New Journal of Chemistry

New NIR-luminescent lanthanides complexes with tridentate oxybenzophenanthrolin ligands

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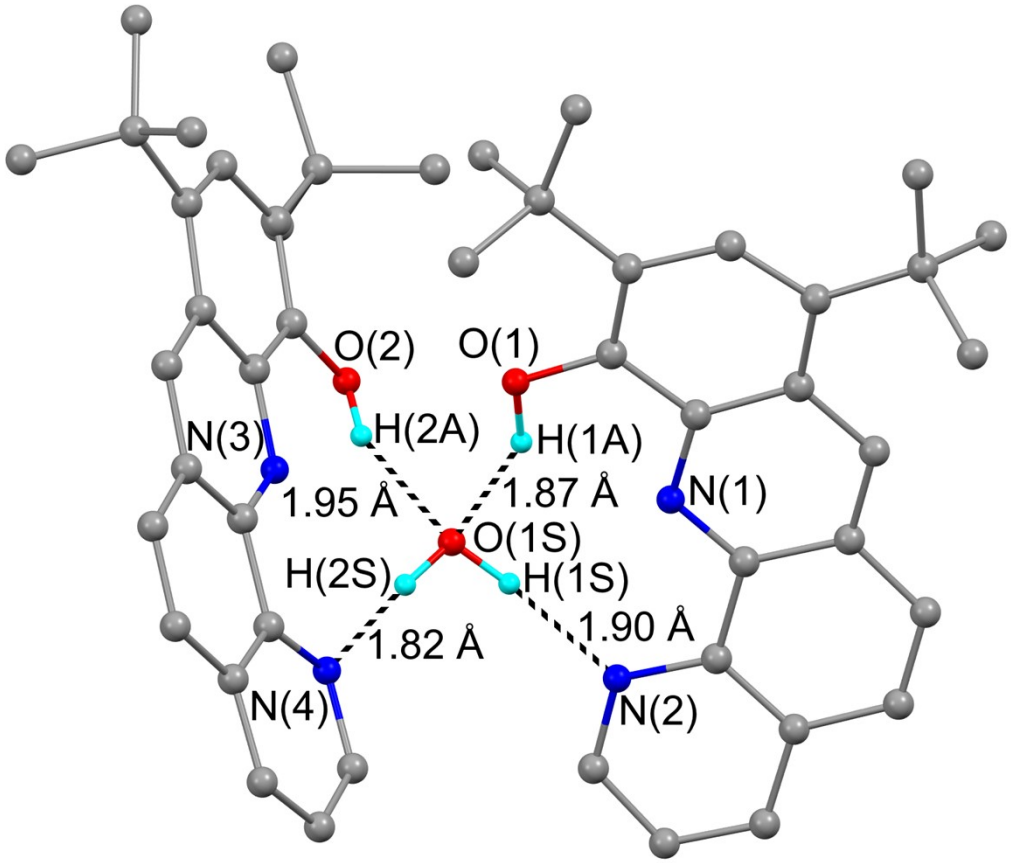


Figure S1. Fragment of the crystal packing of **H(bpen)**. The hydrogen atoms except H(1A), H(2A), H(1S) and H(2S) are omitted for clarity.

