Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Heteroleptic Samarium Complexes with High Quantum Yields for Temperature Sensing Applications

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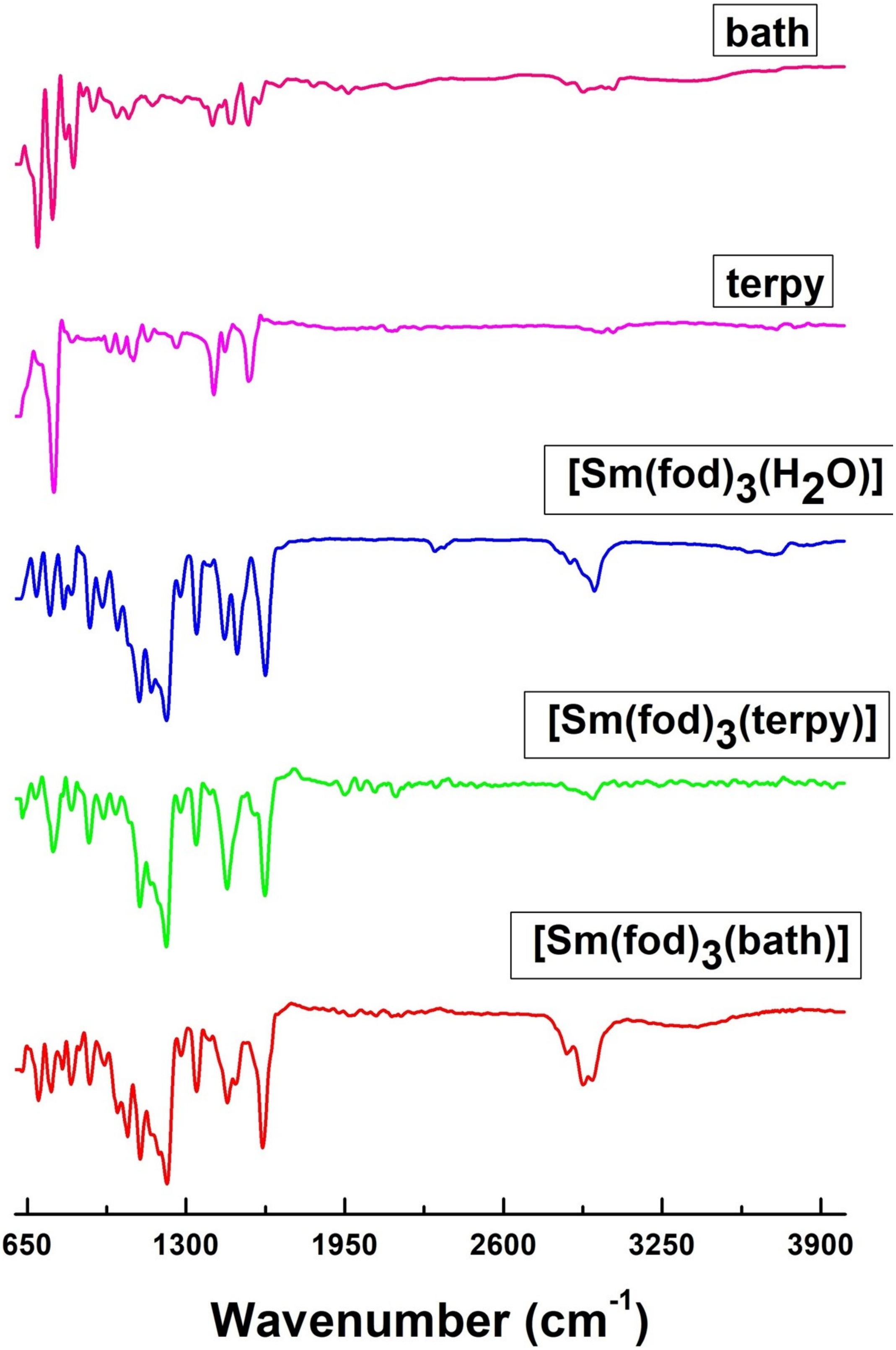

Figure S1 FTIR spectra of ligand and complexes.

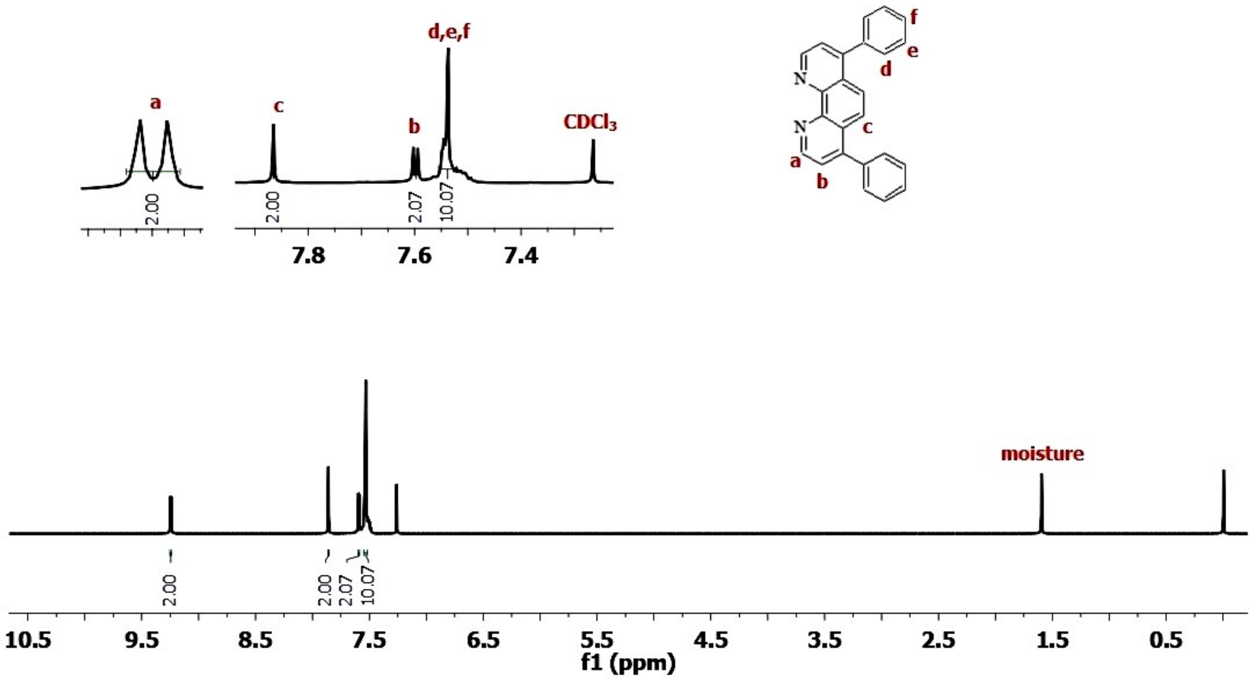

Figure S2 [1]H NMR spectrum of bath in $CDCl_3$.

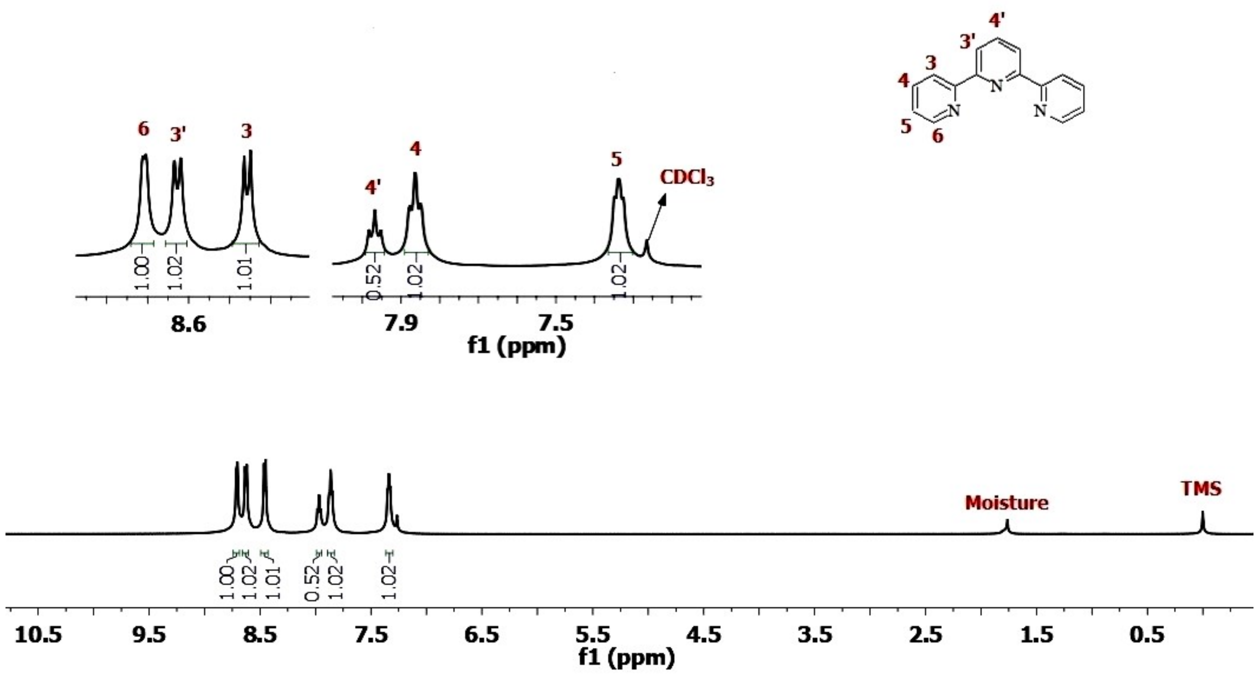

Figure S3 [1]H NMR spectrum of terpy in $CDCl_3$.

