Luminescent Group 12 Metal Tetracarboxylate Networks for Probe Metal Ions

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Tab. S1 Bond lengths [Å] and angles [deg] for **1**

Compound 1			
Zn(1)-O(1)	1.971(2)	Zn(1)-O(8a)	2.028 (2)
Zn(1)-O(7b)	2.043(2)	Zn(1)-O(6c)	2.047(2)
Zn(1)-O(5d)	2.072(2)	Zn(1)…Zn(1e)	3.0268(5)
O(1)-Zn(1)-O(8a)	101.05(7)	O(1)-Zn(1)-O(7b)	101.20(7)
O(8a) -Zn(1)-O(7b)	157.50(7)	O(1)-Zn(1)-O(6c)	107.52(7)
O(8a) -Zn(1)-O(6c)	86.37(8)	O(7b) -Zn(1)-O(6c)	90.17(8)
O(1)-Zn(1)-O(5d)	94.95(7)	O(8a) -Zn(1)-O(5d)	87.41(8)
O(7b) -Zn(1)-O(5d)	87.34(8)	O(6c) -Zn(1)-O(5d)	157.44(7)

Symmetry codes: (a)=-x+1,-y+1,-z; (b)=x+1,y,z; (c)=x,y+1,z; (d)=-x+2,-y,-z; (e)=-x+2,-y+1,-z; (f)=x,y-1,z; (g)=x-1,y,z

Tab. S2 Bond lengths [Å] and angle [deg] for **2**

Compound 2			
Cd(1)-O(1)	2.381(4)	Cd(1)-O(2)	2.344(4)
Cd(1)-O(4a)	2.236(4)	Cd(1)-O(5)	2.448(4)
Cd(1)-O(6)	2.370(5)	Cd(1)-O(7b)	2.277(4)
O(4a)-Cd(1)-O(7b)	85.70(15)	O(4a)-Cd(1)-O(2)	115.32(16)
O(7b) -Cd(1)-O(2)	118.68(15)	O(4a)-Cd(1)-O(6)	89.75(17)
O(7b) -Cd(1)-O(6)	154.06(17)	O(2) -Cd(1)-O(6)	86.28(16)
O(4a)-Cd(1)-O(1)	170.36(17)	O(7b) -Cd(1)-O(1)	100.80(15)
O(6) -Cd(1)-O(1)	87.41(18)	O(4a) -Cd(1)-O(5)	98.05(17)
O(7b)-Cd(1)-O(5)	101.30(14)	O(2) -Cd(1)-O(5)	128.28(14)
O(6) -Cd(1)-O(5)	54.08(15)	O(1) -Cd(1)-O(5)	87.63(15)
O(2) -Cd(1)-O(1)	55.31(15)		

Symmetry codes: (a)= x-1/2,-y+3/2,z-1/2 ; (b)= -x+2,-y+1,-z+1; (c) =-x+1,-y+1,-z+1; (d)= x+1/2,-y+3/2,z+1/2

