\}_2(\mu\text{-bpym-}N,N',C)](2)$

Synthesis

To a 20ml CH_2Cl_2 solution of $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{CO})(\text{py})(\text{H}_2\text{O})]$ (200mg, 0.250mmol) was added 1 eq of $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_5(\text{CO})(\text{py})(\text{bpym-}N,N',C)](1)$ (102mg, 0.116mmol), and the solution was stirred at room temperature for 3 days in the dark. The solution was evaporated to dryness using rotary evaporator, and the residue was dissolved in a minimal amount of CH_2Cl_2 . This solution was placed on a column packed with silica gel (Wakogel C-200) and $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CH}_2\text{OH}$ (98.8/1.2) was used as eluent. The first blue-purple fraction was collected and evaporated to dryness. A blue-purple solid was obtained. Yield: 33mg (18%). The sample contained small amount of isomer that has the same sets of NMR pattern. Since the bpym plane and the Ru_3O planes are not co-planar, there are two isomers with respect to a mutual arrangement of the Ru_3O moieties in relation to the bpym plane. One of the isomers has C_2 symmetry and the other has i symmetry, Fig S2. These isomers could hardly be separated by any effort of purification. However, in a certain case, a mixture with relatively high minor isomer ratio was obtained. It revealed that both the isomers show similar electrochemical property. Fig. S5b shows cyclic voltammograms of two typical isomer mixtures of **2**. In spite of different isomer ratio of the mixtures, which is evaluated by NMR to 5:1 and 1:1, Fig S5a, the two mixtures possess almost the same voltammogram.

Anal. Calcd. for **2** · $\text{CH}_3\text{CH}_2\text{OH}$: C, 30.66, H, 3.06, N 5.11%, Found: C, 30.95, H, 2.95, N, 4.87%
 ^1H NMR(400MHz, δ vs TMS in CDCl_3)

Isomer I (major) : 9.01(d, 4H ,py-*o*), 8.43(d, 2H, bpym), 8.17(t, 2H, py-*p*), 8.09(t, 4H, py-*m*), 7.81(d, 2H, bpym), 2.38(s, 6H, acetate-methyl), 2.33(s, 6H, acetate-methyl), 1.99(s,6H, acetate-methyl), 1.89(s, 6H, acetate-methyl), 1.82(s, 6H, acetate-methyl);

Isomer II (minor) : 9.01(d, 4H ,py-*o*),8.41 (d, 2H, bpym),8.17(t, 2H, py-*p*), 8.09(t, 4H, py-*m*), 7.81(d, 2H, bpym), 2.35(s, 6H, acetate-methyl), 2.32(s, 6H, acetate-methyl), 1.94(s,6H, acetate-methyl), 1.93(s, 6H, acetate-methyl), 1.90(s, 6H, acetate-methyl)

