SUPPORTING INFORMATION

Rational design of triple bridged dinuclear $Zn^{II}Ln^{III}$ based complexes: A structural, magnetic and luminescent study

Andoni Zabala,[a] Javier Cepeda,[a] Itziar Oyarzabal,[a] Antonio Rodríguez-Diéguez,[b] José Ángel García,[c] José Manuel Seco[a] and Enrique Colacio*[b]*

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1. Elemental Analyses and Crystallographic Tables.

Table S1.- Yields and elemental analyses for complexes **1-12**.

Complex	Yield (%)	Formula	% C calc./found	% H calc./found	% N calc./found
1	53	$C_{24}H_{33}N_4O_{12}ZnY$	39.82/39.66	4.60/4.63	7.74/7.87
2	25	$C_{24}H_{33}N_4O_{12}ZnPr$	37.15/37.39	4.29/4.72	7.22/7.44
3	33	$C_{24}H_{33}N_4O_{12}ZnNd$	37.00/37.15	4.27/4.22	7.19/7.04
4	45	$C_{24}H_{33}N_4O_{12}ZnSm$	36.71/36.41	4.24/4.18	7.13/7.16
5	41	$C_{24}H_{33}N_4O_{12}ZnEu$	36.63/36.96	4.23/4.47	7.12/7.33
6	56	$C_{24}H_{33}N_4O_{12}ZnGd$	36.39/36.10	4.20/3.95	7.07/6.82
7	31	$C_{24}H_{33}N_4O_{12}ZnTb$	36.31/36.33	4.19/4.02	7.06/7.25
8	60	$C_{24}H_{33}N_4O_{12}ZnDy$	36.15/36.42	4.17/4.39	7.03/7.29
9	43	$C_{24}H_{33}N_4O_{12}ZnHo$	36.04/35.83	4.16/3.88	7.00/7.12
10	58	$C_{24}H_{33}N_4O_{12}ZnEr$	35.93/36.26	4.15/3.99	6.98/7.16
11	33	$C_{24}H_{33}N_4O_{12}ZnTm$	35.86/36.01	4.14/4.29	6.97/7.21
12	40	$C_{24}H_{33}N_4O_{12}ZnYb$	35.68/35.54	4.12/3.95	6.93/6.72

Table S2.- Bond lengths (Å) and angles (°) for compounds **1**, **8**, **10** and **11**.

Compound	**1**	**8**	**10**	**11**
Ln(1)···Zn(1)	3.3164(4)	3.3237(5)	3.3100(4)	3.2945(5)
Ln(1)-O(1A)	2.2184(17)	2.228(2)	2.210(2)	2.185(3)
Ln(1)-O(2A)	2.5683(18)	2.581(2)	2.564(2)	2.565(3)
Ln(1)-O(3A)	2.3172(16)	2.327(2)	2.302(2)	2.291(3)
Ln(1)-O(4A)	2.4752(18)	2.491(2)	2.469(2)	2.474(3)
Ln(1)-O(2D)bridge	2.2995(18)	2.311(2)	2.288(2)	2.282(3)
Ln(1)-O(5A)nitrate	2.431(2)	2.446(3)	2.423(2)	2.421(3)
Ln(1)-O(6A)nitrate	2.4500(18)	2.465(2)	2.436(2)	2.432(3)
Ln(1)-O(8A)nitrate	2.4278(18)	2.431(2)	2.411(2)	2.401(3)
Ln(1)-O(9A)nitrate	2.4823(19)	2.491(3)	2.477(2)	2.444(3)
Zn(1)-N(1A)	2.101(2)	2.090(3)	2.097(2)	2.086(3)
Zn(1)-N(2A)	2.147(2)	2.149(3)	2.144(3)	2.148(4)
Zn(1)-O(1A)	2.0482(18)	2.054(2)	2.049(2)	2.053(3)
Zn(1)-O(3A)	2.0344(17)	2.030(2)	2.032(2)	2.028(3)
Zn(1)-O(1D)bridge	1.9658(18)	1.974(2)	1.967(2)	1.970(3)
Ln(1)-O(1A)-Zn(1)	101.95(8)	101.73(9)	101.94(8)	102.00(12)
Ln(1)-O(3A)-Zn(1)	99.10(7)	99.20(9)	99.41(8)	99.24(11)
O(1A)-Ln(1)-O(3A)	65.99(6)	65.96(8)	66.12(7)	66.43(10)
O(1A)-Ln(1)-O(2D)bridge	84.49(7)	84.38(9)	84.76(8)	84.89(11)
O(3A)-Ln(1)-O(2D)bridge	77.50(6)	77.40(9)	77.60(8)	78.03(10)
O(1A)-Zn(1)-O(3A)	74.50(7)	74.81(9)	74.24(8)	73.89(11)
O(1A)-Zn(1)-O(1D)bridge	103.86(8)	103.73(10)	103.71(9)	103.31(12)
O(3A)-Zn(1)-O(1D)bridge	109.89(7)	109.77(10)	109.63(9)	110.06(12)
N(1A)-Zn(1)-N(2A)	86.51(9)	86.38(12)	86.80(10)	86.89(14)

Table S3.- Bond lengths (Å) and angles (°) for compounds **1**, **8**, **10** and **11**.

Compound	**1**	**8**	**10**	**11**
Ln(2)···Zn(2)	3.3293(4)	3.3411(5)	3.3270(4)	3.2982(5)
Ln(2)-O(1B)	2.2320(17)	2.244(2)	2.226(2)	2.208(3)
Ln(2)-O(2B)	2.5383(18)	2.559(2)	2.537(2)	2.526(3)
Ln(2)-O(3B)	2.2785(17)	2.294(2)	2.272(2)	2.248(3)
Ln(2)-O(4B)	2.5622(18)	2.564(2)	2.559(2)	2.533(3)
Ln(2)-O(2E)bridge	2.2995(18)	2.319(2)	2.299(2)	2.269(3)
Ln(2)-O(5B)nitrate	2.3960(19)	2.483(3)	2.390(2)	2.371(3)
Ln(2)-O(6B)nitrate	2.468(2)	2.414(2)	2.456(2)	2.392(4)
Ln(2)-O(8B)nitrate	2.432(2)	2.530(3)	2.424(2)	2.300(3)
Ln(2)-O(9B)nitrate	2.537(2)	2.450(3)	2.534(3)	2.591(7)
Zn(2)-N(1B)	2.112(2)	2.109(3)	2.111(3)	2.105(3)
Zn(2)-N(2B)	2.134(2)	2.140(3)	2.135(3)	2.126(3)
Zn(2)-O(1B)	2.0342(18)	2.043(2)	2.035(2)	2.042(3)
Zn(2)-O(3B)	2.0378(17)	2.037(2)	2.038(2)	2.039(3)
Zn(2)-O(1E)bridge	1.9865(18)	1.983(2)	1.979(2)	1.981(3)
Ln(2)-O(1B)-Zn(2)	102.49(7)	102.31(10)	102.55(9)	101.72(11)
Ln(2)-O(3B)-Zn(2)	100.80(7)	100.79(9)	100.90(8)	100.48(11)
O(1B)-Ln(2)-O(3B)	65.36(6)	65.32(8)	65.43(7)	66.12(9)
O(1B)-Ln(2)-O(2E)bridge	83.41(6)	82.91(9)	83.56(8)	85.87(10)
O(3B)-Ln(2)-O(2E)bridge	82.20(6)	81.67(8)	82.35(8)	83.64(10)
O(1B)-Zn(2)-O(3B)	73.48(7)	73.79(9)	73.30(8)	73.13(11)
O(1B)-Zn(2)-O(1E)bridge	103.27(7)	103.22(10)	102.99(9)	103.02(11)
O(3B)-Zn(2)-O(1E)bridge	106.90(7)	107.46(10)	106.78(9)	105.61(11)
N(1B)-Zn(2)-N(2B)	86.31(9)	86.29(12)	86.21(10)	86.22(13)

