

**Manuscript - IC051699I (revised)**

**Multi-site Effects on Intervalence Charge Transfer  
in a “Cluster-like” Trinuclear Assembly  
containing Ruthenium and Osmium**

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**SUPPLEMENTARY INFORMATION**

**Table S1.** Crystal data and structure refinement parameters for  $\Lambda\Delta/\Delta\Lambda$ -  
 $[\{\text{Ru}(\text{bpy})_2\}(\text{HAT})\{\text{Os}(\text{bpy})_2\}](\text{PF}_6)_3\text{Cl}$ .

Crystal Colour	green / purple dichroic
Crystal Dimensions	0.5 x 0.1 x 0.1 mm
Crystal Habit	Plates
Crystal System	monoclinic
space group	P2 <sub>1</sub> /n
<i>a</i> (Å)	10.061(5)
<i>b</i> (Å)	17.521(5)
<i>c</i> (Å)	38.001(19)
$\alpha$ (°)	90
$\beta$ (°)	90.431 (10)
$\gamma$ (°)	90
V (Å <sup>3</sup> )	6685(6)
Z	4
Mol.Wt.	1620.6
T (K)	293
$\lambda$ (MoK $\alpha$ , Å)	0.71069
range <i>h</i>	12< <i>h</i> <12
range <i>k</i>	0< <i>k</i> <21
range <i>l</i>	0< <i>l</i> <47
range $2\theta$ (°)	2.16< $2\theta$ <53.1
No. reflections	14283
No. reflections > $4\sigma$	3195
No. Parameters	820
S	0.818
R <sub>all</sub>	0.3497
R <sub>2σ</sub>	0.117
wR (all)	0.377
wR (2σ)	0.306

Table S2. Fractional Atomic Coordinates for  $\Lambda\Delta/\Delta\Lambda$ -[{Ru(bpy)<sub>2</sub>}(HAT){Os(bpy)<sub>2</sub>}](PF<sub>6</sub>)<sub>3</sub>Cl.

Atom	x	y	z	Uiso
C(1)	0.183(2)	0.595(1)	0.153(1)	0.076
C(10)	0.062(2)	0.401(1)	0.137(1)	0.066
C(11)	-0.071(2)	0.277(1)	0.144(1)	0.079
C(12)	-0.0783(19)	0.3304(10)	0.1691(5)	0.054
C(13)	0.270(2)	0.435(1)	0.215(1)	0.091
C(14)	0.362(2)	0.387(1)	0.235(1)	0.091
C(15)	0.325(3)	0.349(2)	0.263(1)	0.133
C(16)	0.195(3)	0.355(1)	0.273(1)	0.089
C(17)	0.106(2)	0.399(1)	0.254(1)	0.073
C(18)	-0.040(2)	0.407(1)	0.262(1)	0.068
C(19)	-0.100(2)	0.376(1)	0.292(1)	0.084
C(2)	0.261(3)	0.603(2)	0.120(1)	0.093
C(20)	-0.227(3)	0.388(1)	0.297(1)	0.090
C(21)	-0.302(2)	0.431(1)	0.275(1)	0.093
C(22)	-0.240(2)	0.455(1)	0.244(1)	0.073
C(23)	0.082(2)	0.607(1)	0.252(1)	0.088
C(24)	0.058(2)	0.667(1)	0.274(1)	0.083
C(25)	-0.042(3)	0.715(2)	0.270(1)	0.107
C(26)	-0.130(2)	0.696(1)	0.243(1)	0.100
C(27)	-0.109(2)	0.635(1)	0.221(1)	0.082
C(28)	-0.197(2)	0.617(1)	0.191(1)	0.073
C(29)	-0.304(3)	0.662(2)	0.177(1)	0.117
C(3)	0.219(2)	0.486(2)	0.102(1)	0.079
C(30)	-0.373(2)	0.637(2)	0.151(1)	0.130
C(31)	-0.341(3)	0.573(2)	0.134(1)	0.110
C(32)	-0.235(2)	0.528(1)	0.147(1)	0.091
C(33)	-0.194(3)	0.318(2)	0.046(1)	0.106
C(34)	-0.275(3)	0.354(2)	0.022(1)	0.124
C(35)	-0.280(4)	0.323(3)	-0.013(1)	0.168
C(36)	-0.195(3)	0.268(2)	-0.021(1)	0.131
C(37)	-0.095(3)	0.225(2)	0.005(1)	0.125
C(38)	-0.005(3)	0.160(2)	0.000(1)	0.107
C(39)	0.007(4)	0.124(2)	-0.030(1)	0.165
C(4)	0.136(2)	0.471(1)	0.131(1)	0.071
C(40)	0.092(5)	0.068(3)	-0.036(1)	0.187
C(41)	0.158(4)	0.054(2)	-0.009(1)	0.159
C(42)	0.144(3)	0.091(2)	0.023(1)	0.119
C(43)	-0.224(2)	0.119(2)	0.081(1)	0.095
C(44)	-0.305(3)	0.063(2)	0.097(1)	0.105
C(45)	-0.249(3)	0.011(2)	0.118(1)	0.100
C(46)	-0.122(3)	0.013(2)	0.129(1)	0.118
C(47)	-0.046(2)	0.073(1)	0.114(1)	0.069
C(48)	0.099(3)	0.088(1)	0.122(1)	0.093
C(49)	0.164(3)	0.038(1)	0.143(1)	0.102
C(5)	0.230(2)	0.423(1)	0.076(1)	0.078
C(50)	0.297(3)	0.053(2)	0.149(1)	0.118
C(51)	0.358(3)	0.113(2)	0.132(1)	0.107
C(52)	0.278(3)	0.159(2)	0.110(1)	0.097
C(6)	0.154(2)	0.357(2)	0.080(1)	0.075
C(7)	0.244(3)	0.304(2)	0.034(1)	0.115
C(8)	0.326(3)	0.367(2)	0.028(1)	0.100
C(9)	0.065(2)	0.349(1)	0.111(1)	0.076
CL(1)	0.522(3)	0.543(2)	0.038(1)	0.514
F(1)	-0.0489(16)	0.2206(9)	0.2409(6)	0.165
F(10)	-0.1585(15)	0.8697(10)	0.3855(4)	0.129
F(11)	-0.1034(15)	0.8626(9)	0.3287(4)	0.121
F(12)	0.0829(17)	0.7978(11)	0.3454(5)	0.167

