

Supporting Information

Supramolecular Photocatalysts for the Reduction of CO₂

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Synthesis

$[(4\text{dmb})_2\text{Ru}(\text{bpyC}_2\text{bpy})](\text{PF}_6)_2^1$ (bpyC_2bpy = 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**⁴ 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 AgOTf (74 mg, 0.29 mmol) was refluxed for 1 h under a N_2 atmosphere. After cooled to room temperature, the white precipitate (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 PPh_3 (80 mg, 0.31 mmol) was refluxed for 4 h under a 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) ν_{CO} / 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 μmol) and $[\text{Re}(\text{CO})_5(\text{PPh}_3)](\text{OTf})$ (60 mg, 81 μmol) 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– H_2O (1:1 v/v) containing NH_4PF_6). Yield: 62 mg (43%). ^1H NMR (400 MHz, in acetone- d_6) δ / 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) ν_{CO} / 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 μmol) and $[\text{Re}(\text{CO})_5(\text{PPh}_3)](\text{OTf})$ (31 mg, 42 μmol) 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– H_2O (1:1 v/v) containing NH_4PF_6). Yield: 51 mg (65%). ^1H NMR (300 MHz, in acetone- d_6) δ / 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) ν_{CO} / 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 bpyC_2bpy (1386 mg, 3.78 mmol) was dissolved in an ethanol– H_2O (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–H₂O and insoluble unreacted bpyC₂bpy was collected. The product was purified using ion-exchange column chromatography (absorbent: SP Sephadex C-25; eluent: acetonitrile–H₂O (1:1 v/v) containing NH₄PF₆). Yield: 427 mg (54%). ESI-MS (in acetonitrile) *m/z*: 400 ([M – 2PF₆[–] + H⁺]³⁺), 600 ([M – 2PF₆[–]]²⁺), 673 ([M – PF₆[–]]⁺).

[Ru{(bpyC₂bpy)Ru(CO)₂Cl₂}₃](PF₆)₂ (**RuRu6**): An aqueous solution of formic acid (10 mL, 90% v/v) containing RuCl₃·3H₂O (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(bpyC₂bpy)₃](PF₆)₂ (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%). ¹H NMR (400 MHz, in acetonitrile-*d*₃) 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) ν_{CO} / cm^{–1}: 2062, 1999. ESI-MS (in acetonitrile) *m/z*: 943 ([M – 2PF₆[–]]²⁺).

References

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