Supplementary Information

A novel class of oligomeric and polymeric d^{10} metal complexes of asymmetrical N-heterocyclic ligand with strong π stacking and hydrogen bonding, syntheses, structures and photoluminescence

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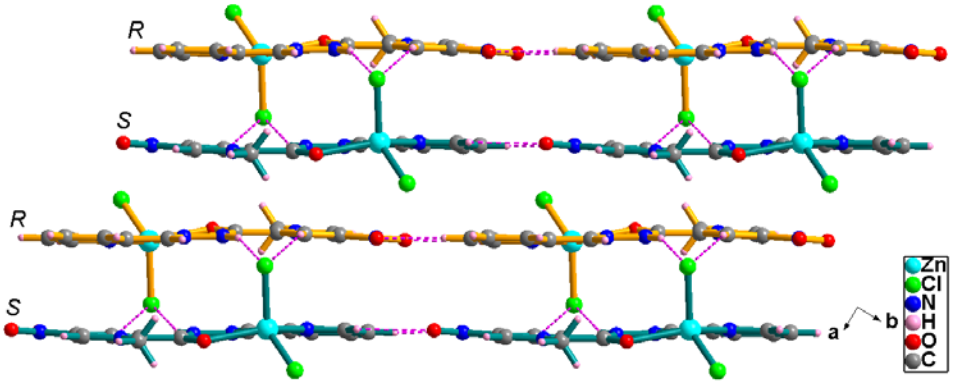

Figure S1. In *ab* plane, the 2-D sheet of alternating chirality is composed of 1-D chains for **2.**

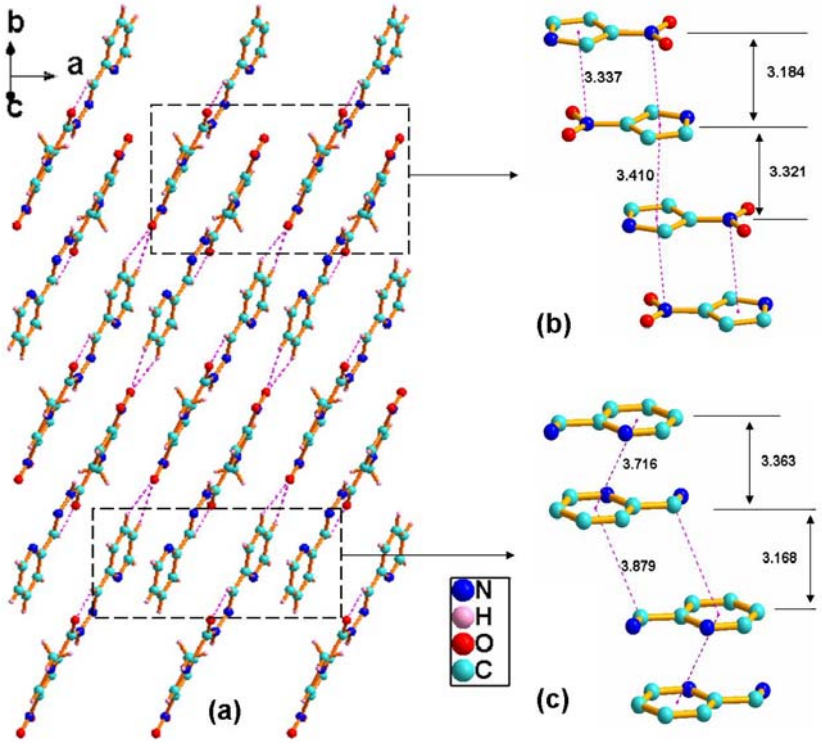

Figure S2. Showing the offset face-to-face $\pi\cdots\pi$ stacking interactions between ligands moieties of **3** in (011) plane (all distances in Å). Hydrogen-bonding interactions are represented by pink dashed lines.

