Table S1. Crystallographic data for **1[PF$_6$]$_2$**, **1[PF$_6$]$_3$** and **1[PF$_6$]$_4$**

	1[PF$_6$]$_2$·4/3CH$_2$Cl$_2$	**1[PF$_6$]$_3$·2CH$_2$Cl$_2$**	**1[PF$_6$]$_4$·1.29CH$_2$Cl$_2$**
Empirical formula	$C_{93.66}H_{101.32}Cl_{3.32}F_{12}Fe_2N_{10}P_6Ru$	$C_{94}H_{102}Cl_4F_{18}Fe_2N_{10}P_7Ru$	$C_{93.29}H_{100.59}Cl_{2.59}F_{24}Fe_2N_{10}P_8Ru$
Formula weight	2111.36	2285.21	2370.09
Temperature/K	100	293	293
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	P21/c
a/Å	15.191(4)	15.130(3)	24.111(9)
b/Å	28.679(7)	26.916(5)	15.177(5)
c/Å	25.451(6)	26.802(5)	30.586(11)
α/°	90	90	90
β/°	93.291(4)	99.730(4)	99.413(8)
γ/°	90	90	90
Volume/Å^3	11070(5)	10758(4)	11042(7)
Z	4	4	4
ρcalcg/cm^3	1.267	1.411	1.426
μ/mm^{-1}	0.625	0.687	0.66
F(000)	4335.0	4668.0	4825
Crystal size/mm	0.25 × 0.2 × 0.17	0.31 × 0.25 × 0.18	0.31 × 0.24 × 0.18
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.062 to 49.426	4.052 to 54.942	5.368 to 51.362
Index ranges	-17 ≤ h ≤ 15, -33 ≤ k ≤ 33, -29 ≤ l ≤ 29	-19 ≤ h ≤ 18, -34 ≤ k ≤ 30, -34 ≤ l ≤ 34	-29 ≤ h ≤ 29, -18 ≤ k ≤ 12, -37 ≤ l ≤ 37
Reflections collected	69001	108081	73481
Independent reflections	18798 [R_{int} = 0.0779, R_{sigma} = 0.0753]	24535 [R_{int} = 0.0541, R_{sigma} = 0.0502]	20850 [Rint = 0.0635, Rsigma = 0.0641]
Data/restraints/parameters	18798/50/1170	24535/641/1354	20850/664/1424
Goodness-of-fit on F^2	1.027	1.026	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0653, wR_2 = 0.1835	R_1 = 0.0634, wR_2 = 0.1807	R1 = 0.1003, wR2 = 0.2349
Final R indexes [all data]	R_1 = 0.0773, wR_2 = 0.2009	R_1 = 0.0773, wR_2 = 0.1996	R1 = 0.1293, wR2 = 0.2629
Largest diff. peak/hole / e Å^{-3}	1.79/-0.68	1.48/-0.65	1.85/-0.73

Table S2. Crystallographic data for **2[PF$_6$]$_2$**, **2[PF$_6$]$_3$** and **2[PF$_6$]$_4$**

	2[PF$_6$]$_{1.78}$I$_{0.22}$·3CH$_2$Cl$_2$	**2[PF$_6$]$_3$·2CH$_2$Cl$_2$**	**2[PF$_6$]$_4$·2CH$_2$Cl$_2$**
Empirical formula	$C_{97}H_{108}Cl_6F_{10.7}Fe_2I_{0.22}N_{10}P_{5.78}Ru$	$C_{96}H_{106}Cl_4F_{18}Fe_2N_{10}P_7Ru$	$C_{96}H_{106}Cl_4F_{24}Fe_2N_{10}P_8Ru$
Formula weight	2249.53	2313.26	2458.23
Temperature/K	100.00(10)	99.9(4)	100.00(10)
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	P2$_1$/c	P-1
a/Å	15.0345(2)	24.6744(5)	15.3832(3)
b/Å	17.0070(2)	14.7327(3)	16.0057(3)
c/Å	23.0440(3)	30.5899(6)	24.4989(4)
α/°	83.6625(10)	90	79.253(2)
β/°	85.3617(10)	100.151(2)	89.686(2)
γ/°	71.1101(12)	90	88.327(2)
Volume/Å^3	5534.36(13)	10946.0(4)	5923.76(19)
Z	2	4	2
ρcalcg/cm^3	1.350	1.404	1.378
μ/mm^{-1}	4.182	3.790	3.651
F(000)	2305.0	4732.0	2504.0
Crystal size/mm	0.45 × 0.4 × 0.22	0.25 × 0.22 × 0.2	0.43 × 0.38 × 0.23
Radiation	GaKα (λ = 1.3405)	Ga Kα (λ = 1.3405)	GaKα (λ = 1.3405)
2Θ range for data collection/°	4.794 to 120.224	5.104 to 109.644	4.888 to 111.678
Index ranges	-19 ≤ h ≤ 16, -21 ≤ k ≤ 21, -29 ≤ l ≤ 29	-29 ≤ h ≤ 30, -17 ≤ k ≤ 17, -35 ≤ l ≤ 37	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -30 ≤ l ≤ 30
Reflections collected	76066	62777	71749
Independent reflections	24465 [Rint = 0.0366, Rsigma = 0.0355]	20728 [R_{int} = 0.0355, R_{sigma} = 0.0380]	23280 [Rint = 0.1086, Rsigma = 0.0740]
Data/restraints/parameters	24465/21/1218	20728/478/1305	23280/6/1316
Goodness-of-fit on F^2	1.029	1.039	1.069
Final R indexes [I>=2σ (I)]	R1 = 0.0416, wR2 = 0.1049	R_1 = 0.0672, wR_2 = 0.1896	R1 = 0.0780, wR2 = 0.2250
Final R indexes [all data]	R1 = 0.0465, wR2 = 0.1073	R_1 = 0.0807, wR_2 = 0.2000	R1 = 0.0934, wR2 = 0.2384
Largest diff. peak/hole / e Å^{-3}	1.39/-1.43	1.47/-1.20	1.21/-1.01

