**The Underlying Spin-Orbit Coupling Structure of Intervalence Charge
Transfer Bands in Dinuclear Polypyridyl Complexes of
Ruthenium and Osmium**

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SUPPLEMENTARY INFORMATION

Table S1. Crystal data and structure refinement parameters for dinuclear osmium complexes incorporating the dpb and dpq' bridging ligands.

Parameter	<i>meso</i> -($\Lambda\Lambda$)-[Os(bpy) ₂] ₂ (μ -dpb)](ZnCl ₄) ₂ ·6H ₂ O	<i>meso</i> -($\Lambda\Lambda$)-[Os(bpy) ₂] ₂ (μ -dpq')](PF ₆) ₄
Crystal Colour	deep green	deep green
Crystal Dimensions	0.5 x 0.3 x 0.05 mm	0.15 x 0.15 x 0.15 mm
Crystal habit	plates	octahedral prisms
Crystal System	monoclinic	orthorhombic
Space Group	P21/c	Pbca
a (Å)	19.598(5)	25.009(3)
b (Å)	16.755(5)	21.978(3)
c (Å)	20.799(5)	26.585(3)
α (°)	90	90
β (°)	96.586(5)	90
γ (°)	90	90
V (Å ³)	6785(3)	14612(3)
Z	4	8
Molecular Weight	1850.86	1867.32
T (K)	293	293
D _{calc} (g cm ⁻³)	1.812	1.698
μ (Mo K α) (cm ⁻¹)	4.806	3.668
range h	-24<h<24	0<h<31
range k	0<k<20	0<k<28
range l	0<l<26	0<l<33
range 2 θ	2.1 < 2 θ < 52.9	2.9 < 2 θ < 54
No reflections	13939	15690
No reflections > 4 σ	5508	9176
No. parameters	828	902
R (all data)	0.2023	0.1477
R (obs data)	0.0637	0.0799
wR (all data)	0.1836	0.2200
wR (obs data)	0.1454	0.1840
S	0.844	1.153

Table S2. Electrochemical data (in mV relative to the Fc^+/Fc^0 couple) for the diastereoisomers of $[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-BL})]^{4+}$ in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$.

BL	Diastereoisomer	K_c ($\times 10^{-3}$)	ΔE_{ox}	$E_{\text{ox}2}$	$E_{\text{ox}1}$	$E_{\text{red}1}$	$E_{\text{red}2}$	$E_{\text{red}3}$	$E_{\text{red}4}$
dpb	<i>meso</i>	256	320	956	636	-664	-1196	-1776	-1868
	<i>rac</i>	86.2	292	944	652	-668	-1200	-1784 ^b	^b
dpb'	<i>meso</i>	3616	388	988	600	-528	-1064	-1836 ^b	-2180 ^b
	<i>rac</i>	4225	392	992	604	-528	-1056	-1840 ^b	-2188 ^b
dpq'	<i>meso</i>	1040	356	960	608	-632	-1240	-1832 ^b	-2208 ^b
	<i>rac</i>	1660	368	976	616	-640	-1232	-1840 ^b	-2184 ^b
ppz	<i>meso</i>	890	352	916	568	-968	-1560	-1794	-1884
	<i>rac</i>	1040	356	924	568	-960	-1556	-1780	-1916
2,3-dpp	<i>meso</i>	378	330	924	594	-1094	-1686	-1800	-1950
	<i>rac</i>	237	318	912	594	-1097	-1690	-1830	-1953

^a Potentials are quoted ± 3 mV.

^b Processes complicated by adsorption/desorption peaks.

Table S3(a). UV/Vis/NIR spectral data for *meso*-[$\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-BL})\}^{n+}$ in 0.1 M [(*n*-C₄H₉)₄N]PF₆/CH₃CN at -35°C.

The parameters of the IVCT and IC transitions in the +5 and +6 states, respectively, are indicated in bold type.

[illegible]

Table S3(b). UV/Vis/NIR spectral data for *rac*-[$\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-BL})\}^{n+}$ in 0.1 M [(*n*-C₄H₉)₄N]PF₆/CH₃CN at -35°C.

The parameters of the IVCT and IC transitions in the +5 and +6 states, respectively, are indicated in bold type.

[illegible]

Table S4. Reduction potentials for $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-BL})]^{4+}$ in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$.^a

BL	Diastereoisomer	E _{red1}	E _{red2}	E _{red3}	E _{red4}	E _{red5}	E _{red6}
dpb	<i>meso</i>	-624	-1268	-1888	-2116	-2240	-2552
	<i>rac</i>	-624	-1260	-1876	^c	-2252	-2640
dpb'	<i>meso</i>	-496	-1128	-1868	-1981	-2144	-2272
	<i>rac</i>	-464	-1116	-1888	-2180	-2716	
dpq'	<i>meso</i>	-596	-1332	-1900	-2178	-2203	
	<i>rac</i>	-592	-1268	-1956	-2177	-2240	
ppz	<i>meso</i>	-956	-1704	-1890	-1956	-2108	-2356
	<i>rac</i>	-944	-1696	-1878	-1975	-2116	-2360
2,3-dpp	<i>meso</i>	-1044	-1540	-1900 ^{b,c}	-2168 ^b		
	<i>rac</i>	-1048	-1560	-1888 ^{b,c}	-2248 ^b		

^a Potentials are quoted ± 3 mV. ^b Processes complicated by adsorption/desorption peaks. ^c Irreversible reduction process. ^d Two-electron reduction process.

Table S5. UV/Vis/NIR spectral data of the reduced absorption spectra (ϵ/ν vs. ν) for the diastereoisomers of $[\{\text{Ru}(\text{pp})_2\}_2(\mu\text{-BL})]^{4+}$ in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$ at -35°C . The parameters of the IVCT transitions are indicated in bold type.^a