1. Experimental XRPD.

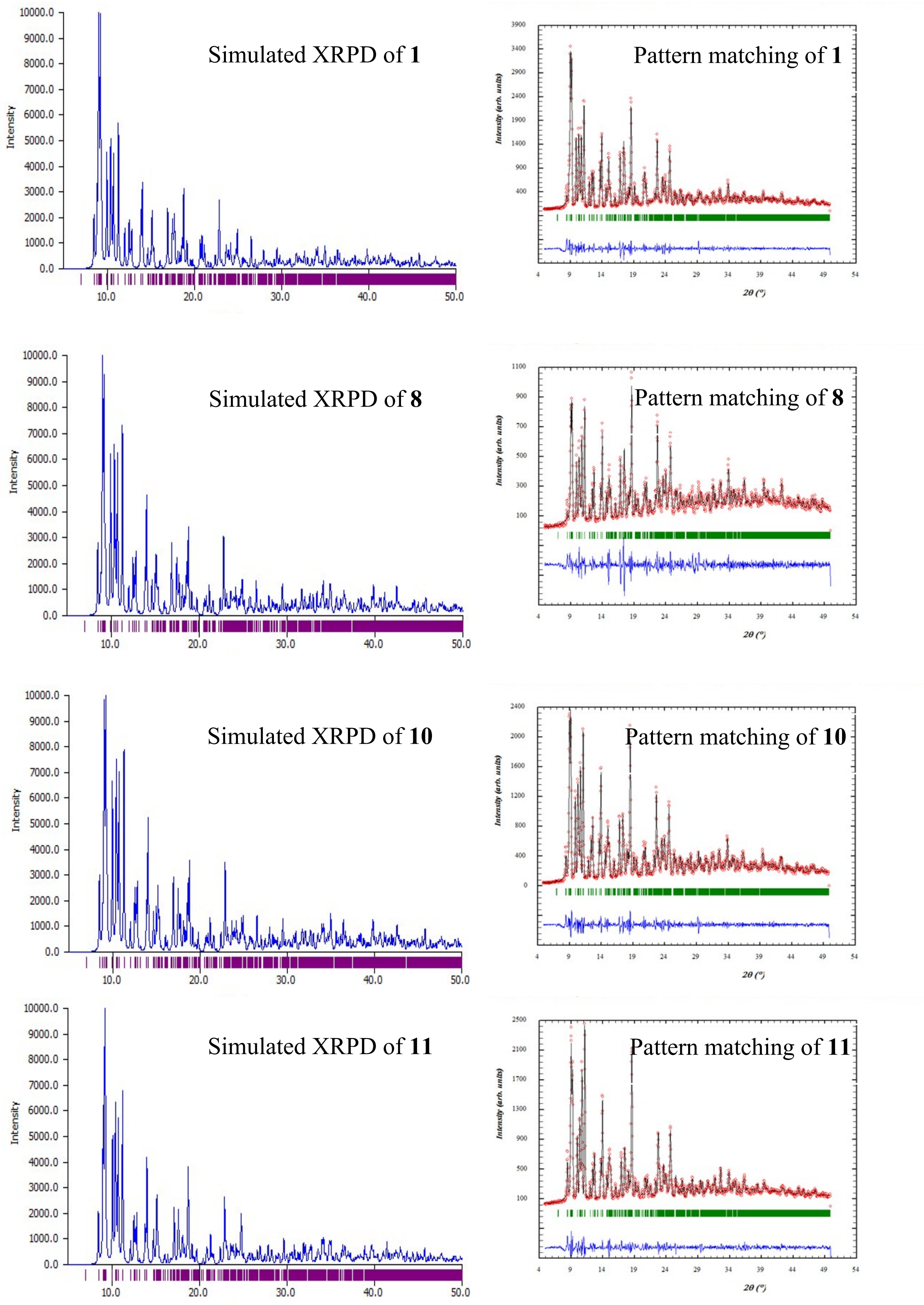

Figure S1.- Pattern-matching analyses and experimental XRPD for complexes **1**, **8**, **10** and **11** together with a simulated pattern from single-crystal X-ray diffractions.

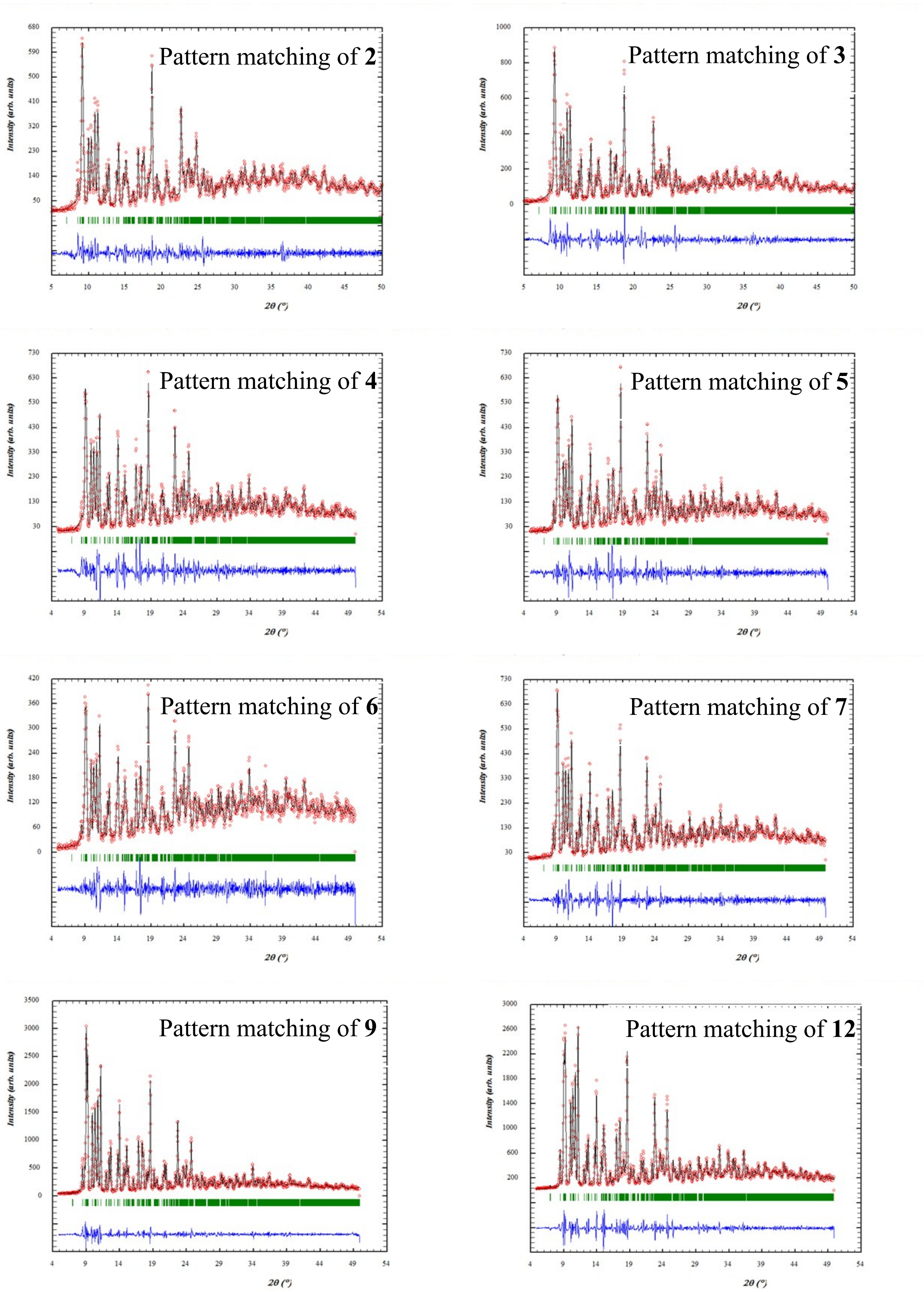

Figure S2.- Pattern-matching analyses and experimental XRPD for complexes **2**-**7**, **9** and **12**.