Table S1. Selected bond lengths (Å) and bond angles (deg) for compounds **1**–**5**

1					
N(1)-C(1)	1.271(2)	O(1)-C(7)	1.218(2)	C(1)-C(2)	1.465(3)
N(1)-N(2)	1.370(2)	N(2)-C(7)	1.355(2)	C(7)-C(8)	1.475(3)
C(1)-N(1)-N(2)	116.30(16)	O(1)-C(7)-C(8)	122.76(18)	N(1)-C(1)-C(2)	119.21(18)
C(7)-N(2)-N(1)	118.27(16)	O(1)-C(7)-N(2)	123.22(18)	C(9)-C(8)-C(7)	130.37(17)
2					
Zn(1)-N(2)	2.110(3)	Zn(1)-Cl(2)	2.2897(11)	N(1)-C(1)	1.371(4)
Zn(1)-N(5)	2.153(3)	Zn(1)-O(1)	2.336(2)	N(2)-C(7)	1.275(4)
Zn(1)-Cl(1)	2.2059(10)	N(1)-N(2)	1.359(3)	O(1)-C(1)	1.226(4)
N(2)-Zn(1)-N(5)	75.35(10)	N(5)-Zn(1)-O(1)	144.83(10)	C(1)-O(1)-Zn(1)	113.2(2)
N(2)-Zn(1)-Cl(1)	135.51(8)	Cl(1)-Zn(1)-O(1)	97.34(7)	N(2)-N(1)-C(1)	115.0(3)
N(5)-Zn(1)-Cl(1)	100.89(8)	Cl(2)-Zn(1)-O(1)	93.50(8)	C(7)-N(2)-N(1)	122.3(3)
N(2)-Zn(1)-Cl(2)	106.00(8)	C(7)-N(2)-Zn(1)	118.3(2)	O(1)-C(1)-N(1)	120.5(3)
N(5)-Zn(1)-Cl(2)	104.09(8)	N(1)-N(2)-Zn(1)	119.2(2)	O(1)-C(1)-C(2)	125.3(3)
Cl(1)-Zn(1)-Cl(2)	117.61(4)	C(12)-N(5)-Zn(1)	127.7(2)	N(2)-C(7)-C(8)	116.4(3)
N(2)-Zn(1)-O(1)	70.56(10)	C(8)-N(5)-Zn(1)	114.6(2)		
3					
Cd(1)-N(1)	2.322(3)	Cd(1)-Cl(1)	2.7077(10)	N(2)-C(6)	1.274(4)
Cd(1)-N(2)	2.411(3)	Cd(1)-Cl(2)^{ii}	2.7898(10)	N(2)-N(3)	1.360(4)
Cd(1)-Cl(1)^{i}	2.5276(9)	Cl(1)-Cd(1)^{i}	2.5276(9)	N(3)-C(7)	1.377(5)
Cd(1)-Cl(2)	2.5716(9)	Cl(2)-Cd(1)^{ii}	2.7898(10)	O(1)-C(7)	1.218(4)
N(1)-Cd(1)-N(2)	69.09(10)	Cl(1)^{i}-Cd(1)-Cl(1)	84.14(3)	Cd(1)^{i}-Cl(1)-Cd(1)	95.86(3)
N(1)-Cd(1)-Cl(1)^{i}	94.19(7)	Cl(2)-Cd(1)-Cl(1)	93.10(3)	Cd(1)-Cl(2)-Cd(1)^{ii}	96.27(3)
N(2)-Cd(1)-Cl(1)^{i}	161.19(7)	N(1)-Cd(1)-Cl(2)^{ii}	84.01(7)	C(1)-N(1)-Cd(1)	123.1(2)
N(1)-Cd(1)-Cl(2)	153.80(8)	N(2)-Cd(1)-Cl(2)^{ii}	89.43(7)	C(5)-N(1)-Cd(1)	118.4(2)
N(2)-Cd(1)-Cl(2)	87.72(7)	Cl(1)^{i}-Cd(1)-Cl(2)^{ii}	97.57(3)	C(6)-N(2)-N(3)	125.0(3)
Cl(1)^{i}-Cd(1)-Cl(2)	110.32(3)	Cl(2)-Cd(1)-Cl(2)^{ii}	83.73(3)	C(6)-N(2)-Cd(1)	117.5(2)
N(1)-Cd(1)-Cl(1)	98.64(7)	Cl(1)-Cd(1)-Cl(2)^{ii}	176.76(3)	N(3)-N(2)-Cd(1)	117.4(2)
N(2)-Cd(1)-Cl(1)	89.77(7)				
4					
Hg(1)-Cl(1)	2.347(6)	Hg(2)-Cl(4)	2.351(6)	N(3)-N(4)	1.37(2)
Hg(1)-Cl(2)	2.348(6)	Hg(2)-N(10)	2.465(17)	N(4)-C(7)	1.25(2)