BL		dpb		dpb'		dpq'		ppz		2,3-dpp ^b	
Diastereoisomer	<i>n</i>	$\nu_{\text{max}}/\text{cm}^{-1}$	$(\epsilon/\nu)_{\text{max}}/\text{M}^{-1}$	$\nu_{\text{max}}/\text{cm}^{-1}$	$(\epsilon/\nu)_{\text{max}}/\text{M}^{-1}$	$\nu_{\text{max}}/\text{cm}^{-1}$	$(\epsilon/\nu)_{\text{max}}/\text{M}^{-1}$	$\nu_{\text{max}}/\text{cm}^{-1}$	$(\epsilon/\nu)_{\text{max}}/\text{M}^{-1}$	$\nu_{\text{max}}/\text{cm}^{-1}$	$(\epsilon/\nu)_{\text{max}}/\text{M}^{-1}$
<i>meso</i>	4	<i>sh</i> 13070	0.2958	<i>sh</i> 11670	0.2646	<i>sh</i> 12900	0.2813	17640	1.4682	19056	1.3356
		15530	1.4440	13880	2.0415	15150	1.9723	23440	0.9021	23361	1.0805
		23520	1.0810	16900	0.2133	18110	0.1567				
		24460	0.9824	24780	1.3524	23480	0.8393				
		26870	1.5690	29140	1.5091	26690	1.0829				
		29450	1.4350								
	5	5205	0.3062	5285	0.8084	5194	0.5934	5370	0.8721	5340	0.2890
		15120	0.7678	9253	0.0998	14900	1.4369	11670	0.1566	18696	0.4676
		<i>sh</i> 17370	0.4504	11420	0.3598	25730	1.0688	13320	0.1400	28680	0.8088
		25920	1.4740	13930	0.9596			17370	0.9003		
				21660	0.3788			24900	0.3950		
				22770	0.4739						
	6	~15000		14210	0.1497			11630	1.9560		
		16870	0.2253	20850	0.8348			16950	0.2601		
		25230	1.2709	22140	0.7751						
				27440	1.5330						
<i>rac</i>	4	<i>sh</i> 13070	0.2269	<i>sh</i> 11770	0.2532	<i>sh</i> 13090	0.4341	17630	1.4715	19070	1.2995
		15420	1.4152	13870	1.8962	15290	1.9334	23420	0.8987	23286	0.8616
		20480	0.3499	16850	0.1661	18280	0.1602				
		23470	1.1100	24780	1.2155	23370	0.8662				
		<i>sh</i> 24400	0.9878	29150	1.3248	26720	1.0949				
		26820	1.4918								
	5	29400	1.5252								
		4998	0.4572	5290	0.7222	5223	0.6329	5390	0.8494	5307	0.5980
		14980	0.6835	9223	0.0878	14980	1.2244	11720	0.1488	18666	0.5886
		25700	1.6362	11250	0.2793	25840	0.8573	13090	0.2145	28642	0.9808
				13920	0.9050			17340	0.9043		
				21630	0.3490			24980	0.3862		
	6			22680	0.4360						
				24570	0.6573						
				27980	1.1377						
		17760	0.1270	12730	0.3188	14450	0.2372	11640	1.9510		
		25170	1.9485	15880	0.2005	21330	0.3455	16930	0.2600		
				20850	0.6463	23560	0.6253				
				22180	0.6198						
				27430	1.3068						

^a Errors in ν_{max} and $(\epsilon/\nu)_{\text{max}}$ are $\pm 10 \text{ cm}^{-1}$ and $\pm 0.001 \text{ M}^{-1}$, respectively. ^b Measurements performed in 0.02 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\{\text{B}(\text{C}_6\text{F}_5)_4\}/\text{CH}_3\text{CN}$; +6 state not measured.

Table S6(a). Parameters obtained from Gaussian deconvolution of the UV/Vis/NIR spectra for *meso*-[Os(bpy)₂]₂(μ-BL)]ⁿ⁺ {BL = dpb, dpb', dpq'} in 0.1 M [(*n*-C₄H₉)₄N]PF₆/CH₃CN at -35°C.^a

Diastereoisomer	<i>n</i>	dpb				dpb'				dpq'			
		$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹	$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹	$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹
<i>meso</i>	5	4910	0.1128	533	63.65	4510	0.0256	249	6.772	4596	0.0307	274	8.920
		5395	0.0433	519	23.94	4757	0.0223	437	10.35	4844	0.0332	331	11.70
		5876	0.0124	508	6.714	5471	0.0355	811	30.64	5339	0.0558	806	47.85
		7385	0.0504	707	37.97	6825	0.2375	831	210.2	6070	0.0127	669	9.075
		8500	0.2611	969	405.8	7590	0.0663	607	42.91	7570	0.0638	1098	74.60
		9177	0.4192	995	444.0	8476	0.7359	791	620.3	8620	0.5516	765	449.4
		9986	0.1940	1085	224.1	9140	0.0866	568	52.39	9168	0.4908	842	440.0
		10810	0.0623	779	51.68	9786	0.1564	1647	274.2	9797	0.1418	876	132.3
		12220	0.3533	1289	484.7	11600	0.5840	1095	681.3	10420	0.0767	1424	116.2
		14130	0.5642	1643	983.5	12540	0.2760	807	237.1	13060	0.4800	1542	787.2
		15630	0.7204	2232	1123	13450	1.3109	927	1293	14900	1.8758	1130	1515
						14600	0.8666	1148	623.0				
	6	4528	0.2226	426	100.2	4520	0.2245	505	120.6	4550	0.2410	428	106.2
		4810	0.0412	289	12.68	5070	0.2376	572	144.9	4845	0.0480	268	13.71
		5134	0.1872	547	110.3	5581	0.0315	522	17.51	5205	0.2786	512	151.3
		5470	0.0442	556	26.22	6096	0.00911	1215	11.75	5613	0.0333	339	12.03
		5840	0.0185	636	12.55	6768	0.00594	433	2.73	5860	0.0311	578	19.15
										6554	0.0164	1305	22.32

^a A number of the Gaussian components are likely to arise due to vibrational progressions due to a more complicated electronic structure than the one already envisioned.