2. Continuous Shape Measurements.

Table S4.- Continuous Shape Measurements for the ZnN_2O_3 coordination environment.

PP-5	1 D5h	Pentagon
vOC-5	2 C4v	Vacant octahedron
TBPY-5	3 D3h	Trigonal bipyramid
SPY-5	4 C4v	Spherical square pyramid
JTBPY-5	5 D3h	Johnson trigonal bipyramid J12

Structure [ML5]	PP-5	Voc-5	TBPY-5	SPY-5	JTBPY-5
Comp1 (Zn1)	30.703	2.847	2.952	1.043	5.425
Comp1 (Zn2)	30.959	2.722	3.714	0.772	6.407
Comp8 (Zn1)	30.747	2.863	2.959	1.068	5.484
Comp8 (Zn2)	30.754	2.756	3.745	0.799	6.509
Comp10 (Zn1)	30.652	2.870	2.974	1.084	5.489
Comp10 (Zn2)	30.763	2.739	3.795	0.803	6.527
Comp11 (Zn1)	30.916	2.933	2.963	1.104	5.421
Comp11 (Zn2)	30.459	2.717	3.907	0.783	6.637

Table S5.- Continuous Shape Measurements for the LnO_9 coordination environment.

EP-9	1 D9h	Enneagon
OPY-9	2 C8v	Octagonal pyramid
HBPY-9	3 D7h	Heptagonal bipyramid
JTC-9	4 C3v	Johnson triangular cupola J3
JCCU-9	5 C4v	Capped cube J8
CCU-9	6 C4v	Spherical-relaxed capped cube
JCSAPR-9	7 C4v	Capped square antiprism J10
CSAPR-9	8 C4v	Spherical capped square antiprism
JTCTPR-9	9 D3h	Tricapped trigonal prism J51
TCTPR-9	10 D3h	Spherical tricapped trigonal prism
JTDIC-9	11 C3v	Tridiminished icosahedron J63
HH-9	12 C2v	Hula-hoop
MFF-9	13 Cs	Muffin

Structure [ML9]	**EP-9**	**OPY-9**	**HBPY-9**	**JTC-9**	**JCCU-9**	**CCU-9**	**JCSAPR-9**
Comp1 (Y1)	35.867	23.037	17.783	15.136	9.857	8.342	3.577
Comp1 (Y2)	35.090	22.969	17.733	15.458	9.041	7.728	4.596
Comp8 (Dy1)	35.800	23.077	17.749	15.261	9.864	8.350	3.487
Comp8 (Dy2)	35.329	23.547	17.129	16.012	9.049	7.642	4.495
Comp10 (Er1)	35.668	23.087	17.900	15.289	10.012	8.489	3.449
Comp10 (Er2)	35.368	23.430	17.212	15.973	9.222	7.836	4.472
Comp11 (Tm1)	35.682	23.004	18.012	15.381	9.931	8.386	3.449
Comp11 (Tm2)	32.350	23.232	18.984	16.258	7.853	6.426	5.925

Structure [ML9]	**CSAPR-9**	**JTCTPR-9**	**TCTPR-9**	**JTDIC-9**	**HH-9**	**MFF-9**
Comp1 (Y1)	2.264	4.876	3.158	9.810	10.067	2.553
Comp1 (Y2)	3.124	6.061	3.412	9.863	7.918	2.831
Comp8 (Dy1)	2.196	4.743	3.050	9.966	10.067	2.510
Comp8 (Dy2)	3.106	5.859	3.610	9.786	7.215	2.640
Comp10 (Er1)	2.137	4.741	3.049	9.893	10.006	2.492
Comp10 (Er2)	3.080	5.913	3.509	9.863	7.360	2.617
Comp11 (Tm1)	2.119	4.721	3.033	9.920	10.184	2.417
Comp11 (Tm2)	4.513	6.135	5.142	10.060	6.361	3.641

3. Magnetic Measurements.

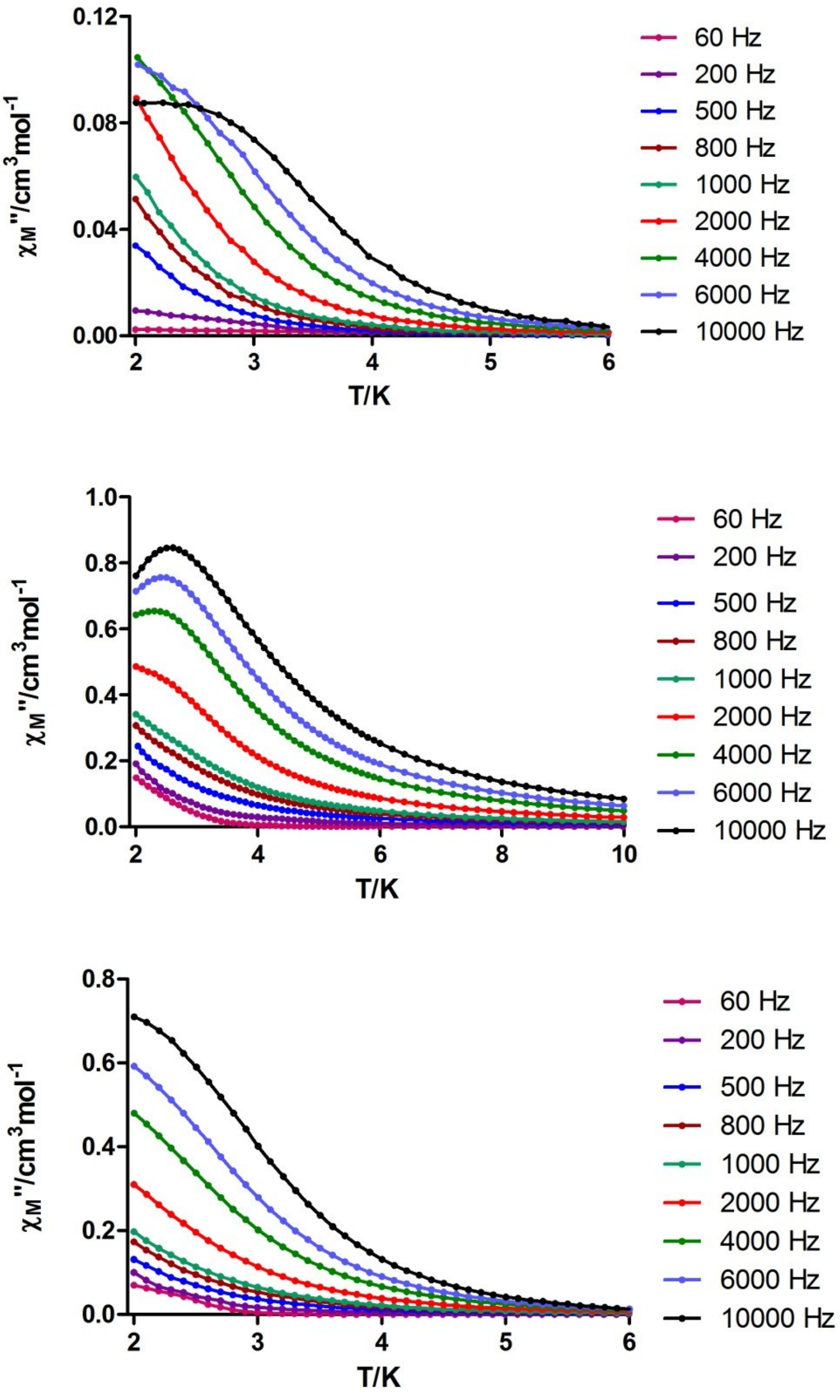

Figure S3.- Temperature dependence of the out-of phase χ_M'' susceptibility signals for complexes **3** (top), **7** (middle) and **10** (bottom) under an applied field of 1000 Oe.