Tab. S3 Bond lengths [Å] and angle[deg] for **3**

Compound 3			
Cd(1)-O(9)	2.196(8)	Cd(1)-O(1a)	2.254(8)
Cd(1)-O(6)	2.260(6)	Cd(1)-O(4)	2.280(5)
Cd(1)-O(5)	2.554(7)	Cd(1)-O(3)	2.603(8)
Cd(1)-O(2a)	2.826(6)	Cd(2)-O(1w)	2.070(15)
Cd(2)-O(13)	2.283(8)	Cd(2)-O(2a)	2.305(8)
Cd(2)-O(17)	2.357(14)	Cd(2)-O(10)	2.371(10)
Cd(2)-O(11)	2.407(7)	Cd(3)-O(14)	2.184(8)
Cd(3)-O(16b)	2.267(7)	Cd(3)-O(7b)	2.345(6)
Cd(3)-O(11)	2.351(6)	Cd(3)-O(8b)	2.401(7)
Cd(3)-O(12)	2.390(8)		
O(1a)-Cd(1)-O(9)	109.3(4)	O(9)-Cd(1)-O(6)	120.0(3)
O(1a)-Cd(1)-O(6)	110.2(3)	O(9)-Cd(1)-O(4)	86.4(3)
O(1a)-Cd(1)-O(4)	91.4(3)	O(6)-Cd(1)-O(4)	134.7(3)
O(9)-Cd(1)-O(5)	167.4(4)	O(4)-Cd(1)-O(5)	92.7(3)
O(6)-Cd(1)-O(5)	53.4(2)	O(9)-Cd(1)-O(3)	84.2(3)
O(1a)-Cd(1)-O(3)	141.9(3)	O(6)-Cd(1)-O(3)	91.2(2)
O(4)-Cd(1)-O(3)	53.0(2)	O(5)-Cd(1)-O(3)	85.3(3)
O(1a)-Cd(1)-O(5)	83.3(3)	O(1w) -Cd(2)-O(11)	84.9(3)
O(1w) -Cd(2)-O(10)	87.6(4)	O(1w) -Cd(2)-O(13)	89.0(4)
O(1w) -Cd(2)-O(2a)	88.6(3)	O(13) -Cd(2)-O(2a)	95.6(3)
O(1w) -Cd(2)-O(17)	175.6(5)	O(13) -Cd(2)-O(17)	94.7(5)
O(2a) -Cd(2)-O(17)	93.3(5)	O(2a)-Cd(2)-O(11)	173.1(2)
O(13)-Cd(2)-O(10)	176.4(4)	O(2a)-Cd(2)-O(10)	83.7(3)

O(17) -Cd(2)-O(10)	88.7(5)	O(17)-Cd(2)-O(11)	93.3(5)
O(13)-Cd(2)-O(11)	81.9(2)	O(10)-Cd(2)-O(11)	98.4(3)
O(14)-Cd(3)-O(16b)	90.0(3)	O(14)-Cd(3)-O(7b)	93.9(3)
O(16b)-Cd(3)-O(7b)	111.7(3)	O(14)-Cd(3)-O(11)	106.3(3)
O(16b)-Cd(3)-O(11)	87.4(3)	O(7b)-Cd(3)-O(11)	152.4(2)
O(14)-Cd(3)-O(12)	161.0(3)	O(16b)-Cd(3)-O(12)	84.2(3)
O(7b)-Cd(3)-O(12)	105.0(2)	O(11) -Cd(3)-O(12)	55.5(2)
O(14)-Cd(3)-O(8b)	95.9(3)	O(16b)-Cd(3)-O(8b)	165.4(3)
O(7b)-Cd(3)-O(8b)	54.6(2)	O(11)-Cd(3)-O(8b)	103.7(2)
O(12)-Cd(3)-O(8b)	94.1(3)		

Symmetry codes: (a)=x-1, y, z; (b)=-x+1, -y+1, -z+2; (c)=x+1, y, z; (d)=-x+2, -y, -z+1; (e)=-x+1, -y, -z+2; (f)= -x+2, -y+1, -z+1; (g)= -x, -y+1, -z+2

Tab. S4 Distances (Å) and angles (deg) of the hydrogen bond interactions in **1**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(D-H···A)
2 N(1) - H(1A) ..O(3d)	0.90	1.76	2.6533	174
2 N(1) - H(1B) ..O(3a)	0.90	1.88	2.7392	158
3 N(2) - H(2A) ..O(2)	0.90	1.88	2.7462	161
3 N(2) - H(2B) ..O(4b)	0.90	1.81	2.7006	169

Symmetry codes: (a) = -x+1, y, z; (b) =x,1+y, z; (c) = 1-x,1-y,1-z; (d) =1-x, -y, 1-z;