Table S6(b). Parameters obtained from Gaussian deconvolution of the UV/Vis/NIR spectra for *rac*-[Os(bpy)₂]₂(μ-BL)]ⁿ⁺ {BL = dpb, dpb', dpq'} in 0.1 M [(*n*-C₄H₉)₄N]PF₆/CH₃CN at -35°C.^a

Diastereoisomer	<i>n</i>	dpb				dpb'				dpq'			
		$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹	$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹	$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹
<i>rac</i>	5	4805	0.0864	583	52.73	4622	0.0271	284	8.189	4924	0.0814	463.9	40.02
		5362	0.0347	577	52.29	4898	0.0528	501	28.03	5310	0.0444	721.3	34.06
		5858	0.0108	500	5.752	5420	0.0369	701	27.50	5865	0.0263	1171	32.75
		7306	0.0482	666	34.21	7011	0.1803	970	186.3	7663	0.0551	977.1	57.28
		8394	0.4495	885	423.7	8698	0.6554	1042	727.0	8816	0.5339	883.2	501.9
		9028	0.3984	863	366.3	9634	0.1677	925	165.2	9419	0.5366	915.1	522.6
		9710	0.1979	924	194.8	10340	0.0950	755	76.43	10110	0.2709	1117	322.1
		10510	0.0856	878	80.05	11850	0.6338	1440	971.9	11070	0.0549	883.3	51.63
		12030	0.3173	1200	405.2	12670	0.1360	668	98.69	12120	0.0374	867.9	34.57
		13930	0.5335	1660	941.6	13640	1.0955	1169	1361	13530	0.6233	1532	1013
		15480	0.6116	2364	1080	14920	0.8030	1151	642.4	15120	2.0561	1103	1582
	6	4474	0.2256	493	117.8	4510	0.2019	510	109.6	4006	0.0304	258	4.355
		5064	0.1906	625	126.8	5080	0.2133	575	130.7	4550	0.2482	502	132.3
		5660	0.0232	508	12.57	5625	0.0296	516	16.26	4897	0.0458	295	14.54
		6060	0.0149	744	11.82	6141	0.00644	585	4.009	5220	0.2601	477	132.3
		6723	0.00385	619	2.282					5586	0.0395	351	14.82
										5821	0.0318	590	19.96
										6380	0.0239	1825	44.36

^a A number of the Gaussian components are likely to arise due to vibrational progressions due to a more complicated electronic structure than the one already envisioned.

Table S6(c). Parameters obtained from Gaussian deconvolution of the UV/Vis/NIR spectra for *meso*-[Os(pp)₂]₂(μ-BL)]ⁿ⁺ {BL = ppz, 2,3-dpp} in 0.1 M [(*n*-C₄H₉)₄N]PF₆/CH₃CN at -35°C.^a

Diastereoisomer	<i>n</i>	ppz				2,3-dpp			
		$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹	$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹
<i>meso</i>	5	4980	0.0704	552	41.24	4950	0.1292	518	70.44
		5594	0.0484	115	59.10	5417	0.0380	436	17.65
		6938	0.0149	211	33.53	5798	0.0455	1018	49.35
		8336	0.4036	701	301.2	8295	0.5043	669	359.3
		8953	0.1229	601	78.62	8867	0.1390	546	80.91
		9521	0.0794	650	54.93	9275	0.1135	1003	121.2
		11140	0.2985	1562	995.4	11650	0.4598	1550	758.8
		12430	0.1565	1161	193.4	12740	0.1328	1186	167.7
		13950	0.1884	2475	496.3	13690	0.1542	1616	265.4
		15790	0.5263	1487	830.7	16100	0.3309	1943	684.1
		17370	1.5005	1380	1313	18210	1.0158	2031	1654
						21960	3.1770	3767	306.4
	6	4395	0.1312	723	98.98	4320	0.2273	460	110.3
		5095	0.1549	725	120.2	4647	0.0500	282	15.01
		5500	0.0363	853	32.92	5100	0.2449	615	160.2
		6290	0.0107	1073	12.20	5640	0.0331	496	17.52
						5976	0.0130	1200	1657

^a A number of the Gaussian components are likely to arise due to vibrational progressions due to a more complicated electronic structure than the one already envisioned.

Table S6(d). Parameters obtained from Gaussian deconvolution of the UV/Vis/NIR spectra for *rac*-[Os(bpy)₂]₂(μ-BL)]ⁿ⁺ {BL = ppz, 2,3-dpp} in 0.1 M [(*n*-C₄H₉)₄N]PF₆/CH₃CN at -35°C.^a

Diastereoisomer	<i>n</i>	ppz				2,3-dpp			
		$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹	$\nu_{\max}$ ± 10 /cm ⁻¹	(ϵ/ν) ± 0.001 /M ⁻¹	$\Delta\nu_{1/2}$ ± 10 /cm ⁻¹	M_0 /M ⁻¹
<i>rac</i>	5	5060	0.1102	993.5	114.3	4949	0.0857	516	46.54
		5970	0.0344	973.9	35.66	5342	0.0553	725	42.54
		8393	0.2986	910.9	289.5	5915	0.0355	1005	38.05
		9237	0.0700	859.6	64.03	8320	0.4416	705	331.7
		11190	0.5336	1686	957.8	8905	0.1278	582	79.25
		12490	0.1152	1207	148.0	9350	0.0959	918	93.72
		13630	0.0840	2056	183.8	11660	0.4251	1600	724.4
		15620	0.3752	1557	621.9	12780	0.0869	1150	106.5
		17470	1.3313	1829	1741	13630	0.1312	1830	266.8
						15980	0.3034	1780	574.5
						18110	0.9490	2090	1650
						20510	1.2492	2870	306.1
	6	4395	0.1310	716	100.3	4270	0.2581	433	117.6
		5095	0.1535	719	120.2	4626	0.0707	321	24.25
		5500	0.0365	856	34.35	5065	0.2397	600	153.4
		6290	0.0109	1080	12.50	5633	0.0376	467	18.73
						6038	0.0115	1385	16.97

^a A number of the Gaussian components are likely to arise due to vibrational progressions due to a more complicated electronic structure than the one already envisioned.

Table S7. Mid-IR spectral data of the reduced absorption spectra (ϵ/ν vs. ν) for *meso*- $[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-BL})]^{5+}$ {BL = dpb, dpb' and ppz} at +25°C. The parameters for the overall NIR band envelopes are shown in bold type and details of the deconvoluted bands are in normal type.

BL	Diastereoisomer	$\nu_{\text{max}} \pm 10$ /cm ⁻¹	$(\epsilon/\nu)_{\text{max}} \pm 0.001$ /M ⁻¹	$\Delta\nu_{1/2} \pm 10$ /cm ⁻¹	M_0 /M ⁻¹	M_1 /cm ⁻¹
dpb	<i>meso</i>	2150	1.8262	1240	2514	2420
		2090	1.7085	963		
		3000	0.7485	1077		
		4850	0.0693	495		
dpb'	<i>meso</i>	2060	3.699	630	2880	2320
		2015	2.7071	426		
		2320	1.5677	646		
		2936	0.5143	1095		
ppz ^a	<i>meso</i>	2275	2.8906	775	2537	2529
		(i)	2318	2.8185		
			2798	0.6803		
			3080	0.4903		
		(ii)	2234	1.7624		
			2535	1.0830		
			2760	0.8324		

^a Results for two different fits to the mid-IR band are reported.