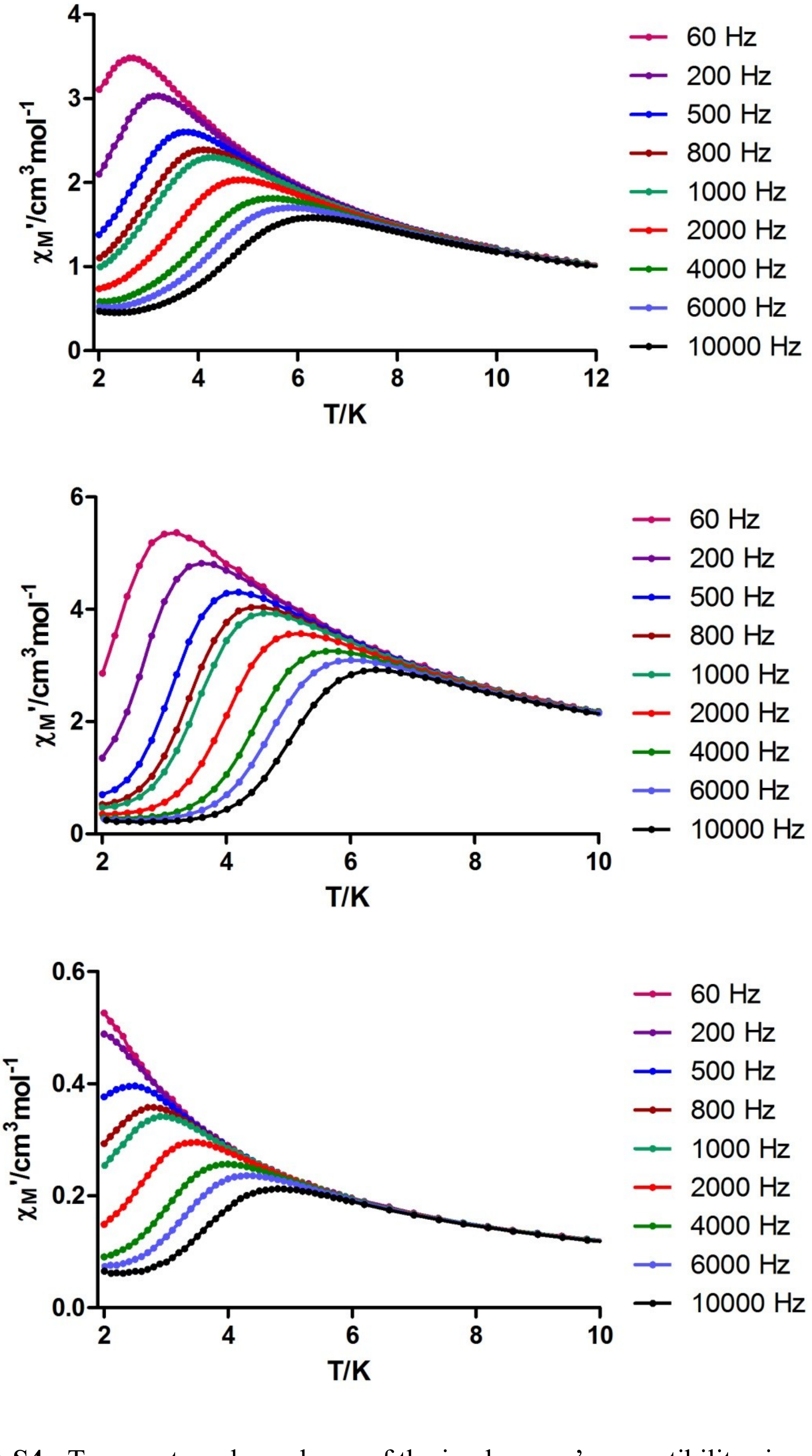

Figure S4.- Temperature dependence of the in phase χ_M' susceptibility signals for complexes **6** (top), **8** (middle) and **12** (bottom) under an applied field of 1000 Oe.