Hg(1)-N(4)	2.502(16)	Hg(2)-N(9)	2.488(16)	N(8)-C(13)	1.35(2)
Hg(1)-N(5)	2.515(16)	Hg(2)-O(6)	2.708(15)	O(6)-C(13)	1.23(2)
Hg(1)-O(3)	2.738(15)	N(3)-C(1)	1.34(2)	N(8)-N(9)	1.38(2)
Hg(2)-Cl(3)	2.350(7)	O(3)-C(1)	1.22(2)	N(9)-C(19)	1.26(2)
Cl(1)-Hg(1)-Cl(2)	149.2(2)	Cl(3)-Hg(2)-Cl(4)	152.3(2)	C(7)-N(4)-Hg(1)	119.2(13)
Cl(1)-Hg(1)-N(4)	103.5(4)	Cl(3)-Hg(2)-N(10)	92.5(5)	N(3)-N(4)-Hg(1)	119.8(12)
Cl(2)-Hg(1)-N(4)	104.5(4)	Cl(4)-Hg(2)-N(10)	110.8(5)	C(8)-N(5)-Hg(1)	116.8(13)
Cl(1)-Hg(1)-N(5)	91.4(4)	Cl(3)-Hg(2)-N(9)	99.6(4)	C(12)-N(5)-Hg(1)	123.5(14)
Cl(2)-Hg(1)-N(5)	111.9(4)	Cl(4)-Hg(2)-N(9)	103.4(4)	C(19)-N(9)-Hg(2)	119.6(13)
N(4)-Hg(1)-N(5)	65.1(5)	N(10)-Hg(2)-N(9)	65.9(5)	N(8)-N(9)-Hg(2)	122.7(11)
Cl(1)-Hg(1)-O(3)	92.4(4)	Cl(3)-Hg(2)-O(6)	91.2(4)	C(20)-N(10)-Hg(2)	117.5(12)
Cl(2)-Hg(1)-O(3)	90.4(4)	Cl(4)-Hg(2)-O(6)	86.9(4)	C(24)-N(10)-Hg(2)	124.2(14)
N(4)-Hg(1)-O(3)	60.3(5)	N(10)-Hg(2)-O(6)	126.1(5)	C(1)-O(3)-Hg(1)	116.0(13)
N(5)-Hg(1)-O(3)	124.6(5)	N(9)-Hg(2)-O(6)	60.5(5)	C(13)-O(6)-Hg(2)	116.0(13)