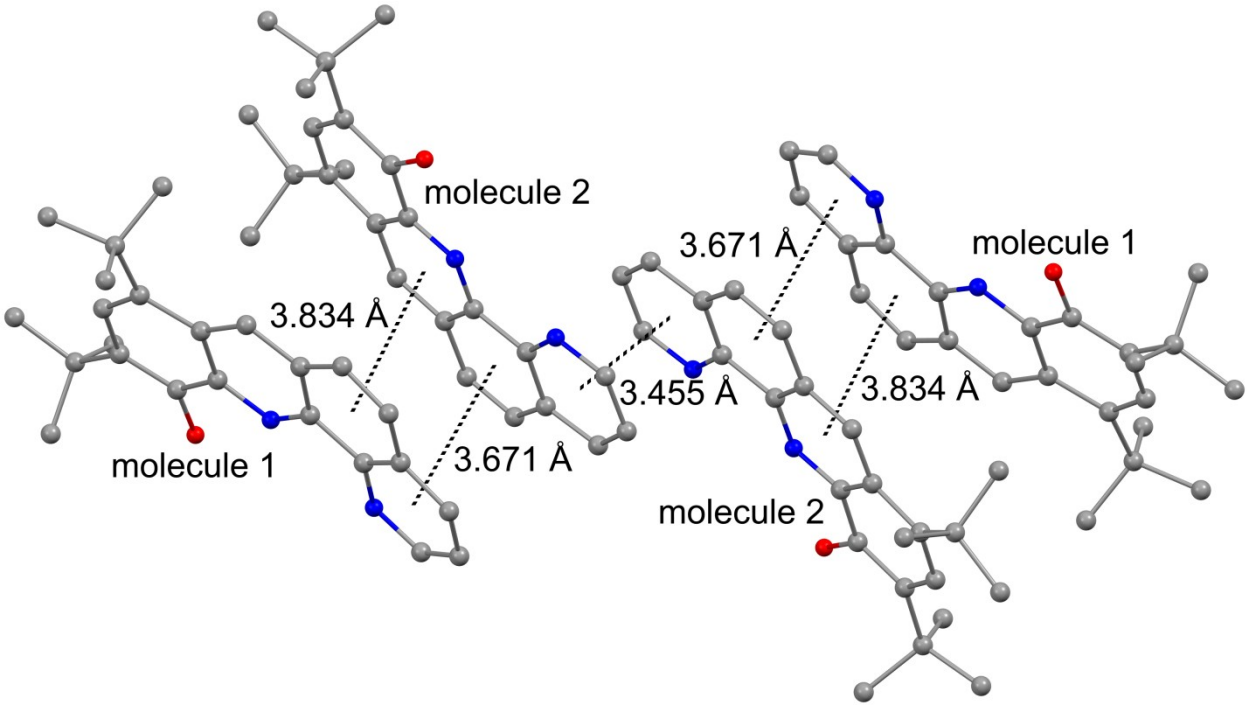


Figure S2. Tetrameric motif with the strong π…π interactions in crystal of compound **H(bpen)**.