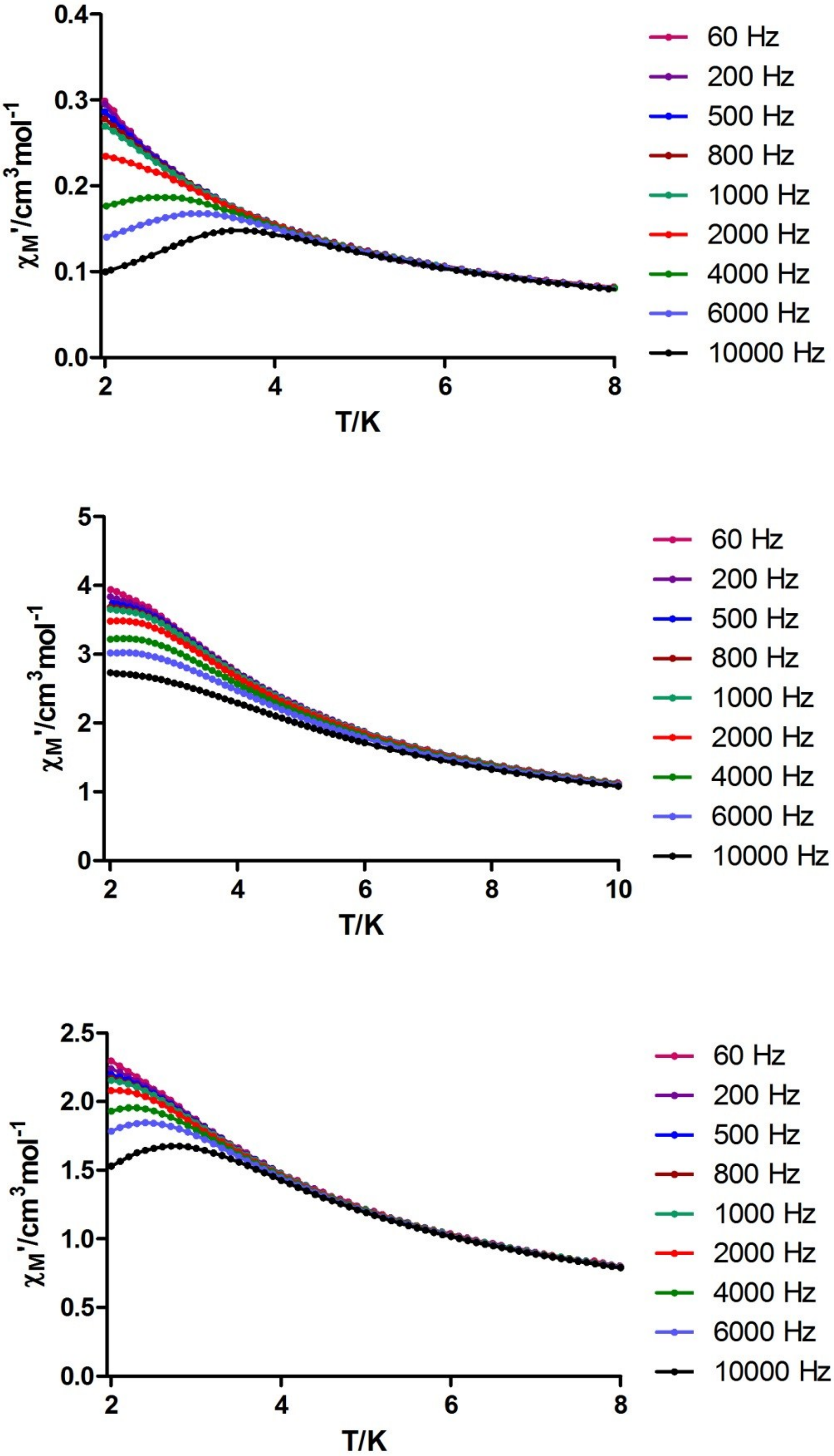

Figure S5.- Temperature dependence of the in phase χ_M' susceptibility signals for complexes **3** (top), **7** (middle) and **10** (bottom) under an applied field of 1000 Oe.

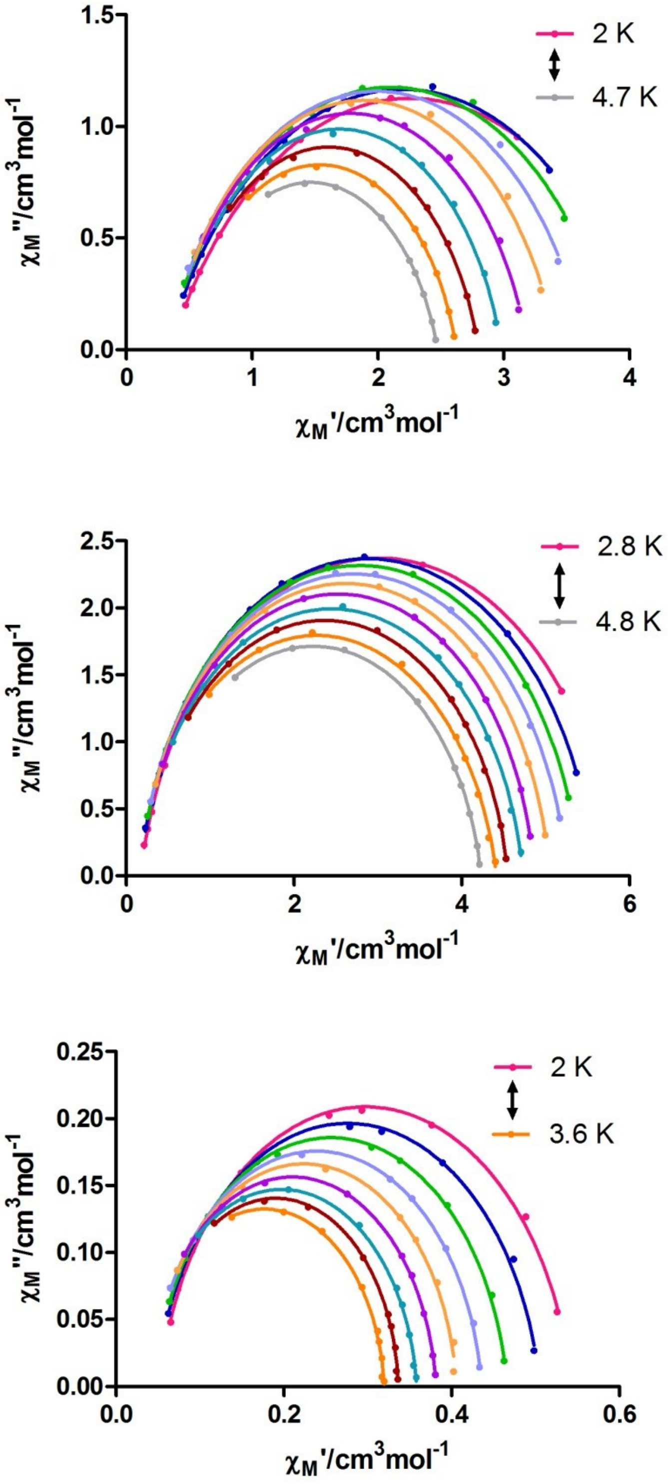

Figure S6.- Cole-Cole plots under 1000 Oe field for **6** (top), **8** (middle) and **12** (bottom). Solid lines represent the best fits to the generalized Debye model.

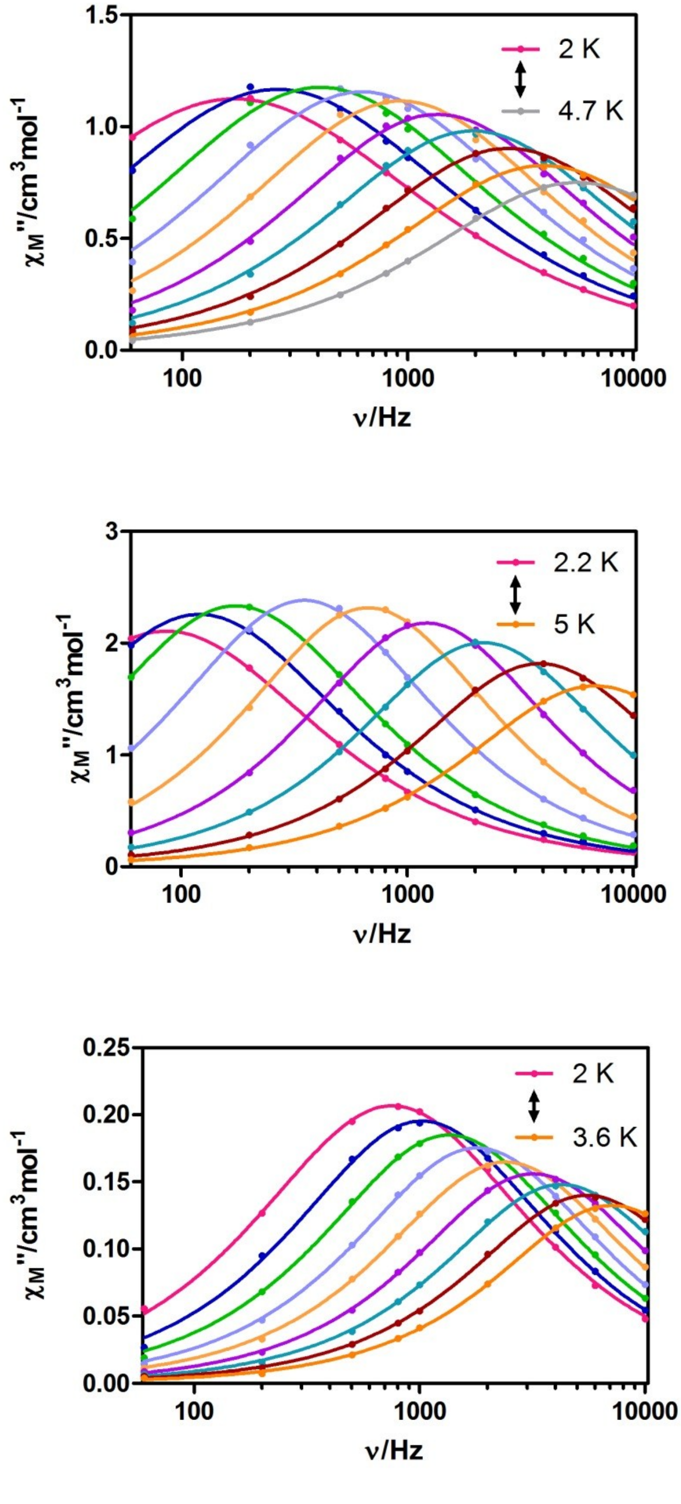

Figure S7.- Variable-temperature frequency dependence of the χ_M'' signal under 1000 Oe applied field for **6** (top), **8** (middle) and **12** (bottom). Solid lines represent the best fitting of the experimental data to the Debye model.

