

Ligand (4): ^1H NMR (CDCl_3): δ = 8.65 (s, 3',5'-tpyH, 4H), 8.58 (d, J = 7.8 Hz, 6,6''-tpyH, 4H), 8.49 (d, J = 4.2 Hz, 3,3''-tpyH, 4H), 7.80 (dd, J = 7.8, 7.5 Hz, 4,4''-tpyH, 4H), 7.66 (dd, J = 3.3, 3.3 Hz, 4-ArH, 2H), 7.43 (dd, J = 3.3, 3.3 Hz, 3-ArH, 2H), 7.24 (dd, J = 6.9, 5.7 Hz, 5,5''-tpyH, 2H). ^{13}C NMR (CDCl_3): δ = 92.14, 92.52, 121.46, 123.42, 124.10, 125.71, 129.14, 132.46, 133.55, 137.21, 149.06, 155.44, 155.56. ESI-MS: m/z = 611.4 [$\text{M}+\text{Na}$] $^+$ (Calcd m/z = 611.20).

[Fe₃(4)₃][6PF₆⁻] (5) ^1H NMR (CD_3CN): δ = 9.19 (s, 3',5'-tpyH, 4H), 8.42 (d, J = 8.1 Hz, 3,3''-tpyH, 4H), 8.04 (dd, J = 3.3, 3.3 Hz, 4-ArH, 2H), 7.78 (dd, J = 3.3, 3.3 Hz, 3-ArH, 2H), 7.56 (dd, J = 7.8, 7.8 Hz, 4,4''-tpyH, 4H), 7.10 (d, J = 5.4 Hz, 6,6''-tpyH, 4H), 6.86 (dd, J = 6.9, 6.3 Hz, 5,5''-tpyH, 4H). ^{13}C NMR (CDCl_3): δ = 91.50, 96.29, 124.83, 125.27, 126.38, 128.44, 131.70, 133.27, 133.92, 139.66, 154.06, 158.23, 161.13.; UV (MeCN) λ_{max} (nm) = 283 (ϵ = $1.27 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 326 (1.27×10^5), 578 (6.43×10^5); ESI-MS: m/z = 2659.7 [$\text{M}+2\text{H}-\text{PF}_6$] $^+$ (Calcd m/z = 2659.3); Elemental Analysis (%) (+6H₂O): calcd. C 49.51, H 2.91, N 8.66; found. C 49.98, H 2.99, N 8.29.

[Ru₃(4)₃][6PF₆⁻] (6) ^1H NMR (CD_3CN): δ = 9.01 (s, 3',5'-tpyH, 4H), 8.44 (d, J = 8.1 Hz, 3,3''-tpyH, 4H), 7.97 (dd, J = 3.3, 3.3 Hz, 4-ArH, 2H), 7.74 (dd, J = 3.3, 3.3 Hz, 3-ArH, 2H), 7.59 (dd, J = 7.8, 7.8 Hz, 4,4''-tpyH, 4H), 7.35 (d, J = 5.7 Hz, 6,6''-tpyH, 4H), 6.95 (dd, J = 6.9, 6.3 Hz, 5,5''-tpyH, 4H). ^{13}C NMR(CDCl_3): δ = 91.50, 95.53, 125.40, 125.56, 126.60, 128.68, 131.19, 131.58, 133.89, 139.04, 153.60, 156.30, 158.46.; UV (MeCN) λ_{max} (nm) = 275 (ϵ = $7.28 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 316 (8.01×10^4), 496 (4.23×10^4); ESI-MS: m/z = 2796.4 [$\text{M}+\text{H}-\text{PF}_6$] $^+$ (Calcd m/z = 2796.17), 2649.8 [$\text{M}-2\text{PF}_6$] $^+$ (Calcd m/z = 2650.20), 2504.6 [$\text{M}-\text{H}-3\text{PF}_6$] $^+$ (Calcd m/z = 2504.23), 2357.7 [$\text{M}-3\text{H}-4\text{PF}_6$] $^+$ (Calcd m/z = 2357.26), 2214.4 [$\text{M}-\text{H}-5\text{PF}_6$] $^+$ (Calcd m/z = 2214.31).

[Ru₂Fe(4)₃][6PF₆⁻] (9) ^1H NMR (CD_3CN): δ = 9.18 (s, 3',5'-tpyH, Fe, 4H), 9.05 (s, 3',5'-tpyH, Ru/Fe, 4H), 9.01 (s, 3',5'-tpyH, Ru, 4H), 8.47-8.42 (m, 3,3''-tpyH, 12H), 8.02-7.95 (m, 4-ArH, 6H), 7.77-7.72 (m, 3-ArH, 6H), 7.60-7.53 (m, 4,4''-tpyH, Ru and 5,5''-tpyH, Fe, 12H), 7.35 (dd, J = 4.8, 5.1 Hz, 4,4''-tpyH, Ru, 8H), 7.12 (d, J = 5.1 Hz, 6,6''-tpyH, Fe, 4H), 6.93 (dd, J = 6.3, 6.6 Hz, 5,5''-tpyH, Ru, 8H), 6.87 (dd, J = 6.6, 6.0 Hz, 5,5''-tpyH, Fe, 4H). ^{13}C NMR(CDCl_3): δ = 91.62, 91.66, 95.56, 125.02, 125.36, 125.49, 125.59, 126.50, 126.64, 126.69, 128.59, 128.70, 131.21, 131.60, 132.37, 133.38, 133.83, 133.95, 139.06, 139.45, 153.64, 154.21, 156.35, 158.38, 158.51, 158.53, 161.23.; UV (MeCN) λ_{max} (nm) = 276 (ϵ = $1.34 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 319 (1.25×10^5), 499 (5.86×10^4), 582 (2.38×10^4); ESI-MS: m/z = 1302.1 [$\text{M}-2\text{PF}_6$] $^{2+}$ (Calcd m/z = 1301.9), 819.8 [$\text{M}-3\text{PF}_6$] $^{3+}$ (Calcd m/z = 819.6), 579.0 [$\text{M}-4\text{PF}_6$] $^{4+}$ (Calcd m/z = 578.5), 433.9 [$\text{M}-5\text{PF}_6$] $^{5+}$ (Calcd m/z = 433.8), 337.3 [$\text{M}-6\text{PF}_6$] $^{6+}$ (Calcd m/z = 337.3).