F(13)	0.474(2)	0.364(1)	0.333(0)	0.192
F(14)	0.320(3)	0.268(2)	0.342(1)	0.284
F(15)	0.591(3)	0.323(2)	0.379(1)	0.295
F(16)	0.406(4)	0.249(1)	0.391(1)	0.284
F(17)	0.497(3)	0.245(2)	0.336(1)	0.262
F(18)	0.389(4)	0.367(2)	0.386(1)	0.379
F(2)	0.1053(17)	0.0709(10)	0.2235(5)	0.154
F(3)	0.1207(18)	0.1589(12)	0.2632(5)	0.160
F(4)	-0.0707(16)	0.1016(8)	0.2561(4)	0.122
F(5)	0.119(2)	0.192(1)	0.206(1)	0.180
F(6)	-0.063(2)	0.135(1)	0.201(1)	0.174
F(7)	-0.1077(18)	0.7571(10)	0.3648(6)	0.165
F(8)	0.0329(18)	0.9157(11)	0.3678(6)	0.171
F(9)	0.0312(17)	0.8084(10)	0.4025(4)	0.137
N(1)	0.1146(17)	0.5261(9)	0.1562(5)	0.065
N(10)	-0.1612(16)	0.5522(9)	0.1753(5)	0.070
N(11)	-0.1101(17)	0.2592(13)	0.0381(5)	0.082
N(12)	0.063(2)	0.144(1)	0.029(1)	0.109
N(13)	-0.1013(18)	0.1253(11)	0.0897(5)	0.078
N(14)	0.1557(18)	0.1432(10)	0.1047(5)	0.076
N(2)	0.2851(17)	0.5488(12)	0.0959(5)	0.072
N(3)	0.1628(18)	0.2926(12)	0.0602(5)	0.084
N(4)	0.3106(19)	0.4293(12)	0.0490(5)	0.085
N(5)	-0.0014(16)	0.2800(10)	0.1131(4)	0.065
N(6)	-0.0136(15)	0.3967(8)	0.1654(4)	0.050
N(7)	0.1400(16)	0.4380(9)	0.2233(5)	0.069
N(8)	-0.1094(16)	0.4492(9)	0.2380(4)	0.063
N(9)	-0.0067(15)	0.5922(7)	0.2243(4)	0.051
OS(1_)	0.0300(10)	0.2078(6)	0.0726(2)	0.087
OS(2_)	-0.0059(6)	0.4870(2)	0.1965(2)	0.067
P(1)	0.0258(8)	0.1460(5)	0.2318(3)	0.105
P(2)	-0.0351(7)	0.8353(5)	0.3662(2)	0.090
P(3)	0.4487(13)	0.3031(7)	0.3609(3)	0.144
RU(1_)	0.0292(15)	0.2082(8)	0.0730(4)	0.055(5)
RU(2_)	-0.0045(12)	0.5008(5)	0.1964(3)	0.044(2)

Table S3. Fractional Hydrogen Positions for  $\Lambda\Delta/\Delta\Lambda$ -[ $\{\text{Ru}(\text{bpy})_2\}$ (HAT) $\{\text{Os}(\text{bpy})_2\}$ ](PF<sub>6</sub>)<sub>3</sub>Cl.

Atom	x	y	z	U <sub>iso</sub>
H(1)	0.17987	0.63317	0.16995	0.092
H(11)	-0.11851	0.23222	0.14796	0.095
H(12)	-0.12852	0.32145	0.18918	0.065
H(13)	0.30059	0.46242	0.19551	0.109
H(14)	0.44995	0.38421	0.22808	0.109
H(15)	0.38506	0.31917	0.27596	0.160
H(16)	0.16542	0.32963	0.29284	0.107
H(19)	-0.05055	0.34734	0.30799	0.101
H(2)	0.29747	0.65133	0.11581	0.111
H(20)	-0.26723	0.36706	0.31714	0.107
H(21)	-0.38960	0.44304	0.27991	0.111
H(22)	-0.29327	0.47649	0.22621	0.088
H(23)	0.15625	0.57622	0.25602	0.105
H(24)	0.11467	0.67448	0.29354	0.100
H(25)	-0.05255	0.75837	0.28313	0.129
H(26)	-0.20734	0.72454	0.24021	0.119
H(29)	-0.32358	0.70881	0.18725	0.141
H(30)	-0.44860	0.66404	0.14417	0.156
H(31)	-0.38765	0.55871	0.11368	0.132
H(32)	-0.21542	0.48138	0.13675	0.110
H(33)	-0.19594	0.33530	0.06915	0.127
H(34)	-0.32459	0.39698	0.02795	0.148
H(35)	-0.34162	0.34155	-0.02917	0.202
H(36)	-0.19327	0.25298	-0.04474	0.157
H(39)	-0.04921	0.13932	-0.04808	0.198
H(40)	0.10058	0.04277	-0.05774	0.224
H(41)	0.22276	0.01608	-0.01057	0.190
H(42)	0.19737	0.07502	0.04133	0.143
H(43)	-0.26012	0.15179	0.06438	0.114
H(44)	-0.39664	0.06169	0.09207	0.125
H(45)	-0.30102	-0.02998	0.12522	0.120
H(46)	-0.08640	-0.02123	0.14533	0.142
H(49)	0.12235	-0.00433	0.15241	0.122
H(50)	0.34584	0.02243	0.16400	0.141
H(51)	0.44830	0.12289	0.13466	0.128
H(52)	0.31529	0.20206	0.10011	0.116
H(7)	0.24717	0.26552	0.01655	0.138
H(8)	0.39036	0.36693	0.01079	0.120

Table S4. Anisotropic Thermal Parameters for  $\Lambda\Delta/\Delta\Lambda$ -[{Ru(bpy)<sub>2</sub>}(HAT){Os(bpy)<sub>2</sub>}](PF<sub>6</sub>)<sub>3</sub>Cl.