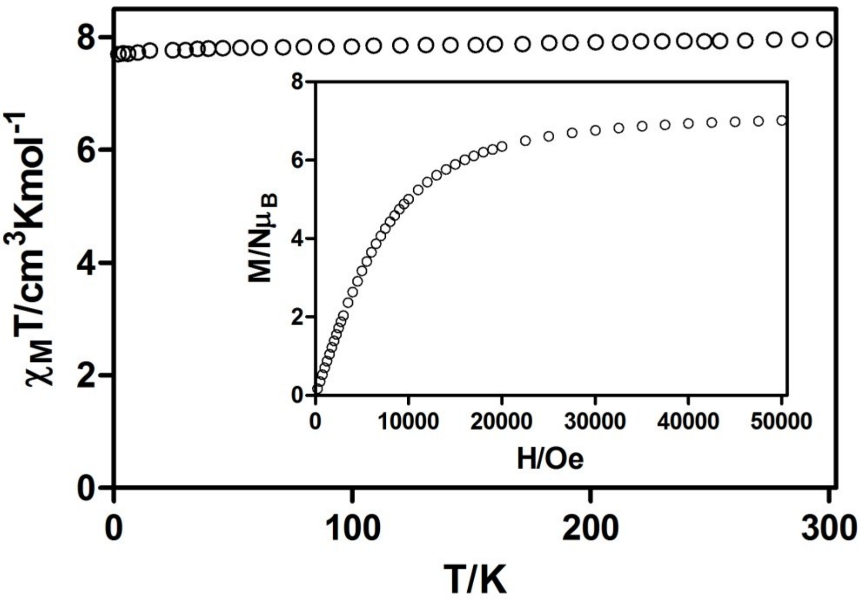

Figure S8.- Temperature dependence of the $\chi_M T$ product at 1000 Oe for complex **6**. Inset: M vs. H plot for **6**.

4. Luminescence Properties.

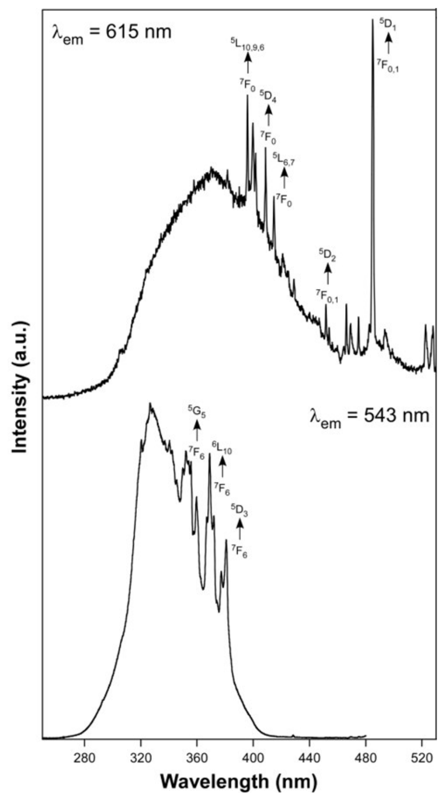

Figure S9.- Excitation spectra monitored at 615 nm for **5** (top) and 543 nm for **7** (down) compounds recorded at 10 K.

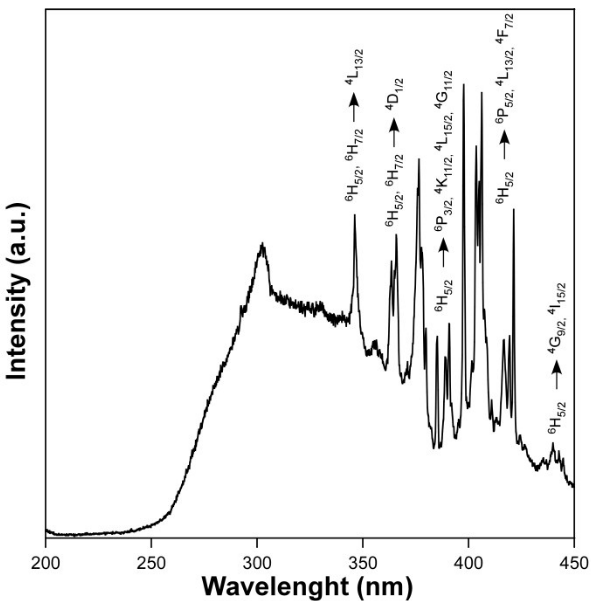

Figure S10.- 10 K excitation spectrum of **4** focusing on the 543 nm.

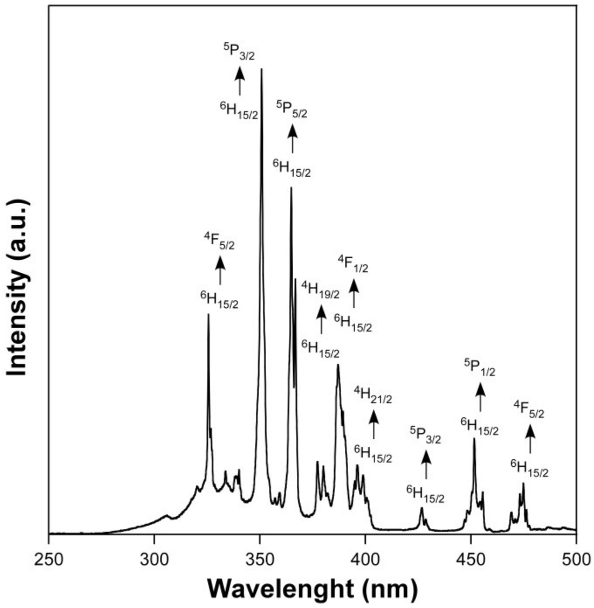

Figure S11.- 10 K excitation spectrum of **8** focusing on the 572 nm.

