

Electronic Supporting Information

Eight Rare Earth Metal Organic Frameworks and Coordination Polymers from 2-Nitroterephthalate: Syntheses, Structures, Solid-State Luminescence and an Unprecedented Topology.

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New Journal of Chemistry

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1. Crystal Data and Hydrogen Bonding Tables

Table S1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1-3, 5, and 7-8

Compound 1					
La1-O2#1	2.4557(17)	La1-O1	2.4746(17)	La1-O7#2	2.4902(17)
La1-O3#3	2.5047(16)	La1-O11	2.5529(18)	La1-O12	2.5579(18)
La1-O13	2.5817(17)	La1-O8	2.5907(17)	La1-O7	2.7806(16)
O2#1-La1-O1	89.93(6)	O2#1-La1-O7#2	147.47(6)	O1-La1-O3#3	136.85(6)
O8-La1-O7	48.28(5)	O3#3-La1-O11	136.73(6)	O11-La1-O12	134.58(6)
O1-La1-O13	73.92(6)	O11-La1-O13	70.13(6)	O12-La1-O13	124.82(6)
symmetry codes: #1: -x+2, -y+1, -z+2; #2: -x+2, -y, -z+2; #3: x+1, y, z+1					
Compound 2					
Nd1-O1	2.545(5)	Nd1-O2	2.424(4)	Nd1-O3	2.562(5)
Nd1-O4	2.513(5)	Nd1-O2#1	2.607(4)	Nd1-O7	2.427(4)
Nd1-O8	2.476(5)	Nd1-OW1	2.479(5)	Nd1-OW2	2.442(5)
O7-Nd1-O3	73.10(15)	OW2-Nd1-O3	71.21(17)	OW1-Nd1-O3	109.62(18)
OW2-Nd1-O2#1	118.85(17)	O4-Nd1-O2#1	145.38(15)	OW1-Nd1-O2#1	111.15(17)
O3-Nd1-O2#1	139.07(14)	O8-Nd1-O3	121.90(16)	O4-Nd1-O3	51.22(15)
symmetry codes: #1: -x,-y,-z+1; #2: x+1,y+1,z; #3: x-1,y-1,z					
Compound 3					
Nd1-O1	2.492(4)	Nd1-O2	2.449(4)	Nd1-O3	2.383(4)
Nd1-O4	2.406(3)	Nd1-O5	2.517(3)	Nd1-O5#2	2.644(3)
Nd1-O6	2.499(4)	Nd1-O6#1	2.588(3)	Nd1-O7	2.465(4)
O2-Nd1-O1	52.86(12)	O3-Nd1-O1	77.46(12)	O4-Nd1-O1	128.78(12)
O2-Nd1-O5	79.66(12)	O2-Nd1-O7	117.18(14)	O3-Nd1-O2	120.57(13)
O3-Nd1-O4	138.33(12)	O6#1-Nd1-O5#2	49.47(11)	O7-Nd1-O5	145.35(13)
symmetry codes: #1: x+1/2,-y+1/2,-z+1; #2: x-1/2,-y+1/2,-z+1; #3: x,-y+1/2,z+1/2; #4: x,-y+1/2,z-1/2					
Compound 5					
Eu1-O1	2.3122(15)	Eu1-O2#1	2.3490(14)	Eu(1)-O(7)	2.3550(15)
Eu1-O3#2	2.3735(15)	Eu1-O11	2.3978(16)	Eu1-O8#3	2.4089(15)

Eu1-O4#4	2.4918(15)	Eu1-O3#4	2.6028(15)	O(1)-C(1)	1.260(3)
O1-Eu1-O2#1	87.44(5)	O1-Eu1-O7	99.63(5)	O2#1-Eu1-O3#2	142.34(5)
O7-Eu1-O11	149.77(5)	O2#1-Eu1-O8#3	144.43(5)	O4#4-Eu1-O3#4	50.89(5)
O1-Eu1-O4#4	157.82(5)	O3#2-Eu1-O11	134.35(5)	O1-Eu1-O8#3	100.88(5)
symmetry codes: #1: -x+1, -y+1, -z+1; #2: -x+1/2, -y+1/2, -z+1; #3: x, y-1, z; #4: x+1/2, -y+1/2, z-1/2					
Compound 7					
Tb1-O1	2.2850(14)	Tb1-O2#1	2.3222(14)	Tb1-O7	2.3269(14)
Tb1-O3#2	2.3479(15)	Tb1-O11	2.3693(16)	Tb1-O8#3	2.3860(15)
Tb1-O4#4	2.4627(15)	Tb1-O3#4	2.5819(15)	O1-C1	1.260(2)
O1-Tb1-O2#1	86.86(5)	O1-Tb1-O7	99.095	O2#1-Tb1-O3#2	142.46(5)
O7-Tb1-O11	149.69(5)	O7-Tb1-O8#3	137.03(5)	O4#4-Tb1-O3#4	51.39(5)
O11-Tb1-O3#4	117.10(5)	O1-Tb1-O4#4	157.62(5)	O11-Tb1-O8#3	70.56(5)
symmetry codes: #1: -x+1, -y+1, -z+1; #2: -x+1/2, -y+1/2, -z+1; #3: x, y-1, z; #4: x+1/2, -y+1/2, z+1/2.					
Compound 8					
Er1-O1	2.2499(16)	Er1-O2#1	2.2904(16)	Er1-O7	2.2925(15)
Er1-O3#2	2.3155(16)	Er1-O11	2.3322(17)	Er1-O8#3	2.3532(15)
Er1-O4#4	2.4250(17)	Er1-O3#4	2.5495(16)	O1-C1	1.262(3)
O1-Er1-O2#1	86.52(6)	O1-Er1-O7	99.25(6)	O2#1-Er1-O3#2	142.49(6)
O7-Er1-O11	149.57(6)	O7-Er1-O8#3	137.55(6)	O4#4-Er1-O3#4	52.01(5)
O11-Er1-O3#4	117.78(6)	O1-Er1-O4#4	157.18(6)	O1-Er1-O8#3	100.38(6)
symmetry codes: #1: -x+1,-y+1,-z+1; #2: -x+1/2,-y+1/2,-z+1; #3: x,y-1,z; #4: x+1/2,-y+1/2,z+1/2					