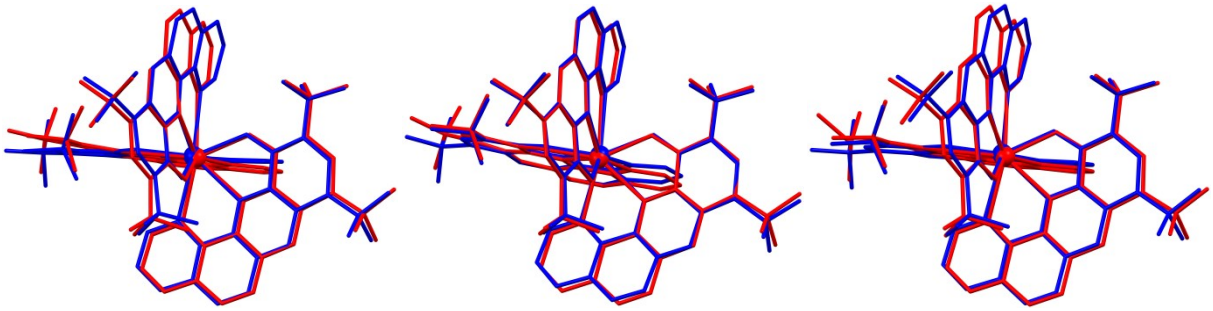
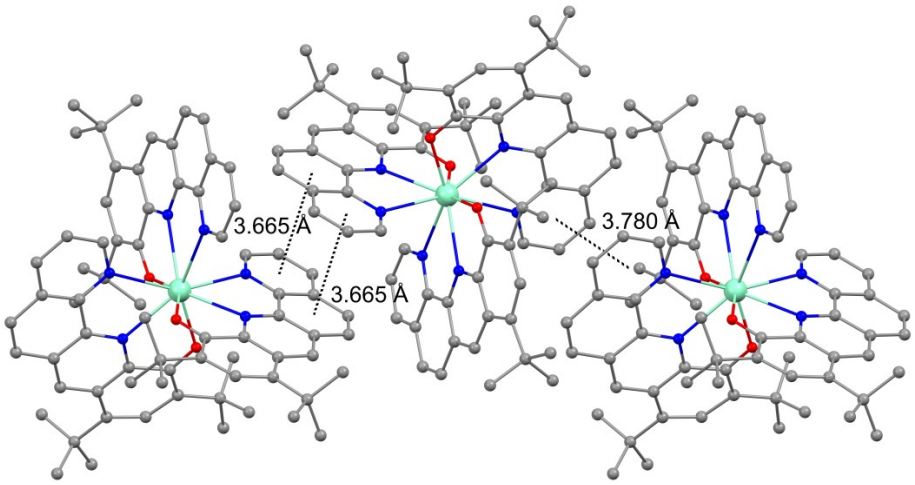
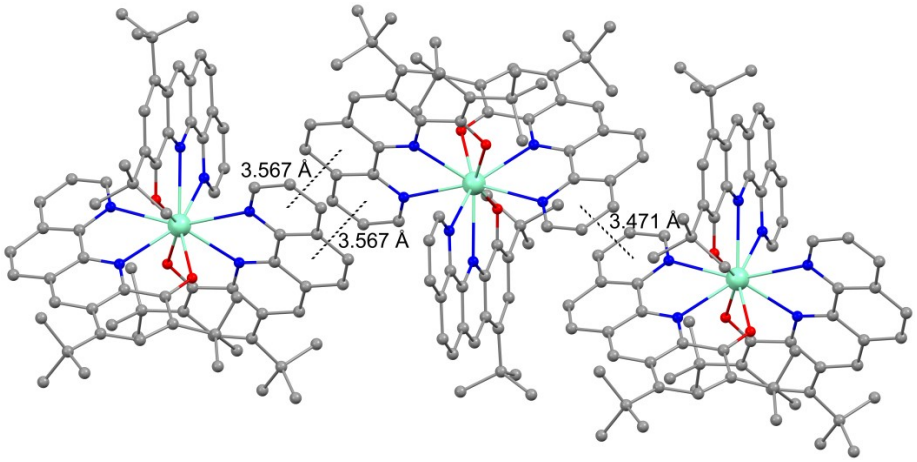


