Supporting Information

Vaduvescu, S.; Potvin, P.G.: “Synthesis and characterization of a novel linear trinuclear ruthenium(II) complex: variation of photosensitization ability with chain length in a homologous series.”

Characterization Details:

L: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.83 (s, 4H, H-4′), 8.79 (d, 4H, H-6, J = 4.2 Hz), 8.74 (d, 4H, H-3, J = 7.0 Hz), 8.09 (s, 4H, H-2″), 7.92 (dd, 4H, H-4, J = 7.0 Hz), 7.39 (dd, 4H, H-5, J = 4.2 Hz) ppm. MALDI–MS: m/z [%] 541 [100, M+1], 443 [27], 324 [10], 221 [17]. EA: Found: C, 79.57, H, 4.73, N, 12.31%, Calc’d for $C_{36}H_{24}N_6$: C, 79.98, H, 4.47, N, 15.54%.

[(ttpy)RuL][PF$_6$]$_2$: ^{1}H-NMR (CD_3CN, 400 MHz): δ 9.12 (s, 2H, H-B4′), 9.02 (s, 2H, H-C4′), 8.97 (s, 2H, H-A4′), 8.79 (m, 4H, H-C3, H-C6), 8.70 (m, 4H, H-B3, H-A3), 8.46 (d, 2H, H-B2″, J = 7.8 Hz), 8.35 (d, 2H, H-B3″, J = 7.8 Hz), 8.13 (m, 4H, H-A2″, H-C4), 7.97 (m, 4H, H-B4, H-A4), 7.60 (m, 4H, H-A3″, H-C5), 7.48 (m, 4H, H-B6, H-A6), 7.22 (m, 4H, H-B5, H-A5), 2.57 (s, 3H, CH_3) ppm. ESI–MS: m/z [%] 483 [100, M], 374 [5], 347 [7], 322 [12]. EA: Found: C, 55.86, H, 3.50, N, 9.77%, Calc’d for $RuC_{58}H_{41}N_9P_2F_{12}$: C, 55.51, H, 3.29, N, 10.04%.

[(ttpy)RuLRu(ttpy)][PF$_6$]$_4$: ^{1}H-NMR (CD_3CN, 400 MHz): δ 9.19 (s, 4H, H-B4′), 9.05 (s, 4H, H-A4′), 8.78 (d, 4H, H-B3, J = 8 Hz), 8.71 (d, 4H, H-A3, J = 8 Hz), 8.62 (s, 4H, H-B2″), 8.17 (d, 4H, J = 7.6, H-A2″), 8.03 (m, 8H, H-A4, H-B4), 7.64 (d, 4H, H-A3″, J = 7.5 Hz), 7.51 (m, 8H, H-A6, H-B6), 7.26 (m, 8H, H-A5, H-B5), 2.58 (s, 6H, CH_3) ppm. ESI–MS: m/z [%] 348 [70, M+1], 322 [8], 271.5 [7], 198.5 [7], 173.5 [10], 157.5 [100], 152 [35], 135.5 [30]. EA reported by Constable *et al.*, *J. Chem Soc. Dalton Trans.* **1992**, 3467.

[(ttpy)RuLRuLRu(ttpy)][PF$_6$]$_6$: ^{1}H-NMR (CD_3CN, 400 MHz): δ 9.23 (s, 4H, H-C4′), 9.21 (s, 4H, H-B4′), 9.06 (s, 4H, H-A4′), 8.79 (t, 8H, H-B3, H-C3), 8.71 (d, 4H, H-A3, J = 7.9 Hz), 8.64 (s, 8H, H-B2″, H-B3″), 8.17 (d, 4H, H-A2″, J = 7.4 Hz), 8.03 (m,12H, H-A4, H-B4, H-C4), 7.64 (d, 4H, H-A3″, J = 7.4 Hz), 7.58 (d, 4H, H-C6, J = 5.3 Hz), 7.52 (m, 8H, H-A6, H-B6), 7.28 (m, 12H, H-A5, H-B5, H-C5), 2.58 (s, 6H, CH_3) ppm. ESI–MS: m/z [%] 339.2 [40, M+1], 200.5 [7], 146.2 [70]. EA: Found: C, 47.52, H, 2.89, N, 7.89%, Calc’d for $Ru_3C_{116}H_{82}N_{18}P_6F_{36}$: C, 48.03, H, 2.85, N, 8.69%.

Table S1. Estimations of the energies of activation for electron transfer ΔG^*.

	$[Ru(bpy)_3]^{2+}$	$[Ru(ttpy)_2]^{2+}$	$[(ttpy)Ru(\mathbf{L})]^{2+}$	$[\{(ttpy)Ru\}_2(\mathbf{L})]^{4+}$	$[\{(ttpy)Ru(\mathbf{L})\}_2Ru]^{6+}$
Λ /eV [a]	0.955	0.955	0.955	0.955	0.955
W_R /eV [b]	0.119	0.119	0.119	0.172	0.207
W_P /eV [b]	0.089	0.089	0.089	0.129	0.155
ΔG^0_{PET} /eV [c]	-0.42	-0.24	-0.22	-0.22	-0.22
ΔG^0_{BET} /eV [c]	-1.71	-1.70	-1.72	-1.72	-1.72
ΔG^*_{PET} /eV [d]	0.19	0.24	0.25	0.29	0.32
ΔG^*_{BET} /eV [d]	0.23	0.22	0.23	0.25	0.26

[a] Reorganizational energy calculated as $\Lambda \approx \Lambda_{out} = e^2(1/2R_A + 1/2R_B - 1/(R_A+R_B)(1/n^2 - 1/\rho)$ since the inner sphere component is near zero.[1] R_B = 3.3 Å for $MV^{2+}/MV^{\bullet+}$ and R_A = 7 Å for all complexes at closest approach.[2] The refractive index n for CH_3CN is 1.3441 and the dielectric constant ρ is 37.5.