Table S2. Hydrogen Bonds for Compound 1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(10)...O(3)#6	0.84	2.02	2.829(3)	161.0
O(11)-H(20)...O(4)#7	0.84	2.17	2.943(3)	153.4
O(12)-H(30)...O(5)#8	0.84	2.14	2.940(3)	158.8
O(12)-H(40)...O(4)#3	0.84	1.96	2.756(3)	157.7
O(13)-H(50)...O(4)#7	0.84	1.89	2.720(2)	169.7
O(13)-H(60)...O(2)	0.84	2.27	2.989(2)	143.6
O(13)-H(60)...O(12)#1	0.84	2.49	3.168(3)	138.0

Symmetry transformations used to generate equivalent atoms:

#1: -x+2,-y+1,-z+2 #2: -x+2,-y,-z+2 #3: x+1,y,z+1 #4: x-1,y,z-1 #5: -x+2,-y,-z+3 #6: -x+1,-y,-z+1

Table S3. Hydrogen Bonds for Compound 5 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(10)...O(6)#9	0.82	2.19	2.977(3)	160.1
O(11)-H(20)...O(1W)	0.78	1.86	2.640(3)	171.3
O(1W)-H(1WA)...O(5)#10	0.91	2.02	2.904(3)	163.8
O(1W)-H(1WB)...O(4)#11	0.99	1.82	2.806(2)	170.9

Symmetry transformations used to generate equivalent atoms:

#1: -x+1,-y+1,-z+1 #2: -x+1/2,-y+1/2,-z+1 #3: x,y-1,z #4: x+1/2,-y+1/2,z-1/2 #5: -x+1,y,-z+1/2
 #6: x-1/2,-y+1/2,z+1/2 #7: x,y+1,z #8: -x+1,-y+2,-z+1 #9: -x+1,-y,-z+1 #10: x+1/2,y+1/2,z
 #11: -x+1,y,-z+3/2

Table S4. Hydrogen Bonds for Compound **6** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(10)...O(6)#9	0.83	2.17	2.978(3)	162.0
O(11)-H(20)...O(1W)	0.81	1.84	2.641(3)	171.0
O(1W)-H(1WA)...O(5)#10	0.92	2.01	2.897(3)	163.3
O(1W)-H(1WB)...O(4)#11	0.99	1.83	2.811(3)	171.0

Symmetry transformations used to generate equivalent atoms:

#1: -x+1,-y+1,-z+1 #2: -x+1/2,-y+1/2,-z+1 #3: x,y-1,z #4: x+1/2,-y+1/2,z+1/2 #5: -x+1,y,-z+3/2
 #6: x-1/2,-y+1/2,z-1/2 #7: x,y+1,z #8: -x+1,-y+2,-z+1 #9: -x+1,-y,-z+1 #10: x+1/2,y+1/2,z
 #11: -x+1,y,-z+1/2

Table S5. Hydrogen Bonds for Compound **7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(10)...O(6)#9	0.85	2.15	2.985(3)	163.8
O(11)-H(20)...O(1W)	0.84	1.82	2.646(3)	170.3
O(1W)-H(1WA)...O(4)#10	0.98	1.86	2.823(3)	170.4
O(1W)-H(1WB)...O(5)#11	0.92	1.99	2.882(3)	162.3

Symmetry transformations used to generate equivalent atoms:

#1: -x+1,-y+1,-z+1 #2: -x+1/2,-y+1/2,-z+1 #3: x,y-1,z #4: x+1/2,-y+1/2,z+1/2 #5: -x+1,y,-z+3/2
 #6: x-1/2,-y+1/2,z-1/2 #7: x,y+1,z #8: -x+1,-y+2,-z+1 #9: -x+1,-y,-z+1 #10: -x+1,y,-z+1/2
 #11: x+1/2,y+1/2,z