Table S3. Crystallographic data for **3[PF$_6$]$_2$**, **3[PF$_6$]$_3$** and **3[PF$_6$]$_4$**

	3[PF$_6$]$_2$·4CH$_2$Cl$_2$	**3[PF$_6$]$_3$·3.08CH$_2$Cl$_2$**	**3[PF$_6$]$_4$**
Empirical formula	$C_{102}H_{118}Cl_8F_{12}Fe_2N_{10}P_6Ru$	$C_{101.08}H_{116.16}Cl_{6.16}F_{18}Fe_2N_{10}P_7Ru$	$C_{98}H_{107}F_{24}Fe_2N_{10}P_8Ru$
Formula weight	2394.25	2461.09	2341.46
Temperature/K	99.9(4)	99.9(7)	99.9(9)
Crystal system	monoclinic	monoclinic	triclinic
Space group	P21/n	C2/c	P-1
a/Å	24.0100(6)	50.6195(4)	15.1437(3)
b/Å	17.3426(4)	14.78570(10)	15.1742(4)
c/Å	28.3067(7)	32.3631(3)	29.2932(4)
α/°	90	90	92.346(2)
β/°	100.424(2)	102.6260(10)	103.657(2)
γ/°	90	90	114.623(2)
Volume/Å^3	11592.3(5)	23636.2(3)	5871.9(2)
Z	4	8	2
ρcalcg/cm^3	1.372	1.383	1.324
μ/mm^{-1}	4.080	3.819	3.132
F(000)	4920.0	10083.0	2394.0
Crystal size/mm	0.23 × 0.2 × 0.14	0.26 × 0.2 × 0.17	0.42 × 0.26 × 0.20
Radiation	GaKα (λ = 1.3405)	Ga Kα (λ = 1.3405)	GaKα (λ = 1.3405)
2Θ range for data collection/°	3.866 to 109.646	5.17 to 113.82	5.466 to 96.27
Index ranges	-29 ≤ h ≤ 29, -16 ≤ k ≤ 21, -34 ≤ l ≤ 34	-62 ≤ h ≤ 63, -18 ≤ k ≤ 16, -40 ≤ l ≤ 40	-16 ≤ h ≤ 15, -13 ≤ k ≤ 16, -32 ≤ l ≤ 32
Reflections collected	60297	163979	67861
Independent reflections	21862 [Rint = 0.0641, Rsigma = 0.0626]	24154 [R_{int} = 0.0484, R_{sigma} = 0.0236]	16848 [Rint = 0.0684, Rsigma = 0.0570]
Data/restraints/parameters	21862/0/1386	24154/672/1528	16848/302/1205
Goodness-of-fit on F^2	1.044	1.050	2.263
Final R indexes [I>=2σ (I)]	R1 = 0.0816, wR2 = 0.2036	R_1 = 0.0738, wR_2 = 0.2156	R1 = 0.1641, wR2 = 0.4787
Final R indexes [all data]	R1 = 0.0950, wR2 = 0.2124	R_1 = 0.0787, wR_2 = 0.2200	R1 = 0.1800, wR2 = 0.4982
Largest diff. peak/hole / e Å^{-3}	2.01/-1.20	3.61/-1.11	5.09/-1.53

Table S4. Crystallographic data for **4[PF$_6$]$_2$** and **4[PF$_6$]$_4$**

	4[PF$_6$]$_2$·CH$_2$Cl$_2$	**4[PF$_6$]$_4$**
Empirical formula	$C_{101}H_{116}Cl_2F_{12}Fe_2N_{10}P_6Ru$	$C_{100}H_{114}F_{24}Fe_2N_{10}P_8Ru$
Formula weight	2167.52	2372.54
Temperature/K	99.9(5)	99.9(5)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	13.16908(10)	31.5906(4)
b/Å	53.1540(5)	14.49020(10)
c/Å	14.27640(11)	27.6689(3)
α/°	90	90
β/°	93.4916(7)	109.893(2)
γ/°	90	90
Volume/Å^3	9974.77(15)	11909.8(3)
Z	4	4
ρcalcg/cm^3	1.443	1.323
μ/mm^{-1}	3.667	3.146
F(000)	4480.0	4864.0
Crystal size/mm	0.34 × 0.25 × 0.2	0.23 × 0.2 × 0.15
Radiation	Ga Kα (λ = 1.3405)	GaKα (λ = 1.3405)
2Θ range for data collection/°	5.582 to 113.818	5.172 to 121.63
Index ranges	-16 ≤ h ≤ 15, -64 ≤ k ≤ 66, -17 ≤ l ≤ 17	-40 ≤ h ≤ 41, -14 ≤ k ≤ 18, -35 ≤ l ≤ 35
Reflections collected	81603	96294
Independent reflections	20380 [R_{int} = 0.0367, R_{sigma} = 0.0327]	26750 [R_{int} = 0.0380, R_{sigma} = 0.0363]
Data/restraints/parameters	20380/180/1278	26750/1016/1573
Goodness-of-fit on F^2	1.021	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0336, wR_2 = 0.0780	R_1 = 0.0572, wR_2 = 0.1411
Final R indexes [all data]	R_1 = 0.0381, wR_2 = 0.0799	R_1 = 0.0774, wR_2 = 0.1517
Largest diff. peak/hole / e Å^{-3}	0.61/-0.66	0.84/-0.92