Figure S3. Overlay of two independent molecules **A** (red) and **B** (blue) for compounds **2** (**a**), **4** (**b**) and **5** (**c**). The root-mean-square deviations of non-hydrogen atomic positions of **A** and **B** molecules are 0.325 Å, 0.232 Å and 0.310 Å, respectively.

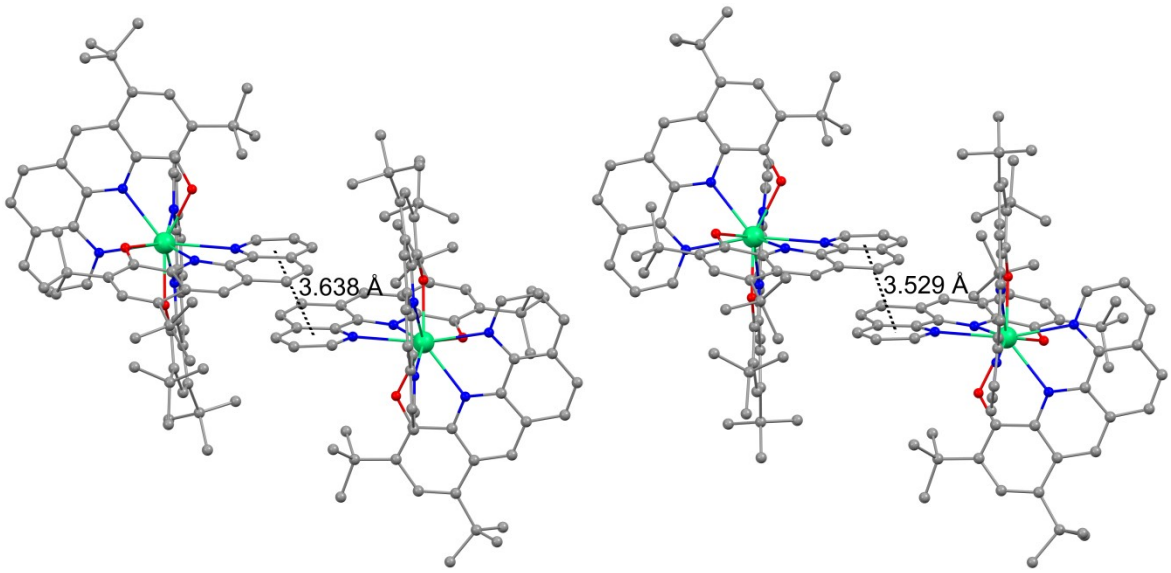


a



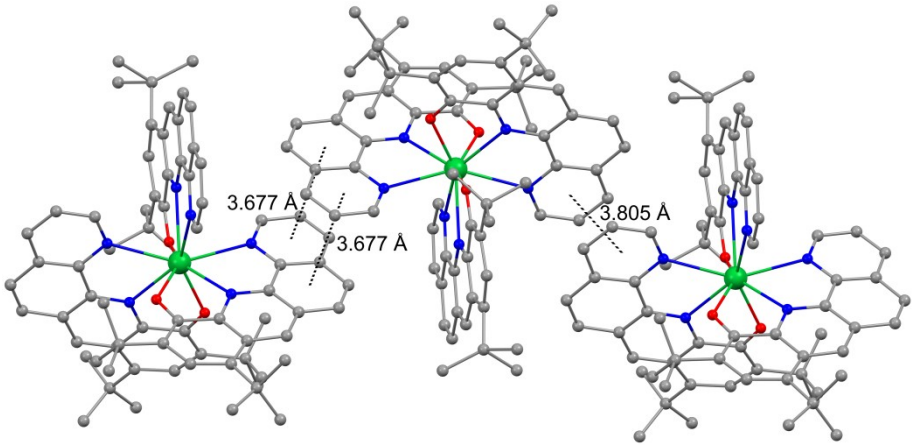
b

Figure S4. Molecular chains with the strong π…π interactions in crystal of complex **2**. The projections of molecular chains …**A**…**A**…**A**… (**a**) and …**B**…**B**…**B**… (**b**) are presented.

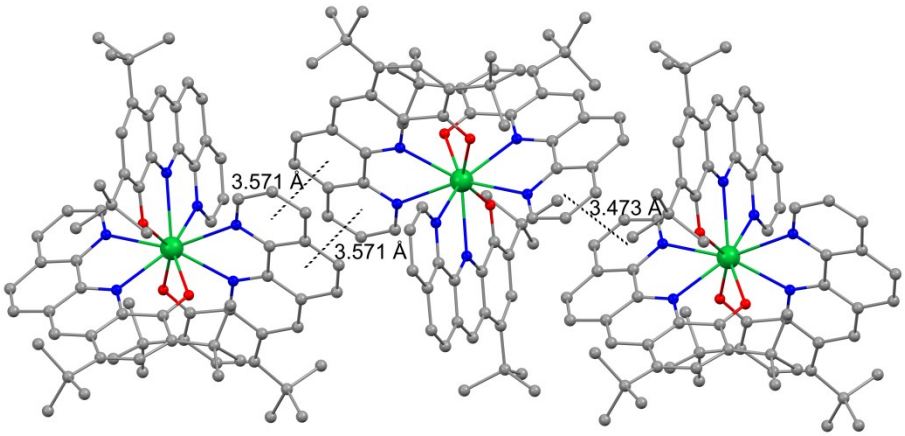


a **b**

Figure S5. Dimeric motifs with the strong π…π interactions in crystal of complex **4**. The projections of dimeric pairs **A**...**A** (**a**) and **B**...**B** (**b**) are presented.



a



b

Figure S6. Molecular chains with the strong π…π interactions in crystal of complex **5**. The projections of molecular chains …**A**…**A**…**A**… (**a**) and …**B**…**B**…**B**… (**b**) are presented.

Table S1. The selected bond lengths (Å) and angles (°) in compound **H(bpen)**.

Bonds	**H(bpen)**, Å	Bonds	**H(bpen)**, Å	Angles	**H(bpen)**, °
O(1)-C(1)	1.354(3)	O(2)-C(25)	1.359(5)	C(1)-O(1)-H(1A)	108(2)
O(1)-H(1A)	0.99(4)	O(2)-H(2A)	0.83(4)	C(15)-N(1)-C(16)	118.9(2)
N(1)-C(15)	1.326(3)	N(3)-C(39)	1.334(4)	C(13)-N(2)-C(14)	117.7(3)
N(1)-C(16)	1.355(3)	N(3)-C(40)	1.348(4)	C(25)-O(2)-H(2A)	108(3)
N(2)-C(13)	1.327(4)	N(4)-C(37)	1.335(5)	C(39)-N(3)-C(40)	119.0(4)
N(2)-C(14)	1.350(4)	N(4)-C(38)	1.346(5)	C(37)-N(4)-C(38)	117.3(4)

Table S2. Geometric characteristics of strong O–H…O and O–H…N interactions in the **H(bpen)** crystal.