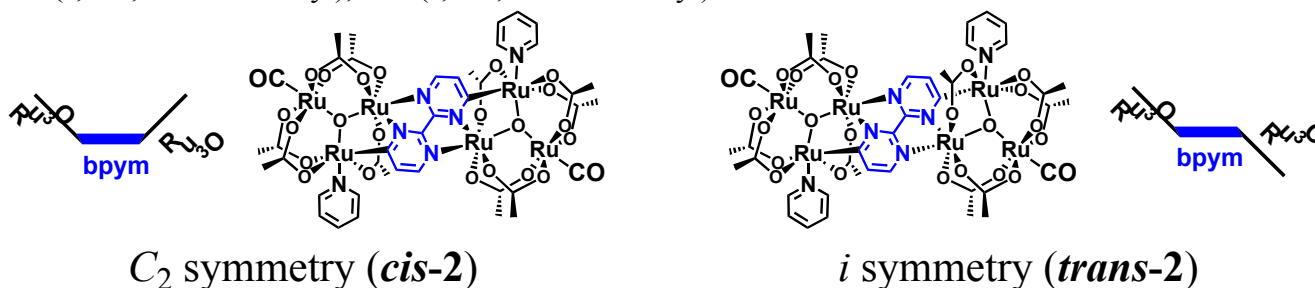
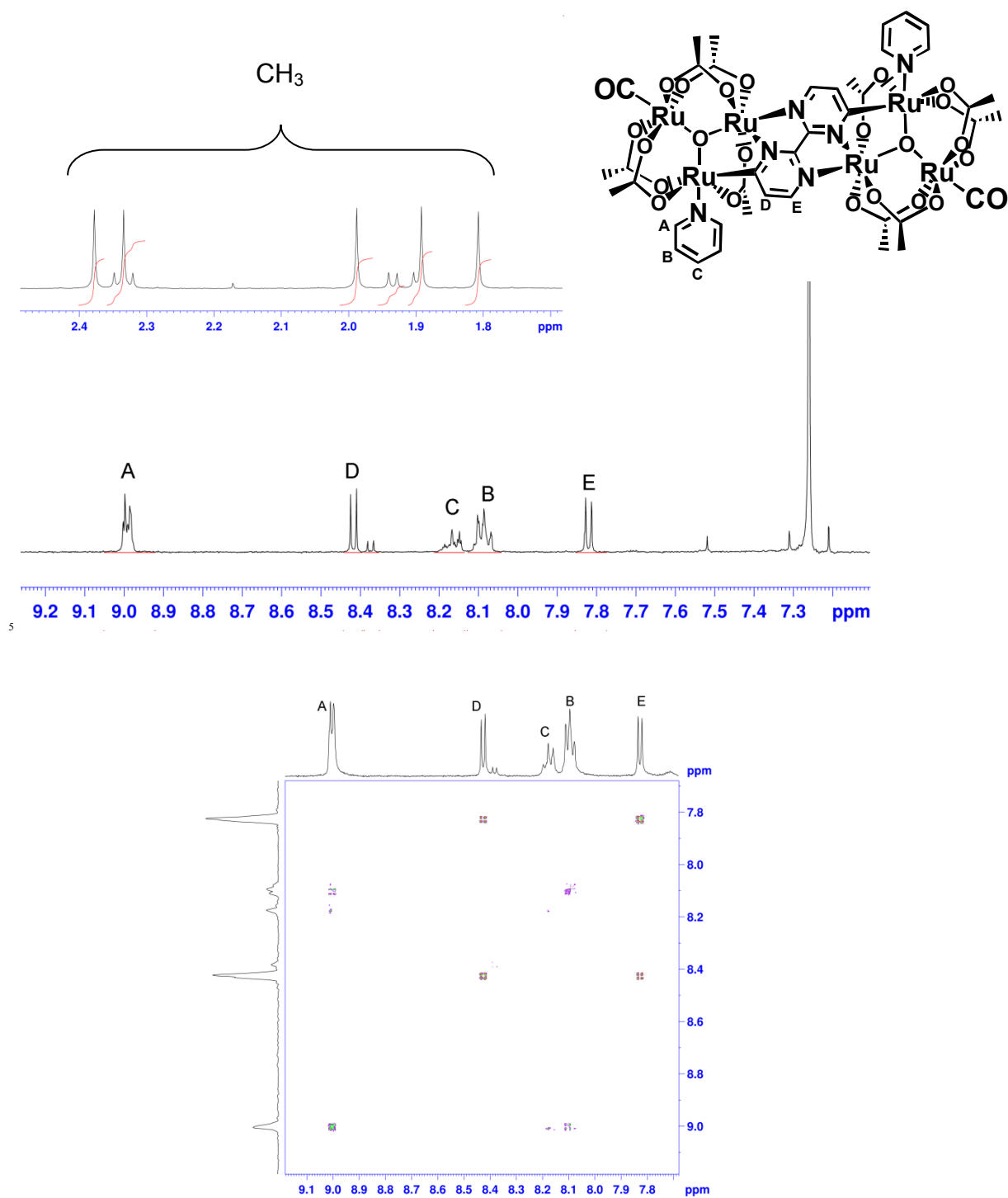


Fig S2. Two isomers of dimer **2**

NMR spectra



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Fig S3. ^1H NMR (400MHz) (top) and COSY (bottom) spectrum of compound **2** in CDCl_3
This sample contains a little minor isomer.