2. IR Spectra and PXRD Patterns

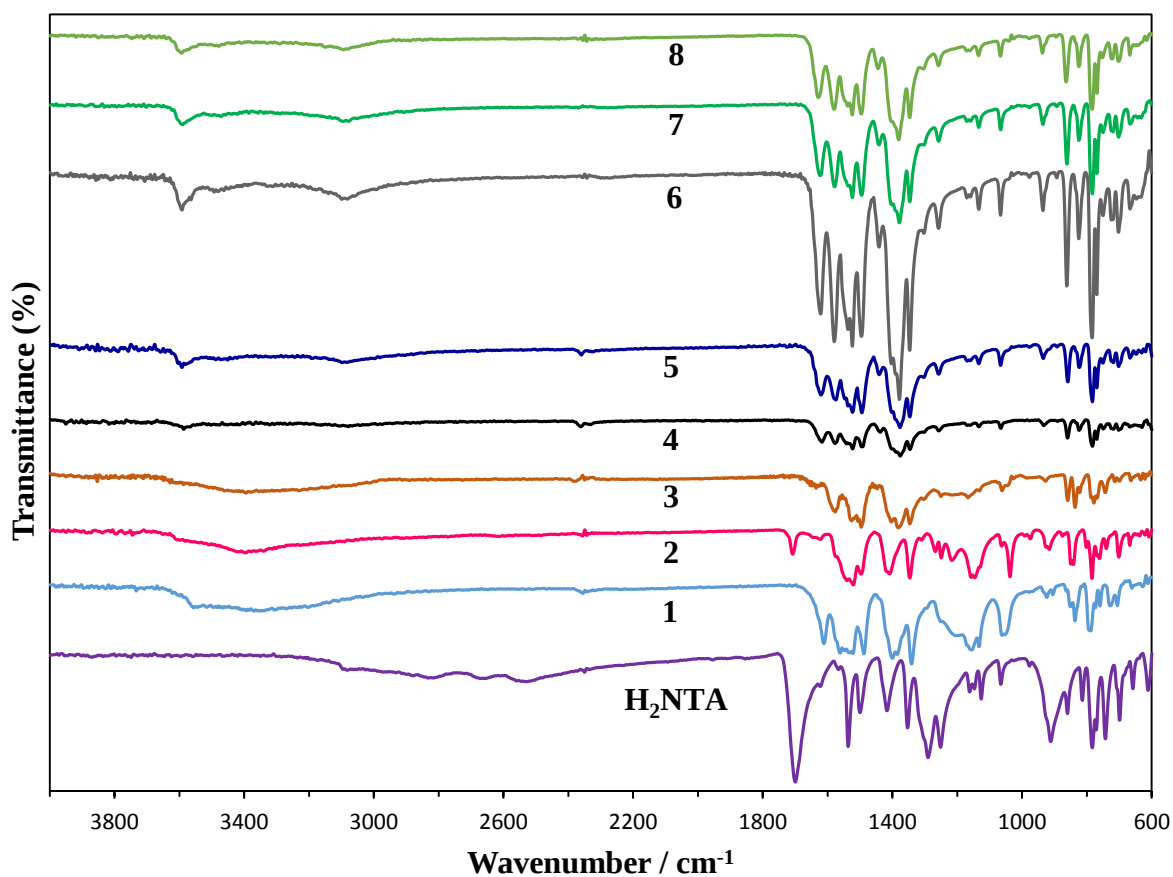


Figure S1. FT-IR spectra of compounds **1-8** and H_2NTA ligand in the solid state at room temperature.

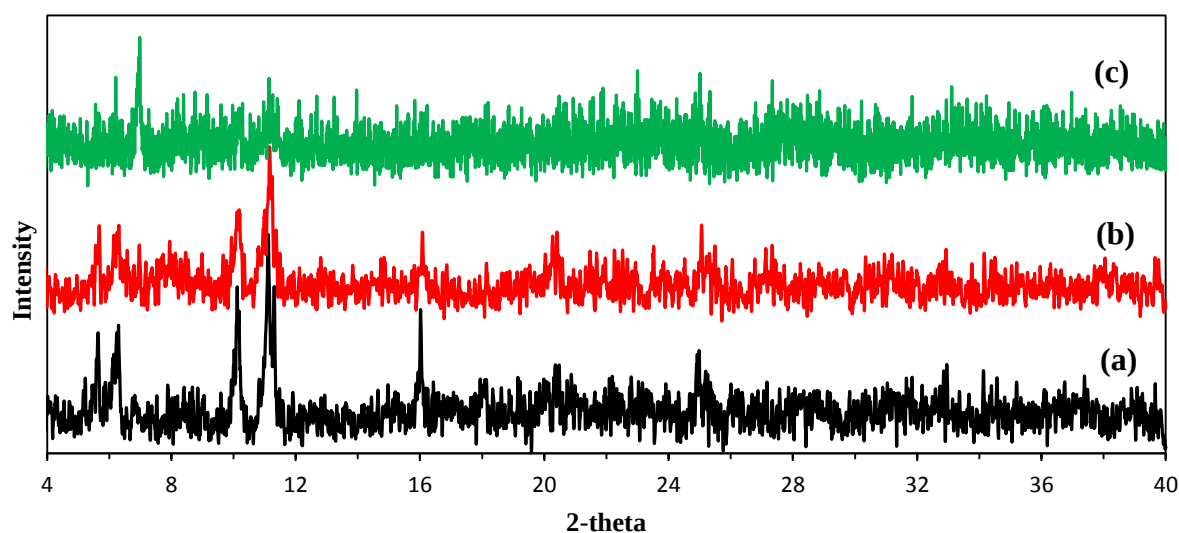


Figure S2. PXRD data for the Eu(III) (a), Tb(III) (b) and Er(III) (c) analogues of compound **2**.