D–H…*A*	*D*–H, Å	H…*A*, Å	*D*…*A*, Å	∠*D*H*A*
O(1)–H(1A)…O(1S)	0.99(4)	1.87(4)	2.754(3)	147(3)
O(2)–H(2A)…O(1S)	0.83(4)	1.95(4)	2.73(3)	156(11)
O(1S)–H(1S)…N(2)	0.94(3)	1.90(3)	2.847(3)	174(3)
O(1S)–H(1S)…N(4)	0.94(3)	1.82(3)	2.759(9)	174(4)

Table S3. The selected bond lengths (Å) in complexes **2**, **4** and **5**.

Bonds	**2** (Ln = Sm), Å		**4** (Ln = Er), Å		**5** (Ln = Yb), Å	
	A	**B**	**A**	**B**	**A**	**B**
Ln(1)-O(1)	2.330(3)	2.319(3)	2.2837(18)	2.2802(18)	2.252(3)	2.238(3)
Ln(1)-O(2)	2.320(2)	2.315(2)	2.2668(18)	2.2627(17)	2.242(3)	2.252(3)
Ln(1)-O(3)	2.341(2)	2.334(2)	2.2860(18)	2.2840(19)	2.268(3)	2.257(3)
Ln(1)-N(1)	2.567(3)	2.571(3)	2.499(2)	2.507(2)	2.473(3)	2.476(3)
Ln(1)-N(2)	2.660(3)	2.672(3)	2.608(2)	2.626(2)	2.601(4)	2.602(3)
Ln(1)-N(3)	2.539(3)	2.522(3)	2.480(2)	2.475(2)	2.448(3)	2.434(3)
Ln(1)-N(4)	2.673(3)	2.693(3)	2.590(2)	2.598(2)	2.605(3)	2.610(3)
Ln(1)-N(5)	2.673(3)	2.662(3)	2.581(2)	2.588(2)	2.584(3)	2.562(3)
Ln(1)-N(6)	2.754(3)	2.748(3)	2.697(2)	2.696(2)	2.697(4)	2.688(4)
O(1)-C(1)	1.305(4)	1.302(4)	1.306(3)	1.307(3)	1.318(5)	1.301(5)
O(2)-C(25)	1.306(4)	1.297(4)	1.305(3)	1.304(3)	1.304(5)	1.295(5)
O(3)-C(49)	1.289(4)	1.294(4)	1.297(3)	1.302(3)	1.295(5)	1.304(5)
N(1)-C(15)	1.331(5)	1.335(4)	1.332(3)	1.334(3)	1.333(5)	1.328(5)
N(1)-C(16)	1.353(5)	1.349(5)	1.352(3)	1.355(3)	1.346(5)	1.345(5)
N(2)-C(13)	1.323(5)	1.324(5)	1.326(4)	1.328(4)	1.322(6)	1.326(6)
N(2)-C(14)	1.356(4)	1.348(5)	1.366(4)	1.354(3)	1.362(5)	1.367(6)
N(3)-C(39)	1.335(4)	1.333(4)	1.321(3)	1.332(3)	1.333(5)	1.332(5)
N(3)-C(40)	1.354(4)	1.351(4)	1.350(3)	1.356(3)	1.345(5)	1.353(5)
N(4)-C(37)	1.329(4)	1.330(5)	1.334(3)	1.339(3)	1.333(5)	1.327(5)
N(4)-C(38)	1.356(5)	1.358(5)	1.361(3)	1.361(4)	1.368(5)	1.354(5)
N(5)-C(63)	1.344(4)	1.329(4)	1.335(3)	1.339(4)	1.333(5)	1.331(5)
N(5)-C(64)	1.356(4)	1.356(4)	1.359(3)	1.354(4)	1.345(5)	1.356(5)
N(6)-C(61)	1.329(5)	1.331(5)	1.333(4)	1.325(4)	1.318(6)	1.329(6)
N(6)-C(62)	1.360(5)	1.360(5)	1.357(3)	1.371(3)	1.358(5)	1.360(5)

Table S4. The selected angles (°) in complexes **2**, **4** and **5**.