5

K(1)-O(6)^{iii}	2.771(5)	K(1)-O(3)^{iv}	2.878(4)	K(1)-O(2)^{iv}	3.018(4)
K(1)-O(1)	2.775(4)	K(1)-N(5)	2.909(5)	K(1)-O(4')	3.02(4)
K(1)-O(5')	2.83(6)	K(1)-O(4)	2.91(3)	K(1)-O(5)	3.17(2)
K(1)-N(2)	2.840(5)				
O(6)^{iii}-K(1)-O(1)	87.33(14)	N(2)-K(1)-O(4)	87.8(8)	N(5)-K(1)-O(5)	123.4(5)
O(6)^{iii}-K(1)-N(2)	89.64(14)	O(3)^{iv}-K(1)-O(4)	100.4(6)	O(4)-K(1)-O(5)	42.4(6)
O(1)-K(1)-N(2)	56.97(12)	N(5)-K(1)-O(4)	86.6(6)	O(2)^{iv}-K(1)-O(5)	92.9(11)
O(6)^{iii}-K(1)-O(3)^{iv}	77.47(14)	O(6)^{iii}-K(1)-O(2)^{iv}	88.15(13)	O(6)^{iii}-K(1)-N(4)^{iv}	83.32(13)
O(1)-K(1)-O(3)^{iv}	161.44(14)	O(1)-K(1)-O(2)^{iv}	127.09(12)	O(1)-K(1)-N(4)^{iv}	147.19(13)
N(2)-K(1)-O(3)^{iv}	132.37(13)	N(2)-K(1)-O(2)^{iv}	175.24(13)	N(2)-K(1)-N(4)^{iv}	153.65(13)
O(6)^{iii}-K(1)-N(5)	87.55(14)	O(3)^{iv}-K(1)-O(2)^{iv}	42.95(12)	O(3)^{iv}-K(1)-N(4)^{iv}	21.30(11)
O(1)-K(1)-N(5)	114.03(13)	N(5)-K(1)-O(2)^{iv}	118.39(12)	N(5)-K(1)-N(4)iv	96.96(13)
N(2)-K(1)-N(5)	57.27(13)	O(4)-K(1)-O(2)^{iv}	94.0(8)	O(4)-K(1)-N(4)^{iv}	96.7(8)
O(3)^{iv}-K(1)-N(5)	76.31(13)	O(6)^{iii}-K(1)-O(5)	143.0(4)	O(2)^{iv}-K(1)-N(4)^{iv}	21.70(11)
O(6)^{iii}-K(1)-O(4)	174.1(6)	N(2)-K(1)-O(5)	91.4(11)	O(5)-K(1)-N(4)^{iv}	109.3(11)
O(1)-K(1)-O(4)	95.7(6)	O(3)^{iv}-K(1)-O(5)	125.7(11)		

Symmetry transformations used to generate equivalent atoms: i [-*x*, 1-*y*, 1-*z*]; ii [1-*x*, 1-*y*, 1-*z*];

iii [*x*, 3/2-*y*, -1/2+*z*]; iv [1+*x*, *y*, *z*].

