Electronic Supplementary Material for Dalton Transactions

Intervalence Charge Transfer in a "Chain-like" Ruthenium Trinuclear Assembly based on the Bridging Ligand 4,7-phenanthrolino-5,6:5',6'-pyrazine (ppz)

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SUPPLEMENTARY INFORMATION

Table S1. ^{1}H Chemical shifts (ppm) for Λ-$[Ru(bpy)(HAT)_2]^{2+}$ and Λ^t-$[Ru(bpy)(ppz)_2]^{2+}$ (CD_3CN, PF_6^- salts). The ^{1}H NMR spectra of the Δ and Λ enantiomers were identical in each case.

		$[Ru(bpy)(HAT)_2]^{2+}$	*trans*-$[Ru(bpy)(ppz)_2]^{2+}$
bpy[a]	H3	8.60	8.58
	H4	8.16	8.14
	H5	7.39	7.34
	H6	7.83	7.83
HAT	H2	8.39 (2H, *J* = 3 Hz, d)	
	H3	9.24 (2H, s)	
	H6	9.39 (2H, s)	
	H7	9.39 (2H, s)	
	H10	9.02 (2H, s)	
	H11	8.29 (2H, *J* = 3 Hz, d)	
ppz	H2		8.86 (2H, *J* = 3 Hz, d)
	H3		8.11 (2H, *J* = 3 Hz, d)
	H6		8.22 (2H, *J* = 5, 1 Hz, dd)
	H7		7.97 (2H, *J* = 10, 8 Hz, dd)
	H8		9.32 (2H, *J* = 8 Hz, d)
	H9		9.32 (2H, *J* = 8 Hz, d)
	H10		8.11 (2H, *J* = 10,8 Hz, dd)
	H11		9.26 (2H, *J* = 3, 1.5 Hz, dd)

[a] H6 (2H, *J* = 5, 1.5 Hz, dd); H5 (2H, *J* = 8, 5 Hz, dd); H4 (2H, *J* = 8, 8 Hz, dd); H3 (2H, *J* = 8, 1.5 Hz, dd).

Table S2. ^{1}H chemical shifts (ppm) for $\Delta\Delta^t\Delta$-[{Ru(bpy)$_2$}$_2${Ru(bpy)(μ-ppz)$_2$}]$^{6+}$ by comparison with the *meso*- and *rac*-[{Ru(bpy)$_2$}$_2$(μ-ppz)]$^{4+}$ (CD_3CN, PF_6^- salts).

		meso (ΔΛ/ΛΔ)	*rac* (ΔΔ/ΛΛ)	$\Delta\Delta^t\Delta$
bpy ring a[a]	H3'	8.58	8.53	8.59
(over bpy)	H4'	8.15	8.13	8.20
	H5'	7.50	7.51	7.52
	H6'	7.73	7.76	7.77
bpy ring b[a]	H3	8.52	8.51	8.50
(over ppz)	H4	8.09	8.07	8.10
	H5	7.39	7.02	7.17
	H6	7.85	7.61	7.42
bpy ring c[a]	H3'	8.43	8.55	8.53
(over bpy)	H4'	8.06	8.15	8.20
	H5'	7.42	7.38	7.36
	H6'	7.75	7.66	7.65
bpy ring d[a]	H3	8.39	8.48	8.53
(over ppz)	H4	7.99	8.00	8.07
	H5	7.25	7.36	7.20
	H6	7.54	7.42	7.65
bpy ring e[a]	H3			8.53
(over ppz)	H4			8.02
	H5			7.36
	H6			7.47
ppz[b]	H2	7.93 (H2/3)	7.96 (H2/3)	7.98
	H3			8.08
	H6	8.23 (H6/11)	8.23 (H6/11)	8.25
	H7	8.01 (H7/10)	8.01 (H7/10)	8.10
	H8	9.32 (H8/9)	9.31 (H8/9)	9.36
	H9			9.33
	H10			8.03
	H11			8.09

[a] H6 (dd; J = 5, 1.5 Hz); H5 (dd; J = 8, 5 Hz); H4 (dd; J = 8, 8 Hz); H3 (dd; J = 8, 1.5 Hz).

[b] H2/3 (s); H 6/11 (dd, J = 5, 1.5 Hz); H7/10 (dd, J = 10, 8 Hz); H8/9 (dd, J = 8, 1.5 Hz).