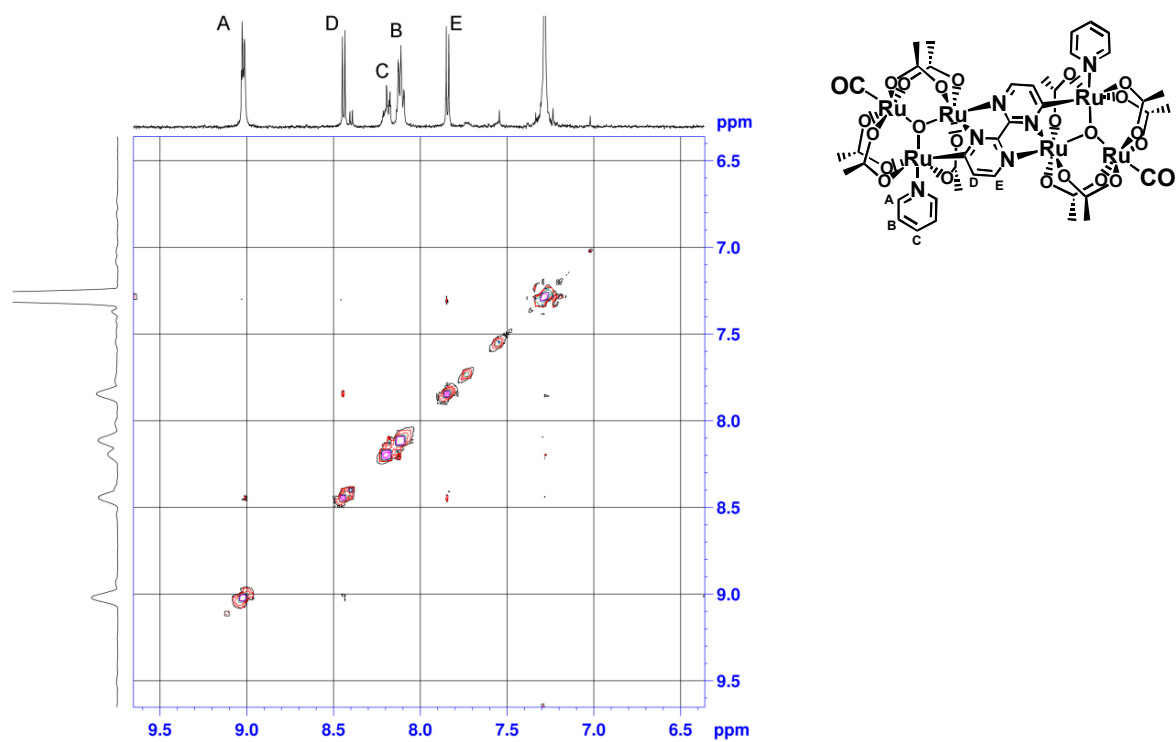


Fig S4. NOESY spectrum of **2** in CDCl₃.

NOE peaks between peak A and peak D are appeared. This spectrum implies py ligands are bound to ruthenium atoms coordinated by bpbm ligand.