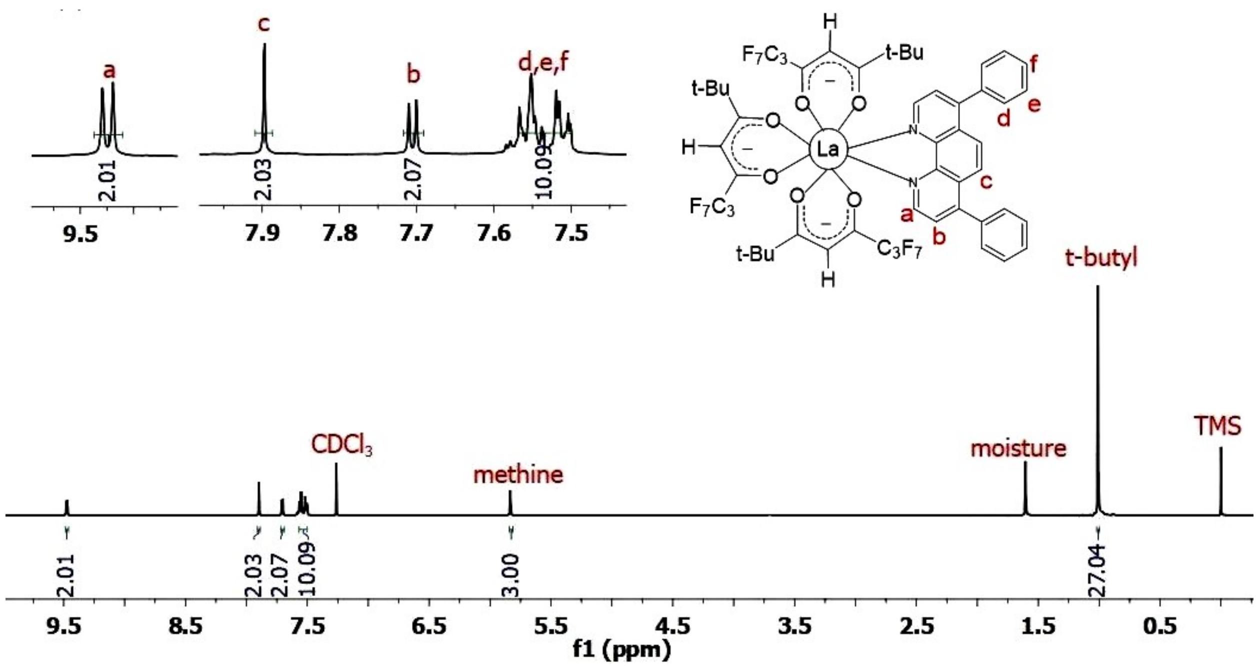

Figure S4 ^{1}H NMR spectra of [La(fod)$_3$(bath)] in CDCl$_3$.

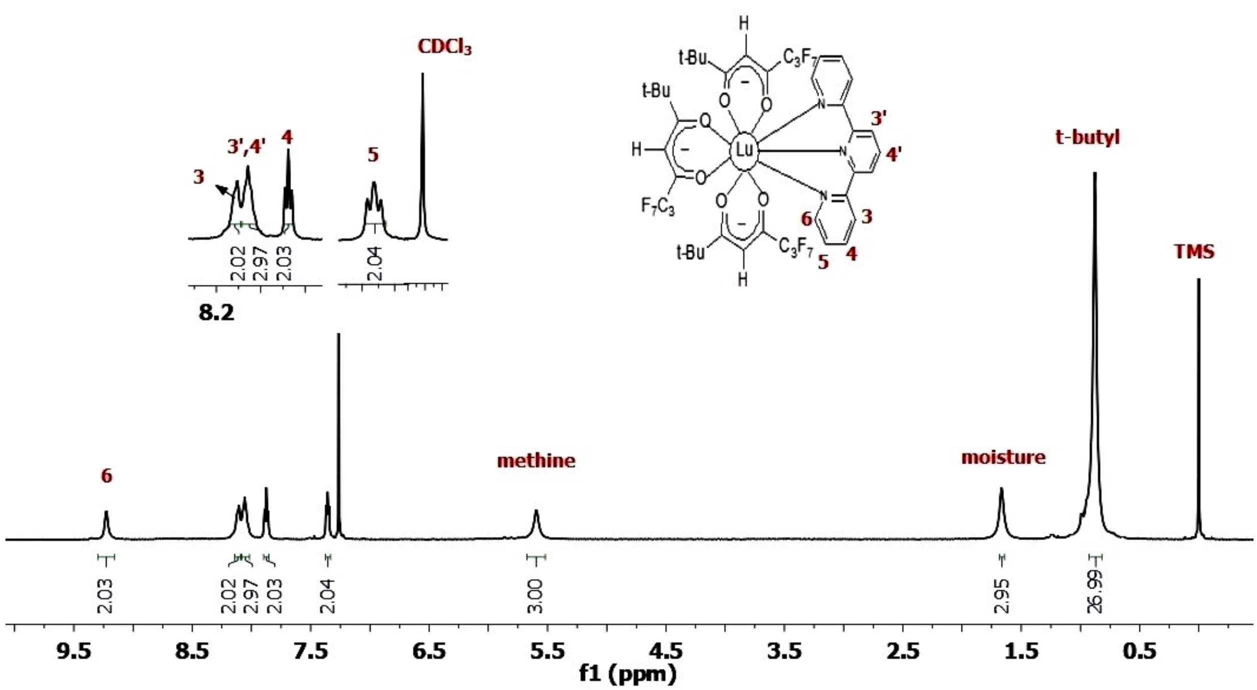

Figure S5 ^{1}H NMR spectra of [Lu(fod)$_3$(terpy)] in CDCl$_3$.

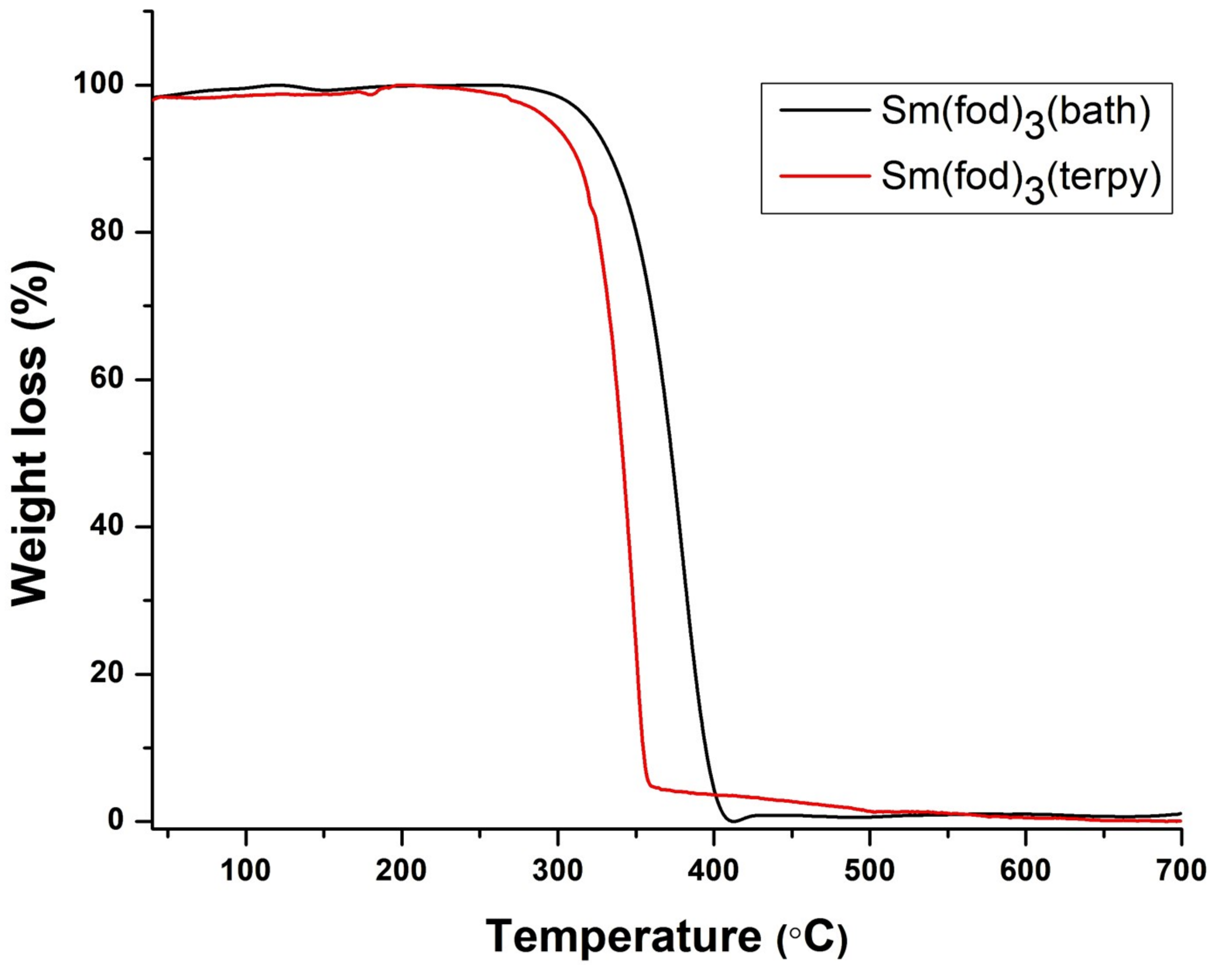

Figure S6 Thermogram of the complexes.

