Supplementary Information

For

Synthesis and properties of rhenium tricarbonyl complex bearing N-fused tetraphenylporphyrin ligand

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1. Experimental Section

Synthesis of NFTPP-Re(CO)$_3$ (4)

(a) From NCTPP (**3**)

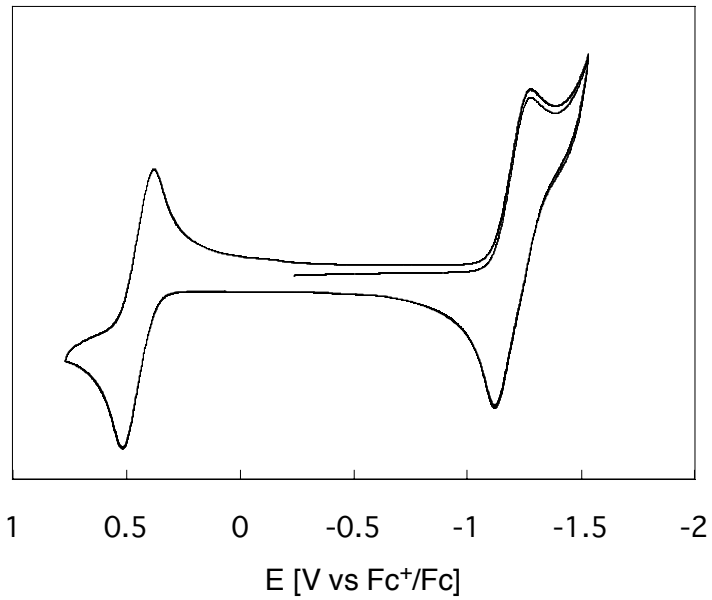
A solution of NCTPP (65.3 mg, 104 μmol, 1.0 equiv) and $Re_2(CO)_{10}$ (37.1 mg, 56.9 μmol, 0.54 equiv) in 1,2-dichlorobenzene (20.0 ml) was degassed under reduced pressure (~0.3 mmHg) at 0 °C. The resulting mixture was heated at 160 °C for 36 h under argon atmosphere. After cooling, 1,2-dichlorobenzene was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane = 1/1). The first violet fraction collected was concentrated to dryness to give **4** in 65% yield (61.0 mg, 69.1 μmol). IR (powder, cm^{-1}): 2080.8, 2008.5; ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ ~7.25 (1H, overlapped with a peak due to $CHCl_3$), 7.34 (d, J = 5.2 Hz, 1H), 7.49 (d, J = 4.6 Hz, 1H), 7.52–7.63 (m, 4H), 7.71–7.84 (m, 11H), 8.00–8.08 (m, 2H), 8.18–8.22 (m, 2H), 8.69 (dd, J = 0.9, 8.2 Hz,

2H), 8.75 (d, J = 5.2 Hz, 1H), 9.21 (d, J = 5.2 Hz, 1H), 9.28 (s, 1H); ^{13}C NMR (CS_2, 75 MHz, ppm): δ 111.87, 112.31, 11947, 121.08, 123.61, 126.05, 127.46, 127.49, 128.21, 128.7, 128.49, 128.88, 129.35, 129.36, 129.82, 131.29, 131.70, 132.32, 133.01, 134.92, 136.72, 137.47, 137.75, 138.20, 140.16, 142.86, 144.92, 149.70, 153.64, 153.80, 153.99, 157.43, 163.51, 193.24, 193.52, 193.71; MS (ESI, positive): 880 (M^+); MS (MALDI, positive): 796 ([M-3(CO)]$^+$); Anal. Calcd for **4**: C, 64.01; H, 3.09; N, 6.35. Found: C, 63.78; H. 3.20; N, 6.25; UV-vis (CH_2Cl_2, λ_{max}/nm (ε)): 358 (42000), 496 (46800), 863 (2650), 950 (2550).

(b) From NFTPP (**7**)

A solution of NFTPP (6.2 mg, 10 μmol, 1.0 equiv) and $Re_2(CO)_{10}$ (3.5 mg, 5.4 μmol, 0.53 equiv) in 1,2-dichlorobenzene (6.0 ml) was degassed under reduced pressure (~0.3 mmHg) at 0 °C. The resulting mixture was heated at 130 °C for 41 h under argon atmosphere. After cooling, 1,2-dichlorobenzene was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane = 1/1). The first violet fraction collected was concentrated to dryness to give **4** in 77% yield (6.9 mg, 7.8 μmol).

2. CV data of 4



Cyclic voltammogram of **4** (multiple scan between −1.53 V and +0.77 V): 0.1 M Bu_4NPF_6 in CH_2Cl_2 at 24 °C with a Pt working electrode. Scan rate = 300 mV/s.