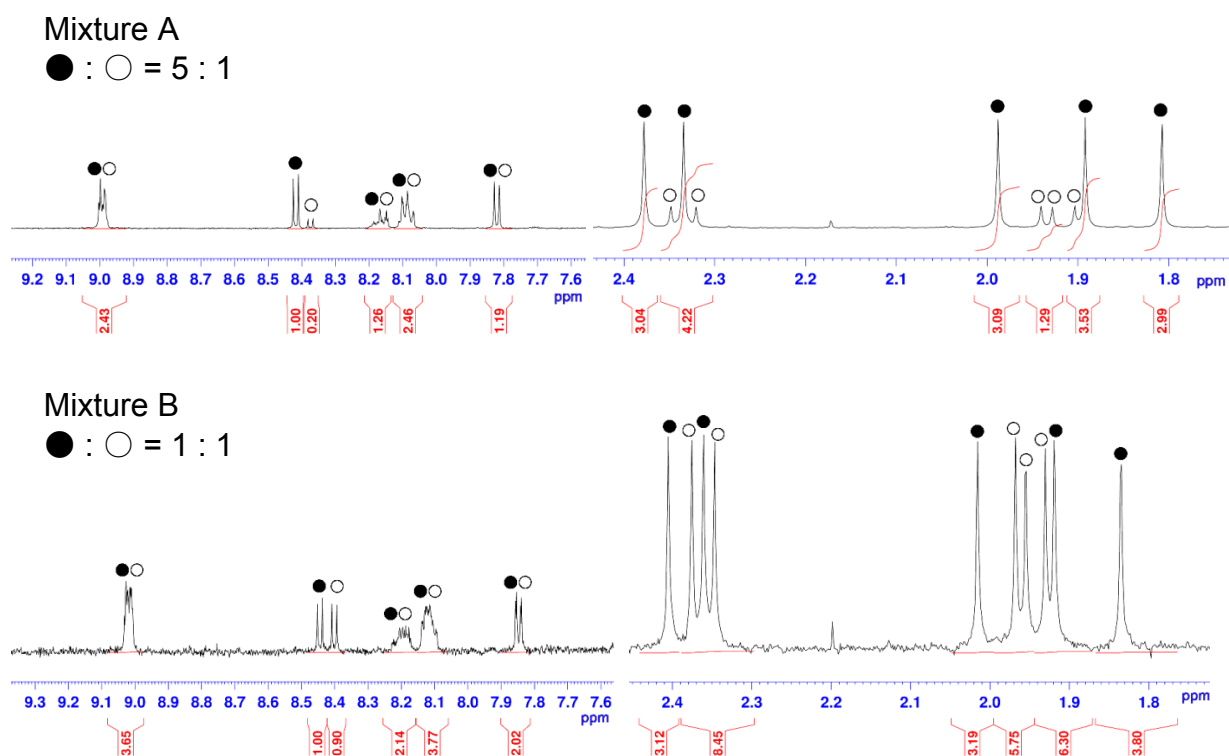
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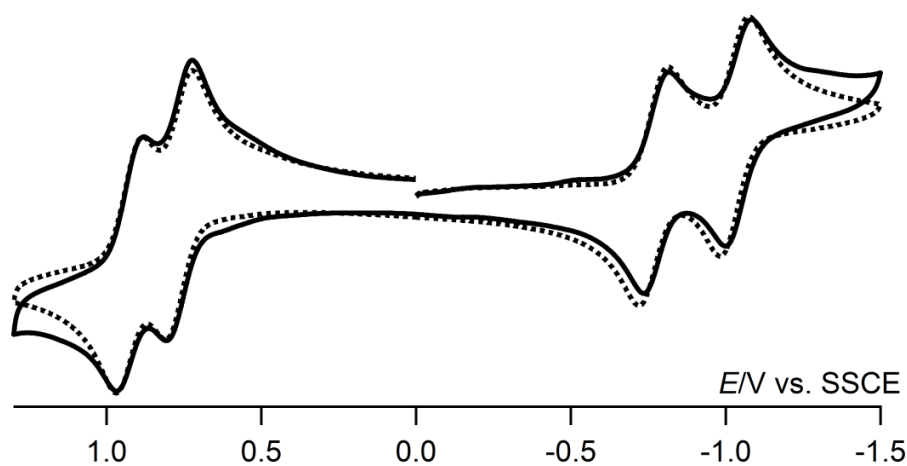
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5 **Fig S5a.** ^1H NMR (400MHz) of mixtures of the two isomers of **2** with different isomer ratio. (**Isomer I** : **Isomer II** = 5:1 for Mixture A, 1:1 for Mixture B) The marks, ● and ○ denote **Isomer I** and **Isomer II** respectively. The red values under the chemical shift scales represent relative intensity ratios of the peaks.



10 **Fig S5b.** Cyclic Voltammograms of mixtures of two isomers of **2** with different isomer ratio, solid line : Mixture A (**Isomer I** : **Isomer II** = 5:1), dotted line : Mixture B (**Isomer I** : **Isomer II** = 1:1).

Reference

15 1 H. Kido, H. Nagino, T. Ito, *Chem. Lett.*, **1996**, 745