Table S5. Crystallographic data for **5[PF$_6$]$_2$**, **5[PF$_6$]$_3$** and **5[PF$_6$]$_4$**

	5[PF$_6$]$_2$·5CH$_2$Cl$_2$	**5[PF$_6$]$_3$·3.38CH$_2$Cl$_2$·0.62H$_2$O**	**5[PF$_6$]$_4$**
Empirical formula	$C_{107}H_{128}N_{10}F_{12}P_6Cl_{10}Fe_2Ru$	$C_{105.38}H_{124.76}Cl_{6.76}F_{18}Fe_2N_{10}O_{0.62}P_7Ru$	$C_{102}H_{118}F_{24}Fe_2N_{10}P_8Ru$
Formula weight	2535.28	2552.59	2400.59
Temperature/K	100	100	232
Crystal system	monoclinic	monoclinic	monoclinic
Space group	Pc	P2/n	$P2_1/c$
a/Å	12.675(8)	14.3274(5)	13.158(3)
b/Å	14.806(9)	16.9831(7)	31.130(7)
c/Å	31.517(19)	24.1522(8)	31.153(7)
α/°	90	90.0000(10)	90
β/°	96.885(11)	95.981(2)	94.169(5)
γ/°	90	90.0000(10)	90
Volume/Å^3	5872(6)	5844.8(4)	12727(5)
Z	2	2	4
ρcalcg/cm^3	1.434	1.450	1.253
μ/mm^{-1}	0.749	0.555	0.521
F(000)	2608.0	2620.0	4928.0
Crystal size/mm	0.4 × 0.32 × 0.25	0.21 × 0.15 × 0.02	0.32 × 0.26 × 0.22
Radiation	MoKα (λ = 0.71073)	synchrotron (λ = 0.65247)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.182 to 49.996	3.114 to 49.692	4.708 to 49.426
Index ranges	-13 ≤ h ≤ 15, -17 ≤ k ≤ 17, -37 ≤ l ≤ 36	-18 ≤ h ≤ 18, -21 ≤ k ≤ 21, -31 ≤ l ≤ 31	-15 ≤ h ≤ 15, -36 ≤ k ≤ 36, -34 ≤ l ≤ 36
Reflections collected	36579	89968	79976
Independent reflections	16458 [R_{int} = 0.0701, R_{sigma} = 0.1080]	12568 [R_{int} = 0.0863, R_{sigma} = 0.0423]	21556 [R_{int} = 0.0828, R_{sigma} = 0.0801]
Data/restraints/parameters	16458/12/1334	12568/43/707	21556/157/1342
Goodness-of-fit on F^2	0.994	1.044	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0849, wR_2 = 0.1756	R_1 = 0.0701, wR_2 = 0.1793	R_1 = 0.0868, wR_2 = 0.2338
Final R indexes [all data]	R_1 = 0.1001, wR_2 = 0.1897	R_1 = 0.0824, wR_2 = 0.1882	R_1 = 0.1089, wR_2 = 0.2626
Largest diff. peak/hole / e Å^{-3}	1.51/-1.11	1.18/-1.22	1.57/-0.94

Table S6. Selected Bond Lengths for $\mathbf{1}^{n+}$ - $\mathbf{5}^{n+}$ (n = 2, 3) and $\mathbf{3}^{4+}$ - $\mathbf{5}^{4+}$.

	Fe1-P[a]	Fe2-P[a]	Fe1-N1[b]	Fe2-N2[b]	Ru-C1[b]	Ru-C2[b]
1^{2+}	2.1918(13)	2.2055(14)	1.943(4)	1.931(4)	2.045(5)	2.043(4)
1^{3+}	2.2584(10)	2.2048(10)	1.888 (3)	1.924(3)	1.984(3)	2.071(3)
1^{4+}	2.263(2)	2.259(2)	1.876(5)	1.873(5)	1.972(7)	2.022(7)
2^{2+}	2.1957(6)	2.1954(6)	1.924(2)	1.927(2)	2.037(2)	2.037(2)
2^{3+}	2.2476(13)	2.2154(13)	1.890(4)	1.914(4)	1.993(4)	2.058(4)
2^{4+}	2.2723(12)	2.2509(13)	1.900(3)	1.908(3)	2.010(4)	2.025(4)
3^{2+}	2.1968(17)	2.1982(14)	1.945(4)	1.949(4)	2.062(6)	2.063(5)
3^{3+}	2.2624(12)	2.2073(12)	1.913(4)	1.942(4)	2.000(4)	2.067(4)
3^{4+}	2.293(6)	2.269(4)	1.890(11)	1.933(11)	1.986(13)	2.001(12)
4^{2+}	2.2196(6)	2.2242(5)	1.9480(14)	1.9557(17)	2.0463(19)	2.0652(19)
4^{3+}	–	–	–	–	–	–
4^{4+}	2.2817(11)	2.2878(11)	1.918(3)	1.914(3)	2.023(3)	2.018(3)
5^{2+}	2.231(5)	2 .234(4)	1.953(12)	1.946(11)	2.054(14)	2.060(14)
5^{3+}	2.2663(12)	–	1.926(3)	–	2.041(4)	–
5^{4+}	2.3119(16)	2.3224(17)	1.934(4)	1.919(4)	2.037(5)	2.003(5)

[a] average Fe-P bond length.
[b] N1 and N2 are nitrogen atoms of the CN bridges, so as the C1 and C2.

