Electronic Supplementary Material (ESI) for *CrystEngComm*.

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Sensitized near-infrared emission of $[Ln(hfac)_4]^-$ [Ln(III) = Nd, Yb, Er] via ruthenium counterions of 2,3,5,6-tetrakis-(2-pyridyl)pyrazine

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1. **Table S1** Crystallographic data and structure refinement parameters for complexes **1**-**3**.

Complex	**1**-Nd	**2**-Yb	**3**-Er
Chemical formula	$C_{88}H_{51}F_{48}N_{12}O_{19}Nd_2Ru$	$C_{88}H_{44}F_{48}N_{12}O_{16}Yb_2Ru$	$C_{88}H_{44}F_{48}N_{12}O_{16}Er_2Ru$
Formula weight	2881.95	2884.50	2868.91
Crystal system	monoclinc	monoclinc	monoclinc
T (K)	150(2)	150(2)	150(2)
Space group	$P2_1/n$	$C2/c$	$C2/c$
a (Å)	23.1251(5)	28.2674(9)	28.2196(7)
b (Å)	18.7945(4)	25.3749(10)	25.4700(8)
c (Å)	25.7849(6)	15.9496(7)	15.9589(5)
α (°)	90	90	90
β (°)	94.6870(10)	100.4430(10)	100.5510(10)
γ (°)	90	90	90
V (Å^3)	11169.3(4)	11250.9(8)	11276.6(6)
Z	4	4	4
ρ_{calc}/ g·cm^{-3}	1.714	1.703	1.690
μ (mm^{-1})	9.412	1.924	1.749
F (000)	5644	5600	5568
θ (°)	2.468-66.586	2.065-25.000	2.171-26.392
Limiting indices	$-27 \le h \le 26$ $-22 \le k \le 22$ $-21 \le l \le 30$	$-33 \le h \le 33$ $-30 \le k \le 30$ $-18 \le l \le 18$	$-35 \le h \le 35$ $-31 \le k \le 31$ $-19 \le l \le 19$
Reflections collected	64827 [$R_{(int)}$ = 0.0665]	131238 [$R_{(int)}$ = 0.0567]	142342 [$R_{(int)}$ = 0.0780]
Data/restraints/parameters	19529/502/1531	9917/1/755	11515/8/755
Goodness-of-fit on F^2	1.036	1.058	1.093
Final R indexes [$I \ge 2\sigma$ (I)]	R_1 = 0.0717 wR_2 = 0.1949	R_1 = 0.0356 wR_2 = 0.0972	R_1 = 0.0482 wR_2 = 0.1200
Final R indexes [all data]	R_1 = 0.0788 wR_2 = 0.2062	R_1 = 0.0411 wR_2 = 0.1004	R_1 = 0.0554 wR_2 = 0.1248
Largest diff. peak/hole [eÅ^{-3}]	1.53 / -0.79	1.33 / -0.61	1.45 / -1.33
CCDC Deposition No.	2168475	2168476	2168477

2. **Table S2** Selected bond lengths [Å] and bond angles [°] for complex **1**.