Table S8. Summary of the energies of the IC transitions obtained by Gaussian deconvolution for $[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-BL})]^{6+}$ complexes.

BL	Diastereoisomer	$\nu_{\text{max}} \pm 10$ /cm ⁻¹	$(\epsilon/\nu)_{\text{max}} \pm 0.001$ /M ⁻¹	$\Delta\nu_{1/2} \pm 10$ /cm ⁻¹	$\Delta\nu_{\text{IC}}^a$ /cm ⁻¹	M_0 /M ⁻¹
dpb	<i>meso</i>	4550	0.2410	428	610	106
		5205	0.2786	512		150
	<i>rac</i>	4550	0.2482	502	595	132
		5220	0.2601	477		132
dpb'	<i>meso</i>	4530	0.2226	426	550	100
		5135	0.1872	547		110
	<i>rac</i>	4470	0.2256	495	575	118
		5065	0.1906	625		127
dpq'	<i>meso</i>	4520	0.2245	505	650	120
		5070	0.2376	573		145
	<i>rac</i>	4505	0.2019	510	670	110
		5080	0.2133	575		130
ppz	<i>meso</i>	4395	0.1312	723	700	98.9
		5095	0.1549	725		120
	<i>rac</i>	4395	0.1310	716	700	100
		5095	0.1535	719		120
2,3-dpp	<i>meso</i>	4320	0.2273	460	780	110
		5100	0.2449	615		160
	<i>rac</i>	4270	0.2581	433	795	117
		5065	0.2397	601		153

^a Difference between the energies of the IC bands.

Table S9. Absorption and electroabsorption properties of the NIR bands for *meso*-
 $[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-BL})]^{5+}$ {BL = dpb, dpq', dpb', ppz} in *n*-butyronitrile glass at 77K and a field
 strength of 4.0 MVcm^{-1} .^a

BL	ν_{max} / cm^{-1}	$\Delta\nu_{1/2}$ / cm^{-1}	$ \Delta\mu_{12} $ / $\text{e}\text{\AA}$	$ \Delta\mu_{12} $ /D	$\text{Tr}(\Delta\alpha)$ / $\text{\AA}^3$	$\Delta\alpha$ / $\text{\AA}^3$
dpb	7485 ^b	833	~ 0	~ 0	957	831
	8930	1358	~ 0	~ 0	572	-221
	10030	1698	~ 0	~ 0	336	130
	12290	1152	0.11(3)	0.50(5)	-84.8	-214
dpb'	6820 ^b	659	0.23(4)	1.12(2)	-380	-408
	8470	656	0.54(1)	2.57(3)	-305	-343
	11590	980	~ 0	~ 0	-215	770
	12615	816	0.63(3)	3.01(5)	-325	-770
dpq'	7650 ^b	814	0.51(5)	2.45(7)	256	-876
	9105	1187	1.3(4)	6.39(3)	-1860	360
	9860	882	0.38(4)	1.83(4)	-370	385
	10550	905	~ 0	~ 0	-264	-50.7
ppz	8280 ^b	439	~ 0	~ 0	-26.3	-76.0
	8620 ^b	338	$4.9(2) \times 10^{-2}$	0.23(7)	102	256
	8900 ^b	576	~ 0	~ 0	-32.9	-5.49

^a The errors in the observed and calculated parameters (not tabulated) are $\pm 10 \text{ cm}^{-1}$ for ν_{max} and $\Delta\nu_{1/2}$ and $\pm 10 \text{ \AA}^3$ for $\text{Tr}(\Delta\alpha)$ and $\Delta\alpha$. ξ was $0 \pm 2^\circ$ in all cases.

^b Absorption bands definitively assigned as IVCT transitions.

Figure S1. Chem 3D representations of *meso*-($\Lambda\Lambda$)- and *rac*-($\Delta\Delta$)- $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-2,3-dpp})]^{4+}$. Hydrogen atoms are omitted for clarity.

$[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-2,3-dpp})](\text{PF}_6)_4$. A suspension of 2,3-dpp (18 mg, 0.0769 mmol) in ethylene glycol (1.5 cm³) was heated in a modified microwave oven (Sharp, Model R-2V55; 600W, 2450 MHz) on medium high power for 20 s to complete dissolution. *cis*- $[\text{Ru}(\text{bpy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ (100 mg, 0.192 mmol) was added and the mixture heated at reflux for a further 5 min on high power during which time the solution attained a dark purple coloration. The crude mixture was diluted with distilled water (50 cm³) and loaded onto a column of SP Sephadex C-25 (dimensions 25 × 3 cm). Separation of the desired dinuclear product from the mixture was achieved via gradient elution procedure with aqueous NaCl solution as the eluent. A band of mononuclear material eluted first (0.2 M NaCl) followed by the desired dark purple product (0.4 M NaCl) which was precipitated as the PF₆⁻ salt by addition of a saturated solution of aqueous KPF₆. The solid was isolated by vacuum filtration and washed with diethyl ether (3 × 10 cm³). Yield: 122 mg (97%). *Anal.* Calcd for C₅₄H₄₂F₂₄N₁₂P₄Ru₂: C, 39.5; H, 2.58; N, 10.2%. Found: C, 39.3; H, 2.22; N, 9.98%.

Separation of the diastereoisomers was achieved using an SP Sephadex C-25 support with aqueous 0.25 M sodium toluene-4-sulfonate solution as the eluent. Rigorous purification methods were employed prior to structural elucidation (via elemental and/or NMR analyses) and physical characterization due to the potentially strong associations between the complex cations and the anions present in the eluents used for the chromatographic separations. The impure complex was dissolved in a minimum volume of acetone and loaded onto a short column of silica gel (200-400 mesh; equilibrated with AR acetone, *ca.* 3 cm in length × 1.5 cm in diameter), washed alternately with copious amounts of water and acetone, and then eluted with AR acetone containing 5% NH₄PF₆. Following the addition of an equal volume of water, and removal of the acetone under reduced pressure, the precipitate was isolated by vacuum filtration, washed with chilled water and diethyl ether and dried *in vacuo*.