Angles	**2** (Ln = Sm), °		**4** (Ln = Er), °		**5** (Ln = Yb), °	
	A	**B**	**A**	**B**	**A**	**B**
O(1)-Ln(1)-O(2)	97.38(9)	95.02(10)	97.57(7)	95.62(7)	95.86(11)	95.58(11)
O(1)-Ln(1)-O(3)	148.89(9)	147.75(9)	143.90(7)	145.36(7)	145.41(10)	143.87(10)
O(2)-Ln(1)-O(3)	78.64(8)	79.95(9)	79.55(7)	79.91(7)	78.85(10)	79.78(10)
O(1)-Ln(1)-N(1)	63.93(9)	64.17(9)	65.32(7)	65.30(7)	65.86(11)	66.16(11)
O(1)-Ln(1)-N(2)	125.99(9)	126.46(9)	128.41(7)	128.04(7)	129.83(11)	130.15(11)
O(1)-Ln(1)-N(3)	80.74(9)	78.16(9)	78.00(7)	79.05(7)	78.05(11)	75.30(11)
O(1)-Ln(1)-N(4)	70.53(9)	67.71(9)	68.87(7)	68.74(7)	69.71(11)	67.97(10)
O(1)-Ln(1)-N(5)	129.32(9)	131.01(9)	129.84(7)	131.68(7)	129.82(11)	130.88(11)
O(1)-Ln(1)-N(6)	77.28(10)	77.16(9)	78.01(7)	77.46(7)	78.02(11)	77.17(11)
O(2)-Ln(1)-N(1)	72.76(9)	72.29(9)	70.01(7)	68.93(7)	71.93(11)	70.68(11)
O(2)-Ln(1)-N(2)	73.29(9)	73.34(9)	73.11(7)	72.86(7)	73.25(11)	72.55(10)
O(2)-Ln(1)-N(3)	64.76(8)	65.01(9)	66.17(7)	66.06(7)	66.83(10)	66.92(11)
O(2)-Ln(1)-N(4)	127.58(9)	127.61(9)	130.34(7)	129.85(7)	131.39(10)	131.89(10)
O(2)-Ln(1)-N(5)	133.30(9)	133.94(9)	132.55(7)	132.53(7)	134.32(11)	133.49(11)
O(2)-Ln(1)-N(6)	147.63(8)	148.34(9)	142.58(7)	143.77(7)	144.52(10)	144.14(10)
O(3)-Ln(1)-N(1)	139.91(9)	140.32(9)	141.60(7)	139.65(7)	140.02(11)	140.82(11)
O(3)-Ln(1)-N(2)	82.85(9)	82.90(9)	85.59(7)	83.78(7)	81.78(11)	82.97(11)
O(3)-Ln(1)-N(3)	69.58(9)	70.82(9)	67.86(7)	67.67(7)	68.39(11)	69.91(11)
O(3)-Ln(1)-N(4)	87.35(9)	90.08(9)	85.54(7)	87.74(7)	88.12(11)	88.46(11)
O(3)-Ln(1)-N(5)	61.84(8)	62.26(9)	63.74(6)	63.68(7)	63.73(10)	64.27(11)
O(3)-Ln(1)-N(6)	121.82(9)	122.41(9)	125.19(7)	125.14(7)	125.03(11)	126.03(10)
N(1)-Ln(1)-N(2)	62.52(10)	62.50(10)	63.86(7)	63.30(7)	64.20(12)	64.22(11)
N(1)-Ln(1)-N(3)	119.54(9)	119.02(9)	116.97(7)	118.00(7)	120.83(11)	118.06(11)
N(1)-Ln(1)-N(4)	132.47(10)	129.34(9)	132.13(7)	131.93(7)	131.76(11)	130.48(11)
N(1)-Ln(1)-N(5)	123.32(9)	121.59(9)	123.42(7)	121.98(7)	122.23(11)	121.18(11)
N(1)-Ln(1)-N(6)	76.37(9)	76.78(9)	74.61(7)	76.04(7)	73.77(11)	74.37(11)
N(2)-Ln(1)-N(3)	133.11(9)	133.56(9)	134.33(7)	132.93(7)	133.58(11)	134.19(11)
N(2)-Ln(1)-N(4)	154.57(9)	156.45(9)	152.52(7)	153.82(7)	150.93(11)	152.13(11)
N(2)-Ln(1)-N(5)	77.80(9)	76.59(9)	75.01(7)	73.84(7)	76.21(11)	74.57(11)
N(2)-Ln(1)-N(6)	84.08(9)	86.66(9)	80.79(7)	83.57(7)	83.99(11)	85.40(11)
N(3)-Ln(1)-N(4)	62.99(9)	63.15(9)	64.31(7)	64.28(7)	64.82(11)	65.22(11)
N(3)-Ln(1)-N(5)	117.09(9)	119.37(9)	119.53(7)	119.71(7)	116.94(11)	120.75(11)
N(3)-Ln(1)-N(6)	142.67(9)	139.74(9)	144.88(7)	143.46(7)	142.27(11)	140.41(11)
N(4)-Ln(1)-N(5)	76.88(9)	80.24(9)	77.73(7)	80.19(7)	74.88(11)	77.81(10)
N(4)-Ln(1)-N(6)	81.28(9)	78.18(9)	83.23(7)	81.20(7)	79.67(11)	78.33(11)
N(5)-Ln(1)-N(6)	60.00(9)	60.22(9)	61.45(7)	61.51(7)	61.33(11)	61.82(11)