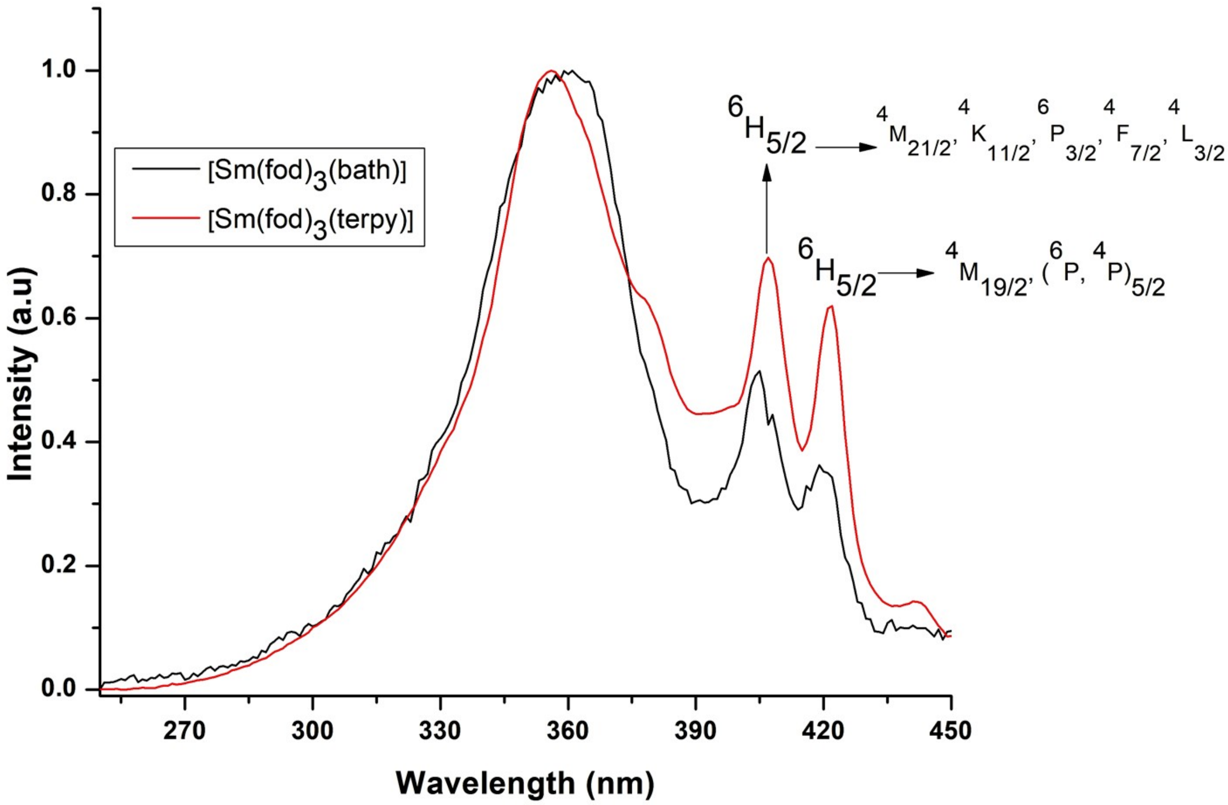

Figure S7 Excitation spectra of the complexes in solid state

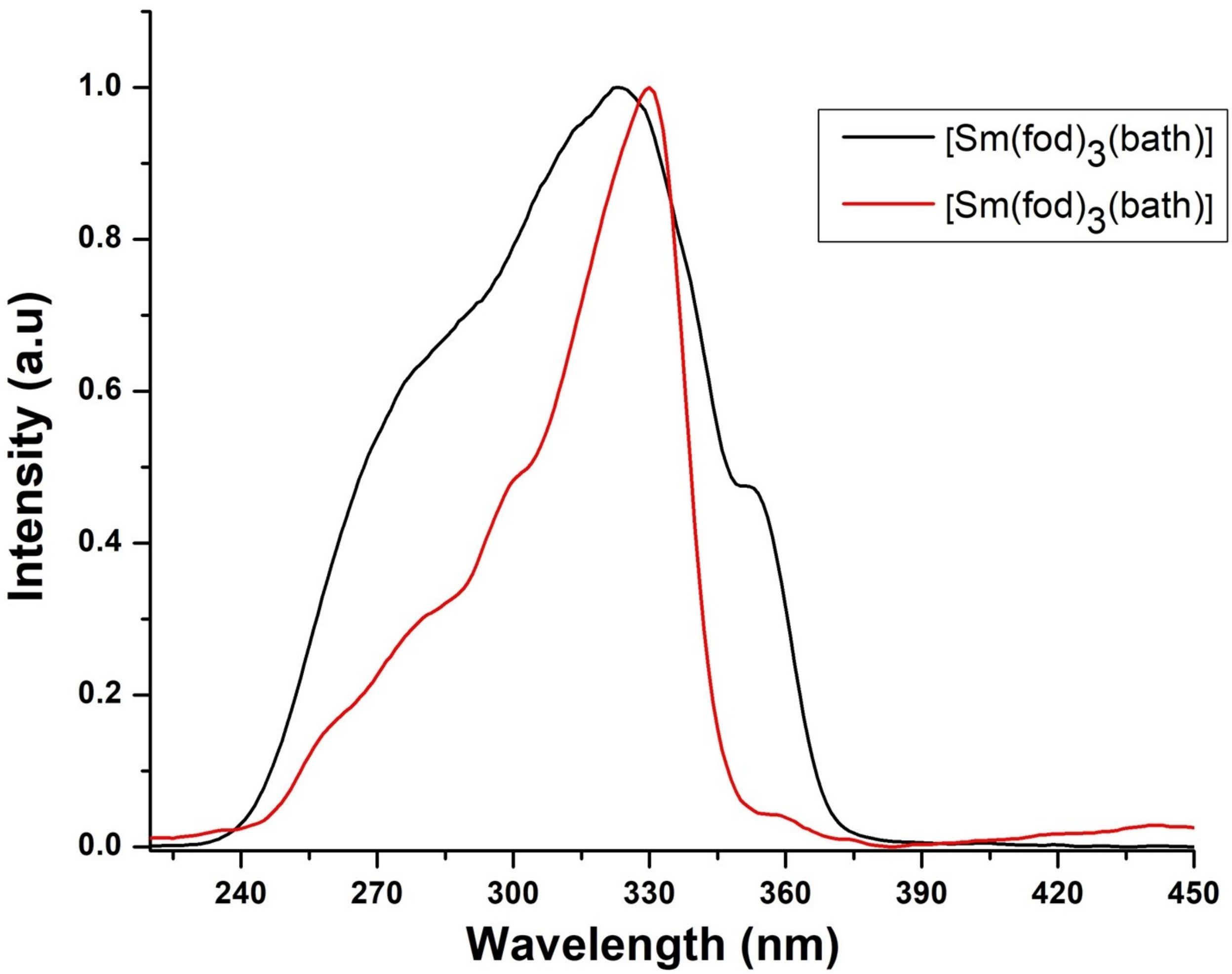

Figure S8 Excitation of the complexes in 3 % PMMA thin film

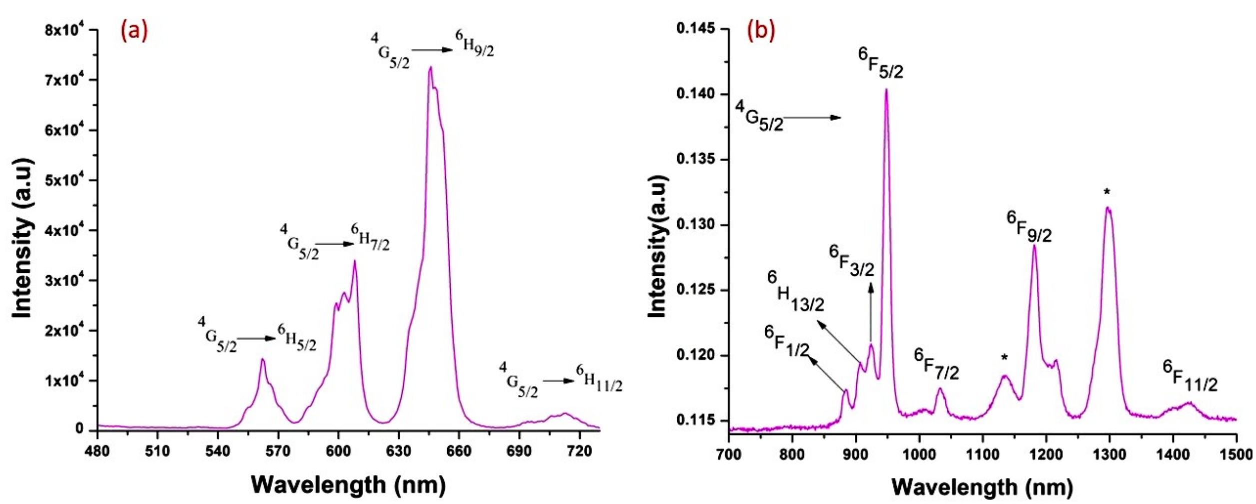

Figure S9 (a) Visible-emission and (b) NIR-emission of the $[Sm(fod)_3(bath)]$ in solid state

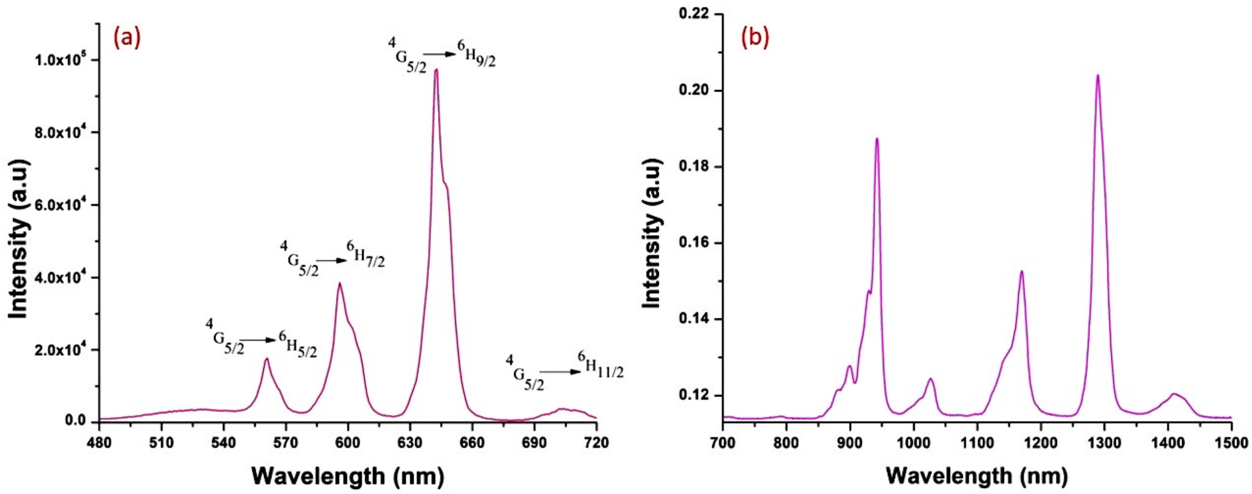

Figure S10 (a) Visible-emission and (b) NIR-emission of the [Sm(fod)$_3$(terpy)] in solid state