Complex	**1**-Nd		
	Bond lengths [Å]		
Nd1—O1	2.544 (4)	Nd2—O13	2.470 (5)
Nd1—O2	2.486 (4)	Nd2—O14	2.541 (5)
Nd1—O3	2.455 (5)	Nd2—O15	2.452 (5)
Nd1—O4	2.438 (4)	Nd2—O16	2.440 (4)
Nd1—O5	2.502 (5)	Nd2—O17	2.543 (5)
Nd1—O6	2.457 (5)	Nd2—O18	2.477 (5)
Nd1—O7	2.445 (4)	Ru1-N1	2.060(5)
Nd1—O8	2.480 (5)	Ru1-N2	1.971(4)
Nd1—O9	2.481 (4)	Ru1-N3	2.069(4)
Nd2—O10	2.482 (5)	Ru1-N6	2.069(5)
Nd2—O11	2.469 (6)	Ru1-N5	1.981(4)
Nd2—O12	2.440 (4)	Ru1-N4	2.071(5)
	Bond angles [°]		
O2-Nd1-O1	70.35(14)	O12-Nd2-O11	69.19(17)
O2-Nd1-O5	125.30(16)	O12-Nd2-O13	77.44(16)
O3-Nd1-O1	136.83(15)	O12-Nd2-O14	144.81(15)
O3-Nd1-O2	70.45(15)	O12-Nd2-O15	135.21(16)
O3-Nd1-O5	67.84(19)	O12-Nd2-O17	67.17(15)
O3-Nd1-O6	143.65(17)	O12-Nd2-O18	75.90(14)
O3-Nd1-O8	69.40(16)	O13-Nd2-O10	109.30(19)
O3-Nd1-O9	137.84(16)	O13-Nd2-O14	68.62(17)
O4-Nd1-O1	69.18(15)	O13-Nd2-O17	125.14(17)
O4-Nd1-O2	71.30(15)	O13-Nd2-O18	140.67(17)
O4-Nd1-O3	81.75(16)	O14-Nd2-O17	126.65(17)
O4-Nd1-O5	69.15(16)	O15-Nd2-O10	76.49(18)
O4-Nd1-O6	88.45(16)	O15-Nd2-O11	144.86(17)
O4-Nd1-O7	138.93(15)	O15-Nd2-O13	129.45(16)
O4-Nd1-O8	139.75(16)	O15-Nd2-O14	67.46(17)
O4-Nd1-O9	132.97(16)	O15-Nd2-O17	68.10(16)
O5-Nd1-O1	124.91(17)	O15-Nd2-O18	89.63(15)
O6-Nd1-O1	68.54(15)	O16-Nd2-O10	136.49(17)
O6-Nd1-O2	138.41(15)	O16-Nd2-O11	141.24(17)
O6-Nd1-O5	75.94(18)	O16-Nd2-O12	89.30(15)
O6-Nd1-O8	131.23(16)	O16-Nd2-O13	70.94(18)
O6-Nd1-O9	71.33(16)	O16-Nd2-O14	71.40(16)
O7-Nd1-O1	128.58(15)	O16-Nd2-O15	72.38(15)
O7-Nd1-O2	145.41(15)	O16-Nd2-O17	68.22(16)
O7-Nd1-O3	94.31(15)	O16-Nd2-O18	136.38(17)

O7-Nd1-O5	71.55(16)	O18-Nd2-O10	71.64(17)
O7-Nd1-O6	70.76(16)	O18-Nd2-O14	137.91(15)
O7-Nd1-O8	72.69(16)	O18-Nd2-O17	68.21(16)
O7-Nd1-O9	74.23(16)	N1-Ru1-N3	157.98(18)
O8-Nd1-O1	114.48(14)	N1-Ru1-N4	89.07(17)
O8-Nd1-O2	72.88(15)	N1-Ru1-N6	95.85(17)
O8-Nd1-O5	120.61(18)	N2-Ru1-N1	79.38(17)
O8-Nd1-O9	68.45(15)	N2-Ru1-N3	78.60(18)
O9-Nd1-O1	63.96(15)	N2-Ru1-N4	101.55(18)
O9-Nd1-O2	96.05(15)	N2-Ru1-N5	176.48(18)
O9-Nd1-O5	138.64(17)	N2-Ru1-N6	100.55(17)
O10-Nd2-O14	68.95(17)	N3-Ru1-N4	95.43(18)
O10-Nd2-O17	125.51(18)	N5-Ru1-N1	97.15(17)
O11-Nd2-O10	69.85(19)	N5-Ru1-N3	104.86(18)
O11-Nd2-O13	73.04(19)	N5-Ru1-N4	78.91(18)
O11-Nd2-O14	107.91(19)	N5-Ru1-N6	79.08(18)
O11-Nd2-O17	125.43(18)	N6-Ru1-N3	88.06(18)
O11-Nd2-O18	70.73(18)	N6-Ru1-N4	157.88(18)
O12-Nd2-O10	134.01(17)		

3. **Table S3** Selected bond lengths [Å] and bond angles [°] for complex **2** and **3**.

Complex	**2**-Yb	**3**-Er
Bond lengths [Å]		
Ln1-O1	2.313(3)	2.333(4)
Ln1-O2	2.261(3)	2.281(4)
Ln1-O3	2.269(3)	2.306(3)
Ln1-O4	2.345(3)	2.363(4)
Ln1-O5	2.327(3)	2.346(3)
Ln1-O6	2.282(3)	2.301(3)
Ln1-O7	2.284(3)	2.289(3)
Ln1-O8	2.344(3)	2.361(3)
Ru1-N3	1.967(4)	1.968(5)
Ru1-N4	2.071(3)	2.074(3)
Ru1-N5	2.062(3)	2.061(3)
Ru1-N6	1.972(4)	1.981(5)
Ru1-N4[1]	2.071(3)	2.074(3)
Ru1-N5[1]	2.062(3)	2.061(3)
Bond angles [°]		
O1-Ln1-O4	132.16(11)	75.92(13)
O1-Ln1-O5	125.91(10)	125.72(12)
O1-Ln1-O8	74.96(11)	131.04(13)
O2-Ln1-O1	75.26(11)	74.87(13)
O2-Ln1-O3	90.78(11)	143.30(13)
O2-Ln1-O4	70.93(11)	74.77(14)