Atom	U11	U22	U33	U12	U13	U23
C(1)	0.06(1)	0.03(1)	0.13(2)	-0.02(1)	0.02(1)	0.00(1)
C(10)	0.08(2)	0.05(1)	0.07(1)	0.01(1)	0.03(1)	0.00(1)
C(11)	0.09(2)	0.09(2)	0.06(1)	-0.02(1)	0.03(1)	-0.02(1)
C(12)	0.06(1)	0.04(1)	0.06(1)	0.00(1)	0.02(1)	0.00(1)
C(13)	0.06(1)	0.13(2)	0.08(2)	0.01(1)	0.00(1)	0.02(1)
C(14)	0.06(1)	0.11(2)	0.10(2)	0.02(1)	-0.01(1)	0.00(1)
C(15)	0.12(2)	0.17(3)	0.10(2)	0.11(2)	0.03(2)	0.04(2)
C(16)	0.11(2)	0.08(2)	0.07(1)	0.04(1)	0.02(1)	0.00(1)
C(17)	0.07(1)	0.08(2)	0.07(1)	0.02(1)	0.00(1)	-0.01(1)
C(18)	0.08(1)	0.05(1)	0.08(1)	0.01(1)	0.01(1)	0.00(1)
C(19)	0.08(1)	0.10(2)	0.08(1)	-0.01(1)	-0.01(1)	0.03(1)
C(2)	0.08(2)	0.07(2)	0.13(2)	-0.02(2)	-0.03(2)	0.03(2)
C(20)	0.11(2)	0.08(2)	0.08(1)	0.02(1)	0.04(1)	0.00(1)
C(21)	0.06(1)	0.12(2)	0.09(2)	0.01(1)	0.02(1)	0.00(1)
C(22)	0.07(1)	0.04(1)	0.11(2)	0.02(1)	0.03(1)	0.01(1)
C(23)	0.07(1)	0.11(2)	0.08(2)	-0.02(1)	0.00(1)	-0.03(1)
C(24)	0.08(2)	0.09(2)	0.07(1)	-0.03(1)	-0.01(1)	-0.02(1)
C(25)	0.10(2)	0.10(2)	0.12(2)	-0.01(1)	0.00(2)	-0.01(2)
C(26)	0.07(2)	0.11(2)	0.13(2)	0.02(1)	0.01(1)	-0.04(1)
C(27)	0.05(1)	0.08(2)	0.11(2)	0.00(1)	0.04(1)	-0.01(1)
C(28)	0.06(1)	0.06(1)	0.10(2)	0.00(1)	0.01(1)	-0.01(1)
C(29)	0.06(2)	0.10(2)	0.19(3)	0.02(1)	-0.01(2)	-0.03(2)
C(3)	0.07(1)	0.12(2)	0.05(1)	-0.01(1)	0.03(1)	0.02(1)
C(30)	0.03(1)	0.13(2)	0.23(4)	0.03(1)	-0.03(2)	-0.02(2)
C(31)	0.11(2)	0.11(2)	0.12(2)	0.00(1)	-0.02(2)	0.02(1)
C(32)	0.08(2)	0.08(2)	0.11(2)	0.00(1)	-0.01(1)	-0.02(1)
C(33)	0.07(2)	0.15(2)	0.10(2)	0.01(1)	0.01(1)	0.01(2)
C(34)	0.12(2)	0.11(2)	0.14(2)	0.03(2)	0.00(2)	0.03(2)
C(35)	0.11(3)	0.28(5)	0.11(2)	0.04(2)	0.00(2)	0.03(2)
C(36)	0.12(3)	0.19(3)	0.08(2)	-0.03(2)	-0.01(2)	-0.01(2)
C(37)	0.10(2)	0.18(3)	0.09(2)	0.00(2)	0.02(2)	0.00(2)
C(38)	0.14(2)	0.12(2)	0.07(1)	-0.05(1)	0.03(1)	-0.04(1)
C(39)	0.18(4)	0.22(4)	0.09(2)	-0.01(2)	0.02(2)	-0.09(2)
C(4)	0.06(1)	0.10(2)	0.06(1)	0.01(1)	-0.01(1)	0.02(1)
C(40)	0.22(5)	0.21(4)	0.13(3)	0.00(3)	0.03(3)	-0.10(3)
C(41)	0.16(3)	0.19(3)	0.13(2)	-0.01(2)	0.06(2)	-0.08(3)
C(42)	0.11(2)	0.13(2)	0.12(2)	-0.02(1)	0.05(1)	-0.07(2)
C(43)	0.07(1)	0.12(2)	0.10(2)	0.00(1)	0.01(1)	-0.03(1)
C(44)	0.06(1)	0.13(2)	0.13(2)	-0.01(1)	0.02(1)	-0.03(2)
C(45)	0.09(1)	0.10(2)	0.12(2)	-0.02(1)	0.02(1)	-0.04(1)
C(46)	0.09(2)	0.15(2)	0.11(2)	-0.03(2)	0.00(2)	0.03(2)
C(47)	0.08(1)	0.09(1)	0.05(1)	-0.01(1)	0.01(1)	-0.04(1)
C(48)	0.08(2)	0.08(2)	0.11(2)	0.01(1)	0.03(1)	0.01(1)
C(49)	0.09(2)	0.06(2)	0.15(3)	0.00(1)	-0.01(2)	0.00(1)
C(5)	0.08(2)	0.09(2)	0.06(1)	0.01(1)	0.01(1)	0.04(1)
C(50)	0.09(2)	0.11(2)	0.16(3)	0.00(2)	0.00(2)	-0.01(2)
C(51)	0.07(2)	0.12(2)	0.14(3)	0.00(1)	0.02(1)	-0.03(2)
C(52)	0.08(1)	0.10(2)	0.11(2)	-0.02(1)	0.00(1)	-0.04(1)
C(6)	0.07(1)	0.11(2)	0.05(1)	-0.02(1)	0.03(1)	-0.02(1)
C(7)	0.10(2)	0.12(2)	0.13(2)	-0.04(2)	0.05(2)	0.02(2)
C(8)	0.09(2)	0.15(3)	0.06(2)	0.00(2)	0.02(1)	-0.01(2)
C(9)	0.08(2)	0.09(2)	0.06(2)	-0.02(1)	0.03(1)	0.01(1)
CL(1)	0.48(4)	0.59(5)	0.47(4)	-0.23(3)	0.03(3)	0.17(4)
F(1)	0.10(1)	0.11(1)	0.28(2)	0.02(1)	0.06(1)	-0.01(1)
F(10)	0.12(1)	0.17(2)	0.10(1)	0.06(1)	0.05(1)	0.00(1)

F(11)	0.11(1)	0.12(1)	0.13(1)	0.01(1)	0.00(1)	0.01(1)
F(12)	0.12(1)	0.20(2)	0.18(2)	0.08(1)	0.07(1)	0.01(1)
F(13)	0.23(2)	0.24(2)	0.11(1)	-0.10(2)	-0.01(1)	0.03(2)
F(14)	0.23(3)	0.31(4)	0.31(4)	-0.06(3)	-0.16(3)	0.02(3)
F(15)	0.23(3)	0.32(4)	0.33(4)	-0.08(3)	-0.09(3)	0.05(3)
F(16)	0.53(5)	0.17(2)	0.15(2)	-0.17(3)	-0.12(3)	0.04(2)
F(17)	0.29(4)	0.24(3)	0.26(3)	0.06(3)	0.08(3)	-0.13(3)
F(18)	0.40(5)	0.22(3)	0.53(6)	0.19(3)	0.28(5)	0.16(4)
F(2)	0.14(1)	0.13(1)	0.19(2)	0.07(1)	0.03(1)	0.03(1)
F(3)	0.13(1)	0.20(2)	0.15(2)	-0.01(1)	-0.04(1)	-0.03(1)
F(4)	0.14(1)	0.09(1)	0.13(1)	-0.02(1)	0.05(1)	0.00(1)
F(5)	0.16(2)	0.19(2)	0.19(2)	0.00(1)	0.09(1)	0.07(2)
F(6)	0.15(2)	0.19(2)	0.18(2)	0.00(2)	-0.05(2)	0.00(2)
F(7)	0.15(2)	0.11(1)	0.24(2)	-0.06(1)	-0.02(1)	0.01(1)
F(8)	0.14(2)	0.15(2)	0.23(2)	-0.05(1)	-0.07(1)	0.00(1)
F(9)	0.15(1)	0.16(1)	0.10(1)	0.03(1)	0.00(1)	-0.02(1)
N(1)	0.07(1)	0.04(1)	0.08(1)	0.01(1)	-0.01(1)	0.02(1)
N(10)	0.06(1)	0.06(1)	0.09(1)	-0.01(1)	0.01(1)	-0.02(1)
N(11)	0.05(1)	0.13(2)	0.07(1)	-0.01(1)	0.01(1)	0.03(1)
N(12)	0.11(2)	0.14(2)	0.08(1)	-0.01(1)	0.04(1)	-0.04(1)
N(13)	0.06(1)	0.09(1)	0.08(1)	0.00(1)	0.04(1)	-0.02(1)
N(14)	0.06(1)	0.06(1)	0.11(1)	0.00(1)	0.03(1)	-0.02(1)
N(2)	0.05(1)	0.07(1)	0.10(1)	-0.01(1)	0.00(1)	0.03(1)
N(3)	0.07(1)	0.12(2)	0.06(1)	-0.01(1)	0.04(1)	-0.01(1)
N(4)	0.08(1)	0.11(2)	0.06(1)	-0.04(1)	0.01(1)	0.01(1)
N(5)	0.07(1)	0.08(1)	0.05(1)	0.00(1)	0.02(1)	-0.01(1)
N(6)	0.05(1)	0.04(1)	0.05(1)	-0.01(1)	0.01(1)	0.00(1)
N(7)	0.057(9)	0.057(11)	0.094(12)	0.010(9)	0.003(9)	0.000(9)
N(8)	0.058(9)	0.063(11)	0.069(10)	0.016(9)	0.012(8)	0.014(8)
N(9)	0.050(9)	0.023(7)	0.080(10)	-0.024(6)	-0.005(8)	-0.007(7)
OS(1_)	0.082(4)	0.101(5)	0.077(4)	-0.021(1)	0.036(2)	-0.033(2)
OS(2_)	0.060(2)	0.056(2)	0.083(2)	-0.004(2)	0.014(1)	-0.007(2)
P(1)	0.081(5)	0.107(6)	0.128(7)	-0.003(5)	0.024(6)	-0.014(6)
P(2)	0.075(5)	0.110(6)	0.086(5)	0.013(5)	0.009(4)	-0.002(5)
P(3)	0.17(1)	0.16(1)	0.10(1)	-0.01(1)	0.04(1)	0.00(1)