Bands 1 and 2 were determined to be the *meso* and *rac* diastereoisomers, respectively, as established by NMR characterization. ^1H NMR (δ ppm; CD_3CN): (**Band 1**; *meso*) 7.41 (2H, $J = 8$ Hz, d), 7.48 (2H, $J = 8$, 5 Hz, dd), 7.50-7.60 (6H, m), 7.85-7.95 (8H, m), 8.07 (2H, $J = 8$, 8 Hz, dd), 8.12 (2H, $J = 8$, 8 Hz, dd), 8.15 (2H, $J = 8$, 8 Hz, dd), 8.20 (2H, $J = 8$, 8 Hz, dd), 8.07 (H7/12 2,3-dpp, 2H, m), 8.38-8.46 (8H, m), 8.59 (4H, $J = 8$, 1.5 Hz, dd), 8.50 (H9/10 2,3-dpp, 2H, $J = 8$, 1.5 Hz, dd); (**Band 2**; *rac*) 7.26 (2H, $J = 8$ Hz, d), 7.38-7.42 (6H, m), 7.48 (4H, $J = 5$ Hz, d), 7.55-7.65 (6H, m), 7.67 (2H, $J = 8$ Hz, dd), 7.78 (2H, m), 7.92 (2H, $J = 8$, 5 Hz, dd), 7.91 (2H, $J = 8$, 5 Hz, dd), 8.07 (2H, $J = 8$, 8 Hz, dd), 8.15 (2H, $J = 8$, 8 Hz, dd), 8.22 (2H, $J = 8$, 8 Hz, dd), 8.43 (2H, $J = 8$ Hz, d), 8.50 (2H, $J = 8$ Hz, d), 8.54 (2H, $J = 8$ Hz, d), 8.59 (2H, $J = 8$ Hz, d), 8.76 (2H, $J = 8$ Hz, d).

Figure S2. Chem 3D representations of *meso*-($\Lambda\Lambda$)- and *rac*-($\Delta\Delta$)- $[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-dpb})]^{4+}$. Hydrogen atoms are omitted for clarity.

$[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-dpb})](\text{PF}_6)_4$. A suspension of dpb (25 mg, 0.0747 mmol) in ethylene glycol (1.5 cm^3) was heated in a modified microwave oven on medium high power for 20 s to complete dissolution. *cis*- $[\text{Os}(\text{bpy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ (94.3 mg, 0.155 mmol) was added and the mixture heated at reflux for a further 5 min on high power during which time the solution attained a dark green colouration. The crude mixture was diluted with distilled water (50 cm^3) and loaded onto a column of SP Sephadex C-25 (dimensions 25 $\times$ 3 cm). Separation of the desired dinuclear product from the mixture was achieved via gradient elution procedure with aqueous NaCl solution as the eluent. A purple band of mononuclear material eluted first (0.2 M NaCl) followed by the desired dark green product (0.4 M NaCl) which was precipitated as the PF_6^- salt by addition of a saturated solution of aqueous KPF_6 . The solid was isolated by vacuum filtration and washed with diethyl ether (3 $\times$ 10 cm^3). Yield: 131 mg (92%). *Anal.* Calcd for $\text{C}_{62}\text{H}_{46}\text{F}_{24}\text{N}_{12}\text{P}_4\text{Os}_2$: C, 38.8; H, 2.42; N, 8.75%.

Found: C, 38.6; H, 2.41; N, 8.67%. Further characterisation was performed following diastereoisomer separation.

Separation of the diastereoisomers was achieved using an SP Sephadex C-25 support with aqueous 0.25 M sodium tosylate solution as the eluent and purification was achieved as described above for $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-}2,3\text{-dpp})]^{4+}$. Bands 1 and 2 were determined to be the *meso* and *rac* diastereoisomers, respectively, as established by X-ray crystallography and NMR characterisation. ^1H NMR (δ ppm; CD_3CN): (**Band 1**; *meso*) 6.41 (H6d, 1H, $J = 5$ Hz, d), 6.94 (H6b, 1H, $J = 5$, 1.5 Hz, dd), 7.09 (H5d, 1H, $J = 8$, 5 Hz, dd), 7.14 (H5d', 1H, $J = 8$, 5 Hz, dd), 7.23 (H5c, 1H, $J = 8$, 5 Hz, dd), 7.33 (H5b, 2H, $J = 8$, 5 Hz, dd), 7.43-7.61 (13H, m), 7.69-8.07 (14H, m), 8.13 (2H, $J = 8$, 8 Hz, dd), 8.28 (1H, $J = 8$ Hz, d), 8.30 (1H, $J = 8$ Hz, d), 8.33 (1H, $J = 8$ Hz, d), 8.36 (1H, $J = 8$ Hz, d), 8.49 (1H, $J = 8$ Hz, d), 8.58 (1H, $J = 8$ Hz, d), 8.60 (1H, $J = 8$ Hz, d), 8.75 (1H, $J = 8$ Hz, d), 8.83 (1H, $J = 8$ Hz, d), 8.90 (1H, $J = 8$ Hz, d); (**Band 2**; *rac*) 6.98 (H5b, 2H, $J = 8$, 5 Hz, dd), 7.21 (H5d, 2H, $J = 8$, 5 Hz, dd), 7.32 (H3/6 dpb, 2H, $J = 10$, 8 Hz, dd), 7.47 (H5c, 2H, $J = 8$, 5 Hz, dd), 7.49 (H6b, 2H, $J = 5$, 1.5 Hz, dd), 7.55 (H6d, 2H, $J = 5$, 1.5 Hz, dd), 7.56 (H4/5 dpb, 2H, $J = 10$, 8 Hz, dd), 7.58 (H6c, 2H, $J = 5$, 1.5 Hz, dd), 7.64 (H5a, 2H, $J = 8$, 5 Hz, dd), 7.76 (H2/7 dpb, 2H, s), 7.87 (H4d, 2H, $J = 8$, 8 Hz, dd), 7.84-7.91 (10H, m), 7.96 (H4b, 2H, $J = 8$, 8 Hz, dd), 8.08 (H4c, 2H, $J = 8$, 8 Hz, dd), 8.29 (H10/17 dpb, 2H, $J = 8$ Hz, d), 8.33 (H13/14 dpb, 2H, $J = 8$ Hz, d), 8.68 (H3b, 2H, $J = 8$ Hz, d), 7.77 (H3c, H3d, 4H, $J = 8$ Hz, d).

Figure S3. Chem 3D representations of *meso*-($\Lambda\Lambda$)- and *rac*-($\Delta\Delta$)- $[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-dpb}')]^{4+}$.

Hydrogen atoms are omitted for clarity.