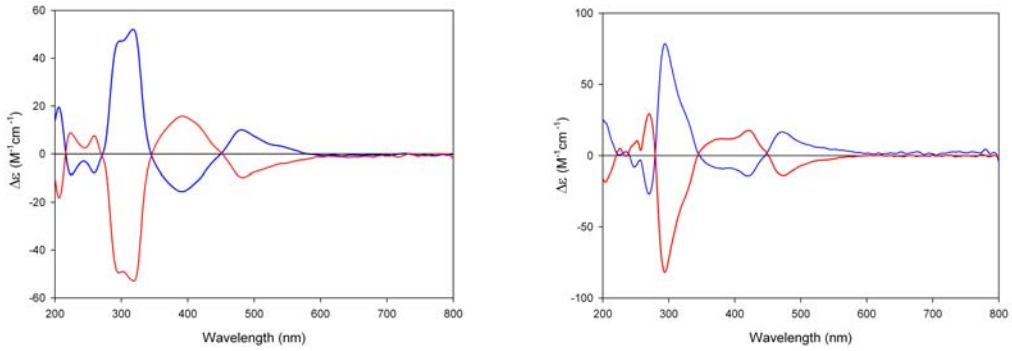
Table S3. Ligand-based reduction potentials[a] data (in mV), and K_c values[b] for the di- and trinuclear complexes in 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ at +25°C. The potentials for $[Ru(bpy)_3]^{2+}$ are included for comparison.

Complex	E_{red1}	E_{red2}	E_{red3}	E_{red4}
$[Ru(bpy)_3]^{2+}$	-1717	-1912	-2160	-2700
trans-$[Ru(bpy)(ppz)_2]^{2+}$ [c]	-1000	-1246	-1700	-1968[b]
meso-$[\{Ru(bpy)_2\}_2(\mu\text{-ppz})]^{4+}$	-956	-1704	-1890	-1956
rac-$[\{Ru(bpy)_2\}_2(\mu\text{-ppz})]^{4+}$	-944	-1696	-1878	-1975
$\Delta\Delta^t\Delta$- $[\{Ru(bpy)_2\}_2\{Ru(bpy)(\mu\text{-ppz})_2\}]^{6+}$	-868	-1036	-1800[b]	-2072[b]

[a] All potentials (± 3 mV) in 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ at +25°C *vs*. Fc^+/Fc^0.

[b] Two-electron reduction process.

[c] The redox properties of the Δ and Λ enantiomers were identical.



(a) **(b)**

Figure S1. CD spectra (CH_3CN) of **(a)** Δ- and Λ-$[Ru(bpy)(HAT)_2]^{2+}$, Band 1 (Δ): (———) and Band 2 (Λ): (———); **(b)** Δ^t- and Λ^t-$[Ru(bpy)(ppz)_2]^{2+}$, Band 1 (Δ) (———) and Band 4 (Λ): (———).

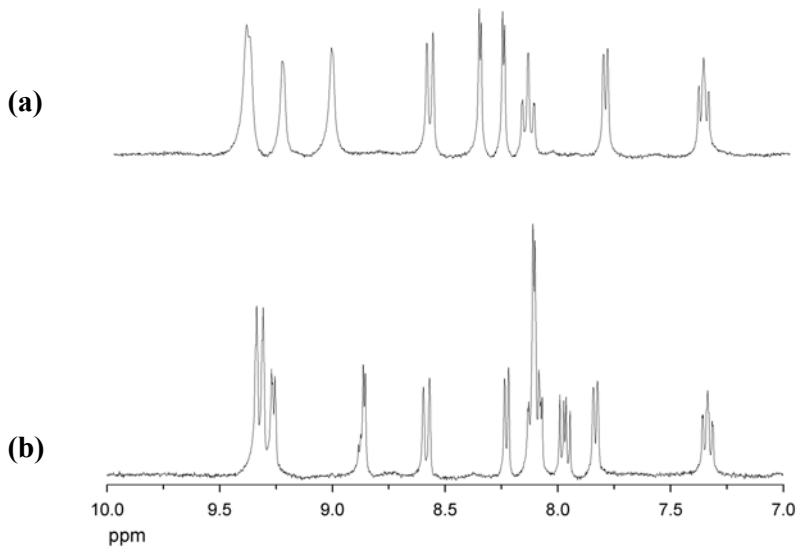


Figure S2. ^{1}H NMR spectra of **(a)** Λ-$[Ru(bpy)(HAT)_2]^{2+}$ and **(b)** Λ^{t}-$[Ru(bpy)(ppz)_2]^{2+}$ (CD_3CN, PF_6^- salts).