Table S5. Bond Lengths ( $\text{\AA}$ ) for  $\Lambda\Delta/\Delta\Lambda$ -[ $\{\text{Ru}(\text{bpy})_2\}\text{(HAT)}\{\text{Os}(\text{bpy})_2\}\text{](PF}_6\text{)}_3\text{Cl}$ .

Bond	Length ( $\text{\AA}$ )	Bond	Length ( $\text{\AA}$ )
OS(2)-RU(2)	0.242(10)	OS(2)-N(6)	1.976(16)
OS(2)-N(7)	1.974(18)	OS(2)-N(8)	2.009(17)
RU(1)-OS(1)	0.019(18)	RU(1)-N(14)	2.08(3)
RU(1)-N(5)	2.00(3)	RU(1)-N(3)	2.06(3)
RU(1)-N(13)	2.06(3)	RU(1)-N(12)	2.06(3)
RU(2)-N(9)	1.920(17)	RU(2)-N(7)	2.08(2)
RU(2)-N(10)	1.98(2)	RU(2)-N(1)	2.00(3)
OS(1)-N(5)	2.019(19)	OS(1)-N(12)	2.04(3)
P(3)-F(13)	1.52(3)	P(3)-F(14)	1.61(4)
P(3)-F(16)	1.57(3)	P(3)-F(18)	1.59(4)
P(3)-F(15)	1.61(4)	P(3)-F(17)	1.48(4)
F(6)-P(1)	1.48(3)	C(36)-H(36)	0.93(4)
C(36)-C(35)	1.34(6)	C(41)-H(41)	0.93(5)
C(41)-C(40)	1.25(6)	C(41)-C(42)	1.38(5)
C(38)-C(37)	1.46(5)	C(38)-C(39)	1.30(5)
C(38)-N(12)	1.31(4)	C(37)-N(11)	1.40(4)
C(40)-H(40)	0.93(5)	C(40)-C(39)	1.33(7)
C(42)-H(42)	0.93(3)	C(42)-N(12)	1.25(4)
C(35)-H(35)	0.93(4)	C(35)-C(34)	1.42(6)
C(39)-H(39)	0.93(4)	C(33)-H(33)	0.93(3)
C(33)-C(34)	1.37(5)	C(33)-N(11)	1.37(4)
C(34)-H(34)	0.93(4)	P(2)-F(12)	1.57(2)
P(2)-F(10)	1.567(17)	P(2)-F(11)	1.646(17)
P(2)-F(9)	1.598(18)	P(2)-F(8)	1.57(3)
P(2)-F(7)	1.553(19)	N(14)-C(48)	1.31(4)
N(14)-C(52)	1.28(4)	N(9)-C(23)	1.41(3)
N(9)-C(27)	1.28(3)	N(6)-C(12)	1.34(3)
N(6)-C(10)	1.32(3)	N(7)-C(17)	1.41(3)
N(7)-C(13)	1.35(3)	C(22)-H(22)	0.93(3)
C(22)-N(8)	1.34(3)	C(22)-C(21)	1.41(4)
N(10)-C(28)	1.33(3)	N(10)-C(32)	1.36(4)
N(8)-C(18)	1.35(3)	N(5)-C(9)	1.39(3)
N(5)-C(11)	1.37(3)	N(1)-C(1)	1.40(3)
N(1)-C(4)	1.37(3)	C(3)-N(2)	1.30(4)
C(3)-C(5)	1.51(4)	C(3)-C(4)	1.42(4)
C(17)-C(18)	1.51(4)	C(17)-C(16)	1.36(4)
N(4)-C(5)	1.31(3)	N(4)-C(8)	1.35(4)
N(3)-C(6)	1.37(4)	N(3)-C(7)	1.32(4)
C(12)-H(12)	0.93(2)	C(12)-C(11)	1.34(3)
N(13)-C(47)	1.40(3)	N(13)-C(43)	1.28(4)
N(2)-C(2)	1.35(4)	C(5)-C(6)	1.39(4)
C(47)-C(48)	1.51(4)	C(47)-C(46)	1.42(4)
C(31)-H(31)	0.93(3)	C(31)-C(32)	1.42(4)
C(31)-C(30)	1.34(5)	C(21)-H(21)	0.93(3)
C(21)-C(20)	1.35(4)	C(23)-H(23)	0.93(3)
C(23)-C(24)	1.36(4)	C(18)-C(19)	1.41(4)
C(29)-H(29)	0.93(3)	C(29)-C(28)	1.42(4)
C(29)-C(30)	1.28(5)	C(28)-C(27)	1.47(4)
C(14)-H(14)	0.93(3)	C(14)-C(15)	1.32(4)
C(14)-C(13)	1.46(4)	C(15)-H(15)	0.93(4)
C(15)-C(16)	1.37(4)	C(6)-C(9)	1.47(4)
C(8)-H(8)	0.93(3)	C(8)-C(7)	1.40(5)
C(24)-H(24)	0.93(3)	C(24)-C(25)	1.32(4)
C(27)-C(26)	1.38(4)	C(9)-C(10)	1.36(4)
C(11)-H(11)	0.93(3)	C(10)-C(4)	1.44(4)
C(19)-H(19)	0.93(3)	C(19)-C(20)	1.31(4)
C(48)-C(49)	1.34(4)	C(50)-H(50)	0.93(4)