Tab. S5 Distances (Å) and angles (deg) of the hydrogen bond interactions in **2**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(D-H···A)
O1w - H1wA .. O(4b)	0.83	2.04	2.8475	165
N(1) - H(1A) .. O(3)	0.90	2.09	2.8841	146
N(1) - H(1A) .. O(2b)	0.90	2.47	2.9198	111
N(1) - H(1B) .. O1w	0.90	1.94	2.8018	158
O1w - H1wB .. O(8)	0.81	1.89	2.7362	165
N(2) - H(2A) .. O(1)	0.90	2.35	3.0428	133
N(2) - H(2A) .. O(8a)	0.90	2.27	2.9783	135
N(2) - H(2B) .. O(5c)	0.90	1.98	2.7903	150

Symmetry codes: (a) = -1/2+x, 1/2-y, -1/2+z; (b) = 1/2-x, -1/2+y, 1/2-z; (c) = 1+x, y, z

Tab. S6 Distances (Å) and angles (deg) of the hydrogen bond interactions in **3**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(D-H···A)
O1W - H(1WA) ..O(16)	1.10	1.84	2.806	145
O1W - H(1WB) ..O(6)	1.09	1.69	2.692	151
N(1) - H(1A) ..O(7)	0.90	2.10	2.826	137
N(1) - H(1B)..O(15)	0.90	1.87	2.692	151

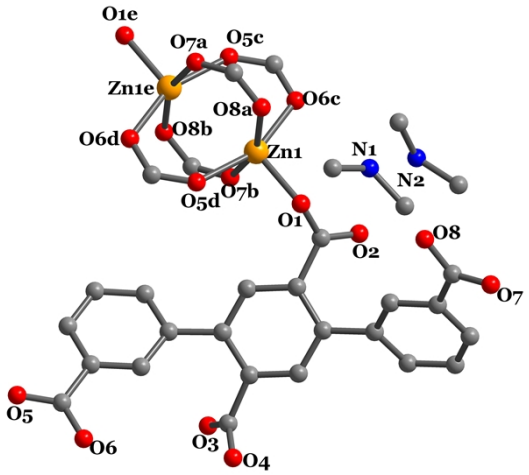

Fig. S1 Views of the coordination environments of Zn(II) atoms and organic $[Me_2NH_2]^+$ cation in **1**