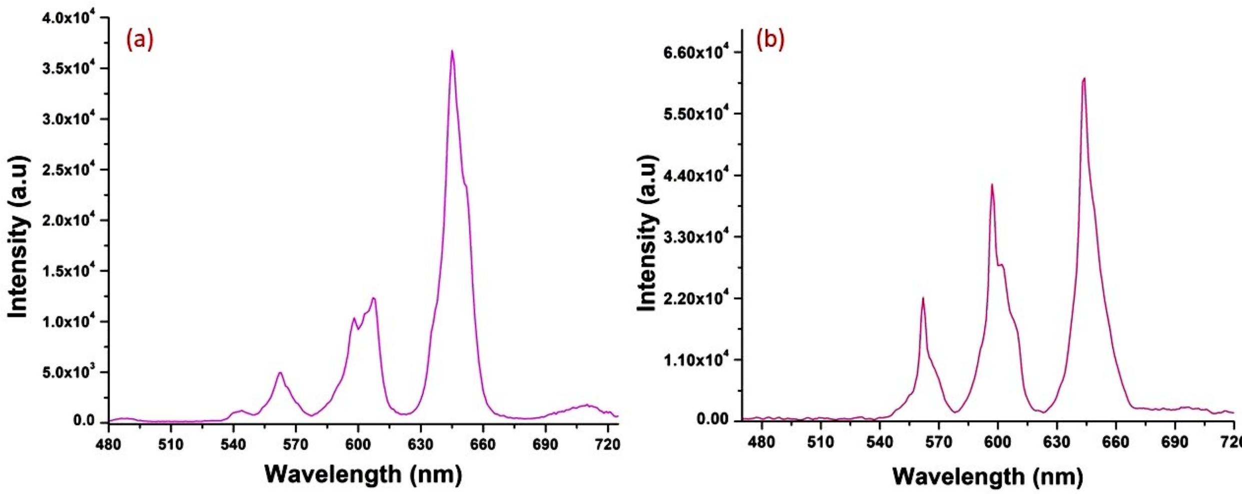

Figure S11 Emission spectra of (a) [Sm(fod)$_3$(bath)] and (b) [Sm(fod)$_3$(terpy)] in 3% PMMA thin film.

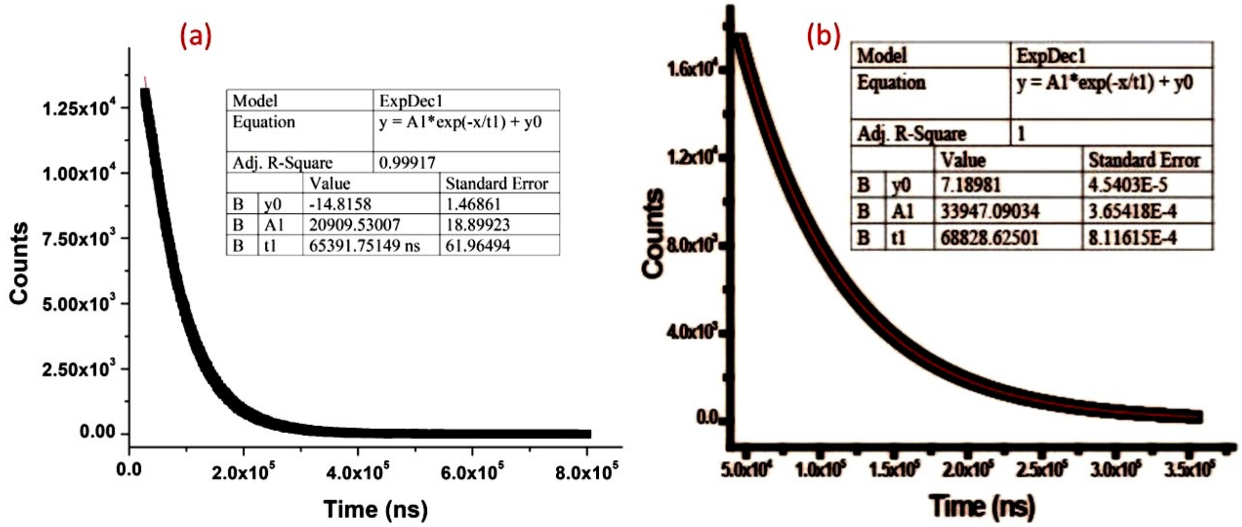

Figure S12 Emission decay time of (a) $[Sm(fod)_3(bath)]$ and (b) $[Sm(fod)_3(terpy)]$ in chloroform.

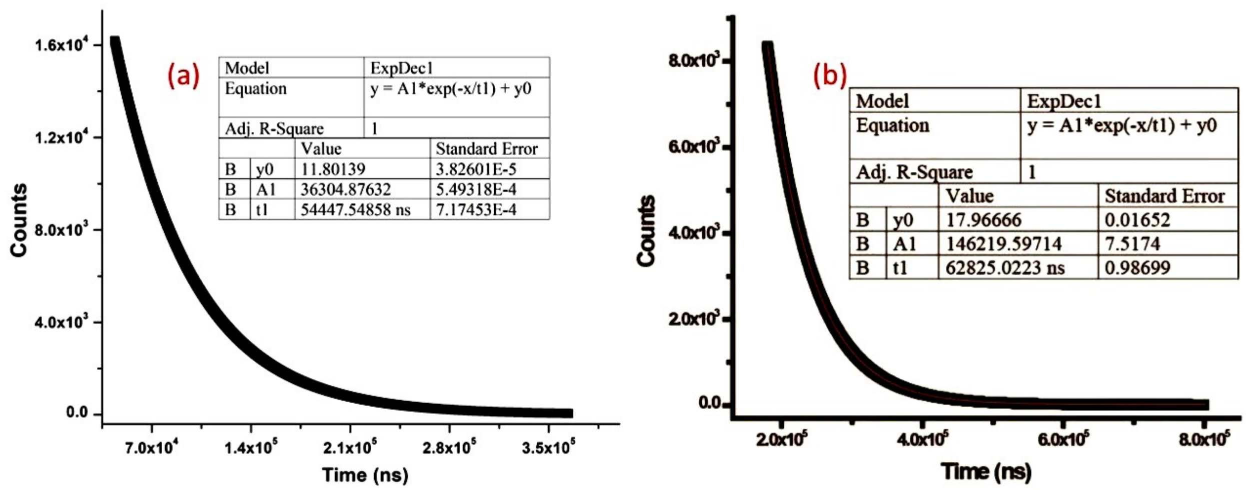

Figure S13 Emission decay time of (a) $[Sm(fod)_3(bath)]$ and (b) $[Sm(fod)_3(terpy)]$ in 3% PMMA thin film.

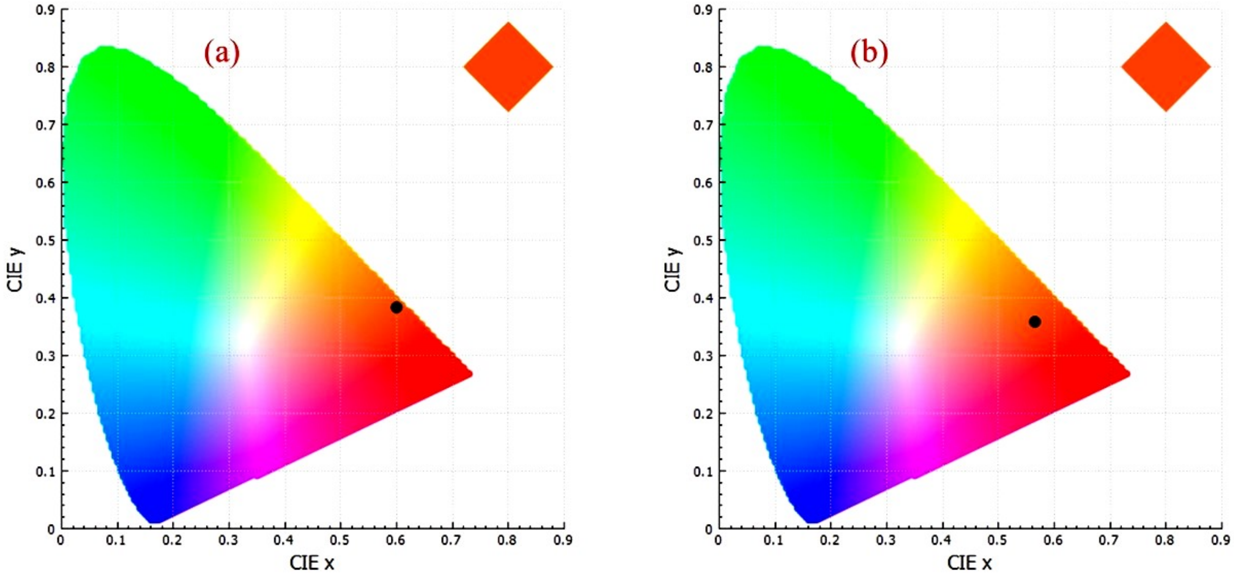

Figure S14 CIE diagram of (a) [Sm(fod)$_3$(bath)] and (b) [Sm(fod)$_3$(terpy)] in chloroform.

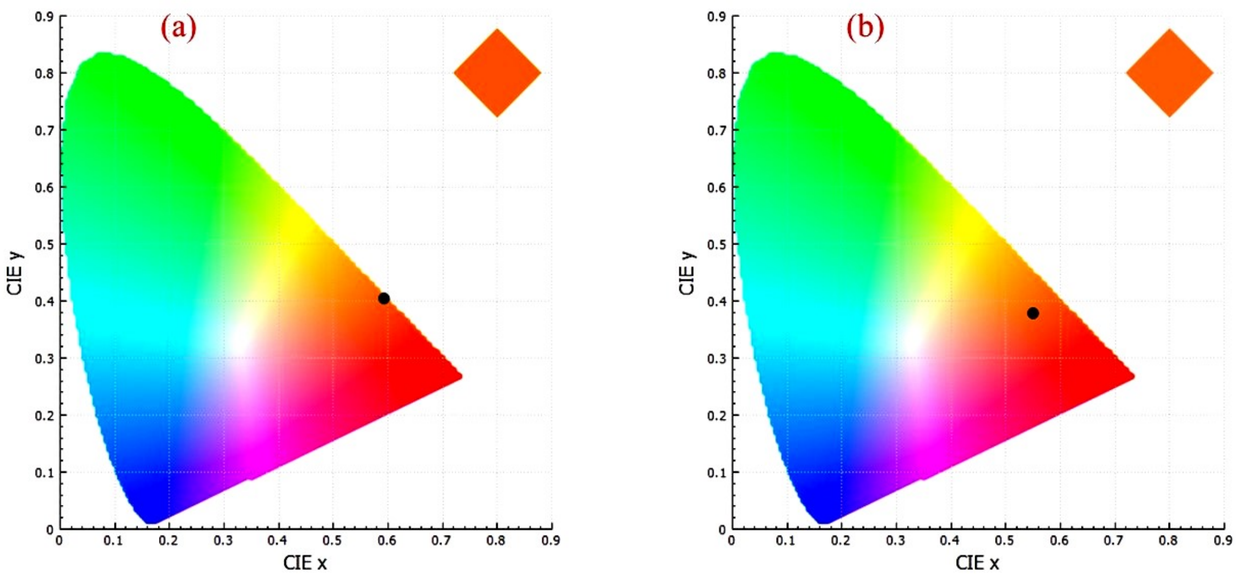

Figure S15 CIE diagram of (a) [Sm(fod)$_3$(bath)] and (b) [Sm(fod)$_3$(terpy)] in 3% PMMA thin film.