Table S2. Shortest D···A distances (Å) and angles (deg) for **1**–**5**

D-H	*d*(*D*-H)	*d*(H···*A*)	∠*D*H*A*	*d*(*D*···*A*)	*A*
			1		
C(12) –H(12B)	0.960	2.566	95.19	2.819	O(1)
C(12) –H(12C)	0.960	2.648	90.20	2.819	O(1)
C(4) –H(4)	0.930	2.574	172.01	3.498	O2[1+*x*, *y*, 1+*z*]
C(11) –H(11)	0.930	2.558	149.98	3.395	O2[-*x*, -*y*, -*z*]
C(6) –H(6)	0.930	2.655	169.19	3.573	O3[2-*x*, 2-*y*, 1-*z*]
N(2) –H(2)	0.860	2.046	154.69	2.847	O(4)
O(4) –H(4A)	0.850	2.013	178.84	2.863	N(3) [2-*x*, 2-*y*, 1-*z*]
O(4) –H(4B)	0.850	2.276	146.51	3.021	O(1) [1-*x*, 1-*y*, 1-*z*]
O(4) –H(4B)	0.850	2.500	129.89	3.114	O(1) [*x*, 1+*y*, *z*]
C(9)–H(9)	0.930	2.463	149.03	3.295	O(4)
C(1) –H(1)	0.930	2.597	135.37	3.324	O(4)
			2		
N(1)–H(1)	0.860	2.420	156.19	3.227	Cl(2) [-*x*, 2-*y*, -*z*]
C(3)–H(3)	0.930	2.760	150.46	3.598	Cl(2) [-*x*, 2-*y*, -*z*]
C(9)–H(9)	0.930	2.708	163.45	3.609	Cl(1) [*x*, 1.5-*y*, -0.5+*z*]
C(11)–H(11)	0.930	2.472	167.16	3.385	O(3) [-1+*x*, -1+*y*, *z*]
C(12)–H(12)	0.930	2.804	132.34	3.499	O(2) [-1+*x*, -1+*y*, *z*]
			3		
C(6)–H(6)	0.930	2.261	121.87	2.863	O(1)
N(3)–H(3)	0.860	2.528	142.08	3.250	Cl(2)
C(11)–H(11)	0.930	2.876	162.55	3.774	Cl(1)[1-*x*, 1-*y*, -*z*]
C(3)–H(3A)	0.930	2.674	149.30	3.506	Cl(1)[-*x*, -*y*, 1-*z*]
C(3)–H(3A)	0.930	2.661	123.85	3.271	O(2)[1+*x*, 1+*y*, -1+*z*]
C(2)–H(2)	0.930	2.676	122.71	3.273	O(2)[1+*x*, 1+*y*, -1+*z*]
			4		
N(3)–H(3)	0.860	1.968	163.88	2.805	O(8) [1+*x*, *y*, *z*]
C(3)–H(3A)	0.930	2.332	152.04	3.184	O(8)[1+*x*, *y*, *z*]
C(10)–H(10)	0.930	2.417	139.84	3.180	O(1) [*x*, *y*, -1+*z*]
N(8)–H(8)	0.860	1.943	168.17	2.788	O(7) [1+*x*, *y*, *z*]
C(15)–H(15)	0.930	2.353	152.08	3.204	O(7) [1+*x*, *y*, *z*]
C(26)–H(26C)	0.930	2.801	163.33	3.731	Cl(4)
C(21)–H(21)	0.930	2.775	161.64	3.670	Cl(3) [2-*x*, 1-*y*, 1-*z*]
C(22)–H(22)	0.930	2.483	143.14	3.278	O(4) [*x*, *y*, -1+*z*]
C(7)–H(7)	0.930	3.035	140.43	3.798	Cl(1) [1-*x*, -*y*, -*z*]
C(9)–H(9)	0.930	2.949	149.43	3.780	Cl(1) [1-*x*, -*y*, -*z*]
			5		
N(1) –H(1)	0.860	2.322	143.52	3.057	O(6) [1-*x*, -1/2+*y*, 3/2-*z*]
N(1) –H(1)	0.860	2.416	157.39	3.233	O(5A) [1-*x*, -1/2+*y*, 3/2-*z*]

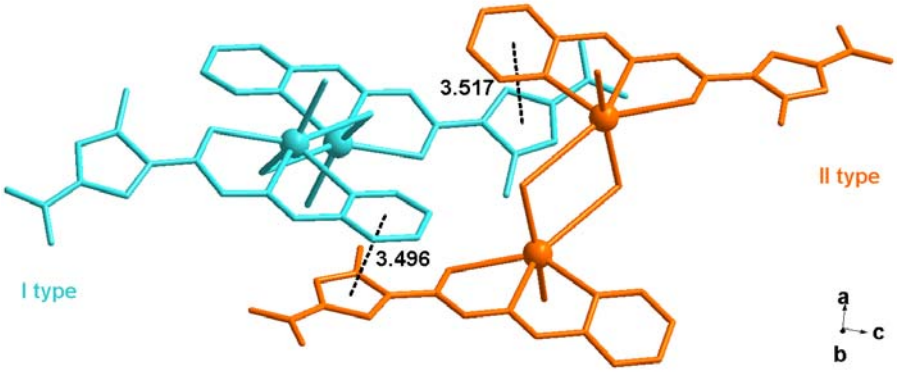

Figure S3. The $\pi\cdots\pi$ interactions between the **I** and **II** type molecule for **4**