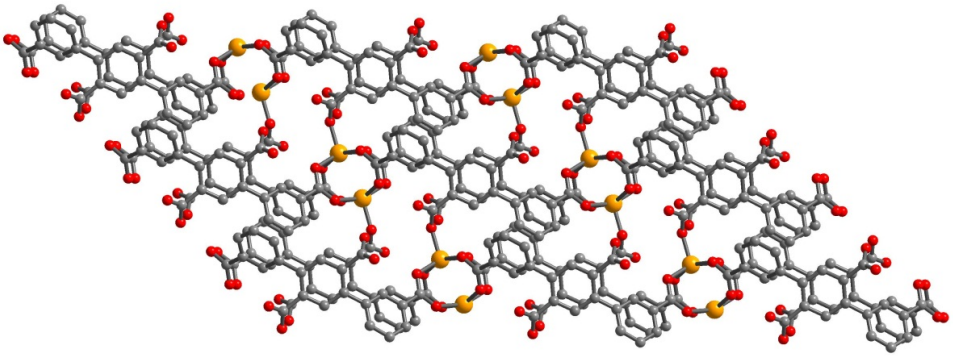

Fig. S2 Perspective view of the 3D supramolecular array of **1**

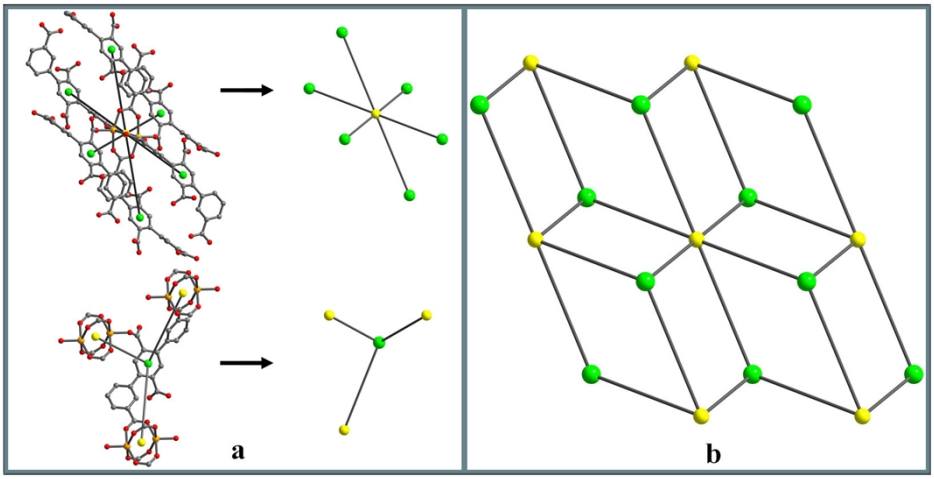

Fig. S3 (a). Tatratopic and tritopic linkers in **1**. (b). Schematic representation of the kgd net in **1**.

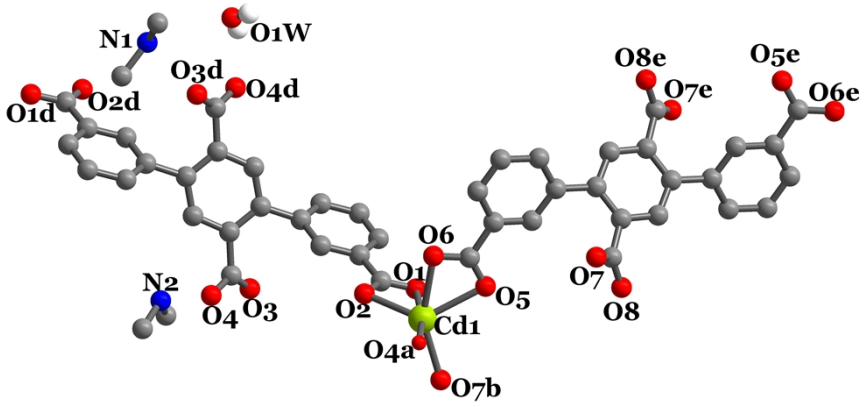

Fig. S4 Views of the coordination environments of Cd(II) atoms and organic $[Me_2NH_2]^+$ cation in **2**

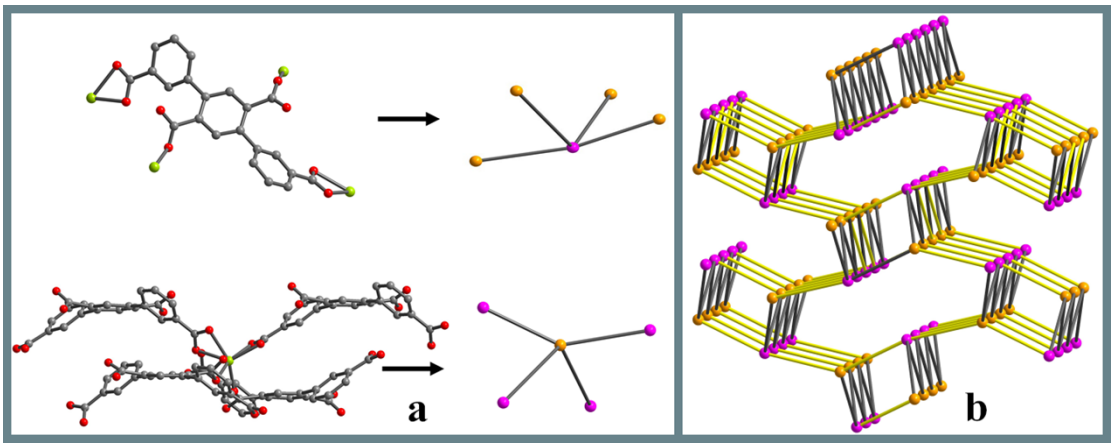

Fig. S5 (a). Two tatratopic linkers in **2**. (b). Schematic representations of the 4-connected sra framework in **2**