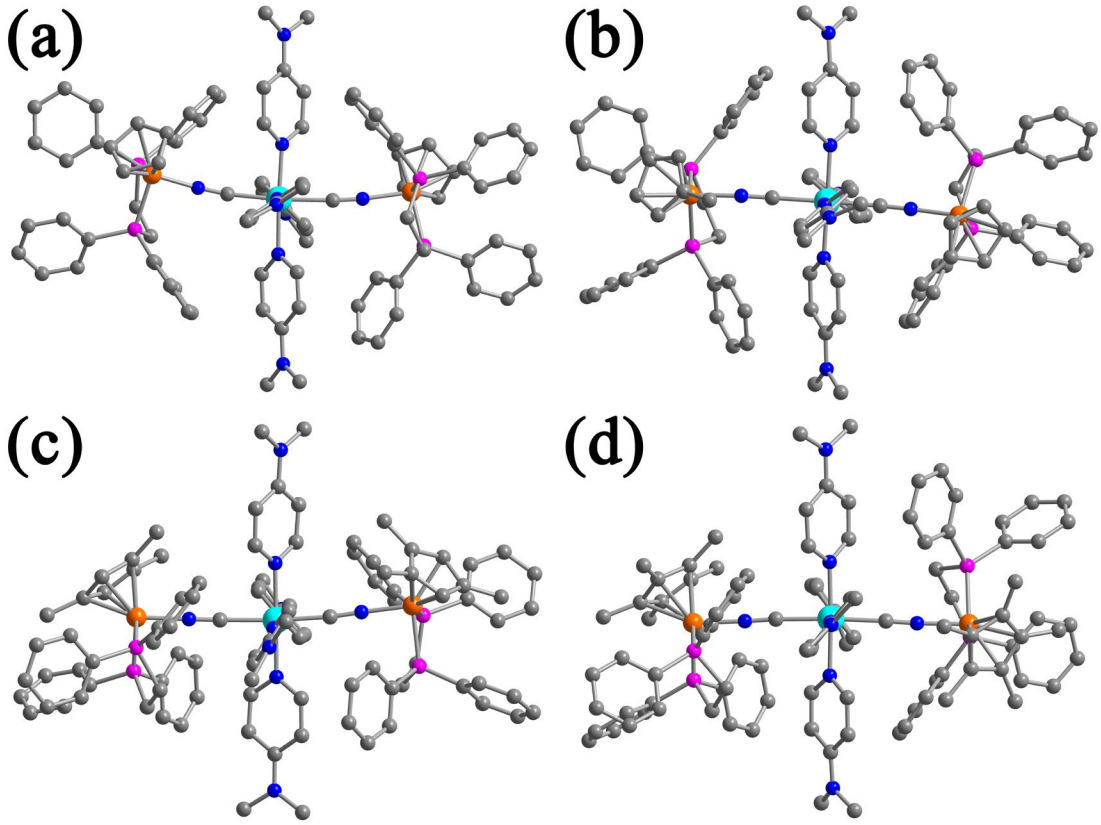

Figure S1. (a), (b), (c), (d) Molecular structure of $\mathbf{1}^{3+}$, $\mathbf{2}^{3+}$, $\mathbf{3}^{3+}$, $\mathbf{5}^{3+}$, respectively. Hydrogen atoms, $[PF_6]^-$ anions, and solvent molecules have been omitted for clarity. Light blue, Ru; orange, Fe; pink, P; gray, C; blue, N.