$[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-dpb}')](\text{PF}_6)_4$. The synthesis, diastereoisomeric separation and purification were performed via a similar procedure to that described above for $[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-dpb})](\text{PF}_6)_4$ involving the reaction of *cis*- $[\text{Os}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ (114 mg, 0.187 mmol) with dpb' (30 mg, 0.0903 mmol). The dinuclear species was isolated as an olive green solid. Yield: 147 mg (85%). *Anal.* Calcd for

$C_{62}H_{44}F_{24}N_{12}P_4Os_2$: C, 38.8; H, 2.31; N, 8.77%. Found: C, 38.5; H, 2.46; N, 8.53%. 1H NMR (δ ppm; CD_3CN): (**Band 1**; *meso*) 6.71 (H6d, 2H, $J = 5$ Hz, d), 7.12 (H5d, 2H, $J = 8, 5$ Hz, dd), 7.17 (H5b, 2H, $J = 8, 5$ Hz, dd), 7.29 (H3/6 dpb', 2H), 7.49 (H5c, 2H, $J = 8, 5$ Hz, dd), 7.55 (H2/7 dpb', 2H), 7.57 (H4/5 dpb', 2H, s), 7.58 (H6c, 2H, $J = 5$ Hz, d), 7.63 (H4d, 2H, $J = 8, 8$ Hz, dd), 7.66 (H5a, 2H, $J = 8, 5$ Hz, dd), 7.76 (H11/14 dpb', 2H, $J = 10, 9$ Hz, dd), 7.91 (H4c, 2H, $J = 8, 8$ Hz, dd), 7.94 (H6a, 2H, $J = 5$ Hz, d), 7.98 (H6b, 2H, $J = 5$ Hz, d), 8.03 (H4b, 2H, $J = 8, 8$ Hz, dd), 8.05 (H10/15 dpb', 2H), 8.06 (H3d, H10/15 dpb', 4H), 8.08 (H4a, 2H, $J = 8, 8$ Hz, dd), 8.26 (H3c, 2H, $J = 8$ Hz, d), 8.69 (H3b, 2H, $J = 8$ Hz, d), 8.78 (H3a, 2H, $J = 8$ Hz, d), 9.06 (H12/13 dpb', 2H, $J = 8, 1.5$ Hz, d); (**Band 2**; *rac*) 6.93 (H5b, 2H, $J = 8, 5$ Hz, dd), 7.12 (H3/6 dpb', 2H), 7.09 (H6d, 2H, $J = 5, 1.5$ Hz, dd), 7.20 (H5d, 2H, $J = 8, 5$ Hz, dd), 7.36 (H6b, 2H, $J = 5, 1.5$ Hz, dd), 7.51 (H2/7 dpb', 2H), 7.54 (H6a, 2H, $J = 5, 1.5$ Hz, dd), 7.55 (H5a, 2H, $J = 8, 5$ Hz, dd), 7.56 (H5c, 2H, $J = 8, 5$ Hz, dd), 7.70 (H4/5 dpb', 2H, s), 7.76 (H6c, 2H, $J = 5, 1.5$ Hz, dd), 7.79 (H11/14 dpb', 2H, $J = 10, 9$ Hz, dd), 7.89 (H4b, 2H, $J = 8, 8$ Hz, dd), 7.93 (H4d, 2H, $J = 8, 8$ Hz, dd), 8.04 (H4a, 2H, $J = 8, 8$ Hz, dd), 8.06 (H4c, 2H, $J = 8, 8$ Hz, dd), 8.05 (H10/15 dpb', 2H, $J = 8, 1.5$ Hz, dd), 8.45 (H3b, 2H, $J = 8$ Hz, d), 8.54 (H3d, 2H, $J = 8$ Hz, d), 8.59 (H3a, 2H, $J = 8$ Hz, d), 8.67 (H3c, 2H, $J = 8$ Hz, d), 9.02 (H12/13 dpb', 2H, $J = 8, 1.5$ Hz, d).

Figure S4. Chem 3D representations of *meso*-($\Lambda\Lambda$)- and *rac*-($\Delta\Delta$)- $[Os(bpy)_2]_2(\mu-dpq')^{4+}$. Hydrogen atoms are omitted for clarity.

$[Os(bpy)_2]_2(\mu-dpq')(PF_6)_4$. The synthesis and purification were performed under similar conditions to those described above for $[Os(bpy)_2]_2(\mu-dpb)(PF_6)_4$ involving the reaction of *cis*- $[Os(bpy)_2Cl_2] \cdot 2H_2O$ (100 mg, 0.164 mmol) with dpq' (22.3 mg, 0.0791 mmol). The dinuclear species was isolated as a dark green solid. Yield: 145 mg (98%). *Anal.* Calcd for $C_{58}H_{42}F_{24}N_{12}P_4Os_2$: C, 37.3; H, 2.27; N, 9.00%. Found: C, 37.0; H, 2.15; N, 8.87%. 1H NMR (δ ppm; CD_3CN): (**Band 1**; *meso*) 6.68 (H6d, 2H, $J = 5$ Hz, d), 7.10 (H5d, 2H, $J = 8, 5$ Hz, dd), 7.21 (H5b, 2H, $J = 8, 5$ Hz, dd), 7.45 (H5c, 2H, $J = 8, 5$ Hz, dd), 7.47 (H5a, 2H, $J = 8, 5$ Hz, dd), 7.46 (H2/5 dpq', 2H), 7.54 (H6c, 2H, $J = 5$ Hz, d), 7.50 (H6a, 2H, $J = 5$ Hz, d), 7.50 (H3/4 dpq', 2H), 7.65 (H4d, 2H, $J = 8, 8$ Hz, dd), 7.77 (H6b, 2H, $J = 5$ Hz, d), 7.81 (H9/12 dpq', 2H), 7.85 (H4a, 2H,