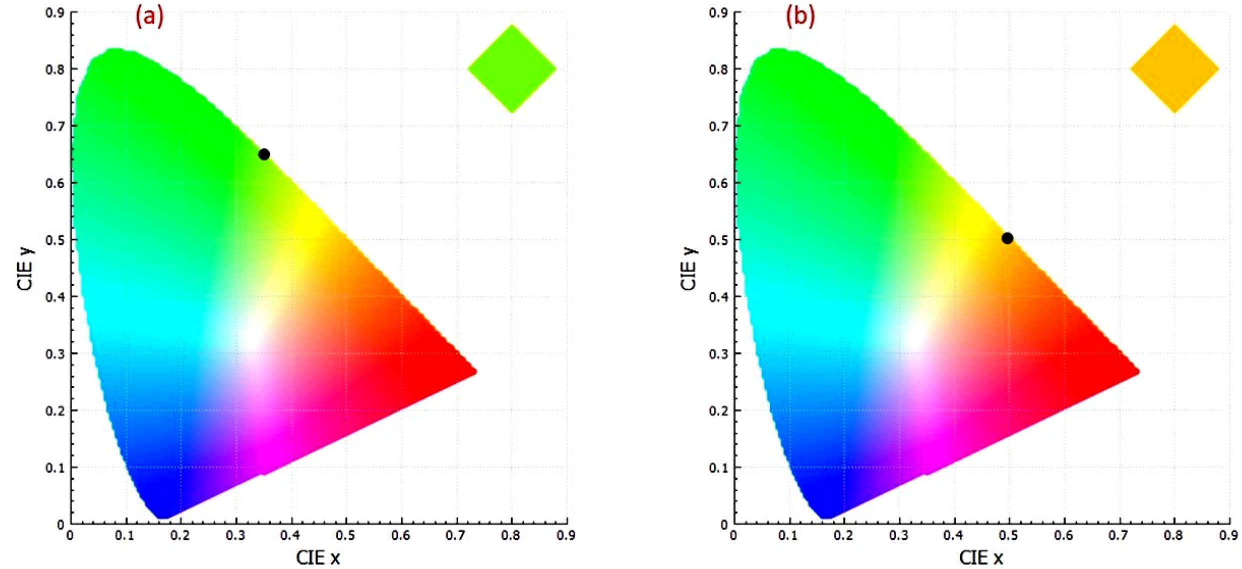

Figure S16 CIE diagram of [Sm(fod)$_3$(bath)] of NIR-region in (a) chloroform and (b) solid state

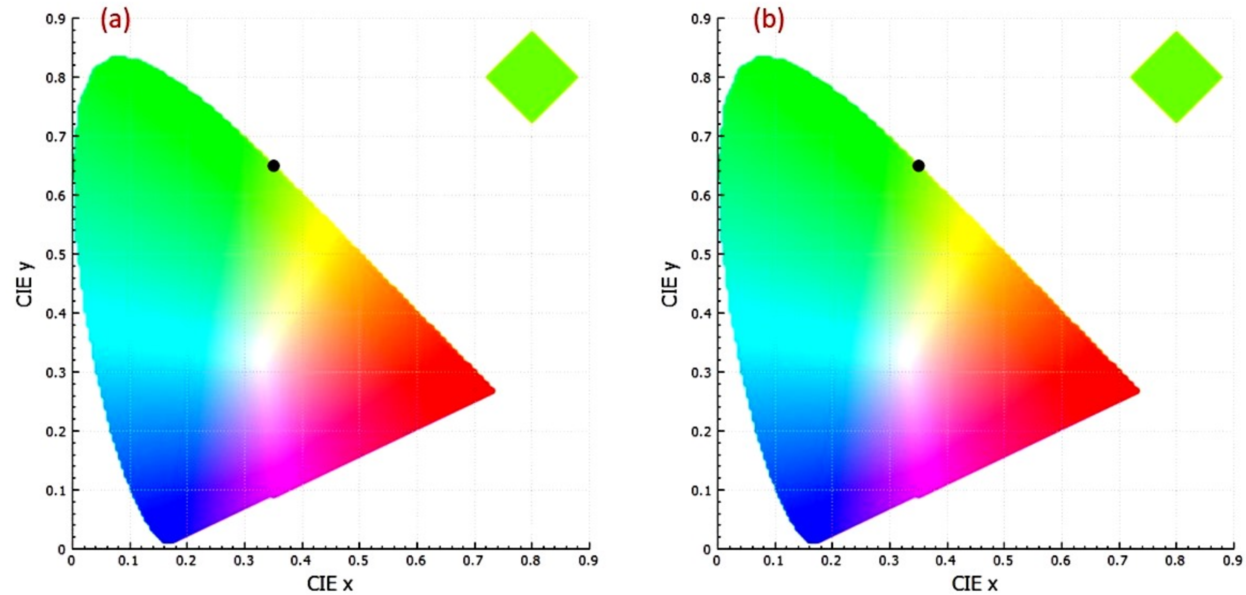

Figure S17 CIE diagram of [Sm(fod)$_3$(terpy)] of NIR-region in (a) chloroform and (b) solid state

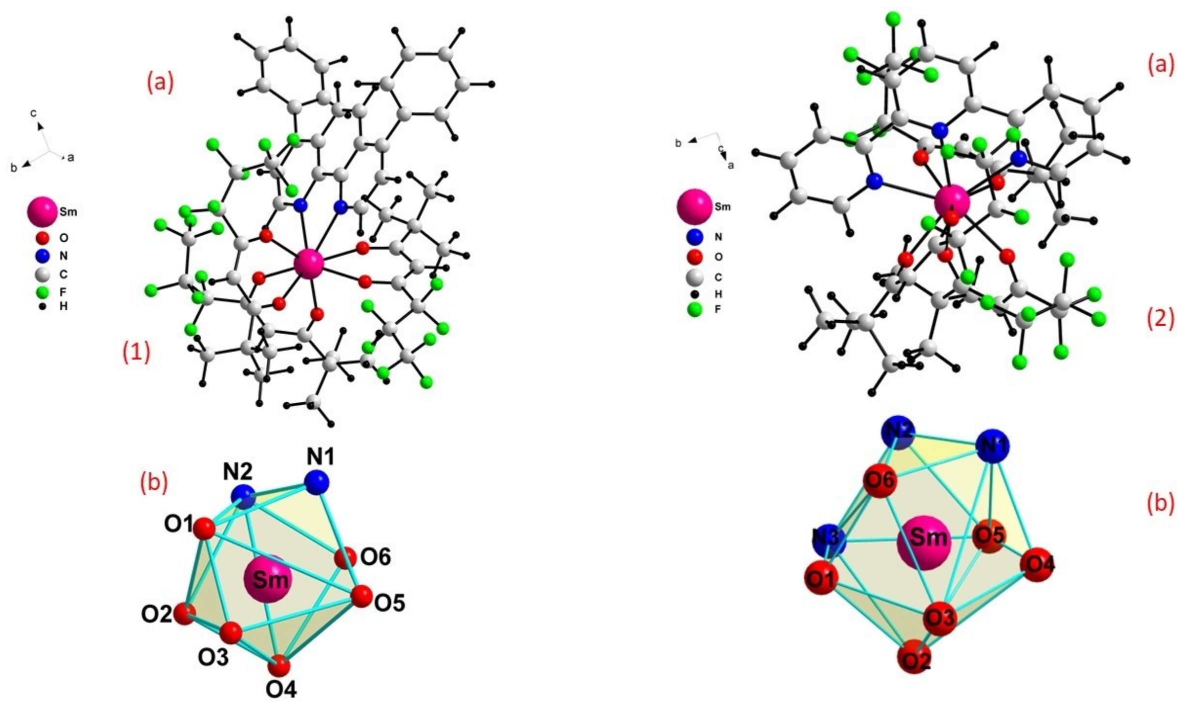

Figure S18 (a) Ground state geometry obtained using Sparkle/PM7 and (b) coordination polyhedron around the metal ion of (1) [Sm(fod)$_3$(bath)] and (2) [Sm(fod)$_3$(terpy)].