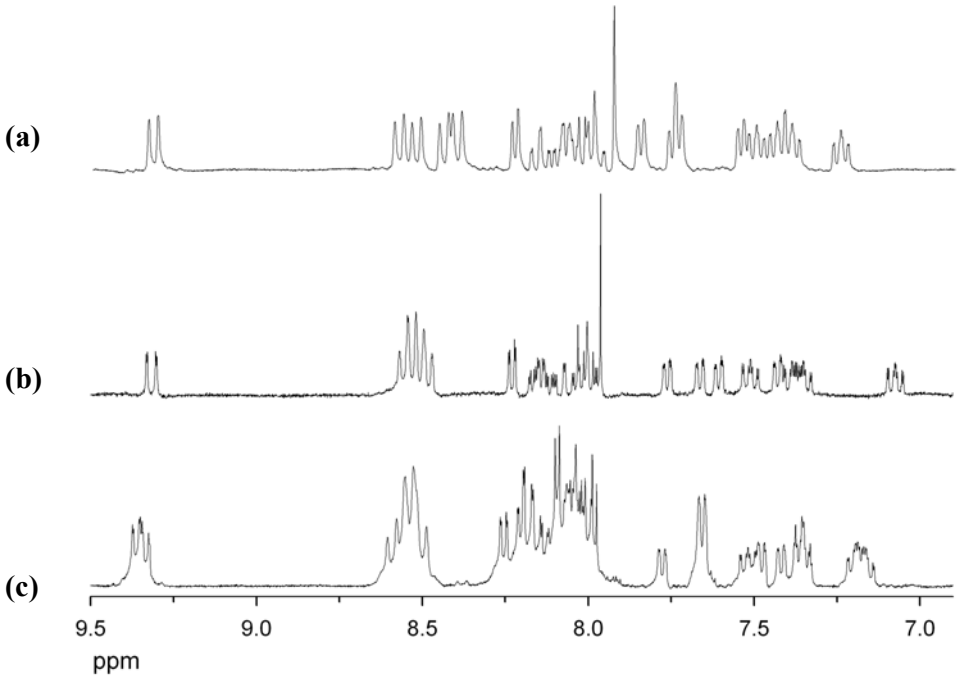


Figure S3. ^{1}H NMR spectra (CH_3CN) for **(a)** *meso*- and **(b)** *rac*-$[\{Ru(bpy)_2\}_2(\mu\text{-ppz})]^{4+}$, and **(c)** $\Delta\Delta^{t}\Delta$-$[\{Ru(bpy)_2\}_2\{Ru(bpy)(\mu\text{-ppz})_2\}]^{6+}$ (CD_3CN, PF_6^- salts).

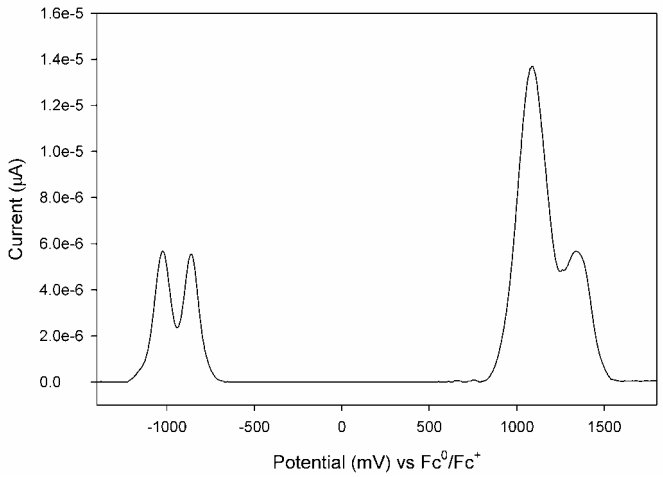


Figure S4. Differential Pulse Voltammogram of $\Delta\Delta^{t}\Delta$- $[\{Ru(bpy)_2\}_2\{Ru(bpy)(\mu\text{-}ppz)_2\}]^{6+}$ in 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ at +25°C.

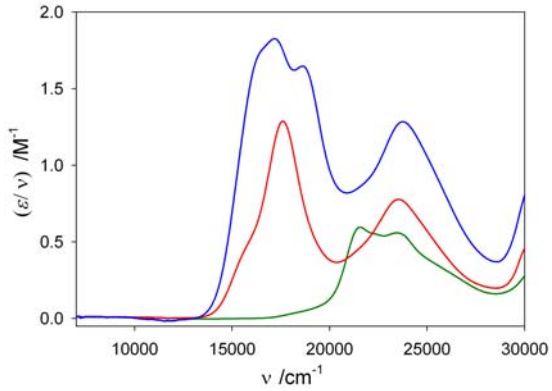


Figure S5. UV/Vis/NIR spectra of $[Ru(bpy)(ppz)_2]^{2+}$ (———), *meso*-$[\{Ru(bpy)_2\}_2(\mu\text{-ppz})]^{4+}$ (———) and $\Delta\Delta^t\Delta$- $[\{Ru(bpy)_2\}_2\{Ru(bpy)(\mu\text{-ppz})_2\}]^{6+}$ (———) in CH_3CN at +25°C.

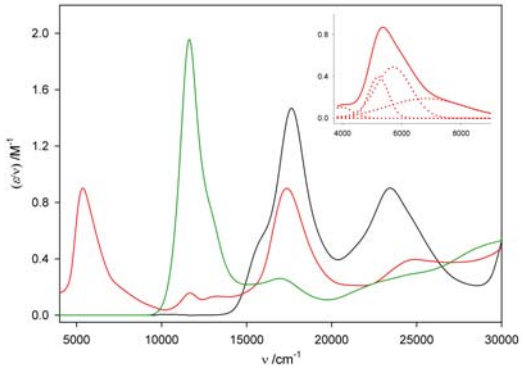


Figure S6. UV/Vis/NIR spectra of *meso*-$[\{Ru(bpy)_2\}_2(\mu\text{-ppz})]^{n+}$ {n = 4 (———), 5 (———), 6 (———)} at -35°C. The inset shows the best fit of the bands obtained by Gaussian deconvolution of the IVCT band.