C(50)-C(49)	1.37(4)	C(50)-C(51)	1.38(5)
C(13)-H(13)	0.93(3)	C(49)-H(49)	0.93(3)
C(46)-H(46)	0.93(3)	C(46)-C(45)	1.34(5)
C(1)-H(1)	0.93(3)	C(1)-C(2)	1.48(4)
C(7)-H(7)	0.93(3)	C(44)-H(44)	0.93(3)
C(44)-C(45)	1.34(4)	C(44)-C(43)	1.41(4)
C(45)-H(45)	0.93(3)	C(20)-H(20)	0.93(3)
C(52)-H(52)	0.93(3)	C(52)-C(51)	1.39(4)
C(16)-H(16)	0.93(3)	C(2)-H(2)	0.93(3)
C(43)-H(43)	0.93(3)	C(51)-H(51)	0.93(3)
C(25)-H(25)	0.93(3)	C(25)-C(26)	1.38(4)
C(26)-H(26)	0.93(3)	C(32)-H(32)	0.93(3)
C(30)-H(30)	0.93(3)	P(1)-F(1)	1.547(19)
P(1)-F(4)	1.552(18)	P(1)-F(3)	1.54(3)
P(1)-F(2)	1.57(2)	P(1)-F(5)	1.59(3)

Table S6. Bond Angles ( $^{\circ}$ ) for  $\Lambda\Delta/\Delta\Lambda$ -[ $\{\text{Ru}(\text{bpy})_2\}(\text{HAT})\{\text{Os}(\text{bpy})_2\}\](PF<sub>6</sub>)<sub>3</sub>Cl.$

Bonds	Bond Angle ( $^{\circ}$ )	Bonds	Bond Angle ( $^{\circ}$ )
RU(2)-OS(2)-N(6)	142.7(29)	RU(2)-OS(2)-N(7)	113.5(31)
RU(2)-OS(2)-N(8)	111.4(30)	N(6)-OS(2)-N(7)	89.2(7)
N(6)-OS(2)-N(8)	100.9(7)	N(7)-OS(2)-N(8)	80.6(8)
OS(1)-RU(1)-N(14)	89.5(520)	OS(1)-RU(1)-N(5)	157.5(533)
OS(1)-RU(1)-N(3)	77.5(525)	OS(1)-RU(1)-N(13)	105.9(526)
OS(1)-RU(1)-N(12)	18.7(531)	N(14)-RU(1)-N(5)	90.0(9)
N(14)-RU(1)-N(3)	97.7(10)	N(14)-RU(1)-N(13)	79.8(9)
N(14)-RU(1)-N(12)	94.2(11)	N(5)-RU(1)-N(3)	80.3(9)
N(5)-RU(1)-N(13)	96.1(10)	N(5)-RU(1)-N(12)	174.0(12)
N(3)-RU(1)-N(13)	175.6(11)	N(3)-RU(1)-N(12)	94.8(11)
N(13)-RU(1)-N(12)	88.9(11)	OS(2)-RU(2)-N(9)	145.7(31)
OS(2)-RU(2)-N(7)	60.4(29)	OS(2)-RU(2)-N(10)	114.5(32)
OS(2)-RU(2)-N(1)	105.2(30)	N(9)-RU(2)-N(7)	100.4(8)
N(9)-RU(2)-N(10)	80.3(8)	N(9)-RU(2)-N(1)	104.2(8)
N(7)-RU(2)-N(10)	171.4(9)	N(7)-RU(2)-N(1)	94.2(9)
N(10)-RU(2)-N(1)	93.9(9)	RU(1)-OS(1)-N(5)	22.3(528)
RU(1)-OS(1)-N(12)	161.1(535)	N(5)-OS(1)-N(12)	174.2(10)
F(13)-P(3)-F(14)	95.3(16)	F(13)-P(3)-F(16)	171.1(17)
F(13)-P(3)-F(18)	88.8(18)	F(13)-P(3)-F(15)	89.3(17)
F(13)-P(3)-F(17)	88.9(16)	F(14)-P(3)-F(16)	83.0(18)
F(14)-P(3)-F(18)	103.5(20)	F(14)-P(3)-F(15)	169.3(20)
F(14)-P(3)-F(17)	73.2(19)	F(16)-P(3)-F(18)	83.1(18)
F(16)-P(3)-F(15)	93.8(19)	F(16)-P(3)-F(17)	98.9(17)
F(18)-P(3)-F(15)	86.1(20)	F(18)-P(3)-F(17)	175.8(22)
F(15)-P(3)-F(17)	97.4(19)	H(36)-C(36)-C(35)	116.9(34)
H(41)-C(41)-C(40)	117.5(41)	H(41)-C(41)-C(42)	117.5(35)
C(40)-C(41)-C(42)	125.0(40)	C(37)-C(38)-C(39)	123.6(31)
C(37)-C(38)-N(12)	112.1(26)	C(39)-C(38)-N(12)	124.3(32)
C(38)-C(37)-N(11)	121.4(26)	C(41)-C(40)-H(40)	125.4(50)
C(41)-C(40)-C(39)	109.2(40)	H(40)-C(40)-C(39)	125.4(45)
C(41)-C(42)-H(42)	117.4(31)	C(41)-C(42)-N(12)	125.1(30)
H(42)-C(42)-N(12)	117.4(29)	C(36)-C(35)-H(35)	120.7(38)
C(36)-C(35)-C(34)	118.7(33)	H(35)-C(35)-C(34)	120.7(40)
C(38)-C(39)-C(40)	126.0(36)	C(38)-C(39)-H(39)	117.0(39)
C(40)-C(39)-H(39)	117.0(36)	H(33)-C(33)-C(34)	117.8(29)
H(33)-C(33)-N(11)	117.9(26)	C(34)-C(33)-N(11)	124.3(27)
C(35)-C(34)-C(33)	117.4(30)	C(35)-C(34)-H(34)	121.3(33)
C(33)-C(34)-H(34)	121.3(32)	F(12)-P(2)-F(10)	176.6(11)
F(12)-P(2)-F(11)	89.9(10)	F(12)-P(2)-F(9)	90.0(10)
F(12)-P(2)-F(8)	93.8(11)	F(12)-P(2)-F(7)	88.3(11)
F(10)-P(2)-F(11)	88.1(9)	F(10)-P(2)-F(9)	91.9(9)
F(10)-P(2)-F(8)	88.9(11)	F(10)-P(2)-F(7)	89.0(10)
F(11)-P(2)-F(9)	179.8(10)	F(11)-P(2)-F(8)	87.2(10)
F(11)-P(2)-F(7)	92.0(10)	F(9)-P(2)-F(8)	93.0(11)
F(9)-P(2)-F(7)	87.9(11)	F(8)-P(2)-F(7)	177.7(11)
RU(1)-N(14)-C(48)	115.7(17)	RU(1)-N(14)-C(52)	124.3(18)
C(48)-N(14)-C(52)	119.6(23)	RU(2)-N(9)-C(23)	124.2(14)
RU(2)-N(9)-C(27)	116.3(16)	C(23)-N(9)-C(27)	118.4(19)
OS(2)-N(6)-C(12)	130.4(13)	OS(2)-N(6)-C(10)	114.6(13)
C(12)-N(6)-C(10)	114.9(17)	OS(2)-N(7)-RU(2)	6.1(3)
OS(2)-N(7)-C(17)	117.5(14)	OS(2)-N(7)-C(13)	127.4(16)
RU(2)-N(7)-C(17)	119.8(14)	RU(2)-N(7)-C(13)	125.0(16)
C(17)-N(7)-C(13)	115.1(19)	H(22)-C(22)-N(8)	118.2(22)
H(22)-C(22)-C(21)	118.3(22)	N(8)-C(22)-C(21)	123.5(21)
RU(2)-N(10)-C(28)	115.5(15)	RU(2)-N(10)-C(32)	127.0(16)