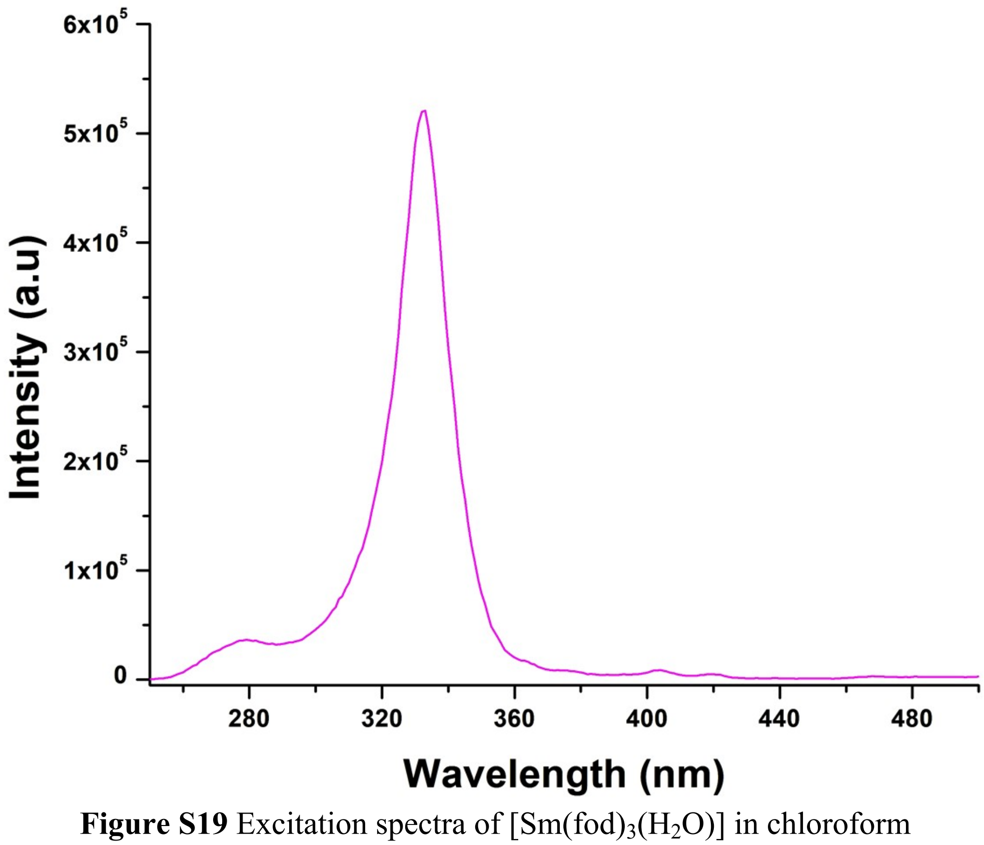

Figure S19 Excitation spectra of [Sm(fod)$_3$(H$_2$O)] in chloroform

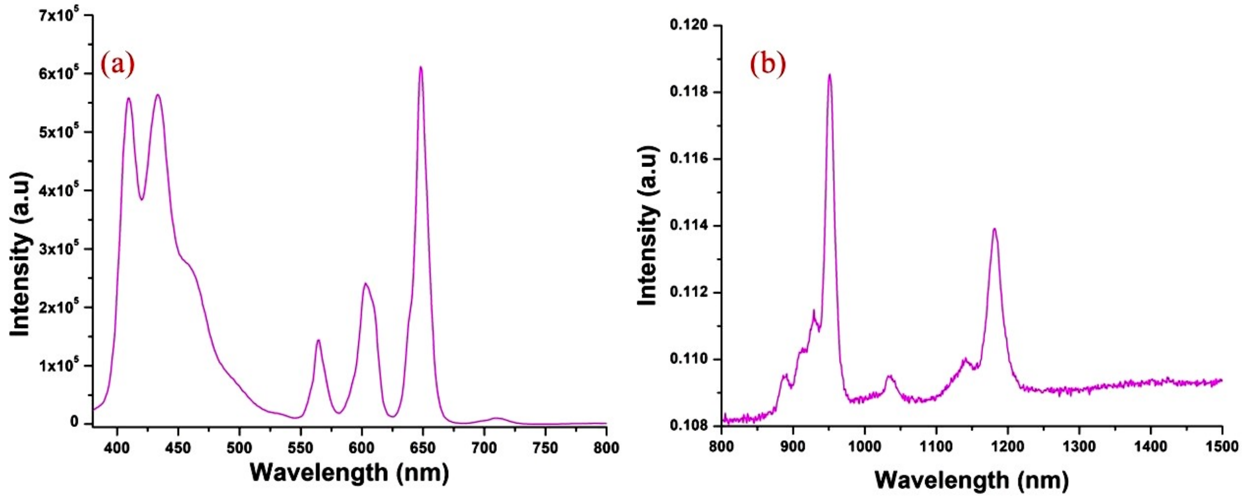

Figure S20 (a) Visible and (b) Near infra-red emission spectra of $[Sm(fod)_3(H_2O)]$ in chloroform

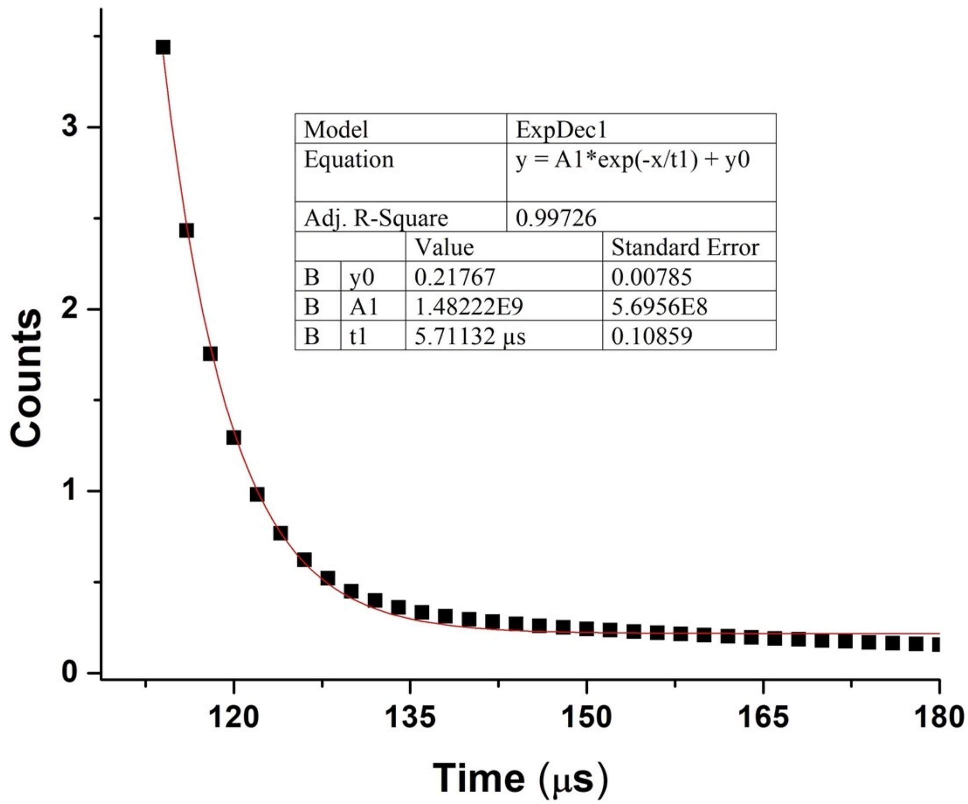

Figure S21 Excitation decay profile of $[Sm(fod)_3(H_2O)]$ in chloroform

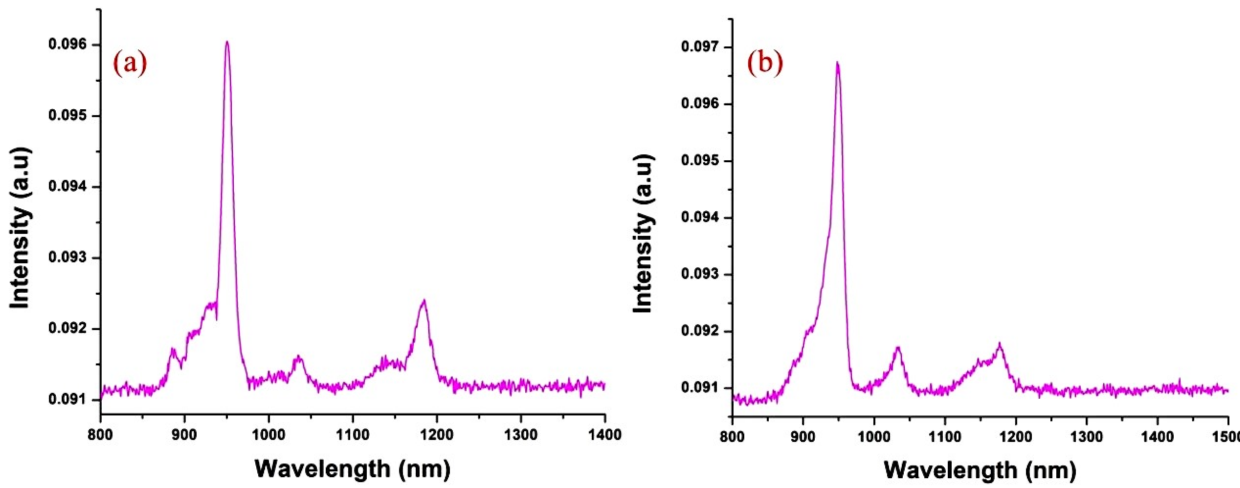

Figure S22 NIR emission spectra of (a) [Sm(fod)$_3$(bath)] and (b) [Sm(fod)$_3$(terpy)] in 3% PMMA thin film.