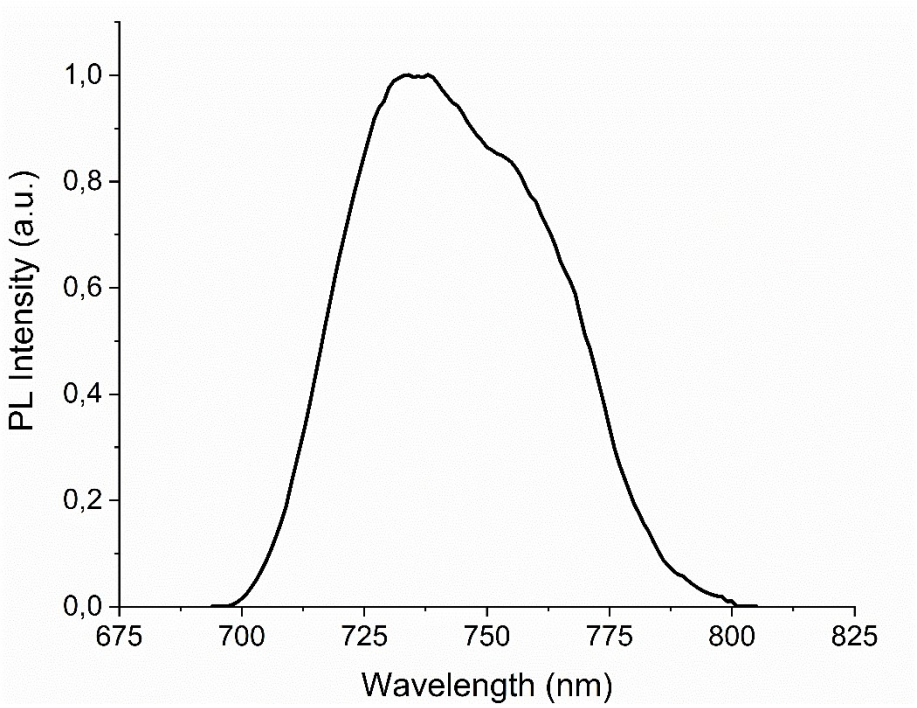


Figure S7. PL spectrum of the solid sample of the samarium complex **2** (λ_{ex} 350 nm) at 293K.