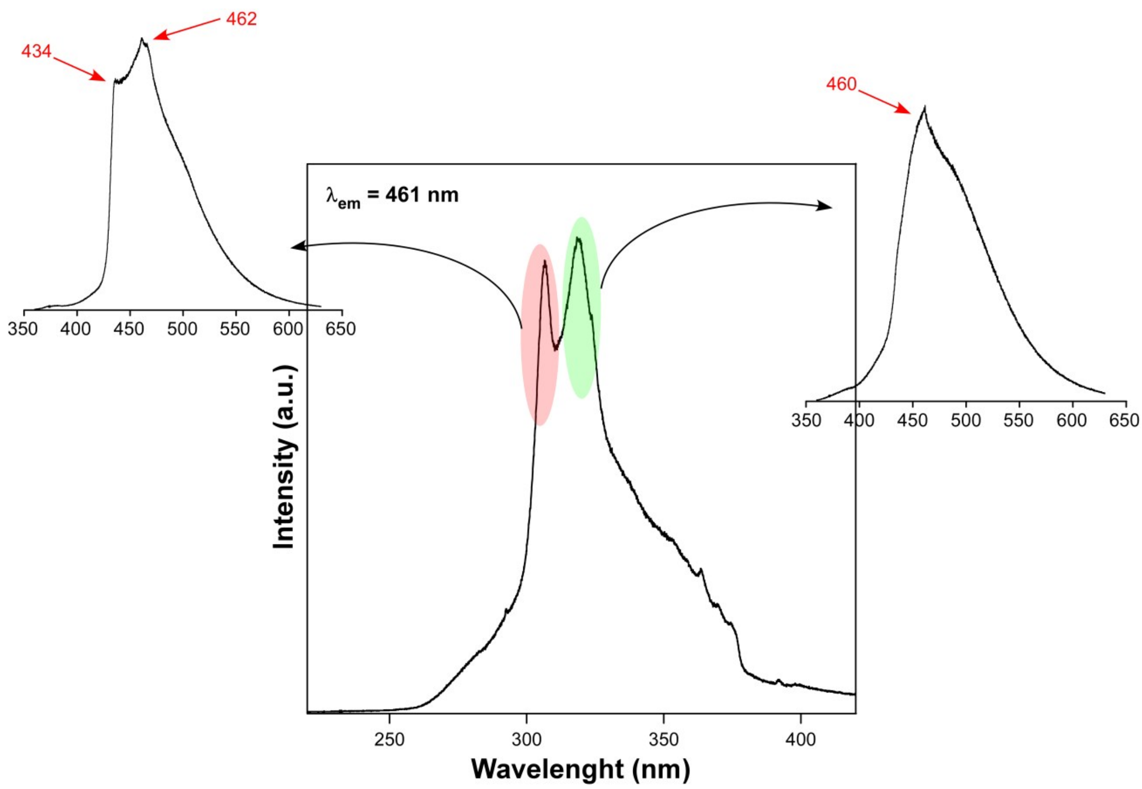

Figure S12.- Excitation spectrum at 10 K of **6** under emission at 461 nm, together with emission spectra excited at the 434 and 462 nm maxima.

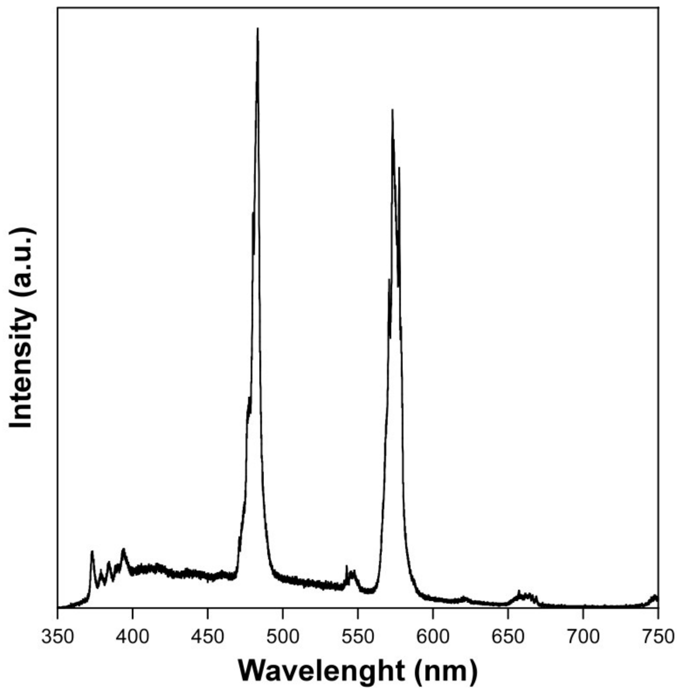

Figure S13.- Emission spectrum at 300 K of **8** excited at 326 nm.

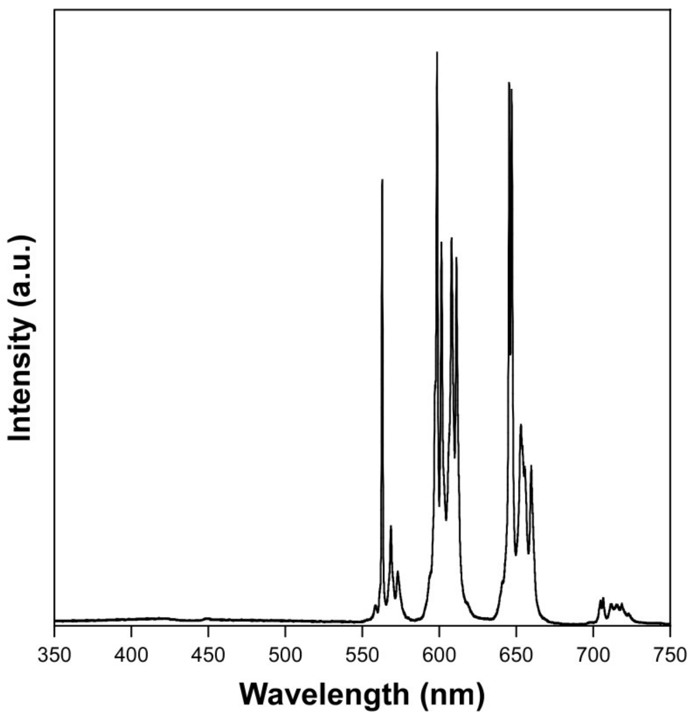

Figure S14.- Emission spectra at 10 K of **4** excited at 305 nm.

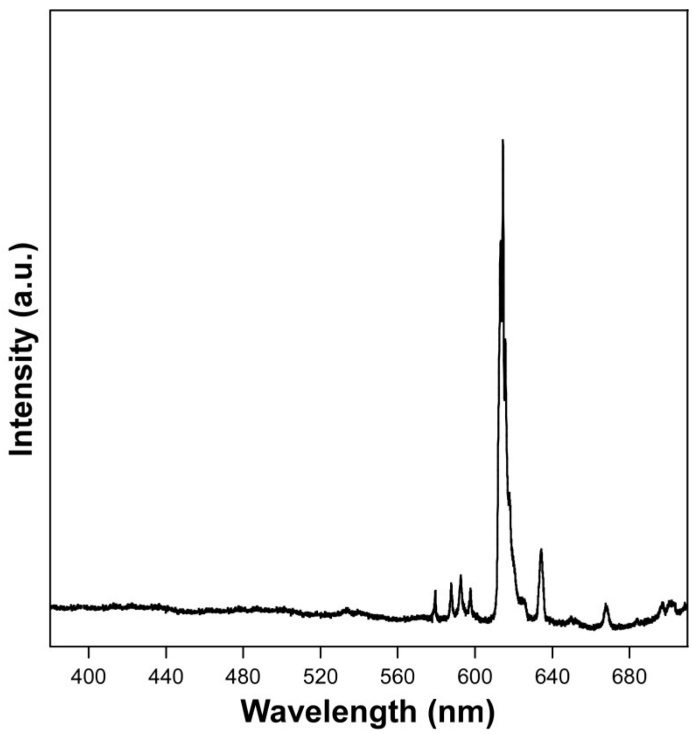

Figure S15.- Emission spectra at 10 K of **5** excited at 368 nm.