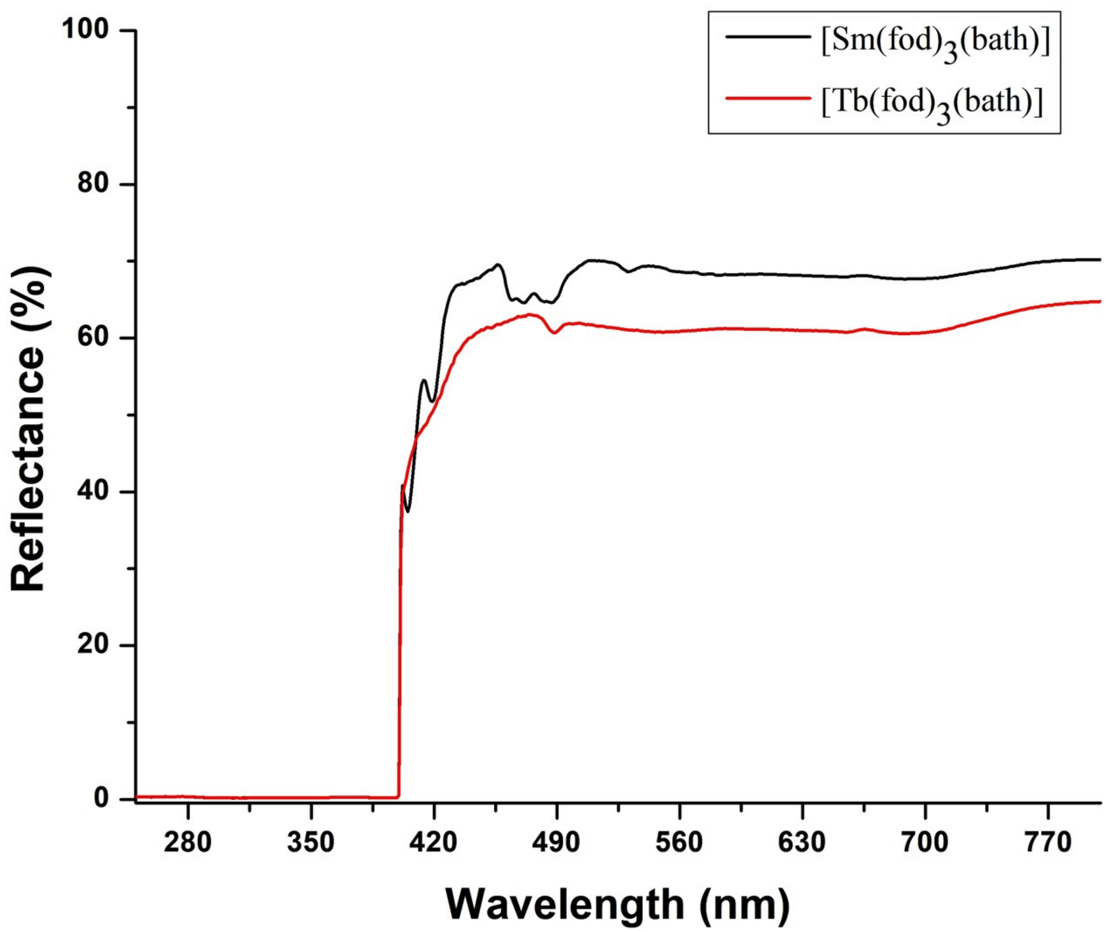

Figure S23 Diffuse reflectance spectra of bathophenanthroline (bath) complexes.

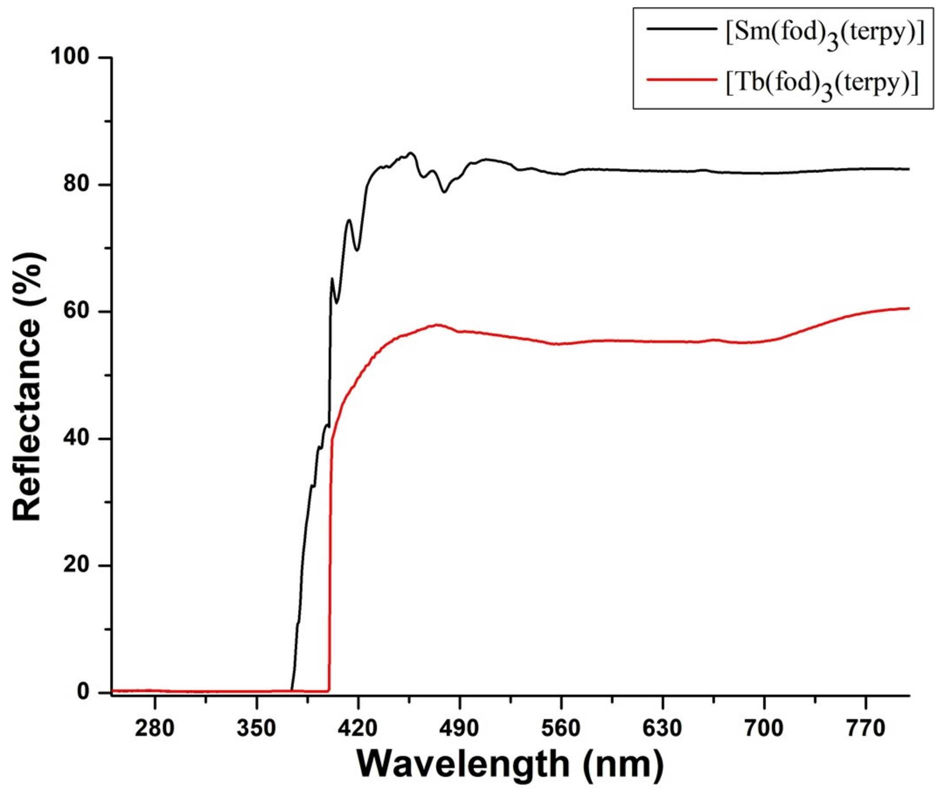

Figure S24 Diffuse reflectance spectra of terpyridine (terpy) complexes.

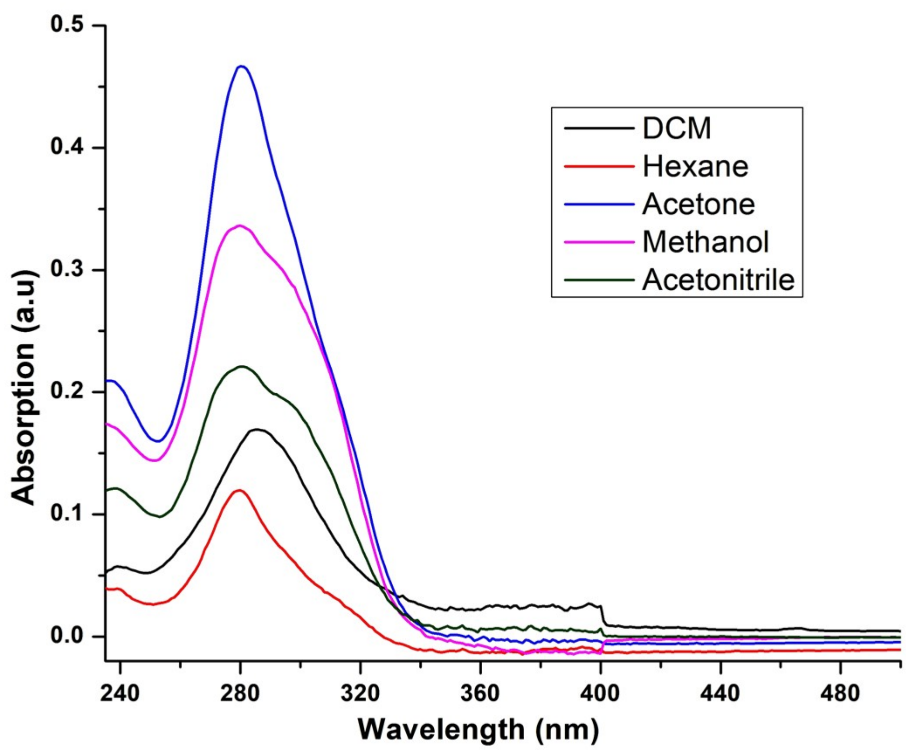

Figure S25 Absorption spectra of $[Sm(fod)_3(bath)]$ in different solvents.

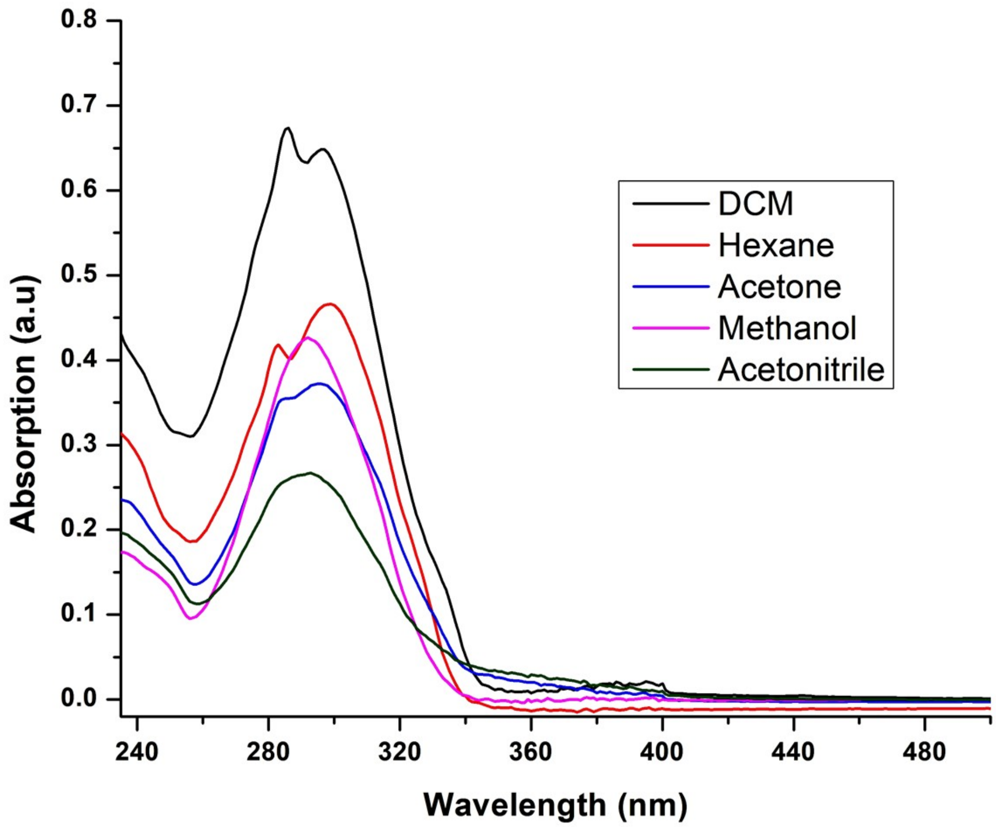

Figure S26 Absorption spectra of $[Sm(fod)_3(terpy)]$ in different solvents.

Table S1 Selected bond angles (˚) for $[Sm(fod)_3(bath)]$ complex.