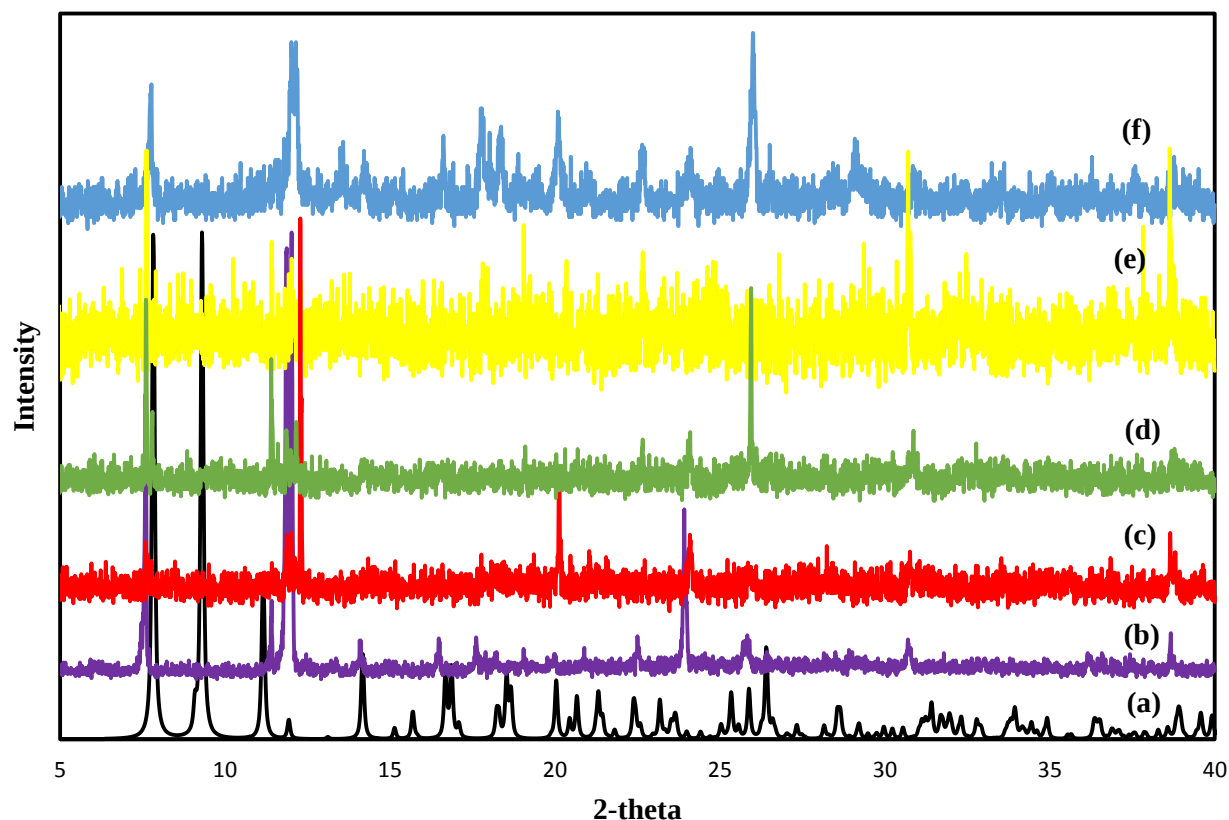


Figure S3. Simulated and as-synthesized PXRD scans of Compound **2** showing preferred orientation effects. Compound **2** simulated (a); specimen #1: crushed and dispersed in acetone on glass slide (b); specimen #2: crushed, thin layer mounted on glass side and pressed (c); specimen #3: crushed, thin layer mounted on glass side and pressed (d); specimen #4: uncrushed single crystals on glass slide (e); specimen #5: dry crushed, un-pressed thin layer on glass slide (f). Note the difference in peak intensities with varying specimen preparation methods.