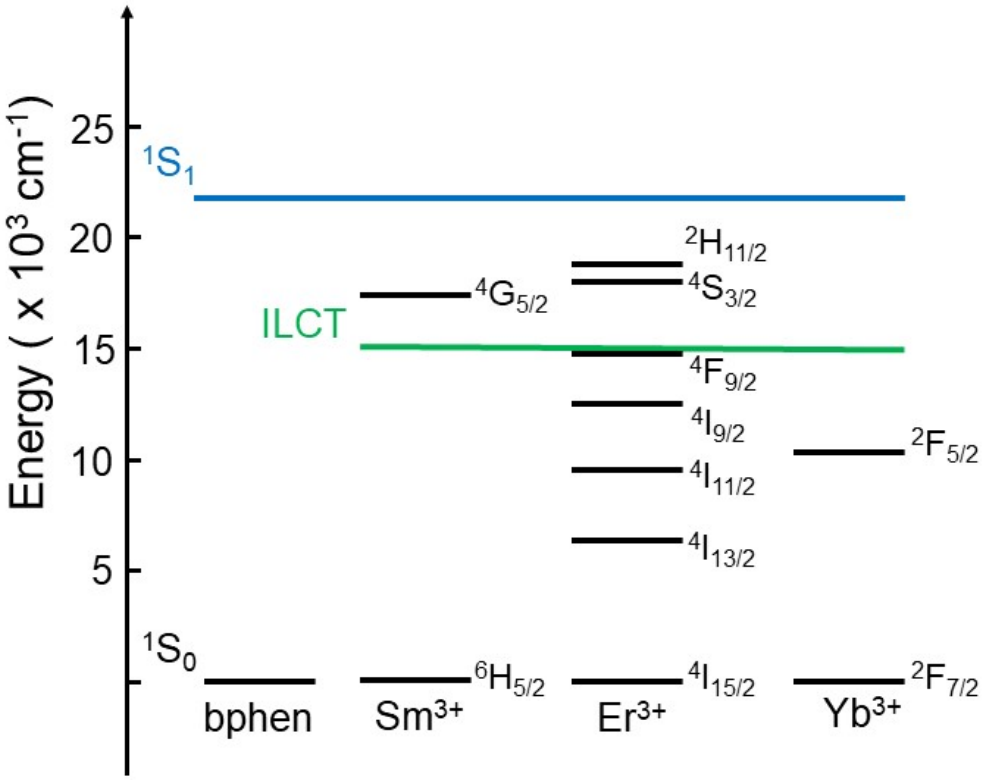


Figure S8. Energy level diagram for complexes **2**, **4** and **5**.

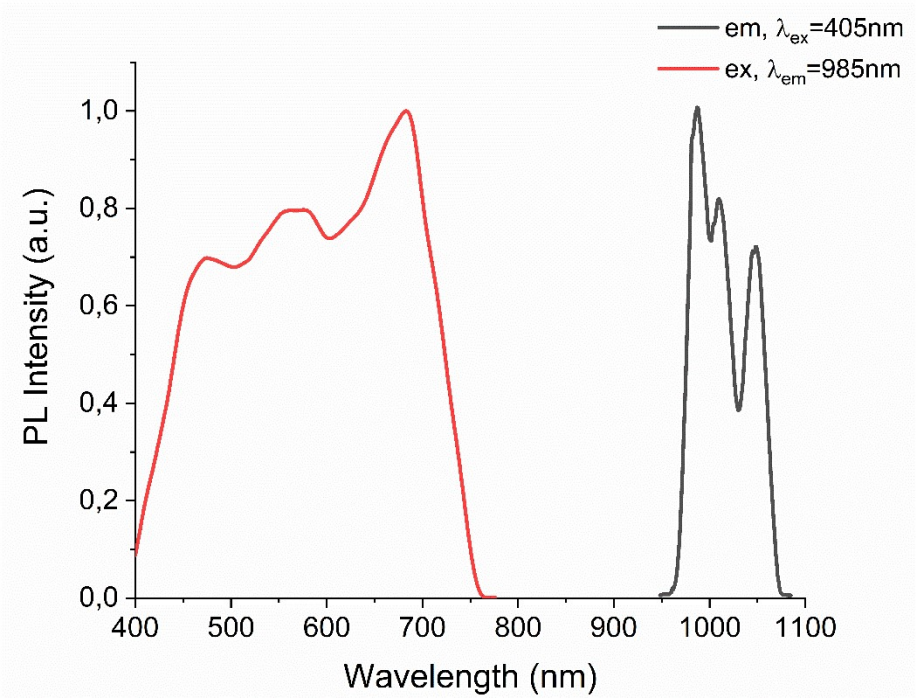


Figure S9. Excitation and emission spectra of the solid sample of the ytterbium complex **5** at 293K.