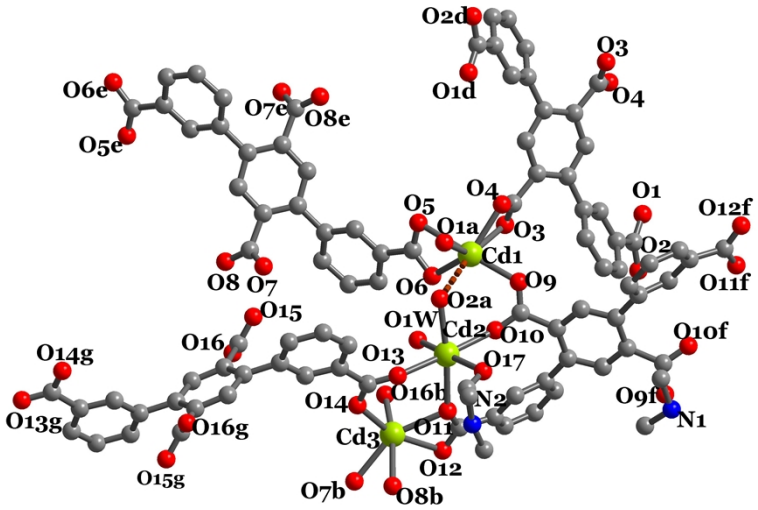

Fig. S6 Views of the coordination environments of Cd(II) atoms in **3.**

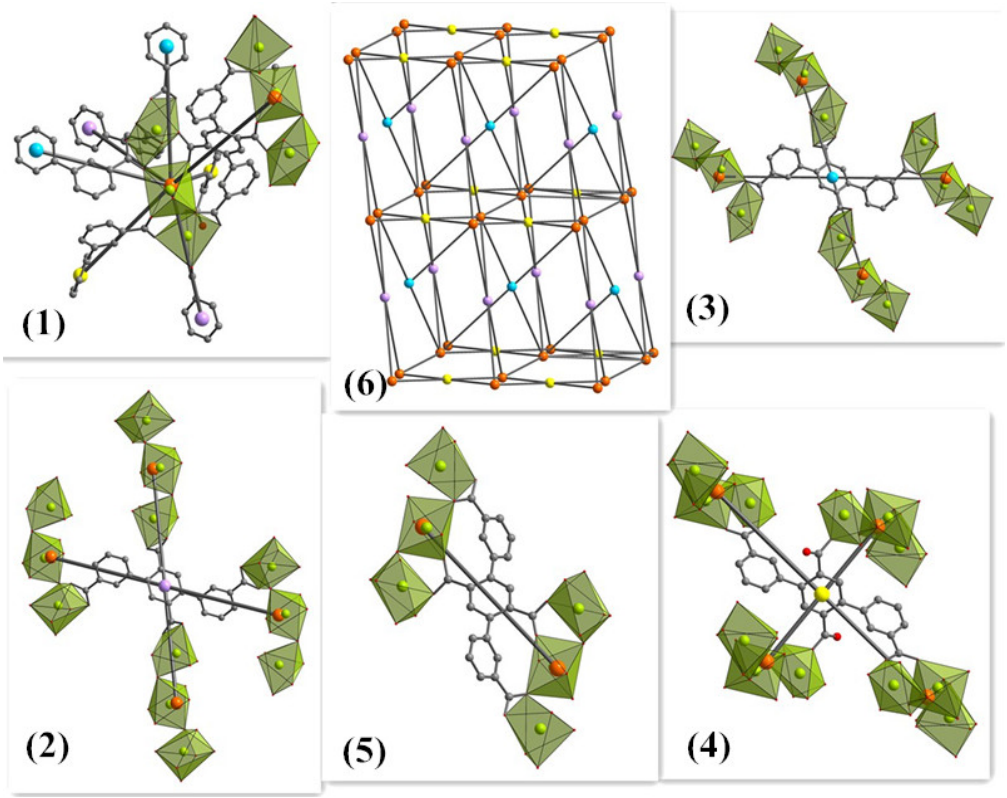

Fig. S7 (1-4). The list of one 7-c node and three 4-c nodes in **3**; (5). The $tpta^{4-}$ as linker; (6). Schematic representations of framework in **3**