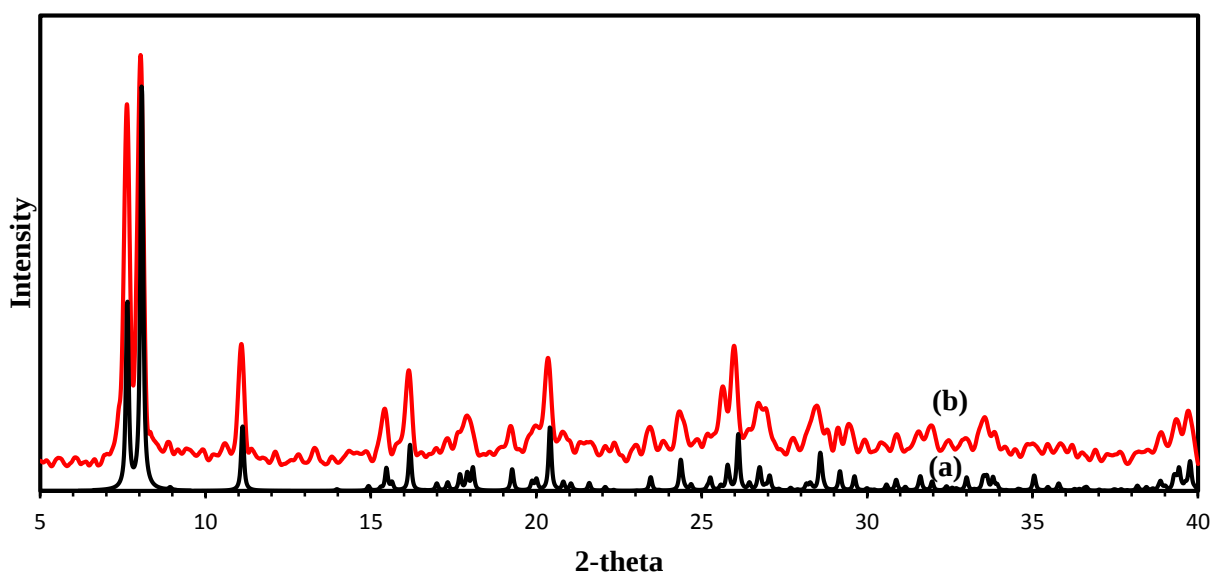


Figure S4. Simulated (a) and as-synthesized (b) PXRD patterns of compound **3**.

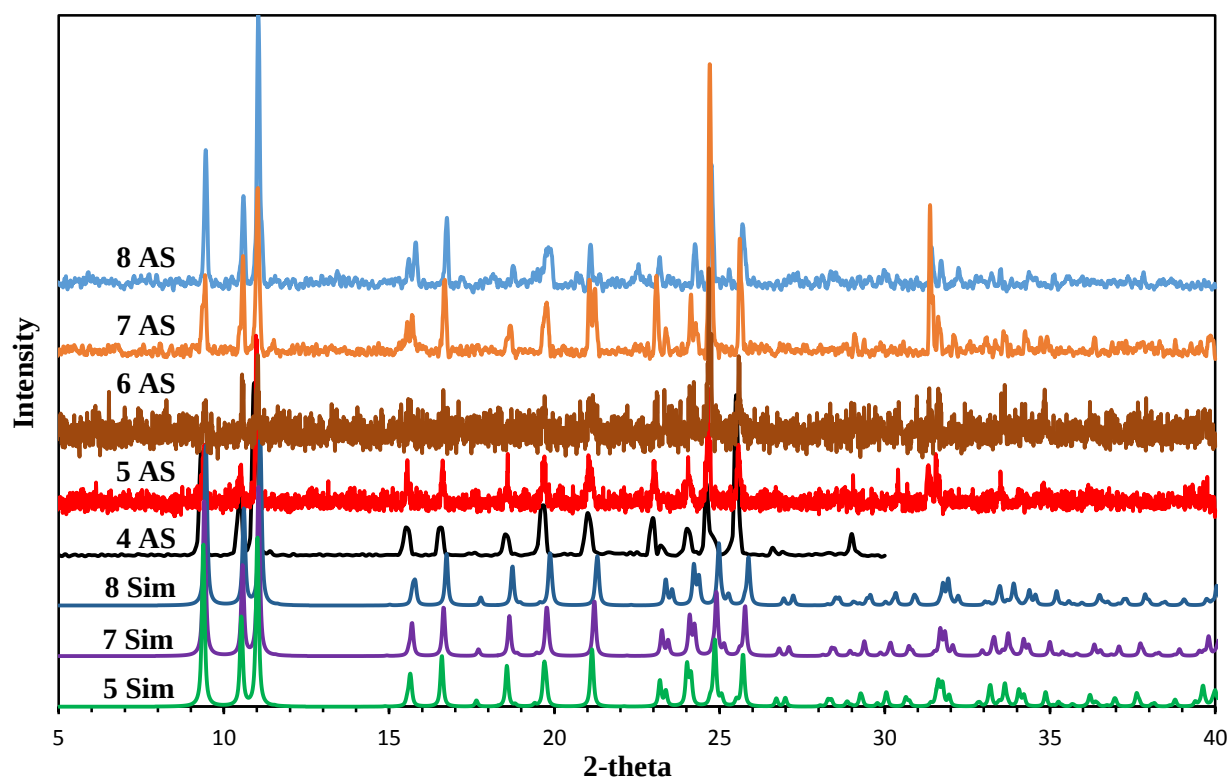


Figure S5. Simulated (Sim) and as-synthesized (AS) PXRD patterns for compounds **4-8**.