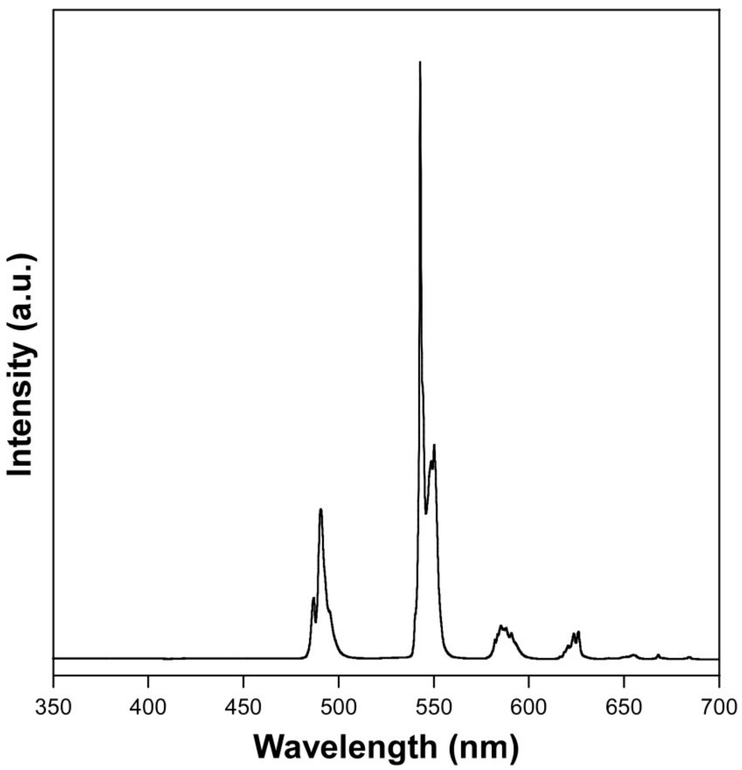

Figure S16.- Emission spectra at 10 K of **7** excited at 327 nm.

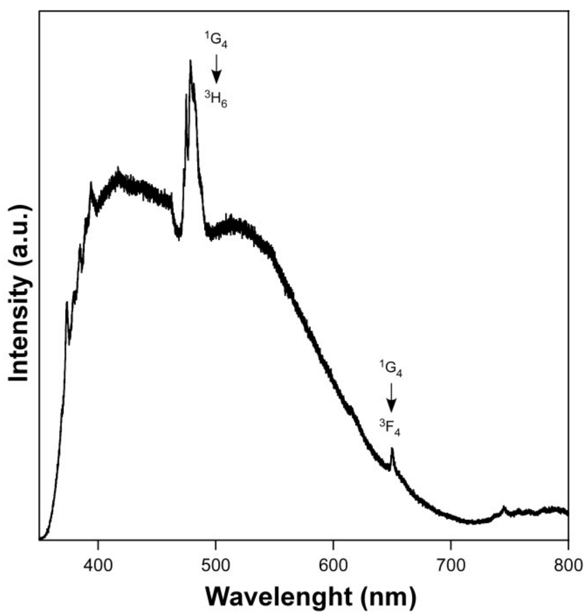

Figure S17.- Emission spectra at 10 K of **11** excited at 325 nm.

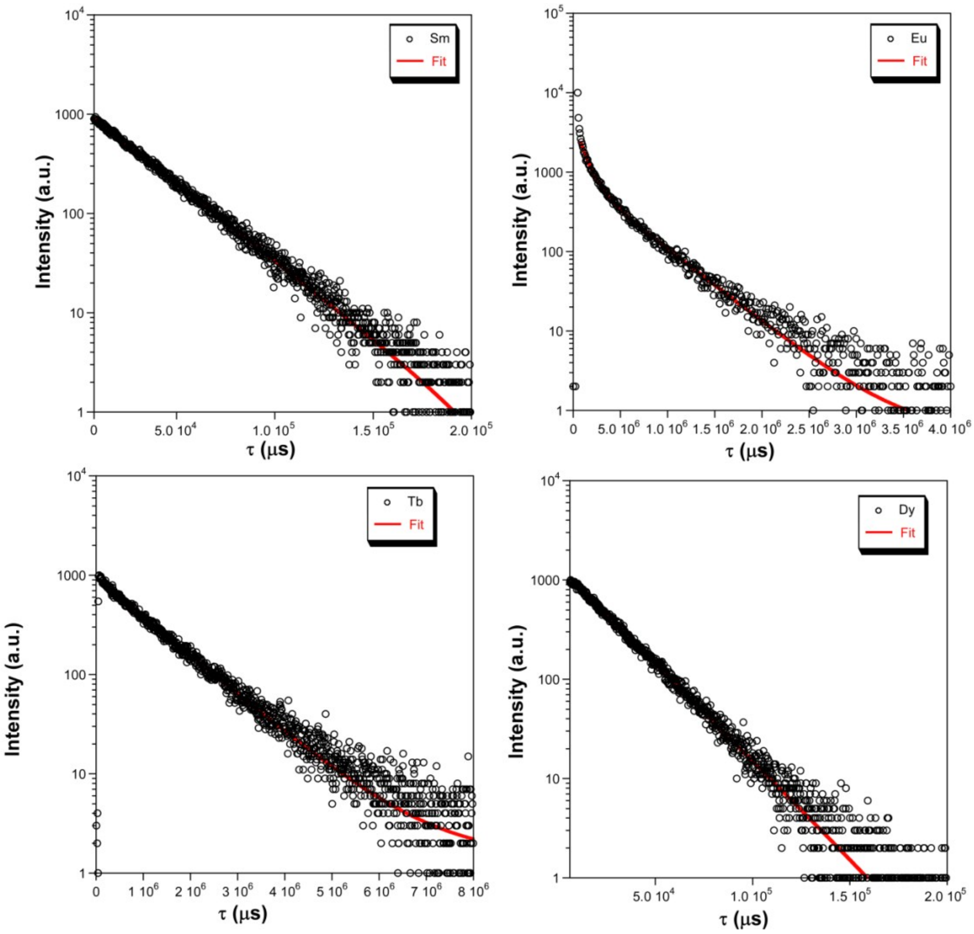

Figure S18.- Luminescence decay curves for **4**, **5**, **7**, and **8** compounds at 10 K.

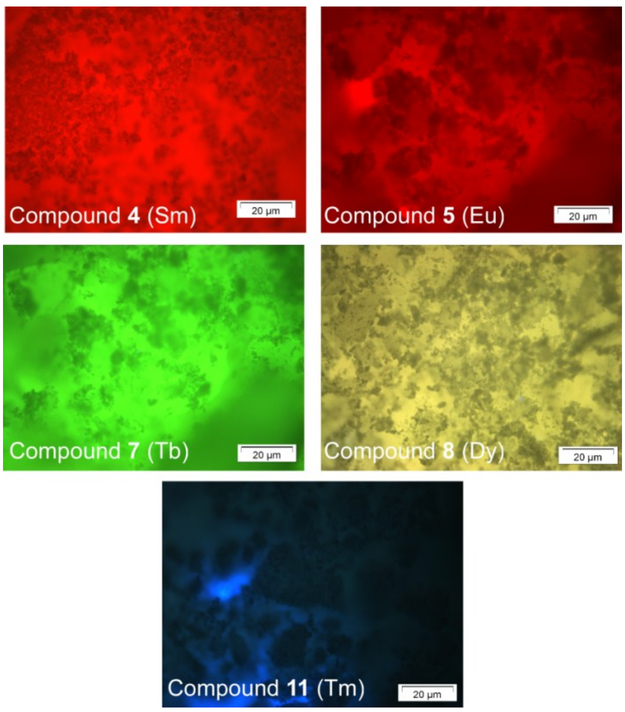

Figure S19.- Micro-photoluminescence images taken on polycrystalline samples at room temperature.