C(28)-N(10)-C(32)	117.5(19)	OS(2_-)-N(8)-C(22)	128.1(15)
OS(2_-)-N(8)-C(18)	116.0(14)	C(22)-N(8)-C(18)	115.7(18)
RU(1_-)-N(5)-OS(1_-)	0.2(6)	RU(1_-)-N(5)-C(9)	115.1(14)
RU(1_-)-N(5)-C(11)	135.1(16)	OS(1_-)-N(5)-C(9)	114.9(14)
OS(1_-)-N(5)-C(11)	135.3(15)	C(9)-N(5)-C(11)	109.7(18)
RU(2_-)-N(1)-C(1)	124.0(15)	RU(2_-)-N(1)-C(4)	117.8(14)
C(1)-N(1)-C(4)	118.0(19)	N(2)-C(3)-C(5)	117.1(20)
N(2)-C(3)-C(4)	127.6(24)	C(5)-C(3)-C(4)	115.3(23)
N(7)-C(17)-C(18)	110.7(18)	N(7)-C(17)-C(16)	123.2(21)
C(18)-C(17)-C(16)	126.0(21)	C(5)-N(4)-C(8)	117.3(23)
C(37)-N(11)-C(33)	126.1(23)	RU(1_-)-N(3)-C(6)	114.7(15)
RU(1_-)-N(3)-C(7)	134.0(19)	C(6)-N(3)-C(7)	110.5(22)
N(6)-C(12)-H(12)	120.0(18)	N(6)-C(12)-C(11)	120.1(19)
H(12)-C(12)-C(11)	120.0(19)	RU(1_-)-N(13)-C(47)	114.2(15)
RU(1_-)-N(13)-C(43)	126.7(18)	C(47)-N(13)-C(43)	119.0(21)
C(3)-N(2)-C(2)	112.0(21)	C(3)-C(5)-N(4)	120.4(22)
C(3)-C(5)-C(6)	118.7(21)	N(4)-C(5)-C(6)	120.8(23)
N(13)-C(47)-C(48)	113.9(20)	N(13)-C(47)-C(46)	122.5(22)
C(48)-C(47)-C(46)	123.6(22)	H(31)-C(31)-C(32)	120.9(28)
H(31)-C(31)-C(30)	120.9(29)	C(32)-C(31)-C(30)	118.2(27)
C(22)-C(21)-H(21)	121.5(24)	C(22)-C(21)-C(20)	117.0(22)
H(21)-C(21)-C(20)	121.5(25)	N(9)-C(23)-H(23)	120.2(22)
N(9)-C(23)-C(24)	119.5(21)	H(23)-C(23)-C(24)	120.2(23)
N(8)-C(18)-C(17)	115.0(19)	N(8)-C(18)-C(19)	122.2(20)
C(17)-C(18)-C(19)	122.8(20)	H(29)-C(29)-C(28)	120.1(29)
H(29)-C(29)-C(30)	120.1(29)	C(28)-C(29)-C(30)	119.8(27)
N(10)-C(28)-C(29)	121.3(23)	N(10)-C(28)-C(27)	110.8(19)
C(29)-C(28)-C(27)	127.8(22)	H(14)-C(14)-C(15)	118.6(27)
H(14)-C(14)-C(13)	118.6(24)	C(15)-C(14)-C(13)	122.9(24)
C(14)-C(15)-H(15)	121.6(30)	C(14)-C(15)-C(16)	116.8(27)
H(15)-C(15)-C(16)	121.6(29)	N(3)-C(6)-C(5)	125.0(20)
N(3)-C(6)-C(9)	113.5(22)	C(5)-C(6)-C(9)	121.3(22)
N(4)-C(8)-H(8)	120.4(29)	N(4)-C(8)-C(7)	119.2(23)
H(8)-C(8)-C(7)	120.4(30)	C(23)-C(24)-H(24)	118.6(24)
C(23)-C(24)-C(25)	122.7(24)	H(24)-C(24)-C(25)	118.6(25)
N(9)-C(27)-C(28)	116.0(21)	N(9)-C(27)-C(26)	120.9(23)
C(28)-C(27)-C(26)	123.0(21)	N(5)-C(9)-C(6)	115.5(21)
N(5)-C(9)-C(10)	121.8(20)	C(6)-C(9)-C(10)	122.1(22)
N(5)-C(11)-C(12)	127.9(21)	N(5)-C(11)-H(11)	116.1(21)
C(12)-C(11)-H(11)	116.1(21)	N(6)-C(10)-C(9)	125.2(20)
N(6)-C(10)-C(4)	118.3(19)	C(9)-C(10)-C(4)	116.2(21)
C(18)-C(19)-H(19)	120.4(24)	C(18)-C(19)-C(20)	119.1(23)
H(19)-C(19)-C(20)	120.4(25)	N(14)-C(48)-C(47)	116.0(22)
N(14)-C(48)-C(49)	124.4(25)	C(47)-C(48)-C(49)	118.9(23)
H(50)-C(50)-C(49)	119.9(30)	H(50)-C(50)-C(51)	119.9(29)
C(49)-C(50)-C(51)	120.2(28)	N(7)-C(13)-C(14)	120.1(21)
N(7)-C(13)-H(13)	119.9(23)	C(14)-C(13)-H(13)	119.9(23)
C(48)-C(49)-C(50)	116.2(26)	C(48)-C(49)-H(49)	121.9(28)
C(50)-C(49)-H(49)	121.9(28)	RU(1_-)-N(12)-OS(1_-)	0.2
RU(1_-)-N(12)-C(38)	118.3(21)	RU(1_-)-N(12)-C(42)	131.4(21)
OS(1_-)-N(12)-C(38)	118.3(21)	OS(1_-)-N(12)-C(42)	131.3(21)
C(38)-N(12)-C(42)	110.4(26)	C(47)-C(46)-H(46)	123.2(28)
C(47)-C(46)-C(45)	113.7(26)	H(46)-C(46)-C(45)	123.2(30)
N(1)-C(1)-H(1)	122.4(23)	N(1)-C(1)-C(2)	115.1(20)
H(1)-C(1)-C(2)	122.5(21)	N(3)-C(7)-C(8)	126.4(26)
N(3)-C(7)-H(7)	116.8(27)	C(8)-C(7)-H(7)	116.8(27)
H(44)-C(44)-C(45)	120.7(29)	H(44)-C(44)-C(43)	120.7(28)
C(45)-C(44)-C(43)	118.6(25)	C(46)-C(45)-C(44)	124.6(27)
C(46)-C(45)-H(45)	117.7(28)	C(44)-C(45)-H(45)	117.7(28)
C(21)-C(20)-C(19)	121.7(24)	C(21)-C(20)-H(20)	119.2(27)