3. TGA-DSC Scans

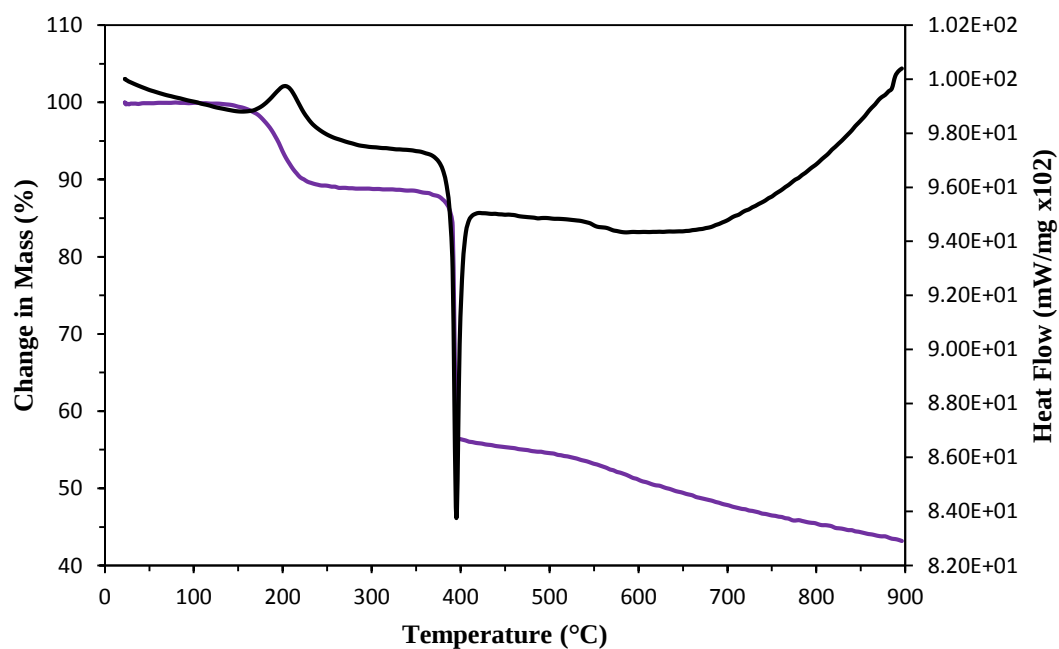


Figure S6. TGA/DSC scan of compound **1**.

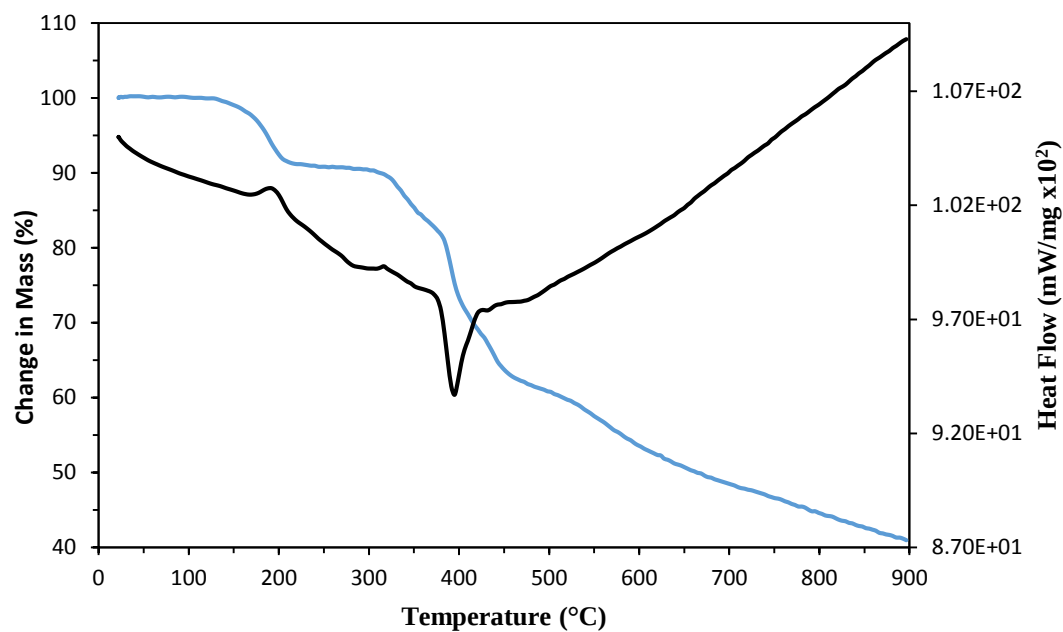


Figure S7. TGA/DSC scan of compound 2.

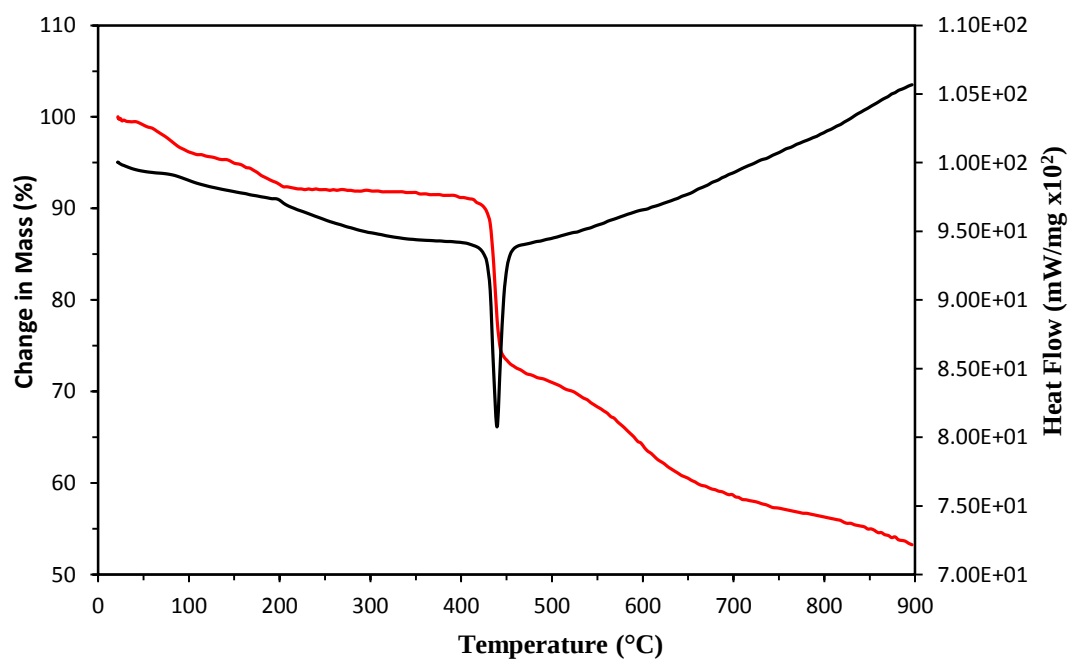


Figure S8. TGA/DSC scan of compound 3.