O2-Ln1-O5	144.72(11)	145.65(13)
O2-Ln1-O6	105.04(11)	105.10(13)
O2-Ln1-O7	144.14(11)	91.63(13)
O2-Ln1-O8	75.18(11)	71.21(13)
O3-Ln1-O1	72.20(11)	79.38(13)
O3-Ln1-O4	75.41(10)	73.90(12)
O3-Ln1-O5	73.27(10)	71.05(12)
O3-Ln1-O6	142.04(10)	82.35(12)
O3-Ln1-O7	104.60(10)	104.84(12)
O3-Ln1-O8	146.63(11)	144.43(13)
O5-Ln1-O4	74.61(10)	132.83(12)
O5-Ln1-O8	133.54(11)	75.09(12)
O6-Ln1-O1	144.82(11)	145.80(13)
O6-Ln1-O4	77.59(10)	71.32(12)
O6-Ln1-O5	74.18(10)	73.60(11)
O6-Ln1-O7	82.57(10)	141.22(12)
O6-Ln1-O8	71.34(10)	77.96(12)
O7-Ln1-O1	78.92(11)	71.99(12)
O7-Ln1-O4	143.94(11)	147.46(12)
O7-Ln1-O5	71.13(10)	73.10(12)
O7-Ln1-O8	74.36(11)	74.76(11)
O8-Ln1-O4	125.31(10)	125.44(12)
N3-Ru1-N4	79.44(9)	79.32(10)
N3-Ru1-N5	100.84(9)	100.78(10)
N3-Ru1-N6	180.0	180.0
N3-Ru1-N4^{1}	79.44(9)	79.32(10)
N3-Ru1-N5^{1}	100.83(9)	100.78(10)
N4-Ru1-N4^{1}	158.88(18)	158.6(2)
N5-Ru1-N4	96.79(12)	86.83(13)
N5-Ru1-N4^{1}	87.17(12)	97.16(13)
N5-Ru1-N5^{1}	158.33(18)	158.4(2)
N6-Ru1-N4	100.56(9)	100.68(10)
N6-Ru1-N5	79.16(9)	79.22(10)
N6-Ru1-N4^{1}	100.56(9)	100.68(10)
N6-Ru1-N5^{1}	79.17(9)	79.22(10)
N5^{1}-Ru1-N4	87.18(12)	97.16(13)
N5^{1}-Ru1-N4^{1}	96.79(12)	86.83(13)

4. **Table S4** Ln···Ru distances in complexes **1**-**3**.

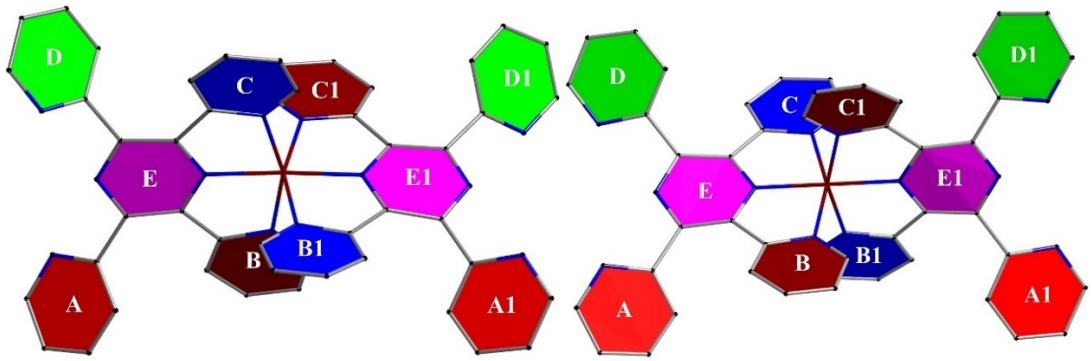
Complex	Ln···Ru distance	Value [Å]
$[Ru(tppz)_2][Nd(hfac)_4(H_2O)]_2$ (**1**)	Nd1···Ru1	8.669
$[Ru(tppz)_2][Yb(hfac)_4]_2$ (**2**)	Yb1···Ru1	8.311
$[Ru(tppz)_2][Er(hfac)_4]_2$ (**3**)	Er1···Ru1	8.290

5. **Table S5** Figures of merits for different geometries of the coordination sphere of Nd(III) centre assuming for **1** calculated with SHAPE software.