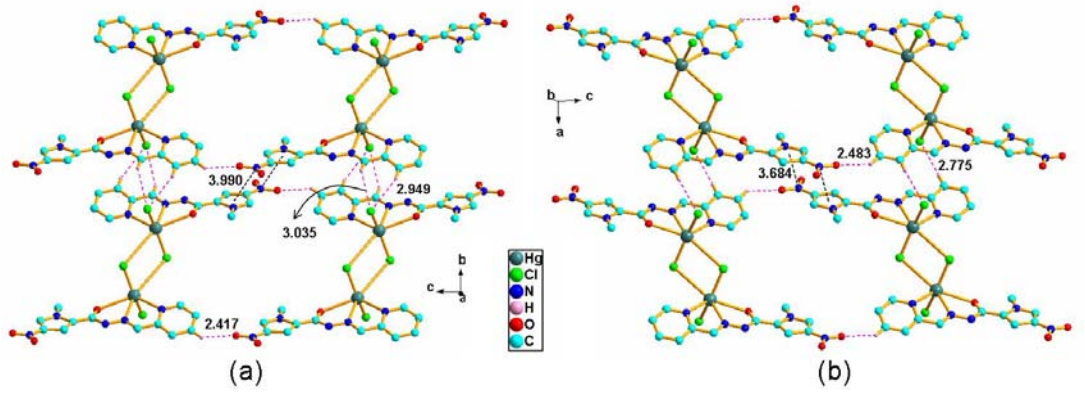

Figure S4. 1-D chains are assembled through H-bonding and $\pi\cdots\pi$ interactions to 2-D network in *bc* plane for **I** type molecule (a) and in *ac* plane for **II** type molecule (b) (all distances in Å). The N,N-Dimethylformamide solvent molecules and H atoms not involved in hydrogen bonds have been omitted for clarity.

The 1-D chains of **I** type molecule (*b*-axis direction) are assembled by intermolecular H-bonds C(10)-H(10)…O(1)(x, y, -1+z) of 2.417 Å and weak $\pi\cdots\pi$ interactions (nitro) N(2)…(pyrrolyl) centroid(1-x, -y, 1-z) of 3.990 Å to form 2-D sheets of parallel staircases in *bc* plane. However, 1-D chains of **II** type molecule (*a*-axis direction) formed 2-D sheets in *bc* plane with stronger $\pi\cdots\pi$ interactions.

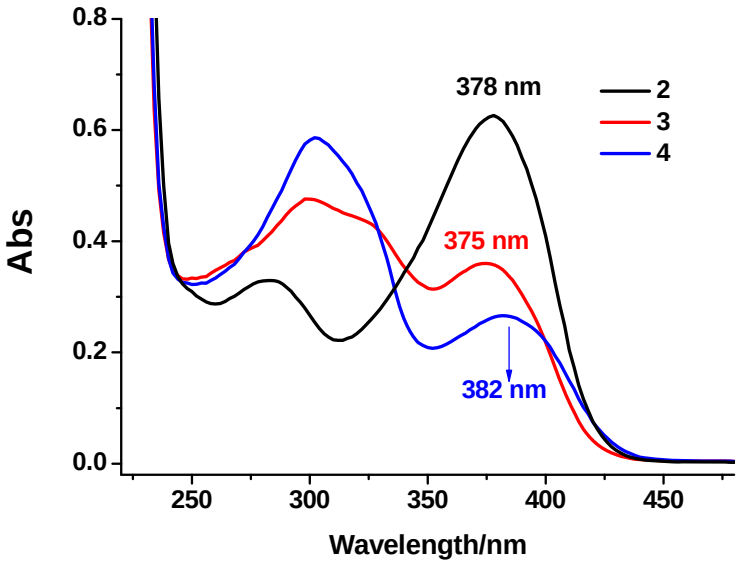

Figure S5. The UV spectra from MeOH solutions of the pure complexes **2-4** ($[M^{2+}]=2.0\times10^{-5}$M)).