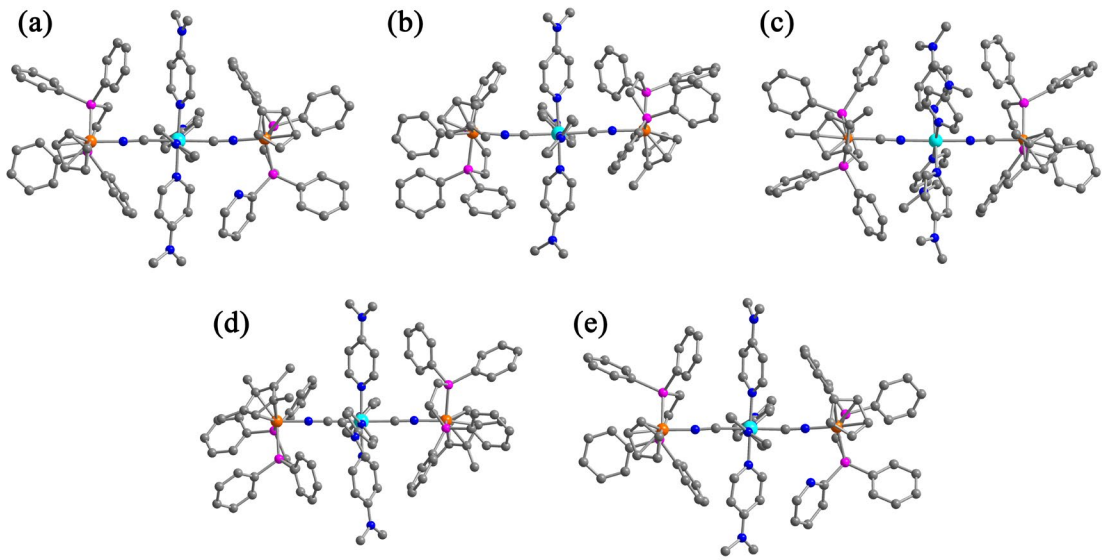

Figure S2. (a), (b), (c), (d), (e) Molecular structure of $\mathbf{1}^{4+}$, $\mathbf{2}^{4+}$, $\mathbf{3}^{4+}$, $\mathbf{4}^{4+}$, $\mathbf{5}^{4+}$, respectively. Hydrogen atoms, $[PF_6]^-$ anions, and solvent molecules have been omitted for clarity. Light blue, Ru; orange, Fe; pink, P; gray, C; blue, N.

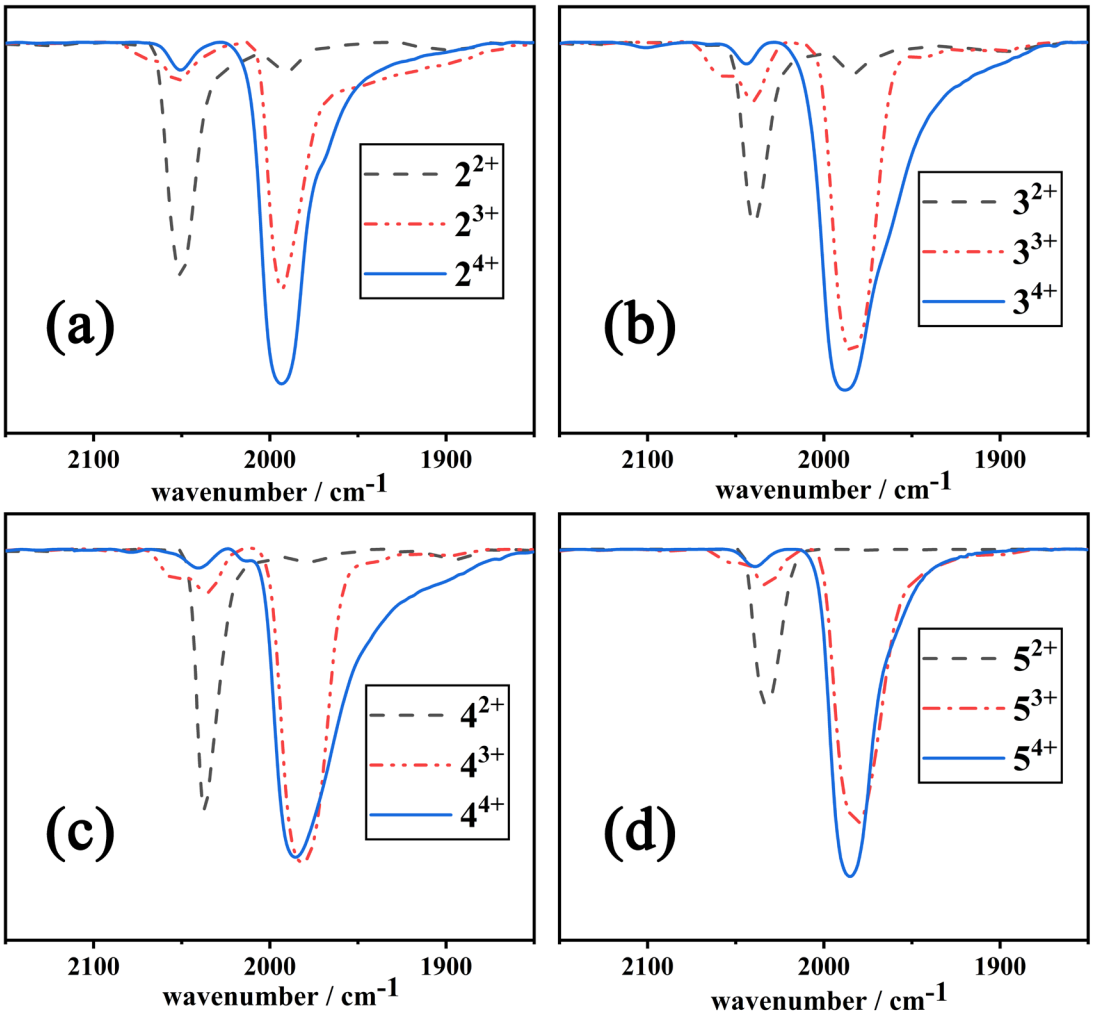

Figure S3. The ν(CN) bands in solid state.

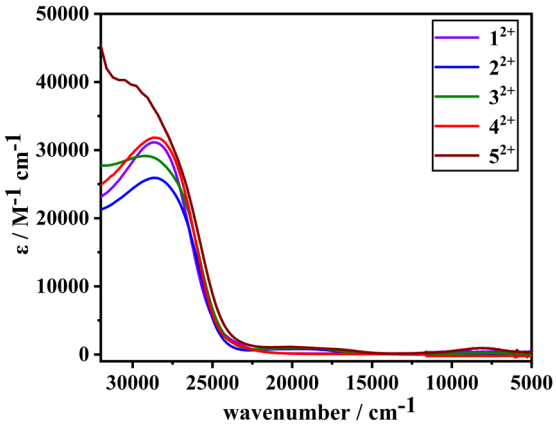

Figure S4. UV/Vis/NIR spectra of the $\mathbf{1}^{2+}$-$\mathbf{5}^{2+}$ in CH_2Cl_2.

