

# Supporting Information

*Supramolecular Photocatalysts for the Reduction of CO<sub>2</sub>*

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## Synthesis

$[(4\text{dmb})_2\text{Ru}(\text{bpyC}_2\text{bpy})](\text{PF}_6)_2^1$  ( $\text{bpyC}_2\text{bpy}$  = 1,2-bis(4'-methyl-[2,2'-bipyridin]-4-yl)ethane),  $[(5\text{dmb})_2\text{Os}(\text{bpyC}_2\text{bpy})](\text{PF}_6)_2^2$ ,  $\text{Ru}(\text{DMSO})_4\text{Cl}_2^3$ , and **RuRu5<sup>4</sup>** were prepared according to the methods reported in the literatures.

$[\text{Re}(\text{CO})_5(\text{PPh}_3)](\text{OTf})$ : A dichloromethane solution (15 mL) of  $\text{Re}(\text{CO})_5\text{Br}$  (104 mg, 0.257 mmol) and  $\text{AgOTf}$  (74 mg, 0.29 mmol) was refluxed for 1 h under a  $\text{N}_2$  atmosphere. After cooled to room temperature, the white precipitate ( $\text{AgBr}$ ) was removed by filtration by passing through Celite, and the solvent was evaporated. A mixed solution of dichloromethane–acetone (2:1 v/v, 15 mL) containing the residue and  $\text{PPh}_3$  (80 mg, 0.31 mmol) was refluxed for 4 h under a  $\text{N}_2$  atmosphere. After the solvent was removed under a reduced pressure, the product was recrystallized from acetone/ether to produce a white powder. Yield: 131 mg (69%). FT-IR (in dichloromethane)  $\nu_{\text{CO}}$  /  $\text{cm}^{-1}$ : 2157, 2097, 2049. ESI-MS (in acetonitrile)  $m/z$ : 589 ( $[\text{M} - \text{PF}_6^-]^+$ ).

$[(4\text{dmb})_2\text{Ru}(\text{bpyC}_2\text{bpy})\text{Re}(\text{CO})_3(\text{PPh}_3)](\text{PF}_6)_3$  (**RuRe15**): A mixed solution of acetone–*o*-dichlorobenzene (1:3 v/v, 20 mL) containing  $[(4\text{dmb})_2\text{Ru}(\text{bpyC}_2\text{bpy})](\text{PF}_6)_2$  (90 mg, 80  $\mu\text{mol}$ ) and  $[\text{Re}(\text{CO})_5(\text{PPh}_3)](\text{OTf})$  (60 mg, 81  $\mu\text{mol}$ ) was heated at 110 °C for 3.5 h and at 140 °C for 20.5 h. After cooled to room temperature, the solvent was removed in vacuo. The product was purified using ion-exchange column chromatography (absorbent: CM Sephadex C-25; eluent: acetonitrile– $\text{H}_2\text{O}$  (1:1 v/v) containing  $\text{NH}_4\text{PF}_6$ ). Yield: 62 mg (43%).  $^1\text{H}$  NMR (400 MHz, in acetone- $d_6$ )  $\delta$  / ppm: 8.80 (s, 1H), 8.66–8.73 (m, 7H), 8.51 (s, 1H), 8.39 (s, 1H), 7.92 (d,  $J$  = 5.6 Hz, 1H), 7.79–7.85 (m, 5H), 7.39–7.54 (m, 17H), 7.22–7.27 (m, 6H), 3.24 (s, 4H), 2.56–2.57 (m, 18H). FT-IR (in dichloromethane)  $\nu_{\text{CO}}$  /  $\text{cm}^{-1}$ : 2038, 1952, 1922. ESI-MS (in acetonitrile)  $m/z$ : 456 ( $[\text{M} - 3\text{PF}_6^-]^{3+}$ ), 758 ( $[\text{M} - 2\text{PF}_6^-]^{2+}$ ). Anal. Calcd for  $\text{C}_{69}\text{H}_{61}\text{F}_{18}\text{N}_8\text{O}_3\text{P}_4\text{ReRu}$ : C, 45.95; H, 3.41; N, 6.21. Found: C, 45.72; H, 3.18; N, 6.15.