$J = 8, 8 \text{ Hz, dd}$), 7.99-8.05 (H4b, H8/13 dpq', 4H, m), 8.05 (H4c, 2H, $J = 8, 8 \text{ Hz, dd}$), 8.09 (H3d, 2H, $J = 8 \text{ Hz, d}$), 8.27 (H3a, 2H, $J = 8 \text{ Hz, d}$), 8.66 (H3b, 2H, $J = 8 \text{ Hz, d}$), 8.73 (H3c, 2H, $J = 8 \text{ Hz, d}$), 9.12 (H10/11 dpq', 2H, $J = 8 \text{ Hz, d}$); (**Band 2; rac**) 6.95 (H5b, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.15 (H5d, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.20 (H6d, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 7.22 (H3/4 dpq', 2H), 7.28 (H6b, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 7.35 (H2/5 dpq', 2H), 7.43 (H5a, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.47 (H6c, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 7.51 (H5c, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.63 (H6a, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 7.83 (H9/12 dpq', 2H, $J = 10, 8 \text{ Hz, dd}$), 7.88 (H4b, 2H, $J = 8, 8 \text{ Hz, dd}$), 7.93 (H4a, 2H, $J = 8, 8 \text{ Hz, dd}$), 7.96 (H4d, 2H, $J = 8, 8 \text{ Hz, dd}$), 8.03 (H4c, 2H, $J = 8, 8 \text{ Hz, dd}$), 8.09 (H8/13 dpq', 2H, $J = 6 \text{ Hz, dd}$), 8.48 (H3d, 2H, $J = 8 \text{ Hz, d}$), 8.51 (H3b, 2H, $J = 8 \text{ Hz, d}$), 8.54 (H3a, 2H, $J = 8 \text{ Hz, d}$), 8.60 (H3c, 2H, $J = 8 \text{ Hz, d}$), 9.06 (H10/11 dpq', 2H, $J = 8 \text{ Hz, d}$).

Figure S5. Chem 3D representations of *meso*-($\Lambda\Lambda$)- and *rac*-($\Delta\Delta$)-[$\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-ppz})\}^{4+}$. Hydrogen atoms are omitted for clarity.

[$\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-ppz})\](PF_6)_4$. The synthesis and purification were performed under similar conditions to those described above for [$\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-dpb})\](PF₆)₄ involving the reaction of *cis*-[Os(bpy)₂Cl₂].2H₂O (54.3 mg, 0.0947 mmol) with ppz (10 mg, 0.0431 mmol). The dinuclear species was isolated as a turquoise solid. Yield: 60 mg (77%). *Anal.* Calcd for C₅₄H₄₀F₂₄N₁₆P₄Os₂: C, 34.6; H, 2.15; N, 12.0%. Found: C, 34.4; H, 2.28; N, 11.8%. ¹H NMR (δ ppm; CD₃CN): (**Band 1; meso**) 7.18 (H5d, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.32 (H5b, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.37 (H5c, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.44 (H6d, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 7.46 (H5a, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.60 (H6a, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 7.65 (H6c, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 7.71 (H2/3 ppz, 2H, s), 7.75 (H6b, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 7.85 (H4d, 2H, $J = 8, 8 \text{ Hz, dd}$), 7.88 (H4c, 2H, $J = 8, 8 \text{ Hz, dd}$), 7.90 (H7/10 ppz, 2H, $J = 10, 8 \text{ Hz, dd}$), 7.90 (H4b, 2H, $J = 8, 8 \text{ Hz, dd}$), 7.97 (H4a, 2H, $J = 8, 8 \text{ Hz, dd}$), 8.16 (H6/11 ppz, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 8.38 (H3d, 2H, $J = 8, 1.5 \text{ Hz, dd}$), 8.42 (H3c, 2H, $J = 8, 1.5 \text{ Hz, dd}$), 8.49 (H3b, 2H, $J = 8, 1.5 \text{ Hz, dd}$), 8.57 (H3a, 2H, $J = 8, 1.5 \text{ Hz, dd}$), 9.09 (H8/9 ppz, 2H, $J = 8, 1.5 \text{ Hz, dd}$); (**Band 2; rac**) 7.00 (H5b, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.29 (H5d, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.30 (H6b, 2H, $J = 5, 1.5 \text{ Hz, dd}$), 7.31 (H5c, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.47 (H5a, 2H, $J = 8, 5 \text{ Hz, dd}$), 7.51 (H6d, 2H, $J =$$

5, 1.5 Hz, dd), 7.53 (H6c, 2H, $J = 5$, 1.5 Hz, dd), 7.64 (H6a, 2H, $J = 5$, 1.5 Hz, dd), 7.74 (H2/3 ppz, 2H, s), 7.83 (H4b, 2H, $J = 8$, 8 Hz, dd), 7.89 (H7/10 ppz, 2H, $J = 10$, 8 Hz, dd), 7.89 (H4c, 2H, $J = 8$, 8 Hz, dd), 7.97 (H4a, 2H, $J = 8$, 8 Hz, dd), 8.01 (H4d, 2H, $J = 8$, 8 Hz, dd), 8.17 (H6/11 ppz, 2H, $J = 5$, 1.5 Hz, dd), 8.45 (H3b, 2H, $J = 8$, 1.5 Hz, dd), 8.52 (H3c, 2H, $J = 8$, 1.5 Hz, dd), 8.52 (H3a, 2H, $J = 8$, 1.5 Hz, dd), 8.56 (H3d, 2H, $J = 8$, 1.5 Hz, dd), 9.09 (H8/9 ppz, 2H, $J = 8$, 1.5 Hz, dd).

Figure S6. Chem 3D representations of *meso*-($\Lambda\Lambda$)- and *rac*-($\Delta\Delta$)-[$\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-2,3-dpp})\}^{4+}$. Hydrogen atoms are omitted for clarity.