C(19)-C(20)-H(20)	119.2(26)	N(14)-C(52)-H(52)	119.2(26)
N(14)-C(52)-C(51)	121.6(25)	H(52)-C(52)-C(51)	119.2(27)
C(17)-C(16)-C(15)	121.8(24)	C(17)-C(16)-H(16)	119.1(26)
C(15)-C(16)-H(16)	119.1(26)	N(2)-C(2)-C(1)	126.9(23)
N(2)-C(2)-H(2)	116.6(27)	C(1)-C(2)-H(2)	116.5(26)
N(13)-C(43)-C(44)	121.1(24)	N(13)-C(43)-H(43)	119.4(26)
C(44)-C(43)-H(43)	119.5(25)	N(1)-C(4)-C(3)	119.8(22)
N(1)-C(4)-C(10)	114.1(19)	C(3)-C(4)-C(10)	126.0(22)
C(50)-C(51)-C(52)	117.3(26)	C(50)-C(51)-H(51)	121.3(29)
C(52)-C(51)-H(51)	121.4(29)	C(24)-C(25)-H(25)	122.2(29)
C(24)-C(25)-C(26)	115.7(26)	H(25)-C(25)-C(26)	122.2(29)
C(27)-C(26)-C(25)	122.4(24)	C(27)-C(26)-H(26)	118.8(26)
C(25)-C(26)-H(26)	118.8(27)	N(10)-C(32)-C(31)	120.6(23)
N(10)-C(32)-H(32)	119.7(24)	C(31)-C(32)-H(32)	119.7(26)
C(31)-C(30)-C(29)	122.1(28)	C(31)-C(30)-H(30)	118.9(33)
C(29)-C(30)-H(30)	118.9(33)	F(6)-P(1)-F(1)	90.0(13)
F(6)-P(1)-F(4)	91.8(11)	F(6)-P(1)-F(3)	178.3(13)
F(6)-P(1)-F(2)	91.7(12)	F(6)-P(1)-F(5)	85.6(12)
F(1)-P(1)-F(4)	89.2(10)	F(1)-P(1)-F(3)	90.2(12)
F(1)-P(1)-F(2)	178.3(12)	F(1)-P(1)-F(5)	90.1(12)
F(4)-P(1)-F(3)	89.9(11)	F(4)-P(1)-F(2)	91.2(10)
F(4)-P(1)-F(5)	177.3(12)	F(3)-P(1)-F(2)	88.1(11)
F(3)-P(1)-F(5)	92.7(12)	F(2)-P(1)-F(5)	89.6(11)

**Table S7.** Redox potentials for the reductions based on the HAT bridging ligand for the di- and trinuclear complexes in 0.1 M [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]PF<sub>6</sub>/CH<sub>3</sub>CN at +25°C.

Complex	E <sub>red1</sub>	E <sub>red2</sub>	E <sub>red3</sub>
[Os(bpy) <sub>2</sub> (HAT)] <sup>2+</sup>	-1101	-1276	
<i>meso</i> -[{Os(bpy) <sub>2</sub> } <sub>2</sub> (μ-HAT)] <sup>4+</sup>	-844	-1320	
<i>rac</i> -[{Os(bpy) <sub>2</sub> } <sub>2</sub> (μ-HAT)] <sup>4+</sup>	-840	-1325	
ΔΛ/ΛΔ-[{Ru(bpy) <sub>2</sub> }({μ-HAT}){Os(bpy) <sub>2</sub> }] <sup>n+</sup>	-804	-1316	
ΔΔ/ΛΛ-[{Ru(bpy) <sub>2</sub> }({μ-HAT}){Os(bpy) <sub>2</sub> }] <sup>n+</sup>	-805	-1320	
Δ <sub>2</sub> Λ'/Λ <sub>2</sub> Δ'-[{Ru(bpy) <sub>2</sub> } <sub>2</sub> {Os(bpy) <sub>2</sub> }({μ-HAT})] <sup>n+</sup>	-624	-956	-1384

<sup>a</sup> All potentials are quoted ±3 mV *vs.* Fc<sup>+</sup>/Fc<sup>0</sup>.

**Table S8.** Deconvoluted NIR spectral data of the reduced absorption spectra ( $\epsilon/v$  vs.  $v$ ) for the di- and trinuclear complexes at -35 and -15°C, respectively.<sup>a</sup>

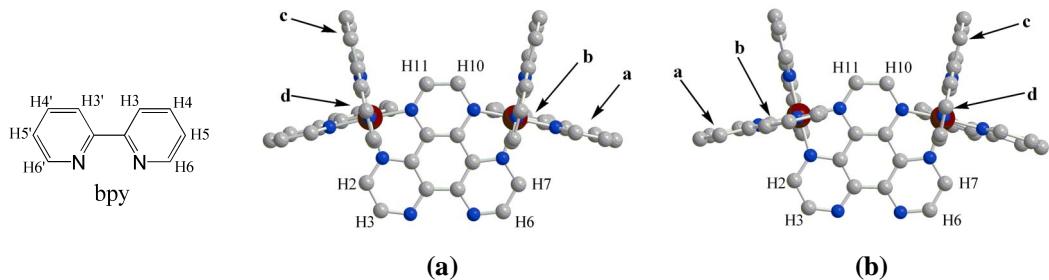
Complex	$v_{\max}$ $\pm 10$ /cm <sup>-1</sup>	$(\epsilon/v)_{\max}$ $\pm 0.0001$ /M <sup>-1</sup>	$\Delta v_{1/2}$ $\pm 10$ /cm <sup>-1</sup>
<i>meso</i> -[{Os(bpy) <sub>2</sub> } <sub>2</sub> (μ-HAT)] <sup>5+</sup>	4980 5420 5770 8200 8780 9325 11110 12470 14285	0.06612 0.02008 0.02298 0.2782 0.07748 0.04413 0.3878 0.1234 0.1241	444 422 1150 663 540 695 1445 1482 1398
<i>rac</i> -[{Os(bpy) <sub>2</sub> } <sub>2</sub> (μ-HAT)] <sup>5+</sup>	5090 5935 8260 9130 11130 12715	0.05752 0.02305 0.2726 0.06784 0.4123 0.1266	932 974 920 848 1654 2030
$\Delta\Lambda/\Lambda\Delta$ -[{Ru(bpy) <sub>2</sub> }(μ-HAT){Os(bpy) <sub>2</sub> }] <sup>5+</sup>	4080 4880 8610 10405 13950	0.4747 0.1107 0.1735 0.02198 0.1145	578 596 2055 2160 1970
$\Delta\Delta/\Lambda\Lambda$ -[{Ru(bpy) <sub>2</sub> }(μ-HAT){Os(bpy) <sub>2</sub> }] <sup>5+</sup>	4060 4880 8695 14060	0.5990 0.1388 0.2125 0.1906	577 591 2060 2857
$\Delta_2\Lambda'/\Lambda_2\Delta'$ -[{Ru(bpy) <sub>2</sub> } <sub>2</sub> {Os(bpy) <sub>2</sub> }](μ-HAT)] <sup>7+</sup>	3975 4620 7670 9480 13080 14650	0.5008 0.1754 0.2193 0.0595 0.07075 0.2518	844 632.8 2597 1695 1345 2197
$\Delta_2\Lambda'/\Lambda_2\Delta'$ -[{Ru(bpy) <sub>2</sub> } <sub>2</sub> {Os(bpy) <sub>2</sub> }](μ-HAT)] <sup>8+</sup>	3530 4040 4470 5530 7765 10550 13110 14890	1.01798 0.20802 0.3064 0.1096 0.1750 0.4488 0.5473 0.2410	414 412 881 1088 2854 2235 2562 1854

<sup>a</sup> Due to the convoluted nature of the NIR spectra, unambiguous determination of the band characteristics for the IC transitions in the +9 species was not possible.