[b] By an end-on approach, the electrostatic work term is $W = q_B f\{q_A/a + q_A/(a+c) + 2i/(a+b) + 2i/(a+b+c) + 2j/(a+2b) + 2j/(a+2b+c)\}$ where q_A is the proximal metal charge, q_B is the charge on each nitrogen of the acceptor $MV^{2+/\bullet+}$, a is the distance of closest approach to the proximal metal (corresponding to R_A+R_B = 10.3 Å), b is the distance between metals, estimated at 15.3 Å,[3] c is the N···N separation in $MV^{2+/\bullet+}$, estimated at 7.0 Å from a crystal structure;[4] $i = j = 0$ for $[(ttpy)Ru(\mathbf{L})]^{3+/2+}$, $i = 1$ and $j = 0$ for $[\{(ttpy)Ru\}_2(\mathbf{L})]^{5+/4+}$ and $i = j = 1$ for $[\{(ttpy)Ru(\mathbf{L})\}_2Ru]^{7+/6+}$; $f = e^2/(4\pi\rho\varepsilon_0)$, where $e = 1.602 \times 10^{-19}$ C and ε_0 is the vacuum permittivity constant, and f has a value in CH_3CN of 37.0 eV Å mol^{-1}. W_R refers to the reactant state (q_A = +2 and q_B = +1) and W_P refers to the product state (q_A = +3 and q_B = +1/2). For an end-on attack of the middle metal in the trinuclear complex, $W = q_B f\{q_A/a + q_A/(a+c) - 4\arctan(a/b)/b - 4\arctan((a+c)/b)/b\}$; W_R increases to 0.289 eV and W_P increases to 0.172 eV. For an end-on attack of the dinuclear complex at its middle, $W = q_B f\{(q_A+2)/a - (q_A+2)\arctan(a/c)/c\}$ where a is now 15.3/2 Å; W_R then increases to 0.338 eV and W_P increases to 0.211 eV.

[c] Using $\Delta G°_{PET} = E_{ox}(Ru^{3+/2+}) - E_{red}(MV^{2+/\bullet+}) - E_{00}$ and $-\Delta G°_{BET} = E_{ox}(Ru^{3+/2+}) - E_{red}(MV^{2+/\bullet+})$.[5] $E_{red}(MV^{2+/\bullet+})$ = -0.45 V (*vs.* SCE in CH_3CN) and E_{ox} is +1.26 V for $[Ru(bpy)_3]^{3+/2+}$,[6] +1.25 V for $[Ru(ttpy)_2]^{3+/2+}$,[7] and +1.27 V for the others (see Table 1), all *vs.* SCE in CH_3CN. E_{00} for $[Ru(bpy)_3]^{2+}$ is 2.12 eV.[8] E_{00} for $[Ru(ttpy)_2]^{2+}$ is calculated at 1.94 eV from the emission λ_{max} at 640 nm,[9] and the same E_{00} value was used for the other cases.

[d] $\Delta G^* = W_R + (\Delta G° + \Lambda + W_P - W_R)/4\Lambda$.[1] ΔG^*_{PET} increases to 0.39 eV for attack of the middle metal in the trinuclear case, and to 0.44 eV for attack of the dinuclear complex at its middle; ΔG^*_{BET} correspondingly increases to 0.29 and 0.32 eV, respectively.

1 Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

2 Sun, H.; Yoshimura, A.; Hoffman, M. Z. *J. Phys. Chem.* **1994**, *98*, 5058.

3 Average of three values from crystal structures in Chamchoumis, C. M.; Potvin, P. G. *J. Chem. Soc. Dalton Trans.* **1999**, 1373 and in Mikel, C.; Potvin, P. G. *Polyhedron* **2002**, *21*, 49.

4 Russell, J. H.; Wallwork, S. C. *Acta Cryst.* **1972**, *B28*, 1527.

5 Rehm, D.; Weller, A. *Ber. Bunsges. Phys. Chem.* **1969**, *73*, 834.

6 Kavarnos, G. J. *Fundamentals of Photoinduced Electron Transfer*; VCH: New York, 1993.

7 K. Kalyanasundaram, M.K. Nazeeruddin, M. Grätzel, G. Viscardi, P. Savarino, E. Barni, *Inorg. Chim. Acta* **1992**, *198*, 831.

8 Balzani, V.; Barigelletti, F.; De Cola, L. *Top. Curr. Chem.* **1990**, *158*, 31.

9 Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc. Chem. Commun.* **1993**, 942.