Lable	Symmetry	Shape	Calculated results **1**-Nd
EP-9	D9h	Enneagon	37.678
OPY-9	C8v	Octagonal pyramid	21.406
HBPY-9	D7h	Heptagonal bipyramid	18.974
JTC-9	C3v	Johnson triangular cupola J3	16.949
JCCU-9	C4v	Capped cube J8	9.843
CCU-9	C4v	Spherical-relaxed capped cube	8.631
JCSAPR-9	C4v	Capped square antiprism J10	1.909
CSAPR-9	C4v	Spherical capped square antiprism	0.813
JTCTPR-9	D3h	Tricapped trigonal prism J51	2.420
TCTPR-9	**D3h**	**Spherical tricapped trigonal prism**	**0.447**
JTDIC-9	C3v	Tridiminished icosahedron J63	12.267

6. **Table S6** Figures of merits for different geometries of the coordination spheres of Yb(III) and Er(III) centres assuming for **2** and **3** calculated with SHAPE software.

Lable	Symmetry	Shape	Calculated results	
			2-Yb	**3**-Er
OP-8	D8h	Octagon	29.396	29.436
HPY-9	C7v	Heptagonal pyramid	23.702	23.541
HBPY-8	D6h	Hexagonal bipyramid	16.119	15.662
CU-8	Oh	Cube	9.145	15.662
SAPR-8	D4d	Square antiprism	1.189	1.253
TDD-8	**D2d**	**Triangular dodecahedron**	**0.571**	**0.547**
JGBF-8	D2d	Johnson gyrobifastigium J26	14.470	14.801
JETBPY-8	D3h	Johnson elongated triangular bipyramid J14	28.669	28.567
JBTPR-8	C2v	Biaugmented trigonal prism J50	2.370	2.444
BTPR-8	C2v	Biaugmented trigonal prism	1.869	1.963
JSD-8	D2d	Snub diphenoid J84	2.865	2.934



(a) (b)

7. **Fig 1S** Perspective views of the $[Ru(tppz)_2]^{2+}$ cations in (a) **1**-Nd and (b) **2**-Yb with the pyrazine and pyridyl rings numbering.

8. **Table S7** The dihedral angles of the pyridyl rings (A–D) with respect to the pyrazine ring (E) in the $[Ru(tppz)_2]^{2+}$ cation of complex **1.**

Rings	Angle (º)	Rings	Angle (º)
A-E	44.97	B-E	18.12
A-B	56.04	C-D	56.73
A-C	53.48	C-E	11.69
A-D	59.53	D-E	47.39
B-C	7.08	E-E1	82.74
B-D	63.80		

9. **Table S8** The dihedral angles of the pyridyl rings (A–D) with respect to the pyrazine ring (E) in the $[Ru(tppz)_2]^{2+}$ cation of complex **2**.

Rings	Angle (º)	Rings	Angle (º)
A-E	38.14	B-E	21.56
A-B	57.71	C-D	57.71
A-C	57.95	C-E	21.56
A-D	34.53	D-E	28.14
B-C	7.10	E-E1	38.82
B-D	57.95		

10. **Table S9** π-π stacking interactions are observed between the aromatic rings in complex **1**.

Rings	Centroid distance (Å)	Vertical distance (Å)	Offset angle (º)
A•••A1	4.214(4)	3.651(8)	19.9(4)
B•••B1	3.611(4)	3.456(5)	0.0(8)
D•••D1	4.673(6)	3.351(12)	0.0(13)