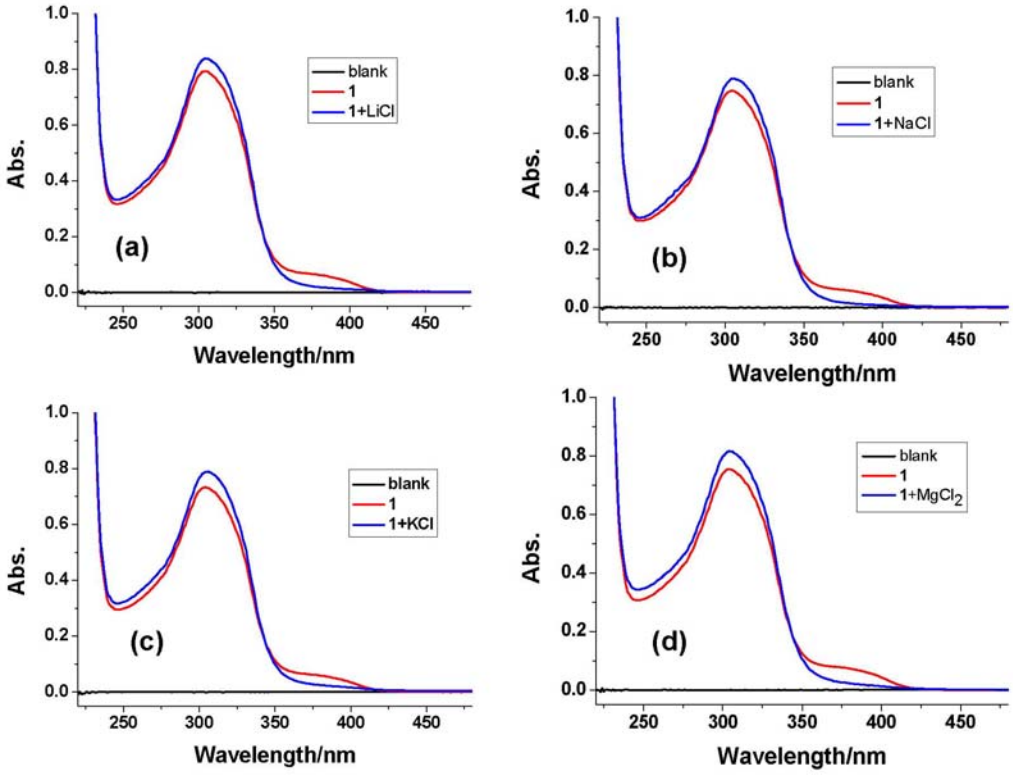

Figure S6. The variation of spectra upon addition of a small quantity solids of LiCl(a), NaCl(b), KCl(c), and $MgCl_2$(d) to the MeOH solution of **1** (1.4×10^{-5}M) at 25 ºC.

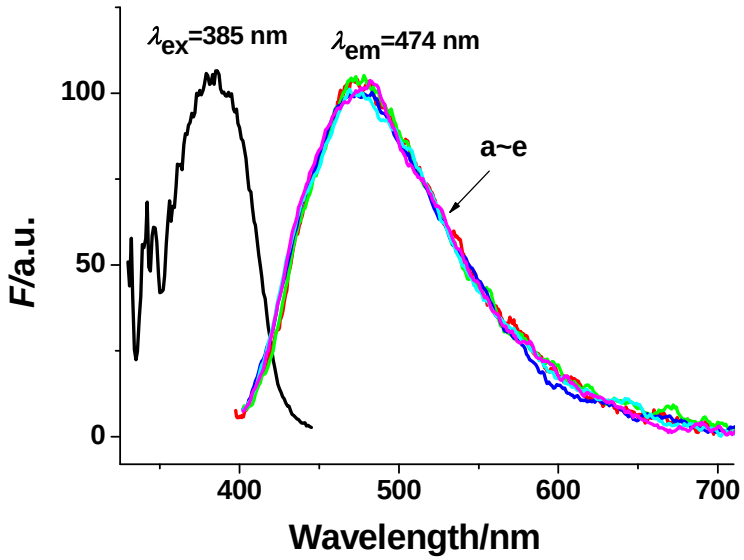

Figure S7. The fluorescence spectra upon addition of KNO_3 to the MeOH solution of **1** (1.1×10^{-5} M) at 25 ºC, slit width, 5 nm.