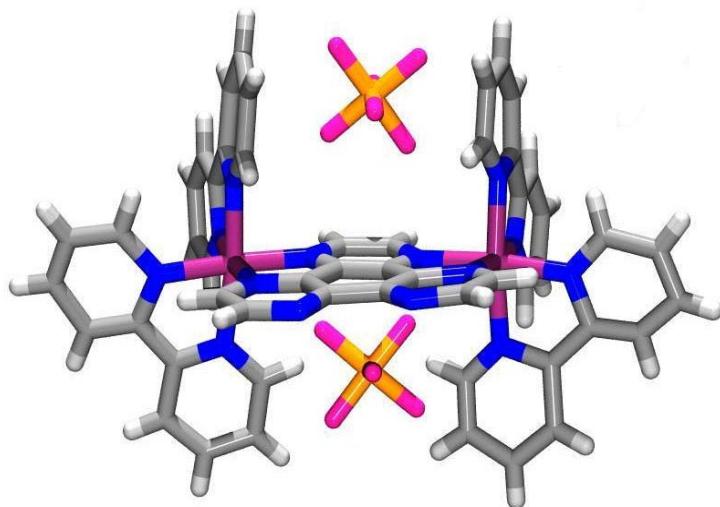
**Table S9.** Deconvoluted NIR spectral data ( $\varepsilon/\nu$  vs.  $\nu$ ) of the fully-oxidized forms of the mono- and dinuclear complexes at -35°C. The parameters for the IC bands are indicated in bold type.<sup>a</sup>

Complex	$\nu_{\text{max}}$ $\pm 10$ /cm <sup>-1</sup>	$(\varepsilon/\nu)_{\text{max}}$ $\pm 0.0001$ /M <sup>-1</sup>	$\Delta\nu_{1/2}$ $\pm 10$ /cm <sup>-1</sup>
$[\text{Os}(\text{bpy})_2(\text{HAT})]^{3+}$	<b>4435</b>	0.06315	485
	<b>5090</b>	0.05405	645
	5735	0.004250	330
	6060	0.003798	1280
	10460	0.02746	1820
	12120	0.004165	908
<i>meso</i> -[ $\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-HAT})]^{6+}$	<b>4320</b>	0.2144	514
	<b>5060</b>	0.1500	746
	5790	0.02133	560
	6645	0.03988	1210
<i>rac</i> -[ $\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-HAT})]^{6+}$	<b>4280</b>	0.2788	396
	4600	0.06351	302
	<b>5030</b>	0.1457	600
	5607	0.01473	503
	6695	0.03058	990
$\Delta\Lambda/\Lambda\Delta$ -[ $\{\text{Ru}(\text{bpy})_2\}(\mu\text{-HAT})\{\text{Os}(\text{bpy})_2\}]^{6+}$	<b>4430</b>	0.2642	697
	5035	0.04626	405
	5335	0.06867	600
	6075	0.01228	1117
	9090	0.04851	1736
$\Delta\Delta/\Lambda\Lambda$ -[ $\{\text{Ru}(\text{bpy})_2\}(\mu\text{-HAT})\{\text{Os}(\text{bpy})_2\}]^{6+}$	<b>3920</b>	0.3529	578
	4720	0.1477	942
	8300	0.1677	2100
	10778	0.2550	2226

<sup>a</sup> Due to the convoluted nature of the NIR spectra, unambiguous determination of the band characteristics for the IC transitions in the +9 species was not possible.



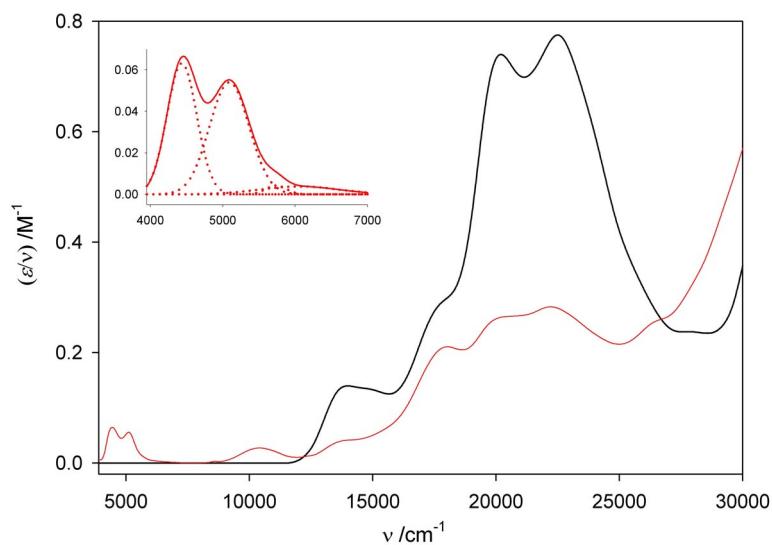
**Figure S1.** Proton numbering schemes for **(a)**  $\Lambda\Delta$ - and **(b)**  $\Delta\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}(\mu\text{-HAT})\{\text{Os}(\text{bpy})_2\}]^{4+}$  ( $\text{M}, \text{M}' = \text{Os}, \text{Os}$  or  $\text{Ru}, \text{Os}$ ) (Hydrogen atoms are omitted for clarity). *Left:* proton numbering scheme for bpy.



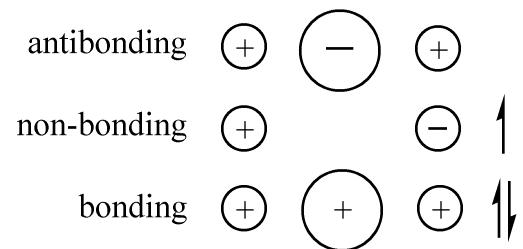
**Figure S2.** The  $\Lambda\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}(\mu\text{-HAT})\{\text{Os}(\text{bpy})_2\}]^{4+}$  cation showing the association of two  $\text{PF}_6^-$  anions within the clefts between the bpy ligands.



**Figure S3.** Schematic illustration of the relative potentials of the metal-based oxidation processes in selected mono-, di- and trinuclear ruthenium and osmium complexes in this study.



**Figure S4.** UV/Vis/NIR spectra of  $[\text{Os(bpy)}_2(\text{HAT})]^{n+}$  { $n = 2$  (—), 3 (—)} at -35°C. The inset shows the interconfigurational (IC) bands for the  $n = 3$  species and the components of the Gaussian deconvolution of the bands (·····).



**Figure S5.** Qualitative molecular orbital diagram for the dinuclear  $\left[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-BL})\right]^{5+}$  systems showing the bonding, non-bonding and antibonding molecular orbitals. The IVCT corresponds to a bonding  $\rightarrow$  non-bonding transition.