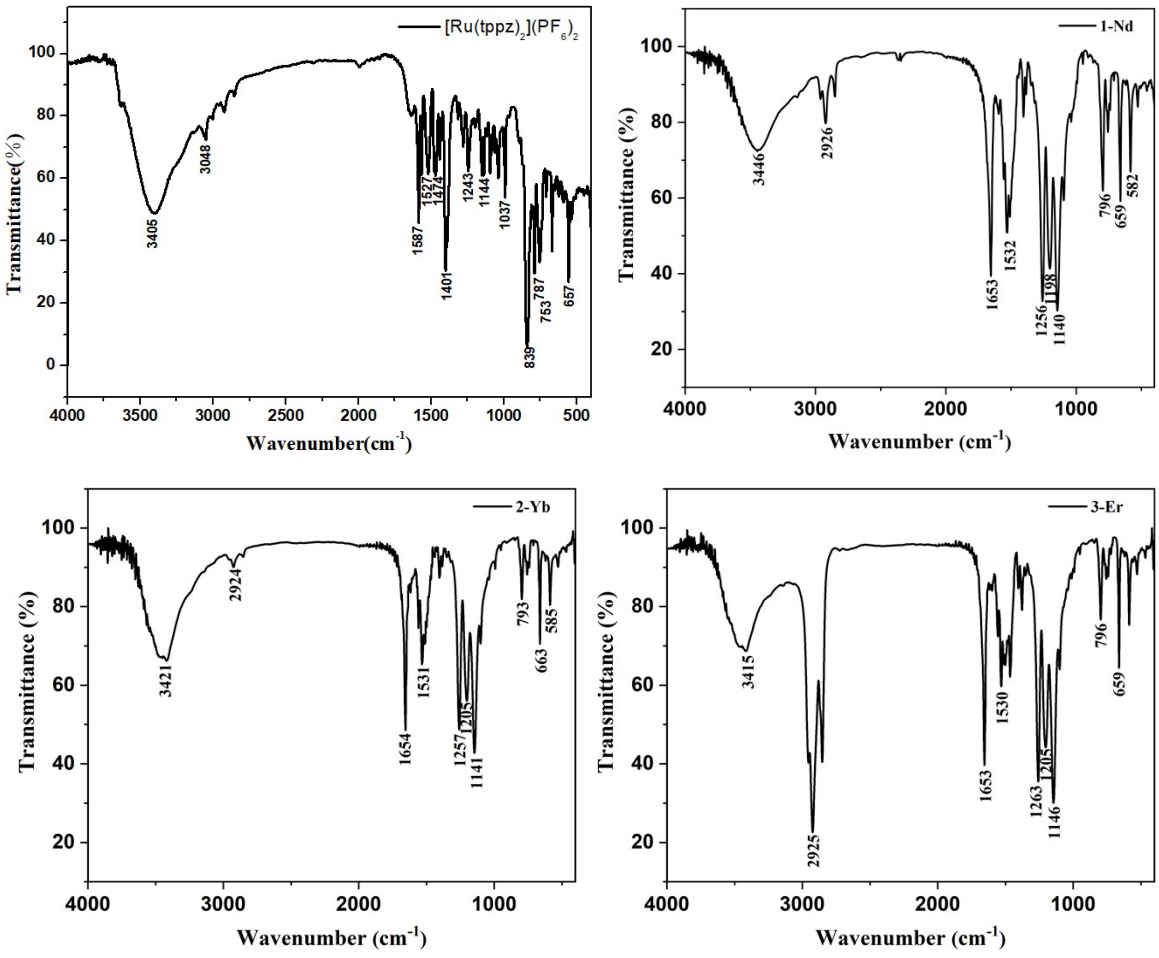
11. **Table S10** π-π stacking interactions are observed between the aromatic rings in complex **2**.

Rings	Centroid distance (Å)	Vertical distance (Å)	Offset angle (º)
C•••C	3.621(3)	3.569(2)	0.0(6)
C1•••C1	3.621(3)	3.515(2)	0.0(6)
D•••D1	3.889(4)	3.410(3)	18.5(3)