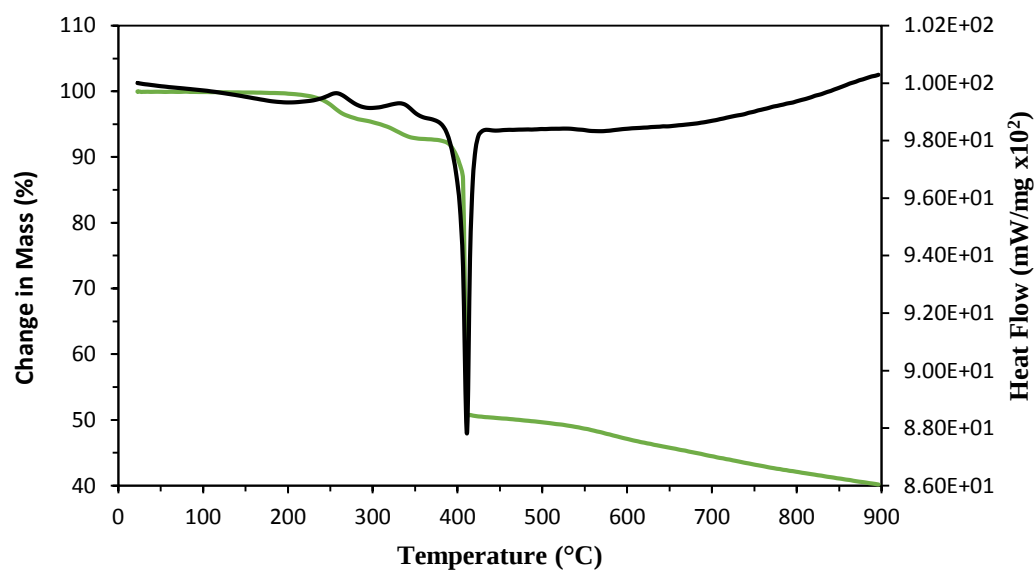


Figure S9. TGA/DSC scan of compound 5.

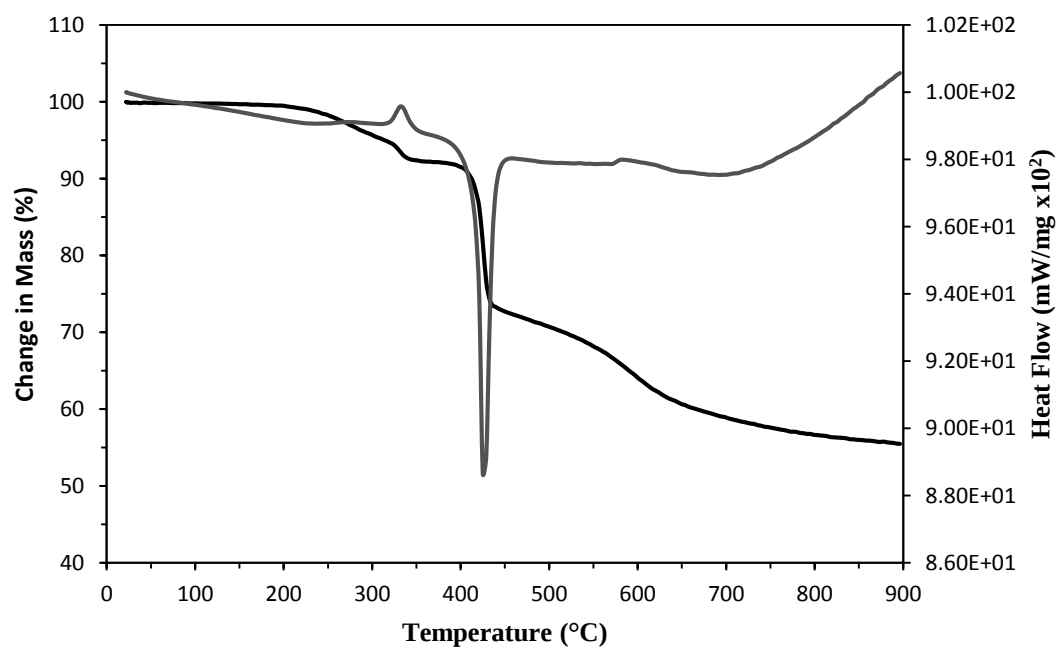


Figure S10. TGA/DSC scan of compound 8.