$[(5\text{dmb})_2\text{Os}(\text{bpyC}_2\text{bpy})\text{Re}(\text{CO})_3(\text{PPh}_3)](\text{PF}_6)_3$  (**OsRe3**): A mixed solution of acetone–*o*-dichlorobenzene (1:3 v/v, 12 mL) containing  $[(5\text{dmb})_2\text{Os}(\text{bpyC}_2\text{bpy})](\text{PF}_6)_2$  (53 mg, 44  $\mu\text{mol}$ ) and  $[\text{Re}(\text{CO})_5(\text{PPh}_3)](\text{OTf})$  (31 mg, 42  $\mu\text{mol}$ ) was heated at 140 °C for 10.5 h. After cooled to room temperature, the solvent was removed in vacuo. The product was purified using ion-exchange column chromatography (absorbent: CM Sephadex C-25; eluent: acetonitrile– $\text{H}_2\text{O}$  (1:1 v/v) containing  $\text{NH}_4\text{PF}_6$ ). Yield: 51 mg (65%).  $^1\text{H}$  NMR (300 MHz, in acetone- $d_6$ )  $\delta$  / ppm: 8.68–8.76 (m, 3H), 8.57–8.62 (m, 5H), 8.50 (s, 1H), 8.39 (s, 1H), 7.67–7.81 (m, 10H), 7.36–7.49 (m, 12H), 7.21–7.31 (m, 7H), 3.25–3.28 (m, 4H), 2.64 (s, 3H), 2.57 (s, 3H), 2.20 (s, 12H). FT-IR (in acetonitrile)  $\nu_{\text{CO}}$  /  $\text{cm}^{-1}$ : 2039, 1952, 1923. ESI-MS (in acetonitrile)  $m/z$ : 486 ( $[\text{M} - 3\text{PF}_6^-]^{3+}$ ), 802 ( $[\text{M} - 2\text{PF}_6^-]^{2+}$ ).

$[\text{Ru}(\text{bpyC}_2\text{bpy})_3](\text{PF}_6)_2$ : An excess amount of  $\text{bpyC}_2\text{bpy}$  (1386 mg, 3.78 mmol) was dissolved in an ethanol– $\text{H}_2\text{O}$  (100:3 v/v, 103 mL) mixed solvent by heating at reflux and then, an ethanol solution (50 mL) of  $\text{Ru}(\text{DMSO})_4\text{Cl}_2$  (253 mg, 0.535 mmol) was added, followed by reflux for 20.5 h. After cooled to room temperature, the solvent was removed in vacuo. The residue was dissolved in a 1:1 mixture of

acetonitrile–H<sub>2</sub>O and insoluble unreacted bpyC<sub>2</sub>bpy was collected. The product was purified using ion-exchange column chromatography (absorbent: SP Sephadex C-25; eluent: acetonitrile–H<sub>2</sub>O (1:1 v/v) containing NH<sub>4</sub>PF<sub>6</sub>). Yield: 427 mg (54%). ESI-MS (in acetonitrile) *m/z*: 400 ([M – 2PF<sub>6</sub><sup>–</sup> + H<sup>+</sup>]<sup>3+</sup>), 600 ([M – 2PF<sub>6</sub><sup>–</sup>]<sup>2+</sup>), 673 ([M – PF<sub>6</sub><sup>–</sup>]<sup>+</sup>).

[Ru{(bpyC<sub>2</sub>bpy)Ru(CO)<sub>2</sub>Cl<sub>2</sub>}<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (**RuRu6**): An aqueous solution of formic acid (10 mL, 90% v/v) containing RuCl<sub>3</sub>·3H<sub>2</sub>O (50 mg, 0.19 mmol) and paraformaldehyde (26 mg) was refluxed for 6 h, and then kept in refrigerator overnight. After the solvent was removed in vacuo, the residue and [Ru(bpyC<sub>2</sub>bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (85 mg, 57 μmol) were dissolved in acetone–methanol (1:1 v/v, 20 mL) mixture. The solution was refluxed for 5 h. The product was isolated using a preparative recycle HPLC equipped with size-exclusion chromatography columns. Yield: 57 mg (46%). <sup>1</sup>H NMR (400 MHz, in acetonitrile-*d*<sub>3</sub>) δ / ppm: 8.93-8.99 (m, 6H), 8.20-8.33 (m, 12H), 7.34-7.59 (m, 12H), 7.10-7.34 (m, 6H), 3.24 (s, 12H), 2.45-2.55 (m, 18H). FT-IR (in acetonitrile) *v*<sub>CO</sub> / cm<sup>–1</sup>: 2062, 1999. ESI-MS (in acetonitrile) *m/z*: 943 ([M – 2PF<sub>6</sub><sup>–</sup>]<sup>2+</sup>).

## References

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