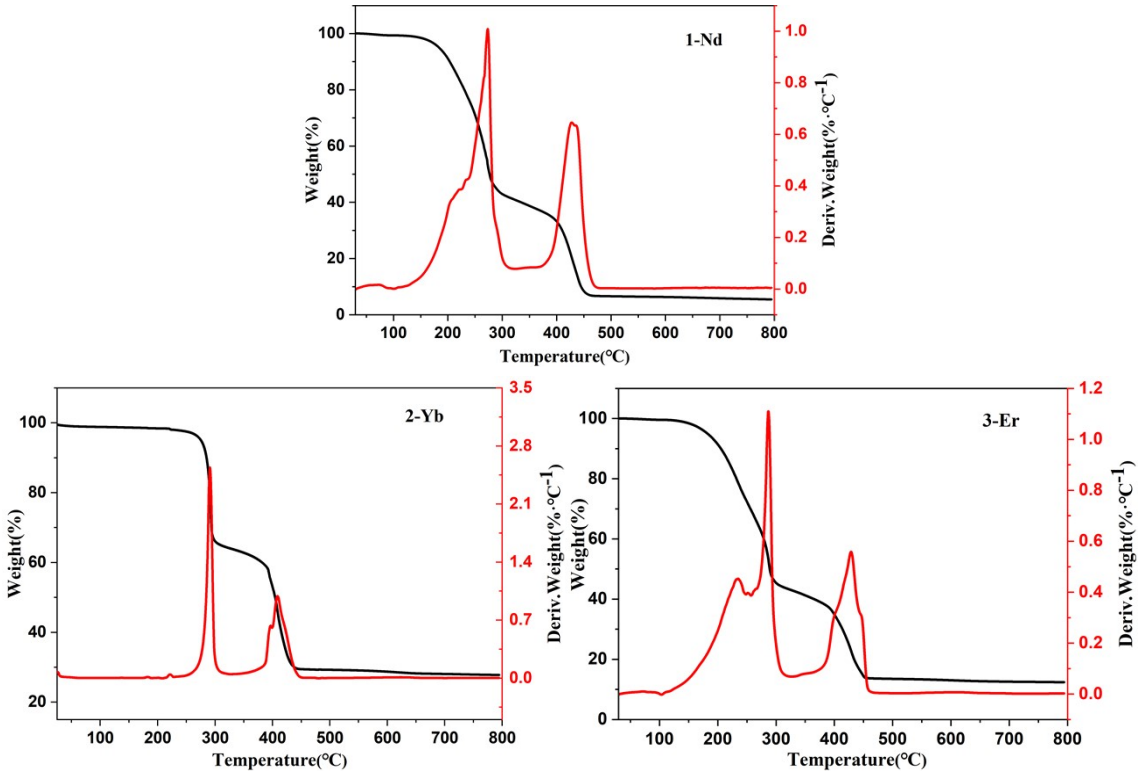
A•••A1	4.069(4)	3.839(4)	20.5(4)

12. **Table S11** IR data for $[Ru(tppz)_2](PF_6)$ and complexes **1**-**3**.

Compounds	ν (C-H) cm^{-1}	ν (C=O) cm^{-1}	ν (C=C) ν (C=N) cm^{-1}	ν (C-F) cm^{-1}	δ (C-H) cm^{-1}
$[Ru(tppz)_2](PF_6)_2$	3048	/	1587,1527	/	839,787,753,657
1-Nd	2926	1653	1532	1256,1198,1140	796,659
2-Yb	2924	1654	1531	1257,1205,1141	793,663
3-Er	2925	1653	1530	1263,1205,1146	796,659



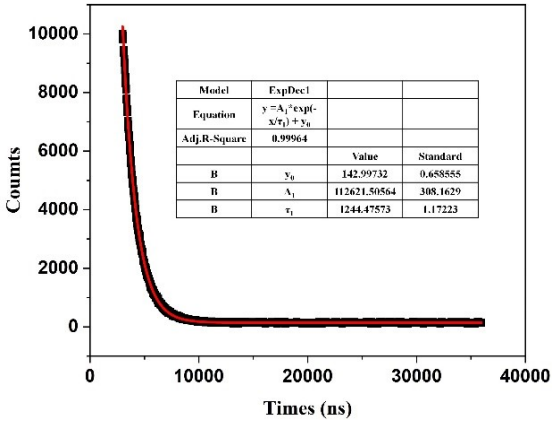
13. **Fig 2S** IR spectra of $[Ru(tppz)_2](PF_6)$ and complexes **1**-**3**.



14. **Fig S3** TGA (black) and DTG (red) curves for complexes **1**-**3**.

15. **Table S12** Relative contributions of various intermolecular interactions to the Hirshfeld surfaces for complexes **1**-**3**.

Complex (%)	H-F/ F-H	F-F	H-H	C-F/ F-C	H-O/ O-H	H-C/ C-H	H-N/ N-H	C-C	O-F/ F-O	C-N/ N-C	N-F/ F-N	C-O/ O-C
1-Nd	**41.7**	**24.7**	**12.6**	6.6	6.4	4.6	1.3	0.9	0.6	0.3	0.2	-
2-Yb	**37.9**	**28.8**	**13.0**	5.6	3.9	4.2	2.2	1.8	1.2	0.7	0.3	0.4
3-Er	**38.1**	**28.7**	**9.4**	6.1	3.9	5.6	4.1	1.8	1.2	0.8	-	0.4



16. **Fig S4** Solid-state $^4F_{3/2} \rightarrow {}^4I_{11/2}$ decay profile for **1**-Nd at 1062 nm.