Tab. S6 Solid-state emission and excitation from 4K to 298K for **1**−**3**

Compound	Temperature(K)	λ_{ex}	λ_{em1}	λ_{em2}
H_4TPTA	298	367	435	462
1	4	374	420	467
	100	374	430	467
	200	374	439	467
	298	374	443	467
2	4	377	410.5	470
	100	377	417	470
	200	377	424	468.5
	298	377	446	470
3	4	378	408	467
	100	378	412	467
	150	378	425	467
	200	378	427	467
	250	378	434	467
	298	378	439	467

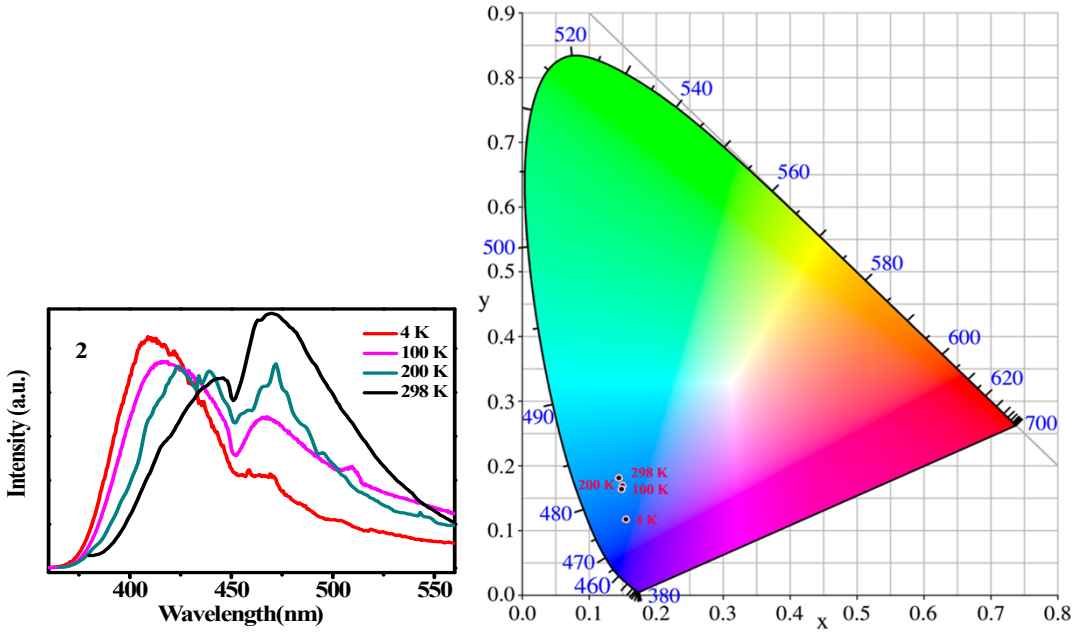

Fig. S8 (a) Emission spectra of **2** from 4K to 298K with λ_{ex}= 377 nm; (b) The CIE coordinates (marked by the circles) for **2** at various temperature