Unit 1				Unit 2			
O(1)-Sm(1)-N(1)	141.43(11)	O(3)-Sm(1)-N(2)	76.01(12)	O(7)-Sm(2)-O(8)	70.36(12)	O(10)-Sm(2)-N(3)	79.32(14)
O(1)-Sm(1)-N(2)	78.88(12)	O(4)-Sm(1)-O(1)	134.01(13)	O(7)-Sm(2)-O(9)	143.87(12)	O(10)-Sm(2)-N(4)	72.42(14)
O(2)-Sm(1)-O(1)	70.77(12)	O(4)-Sm(1)-O(6)	144.46(12)	O(7)-Sm(2)-N(3)	107.82(14)	O(11)-Sm(2)-O(7)	78.48(14)
O(2)-Sm(1)-O(4)	76.13(12)	O(4)-Sm(1)-N(1)	74.36(12)	O(7)-Sm(2)-N(4)	81.00(14)	O(11)-Sm(2)-O(8)	84.07(13)
O(2)-Sm(1)-O(5)	85.28(12)	O(4)-Sm(1)-N(2)	122.04(12)	O(8)-Sm(2)-O(9)	78.98(13)	O(11)-sm(2)-O(9)	79.81(12)
O(2)-Sm(1)-O(6)	109.90(13)	O(5)-Sm(1)-O(1)	130.48(12)	O(8)-Sm(2)-N(3)	71.43(13)	O(11)-Sm(2)-N(3)	150.08(12)
O(2)-Sm(1)-N(1)	147.45(12)	O(5)-Sm(1)-O(4)	75.78(12)	O(8)-Sm(2)-N(4)	113.07(14)	O(11)-Sm(2)-N(4)	146.76(12)
O(2)-Sm(1)-N(2)	148.26(12)	O(5)-Sm(1)-O(6)	70.07(11)	O(9)-Sm(2)-N(3)	78.88(13)	O(12)-Sm(2)-O(7)	77.47(13)
O(3)-Sm(1)-O(1)	77.95(13)	O(5)-Sm(1)-N(1)	74.46(12)	O(9)-Sm(2)-N(4)	129.88(13)	O(12)-Sm(2)-O(8)	142.83(12)
O(3)-Sm(1)-O(2)	88.54(13)	O(5)-Sm(1)-N(2)	122.69(13)	O(10)-Sm(2)-O(7)	145.12(12)	O(12)-Sm(2)-O(9)	121.71(14)
O(3)-Sm(1)-O(4)	70.07(12)	O(6)-Sm(1)-O(1)	78.20(12)	O(10)-Sm(2)-O(8)	141.10(11)	O(12)-Sm(2)-O(11)	71.49(13)
O(3)-Sm(1)-O(5)	145.78(12)	O(6)-Sm(1)-N(1)	87.11(12)	O(10)-Sm(2)-O(9)	70.52(12)	O(12)-Sm(2)-N(3)	138.19(14)
O(3)-Sm(1)-O(6)	142.73(11)	O(6)-Sm(1)-N(2)	71.58(12)	O(10)-Sm(2)-O(11)	112.69(14)	O(12)-Sm(2)-N(4)	78.73(14)
O(3)-Sm(1)-N(1)	94.07(13)	N(2)-Sm(1)-N(1)	62.62(12)	O(10)-Sm(2)-O(12)	75.54(12)	N(4)-Sm(2)-N(3)	61.96(13)

Table S2 Selected bond lengths (Å) and bond angles (˚) of [Sm(fod)$_3$(terpy)]

Sm(1)-O(3)	2.373(6)	O(3)-Sm(1)-O(4)	80.0(3)	O(4)-Sm(1)-O(2)	69.8(2)	O(2)-Sm(1)-O(1)	69.2(2)
Sm(1)-O(4)	2.348(7)	O(3)-Sm(1)-O(6)	134.9(2)	O(6)-Sm(1)-O(2)	125.0(3)	O(3)-Sm(1)-N(1)	146.1(3)
Sm(1)-O(6)	2.465(6)	O(4)-Sm(1)-O(6)	73.7(2)	O(5)-Sm(1)-O(2)	133.9(3)	O(4)-Sm(1)-N(1)	84.9(3)
Sm(1)-O(5)	2.480(7)	O(3)-Sm(1)-O(5)	69.2(3)	O(3)-Sm(1)-O(1)	79.0(2)	O(6)-Sm(1)-N(1)	67.1(3)
Sm(1)-O(2)	2.455(6)	O(4)-Sm(1)-O(5)	74.7(3)	O(4)-Sm(1)-O(1)	137.2(2)	O(5)-Sm(1)-N(1)	135.0(2)
Sm(1)-O(1)	2.413(5)	O(6)-Sm(1)-O(5)	68.8(2)	O(6)-Sm(1)-O(1)	143.0(2)	O(2)-Sm(1)-N(1)	69.9(2)
Sm(1)-N(1)	2.598(8)	O(3)-Sm(1)-O(2)	76.4(2)	O(5)-Sm(1)-O(1)	129.7(3)	O(1)-Sm(1)-N(1)	92.2(2)
Sm(1)-N(2)	2.640(7)	O(1)-Sm(1)-N(3)	67.2(2)	N(3)-Sm(1)-N(1)	124.4(2)	O(2)-Sm(1)-N(2)	112.0(2)
Sm(1)-N(3)	2.598(8)	O(2)-Sm(1)-N(3)	134.2(2)	O(4)-Sm(1)-N(2)	141.4(3)	O(6)-Sm(1)-N(2)	75.2(2)
O(4)-Sm(1)-N(3)	144.9(3)	O(6)-Sm(1)-N(3)	98.6(3)	O(3)-Sm(1)-N(2)	138.5(2)	O(5)-Sm(1)-N(2)	114.1(3)
O(3)-Sm(1)-N(3)	82.5(2)	O(5)-Sm(1)-N(3)	70.7(3)	O(1)-Sm(1)-N(2)	67.9(2)	N(3)-Sm(1)-N(2)	62.3(2)

Table S3 Spherical coordinates of the coordination polyhedron for Sparkle/PM7 optimized structure of Sm(fod)$_3$(bath).

PM7	R (Å)	(θ)°	(Φ)°
Sm	0.00000	0.000	0.000
O(fod)	2.36710	127.268	141.708
O(fod)	2.38630	69.189	169.630
O(fod)	2.39881	71.238	75.233
O(fod)	2.37450	117.103	29.911
O(fod)	2.39597	83.535	318.984
O(fod)	2.38194	134.487	275.823
N(bath)	2.55029	67.658	250.980
N(bath)	2.54781	15.632	328.248

Table S4 Spherical coordinates of the coordination polyhedron for Sparkle/PM7 optimized structure of $Sm(fod)_3(terpy)$.

PM7	R (Å)	(θ)°	(Φ)°
Sm	0.00000	0.000	0.000
O(fod)	2.40388	59.915	164.901
O(fod)	2.41111	41.057	247.030
O(fod)	2.40190	153.754	5.303
O(fod)	2.40057	100.217	54.938
O(fod)	2.40667	73.306	332.187
O(fod)	2.39699	31.306	40.243
N(terpy)	2.55398	132.257	192.496
N(terpy)	2.55291	103.611	259.348
N(terpy)	2.55751	108.835	121.083

Table S5 SHAPE measured deviations from ideal eight coordinate geometries of $[Sm(fod)_3(bath)]$ complex.

S. No.	SHAPE	Symmetry	Deviation $[Sm(fod)_3(bath)]$
1	Octagon	D_{8h}	30.111
2	Heptagonal pyramid	C_{7v}	20.939
3	Hexagonal bipyramid	D_{6h}	16.673
4	Cube	Oh	10.484
5	Square antiprism	D_{4d}	**0.691**
6	Triangular dodecahedron	D_{2d}	2.100
7	Johnson gyrobifastigium J26	D_{2d}	15.093
8	Johnson elongated triangular bipyramid J14	D_{3h}	27.657
9	Biaugmented trigonal prism J50	C_{2v}	3.014
10	Biaugmented trigonal prism	C_{2v}	2.336
11	Snub diphenoid J84	D_{2d}	4.907
12	Triakis tetrahedron	Td	11.178
13	Elongated trigonal bipyramid	D_{3h}	22.917

Table S6 SHAPE measured deviations from ideal nine coordinate geometries of $Sm(fod)_3(terpy)$ complex.

S. No.	SHAPE	Symmetry	Deviation $[Sm(fod)_3(terpy)]$
1	Enneagon	D_{9h}	36.838
2	Octagonal pyramid	C_{8v}	21.070
3	Heptagonal bipyramid	D_{7h}	16.693
4	Johnson triangular cupola J3	C_{3v}	15.792
5	Capped cube J8	C_{4v}	9.737
6	Spherical-relaxed capped cube	C_{4v}	8.422
7	Capped square antiprism J10	C_{4v}	2.206
8	Spherical capped square antiprism	C_{4v}	1.153
9	Tricapped trigonal prism J51	D_{3h}	2.833
10	Spherical tricapped trigonal prism	D_{3h}	1.328
11	Tridiminished icosahedron J63	C_{3v}	11.538
12	Hula-hoop	C_{2v}	11.491
13	Muffin	C_S	**1.029**

Table S7 SHAPE measured deviations from ideal eight coordinate geometry in Sparkle/PM7 predicted $Sm(fod)_3(bath)$ complex.

S.No.	SHAPE	Symmetry	Deviation $[Sm(fod)_3(bath)]$
1	Octagon	D8h	30.397
2	Heptagonal pyramid	C7v	20.296
3	Hexagonal bipyramid	D6h	16.954
4	Cube	Oh	9.790
5	Square antiprism	D4d	**1.405**
6	Triangular dodecahedron	D2d	3.153
7	Johnson gyrobifastigium J26	D2d	15.747
8	Johnson elongated triangular bipyramid J14	D3h	26.165
9	Biaugmented trigonal prism J50	C2v	3.858
10	Biaugmented trigonal prism	C2v	3.123
11	Snub diphenoid J84	D2d	6.103

Table S8 SHAPE measured deviations from ideal seven coordinate geometries in Sparkle/PM7 predicted $Sm(fod)_3(terpy)$ complex.

S. No.	SHAPE	Symmetry	Deviation $[Sm(fod)_3(terpy)]$
1	Enneagon	D_{9h}	33.356
2	Octagonal pyramid	C_{8v}	21.936
3	Heptagonal bipyramid	D_{7h}	15.128
4	Johnson triangular cupola J3	C_{3v}	16.005
5	Capped cube J8	C_{4v}	7.891
6	Spherical-relaxed capped cube	C_{4v}	6.570
7	Capped square antiprism J10	C_{4v}	3.777
8	Spherical capped square antiprism	C_{4v}	2.565
9	Tricapped trigonal prism J51	D_{3h}	5.234
10	Spherical tricapped trigonal prism	D_{3h}	2.979
11	Tridiminished icosahedron J63	C_{3v}	11.088
12	Hula-hoop	C_{2v}	8.461
13	Muffin	C_S	**1.493**