4. Emission Spectra

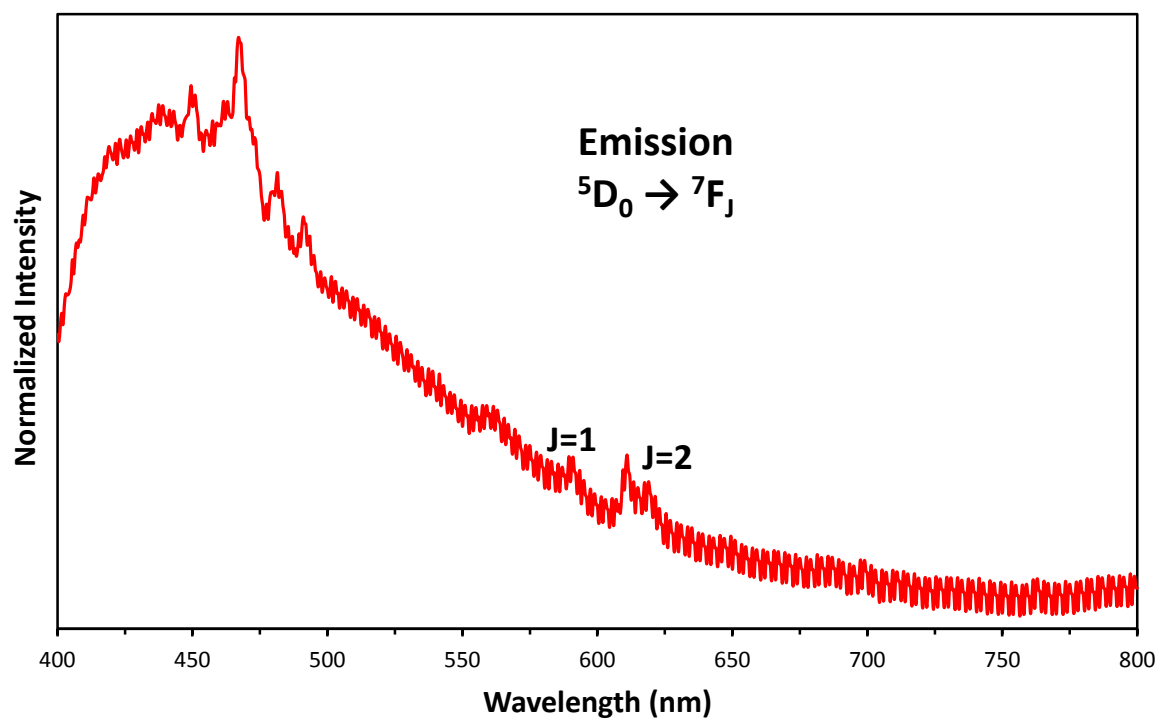


Figure S11. 298 K solid state emission spectrum for compound **5** exciting into the ligand at 327 nm.

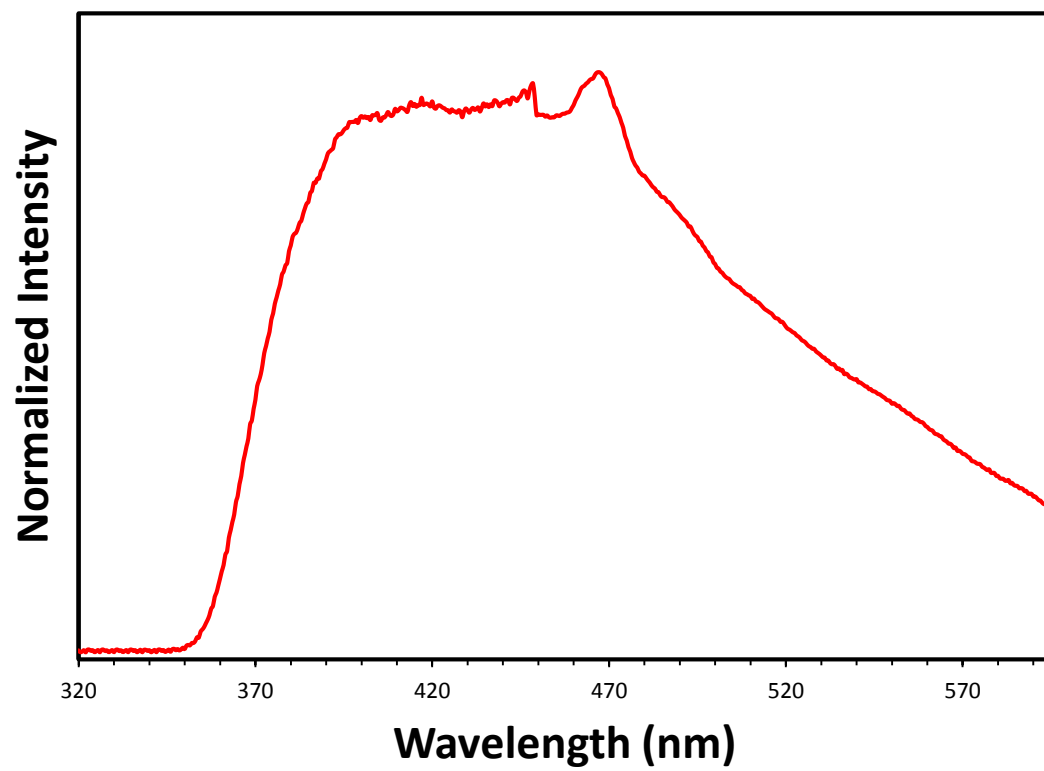


Figure S12. 77 K solid state emission spectrum of compound **6** ($\lambda_{\text{exc}} = 250$ nm).