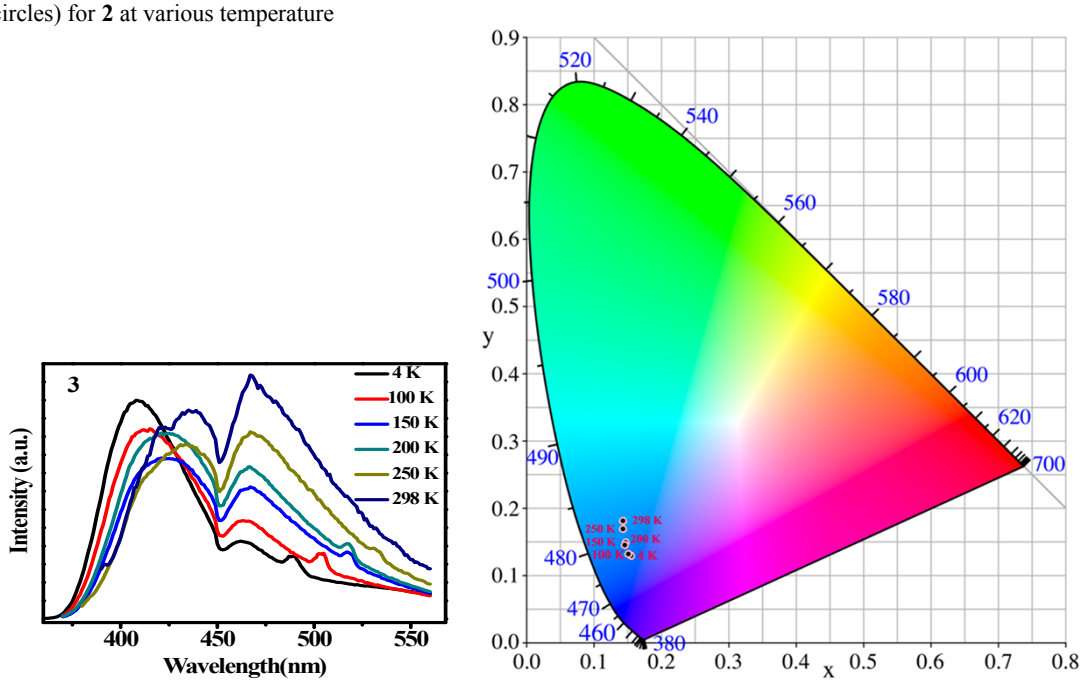

Fig. S9 (a) emission spectra of **3** from 4k to 298k with λex= 378 nm; (b) The CIE coordinates (marked by the circles) for **3** at various temperature

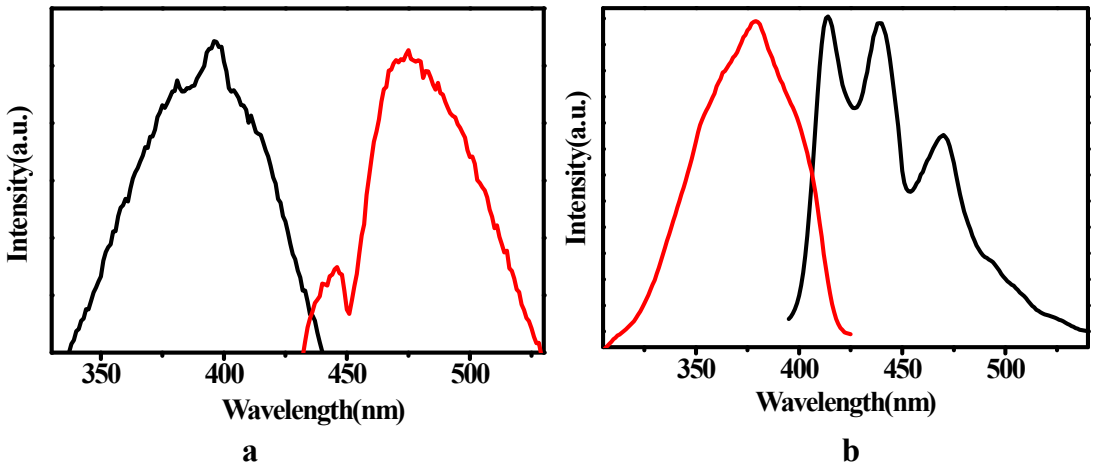

Fig. S10 (a). Emission and excitation spectra of H_4tpta: excitation spectrum (λmax = 396 nm) (black) and emission spectrum (λmax = 475 nm) (red) in pyridine; (b). Emission and excitation spectra of H4tpta: excitation spectrum (λmax = 379 nm) (red) and emission spectrum (central peak at around 440 nm additional peaks at higher 470 nm and lower wavelengths at 414nm) (black) in 1,2,4-trichlorobenzene