[$\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-2,3-dpp})\](\text{PF}_6)_4$. The synthesis and purification were performed under similar conditions to those described above for [$\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-dpp})\](PF_6)₄ involving the reaction of *cis*-[Os(bpy)₂Cl₂].2H₂O (94.3 mg, 0.164 mmol) with 2,3-dpp (17.5 mg, 0.0747 mmol). The dinuclear species was isolated as a dark purple solid. Yield: 130 mg (96%). *Anal.* Calcd for C₅₄H₄₂F₂₄N₁₂P₄Os₂: C, 35.7; H, 2.33; N, 9.24%. Found: C, 35.5; H, 2.14; N, 9.20%. ¹H NMR (δ ppm; CD₃CN): (**Band 1; meso**) 7.16 (H5d, 2H, $J = 8$ Hz, d), 7.33 (H5b, 2H, $J = 8$, 5 Hz, dd), 7.40 (H8/11 2,3-dpp, 2H, m), 7.42 (H5c, 2H, $J = 8$, 5 Hz, dd), 7.49 (H6d, 2H, $J = 5$, 1.5 Hz, dd), 7.51 (H5a, 2H, $J = 8$, 5 Hz, dd), 7.69 (H6a, 2H, $J = 5$, 1.5 Hz, dd), 7.72 (H6b, H6c, 4H, $J = 5$, 1.5 Hz, dd), 7.78 (H2/3 2,3-dpp, 2H, s), 7.85 (H4d, 2H, $J = 8$, 8 Hz, dd), 7.95 (H4b, H4c, 4H, $J = 8$, 8 Hz, dd), 7.98 (H7/12 2,3-dpp, 2H, $J = 10$, 8 Hz, dd), 8.00 (H4a, 2H, $J = 8$, 8 Hz, dd), 8.39 (H6/13 2,3-dpp, 2H, m), 8.39 (H3c, H3d, 4H, $J = 8$, 1.5 Hz, dd), 8.56 (H3b, 2H, $J = 8$, 1.5 Hz, dd), 8.58 (H3a, 2H, $J = 8$, 1.5 Hz, dd), 8.74 (H9/10 2,3-dpp, 2H, $J = 8$, 1.5 Hz, dd); (**Band 2; rac**) 6.98 (H5b, 2H, $J = 8$, 5 Hz, dd), 7.30 (H5d, 2H, $J = 8$, 5 Hz, dd), 7.33 (H6b, 2H, $J = 5$, 1.5 Hz, dd), 7.29 (H5c, 2H, $J = 8$, 5 Hz, dd), 7.50 (H8/11 2,3-dpp, 2H, m), 7.48 (H5a, 2H, $J = 8$, 5 Hz, dd), 7.51 (H6d, 2H, $J = 5$, 1.5 Hz, dd), 7.53 (H6c, 2H, $J = 5$, 1.5 Hz, dd), 7.64 (H6a, 2H, $J = 5$, 1.5 Hz, dd), 7.77 (H2/3 2,3-dpp, 2H, s), 7.90 (H4b, 2H, $J = 8$, 8 Hz, dd), 8.40 (H6/13 2,3-dpp, 2H, m), 7.89-7.99 (6H, m), 8.00$

(H7/12 2,3-dpp, 2H, $J = 10, 8$ Hz, dd), 8.30 (H3b, 2H, $J = 8, 1.5$ Hz, dd), 8.35 (H3c, 2H, $J = 8, 1.5$ Hz, dd), 8.53 (H3a, 2H, $J = 8, 1.5$ Hz, dd), 8.56 (H3d, 2H, $J = 8, 1.5$ Hz, dd), 8.70 (H9/10 2,3-dpp, 2H, $J = 8, 1.5$ Hz, dd). The proton numbering scheme was identical to that employed for the dinuclear ruthenium analogue.

Figure S7. ORTEP plot (30% thermal ellipsoids) of the cation of *meso*-[$\{Os(bpy)_2\}_2(\mu\text{-dpb})](ZnCl_4)_2 \cdot 6H_2O$ with atomic numbering.

Figure S8. ORTEP plot (30% thermal ellipsoids) of the cation of *meso*-[$\{Os(bpy)_2\}_2(\mu\text{-dpq}')](PF_6)_4$ with atomic numbering.

Figure S9. (a) Differential mid-IR spectra (CH₃CN) for *meso*-[Os(bpy)₂]₂(μ-BL)]⁵⁺ {BL = dpb, dpb'} obtained by chemical oxidation with NOPF₆, and *meso*-[Os(bpy)₂]₂(μ-ppz)]ⁿ⁺ {n = 5 (—), 6 (—); reference species is the +4 state (—)} obtained by spectroelectrochemical oxidation. (b) UV/Vis/NIR spectra of *meso*-[Os(bpy)₂]₂(μ-BL)]ⁿ⁺ {BL = dpb, dpb', dpq', ppz, 2,3-dpp; n = 4 (—), 5 (—), 6 (—)} in [(*n*-C₄H₉)₄N]PF₆/CH₃CN at -35°C. The insets show the best fits of the bands obtained by Gaussian deconvolution of the spectra. The deconvolutions of the mid-IR band for *meso*-[Os(bpy)₂]₂(μ-ppz)]⁵⁺ were not unique and the two best-fit solutions {(i) and (ii)} are shown.

Figure S10. Overlay of the IVCT bands in CH₃CN for the angular bridging ligands for *meso*- and *rac*- [{Ru(bpy)₂}₂(μ-BL)]⁵⁺ {BL = dpb, dpb' and dpq'} in 0.1 M [(*n*-C₄H₉)₄N]PF₆/CH₃CN at -35°C.

Figure S11. Overlay of the NIR spectra of the +5 (a) and +6 (b) forms of *meso*- and *rac*- $[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-BL})]^{5+}$ {BL = dpb, dpb', dpq', ppz, 2,3-dpp} in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$ at -35°C with the bands obtained by Gaussian deconvolution of the *meso* diastereoisomers of the +6 forms.

Figure S12. Differential mid-IR spectra for *meso*-[$\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-ppz})\}^{n+}$ $\{n = 5 (—), 6 (----)\}$. The reference species is the +4 state. The asterisk denotes the new band at 1625 cm^{-1} .

Figure S13. Liptay analysis of the Stark absorption spectrum (A vs. ν) for *meso*- $[(\text{Os}(\text{bpy})_2)(\mu\text{-dpq}')]^{5+}$ in *n*-butyronitrile glass at 77K, with a field strength of 4.0 MVcm^{-1} . (a) Unperturbed absorption spectrum with the bands obtained by Gaussian deconvolution and energy weighted first (b) and second (c) derivatives of the absorption spectrum. (d) Measured (—) and fitted (—) Stark signals (ΔA vs. ν) at 45° . **(A)** and **(B)** show the fits for two different spectral regions.

Figure S14. Liptay analysis of the Stark absorption spectrum (A vs. ν) for *meso*- $[(\text{Os}(\text{bpy})_2)_2(\mu\text{-dpb}')]^{5+}$ in *n*-butyronitrile glass at 77K, with a field strength of 4.0 MVcm^{-1} . (a) Unperturbed absorption spectrum with the bands obtained by Gaussian deconvolution and energy weighted first (b) and second (c) derivatives of the absorption spectrum. (d) Measured (—) and fitted (—) Stark signals (ΔA vs. ν) at 45° . (A) and (B) show the fits for two different spectral regions.

Figure S15. Liptay analysis of the Stark absorption spectrum (ΔA vs. ν) for *meso*- $[(\text{Os}(\text{bpy})_2)_2(\mu\text{-ppz})]^{5+}$ in *n*-butyronitrile glass at 77K (and 45°), with a field strength of 4.0 MVcm^{-1} . The result for the fit using a single set of Liptay parameters over the entire spectral region is shown as open circles, against the measured Stark signal (black line).