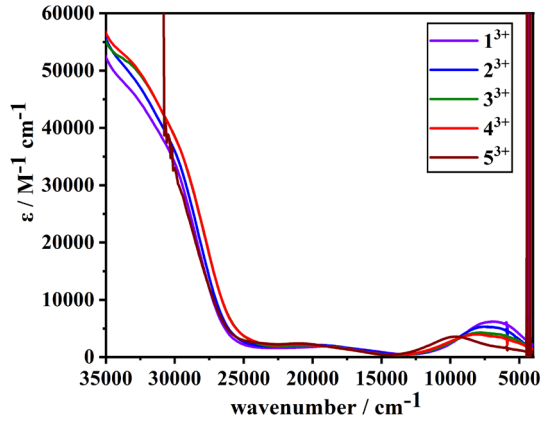

Figure S5. UV/Vis/NIR spectra of the $\mathbf{1}^{3+}$-$\mathbf{5}^{3+}$ in CH_2Cl_2.

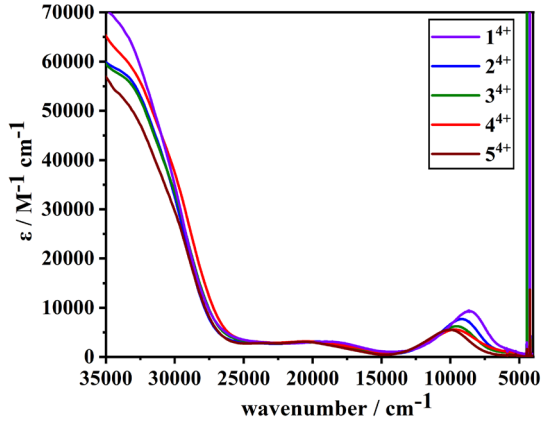

Figure S6. UV/Vis/NIR spectra of the $\mathbf{1}^{4+}$-$\mathbf{5}^{4+}$ in CH_2Cl_2.

Table S7. ^{57}Fe Mössbauer Fitting Parameters for Selected Complexes

	IS (mm.s^{-1})	QS (mm.s^{-1})	Relative Area (%)
$\mathbf{1}^{2+}$	0.39	1.87	100
$\mathbf{1}^{3+}$	0.37	1.87	49.6
	0.32	0.74	50.4
$\mathbf{1}^{4+}$	0.30	0.76	100
$\mathbf{5}^{2+}$	0.37	1.93	100
$\mathbf{5}^{3+}$	0.38	1.95	49.1
	0.37	0.72	50.9
$\mathbf{5}^{4+}$	0.36	0.76	100

Table S8. Mulliken spin densities of **the MV compounds**.

	Ru	Fe1	Fe2
$\mathbf{1}^{3+}$	0.162964	0.946180	0.009151
$\mathbf{2}^{3+}$	0.167755	0.924511	0.028568
$\mathbf{3}^{3+}$	0.080989	1.095698	0.007498
$\mathbf{5}^{3+}$	0.080253	1.127621	0.017721
$\mathbf{1}^{4+}$	0.088287	1.076182	1.095622
$\mathbf{2}^{4+}$	0.058455	1.126289	1.100173
$\mathbf{3}^{4+}$	0.042816	1.194779	1.230900
$\mathbf{4}^{4+}$	0.042165	1.207083	1.160610
$\mathbf{5}^{4+}$	0.038554	1.256374	1.254484

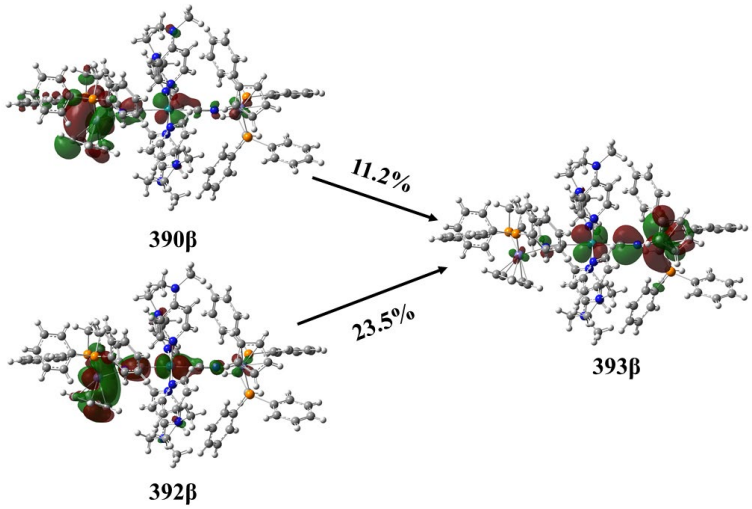

Figure S7. The major electronic transitions corresponding to the NIR band (λ = 1475 nm, f = 0.0945) of $\mathbf{1}^{3+}$.

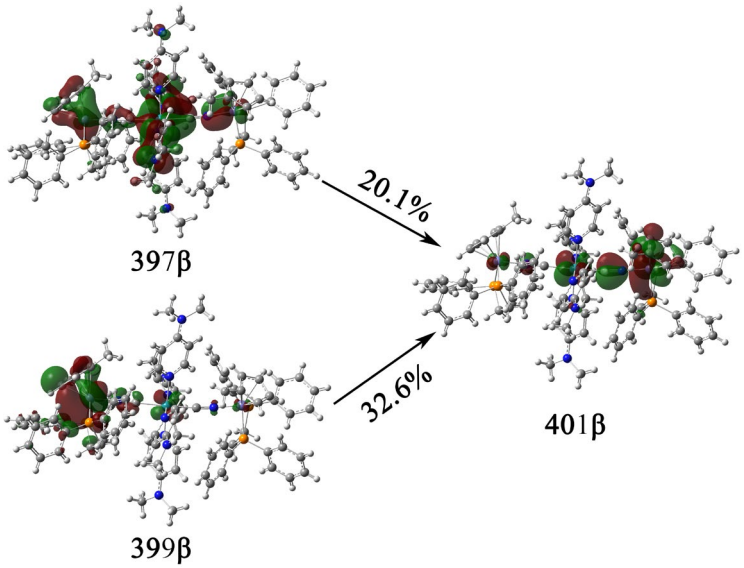

Figure S8. The major electronic transitions corresponding to the NIR band (λ = 1316.44 nm, f = 0.0250) of $\mathbf{2}^{3+}$.

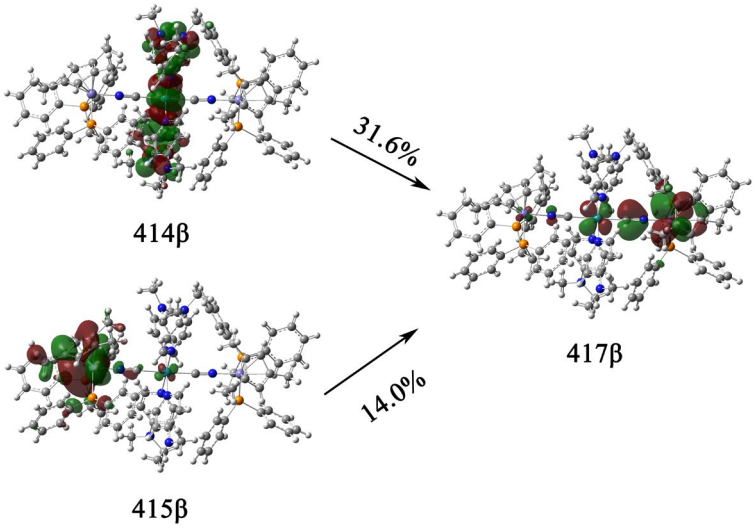

Figure S9. The major electronic transitions corresponding to the NIR band (λ = 1195.94 nm, f = 0.0103) of $\mathbf{3}^{3+}$.

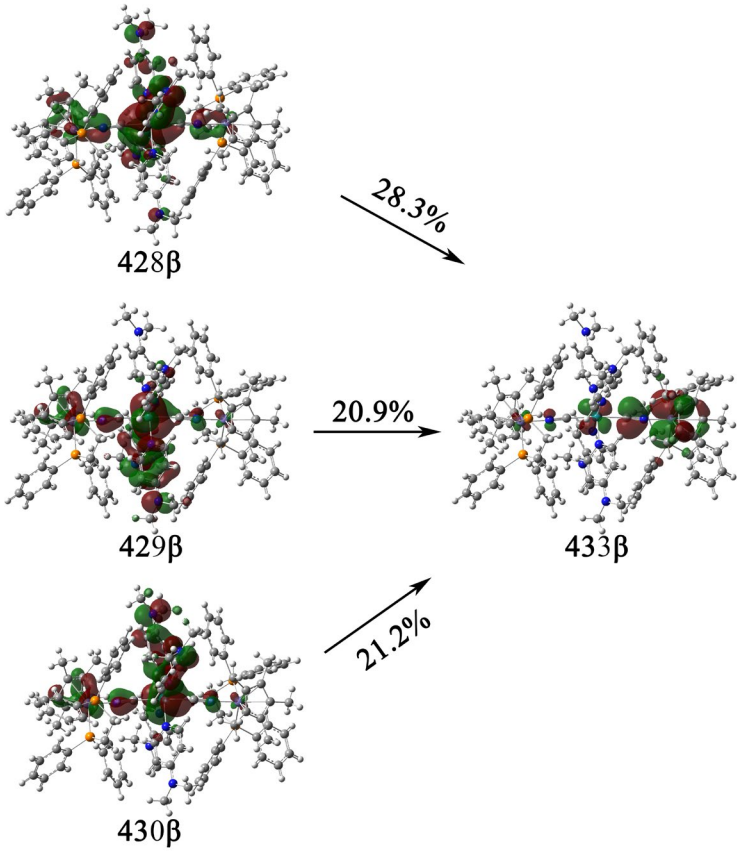

Figure S10. The major electronic transitions corresponding to the NIR band (λ = 992.52 nm, f = 0.0363) of $\mathbf{5}^{3+}$.

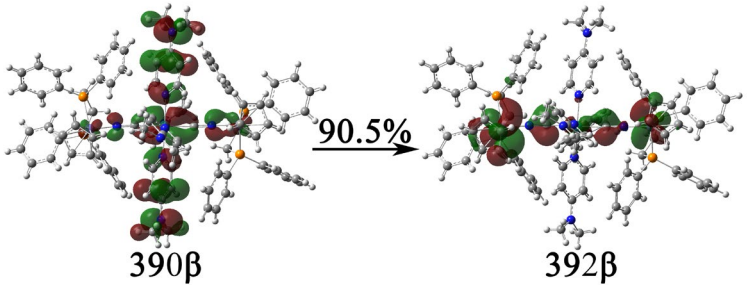

Figure S11. The major electronic transitions corresponding to the NIR band of (λ = 876.33 nm, f = 0.1137) $\mathbf{1}^{4+}$.

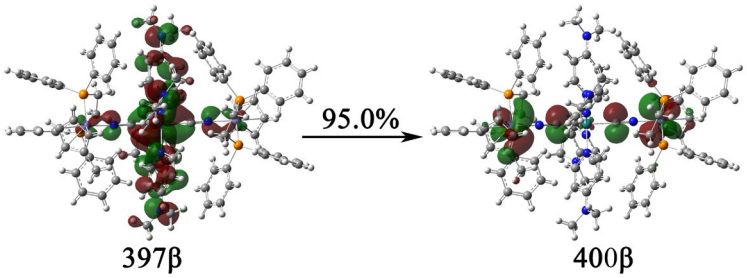

Figure S12. The major electronic transitions corresponding to the NIR band (λ = 785.08 nm, f = 0.1089) of $\mathbf{2}^{4+}$.

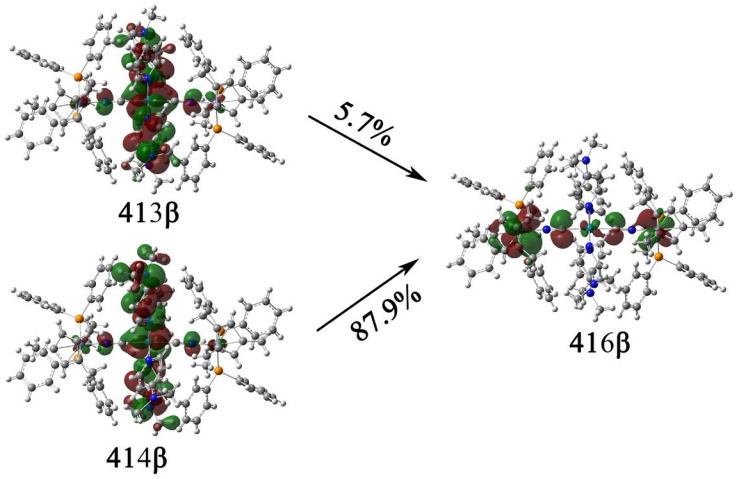

Figure S13. The major electronic transitions corresponding to the NIR band (λ = 685.21 nm, f = 0.0627) of $\mathbf{3}^{4+}$.

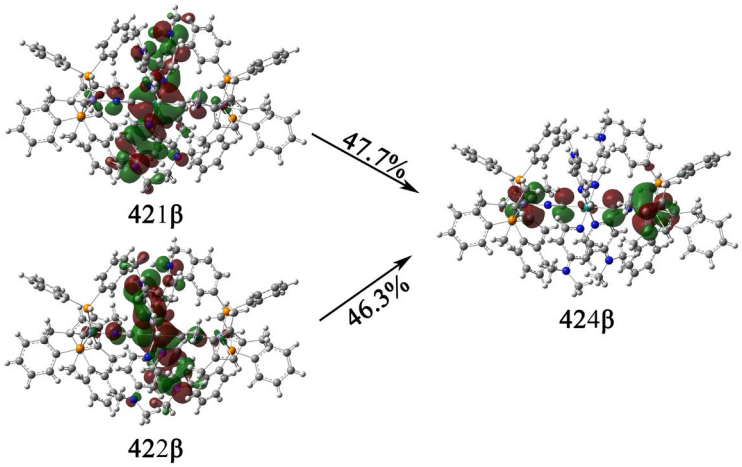

Figure S14. The major electronic transitions corresponding to the NIR band (λ = 691.77 nm, f = 0.0868) of $\mathbf{4}^{4+}$.

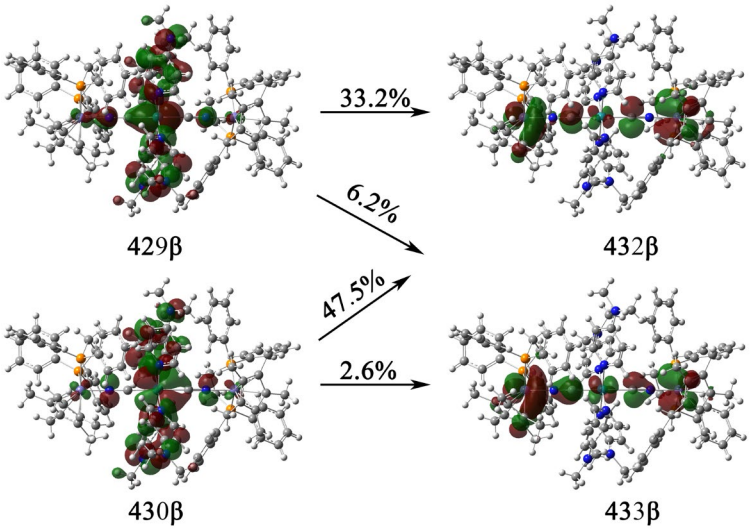

Figure S15. The major electronic transitions corresponding to the NIR band (λ = 611.57 nm, f = 0.1066) of $\mathbf{5}^{4+}$.