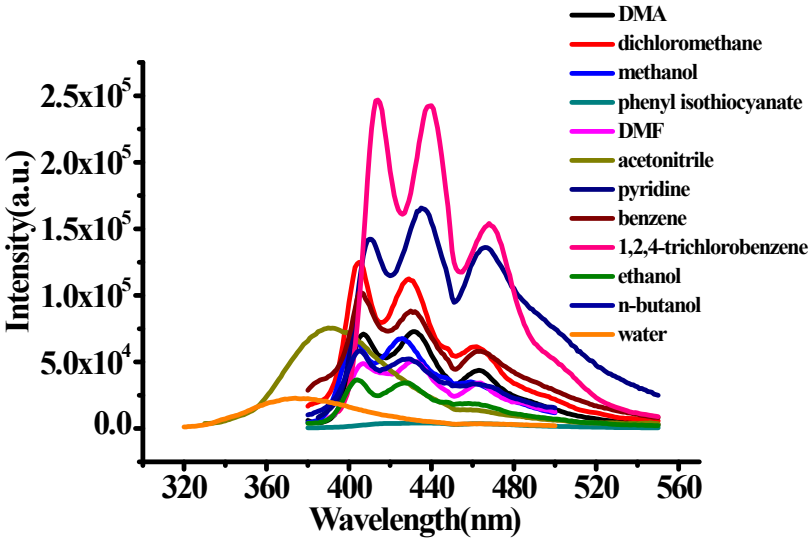

Fig. S11 Phosphorescence emission changes of **2** in different solvents.

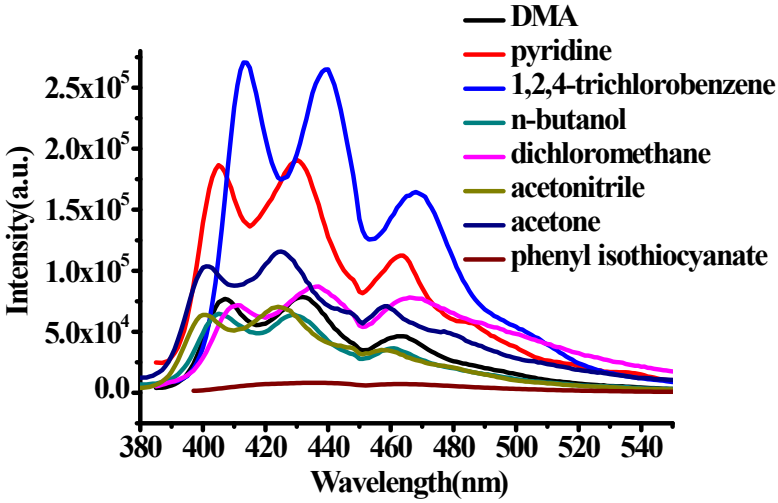

Fig. S12 Phosphorescence emission changes of **3** in different solvents

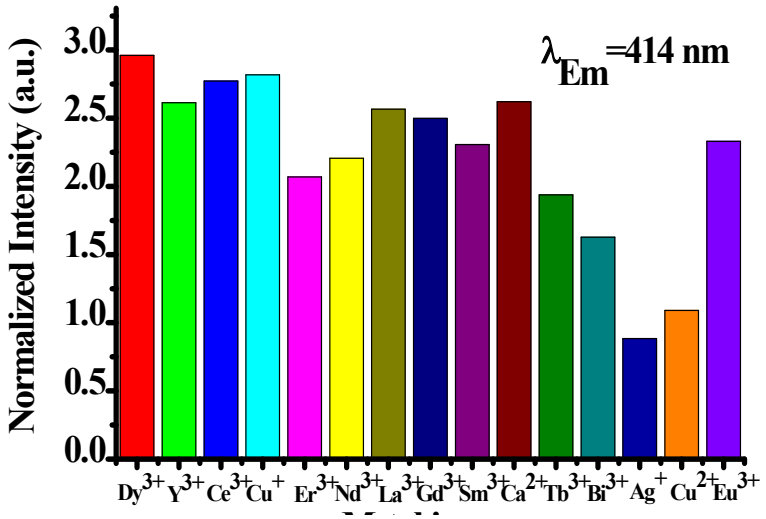

Fig. S13 Phosphorescence response of **2** to various cations.

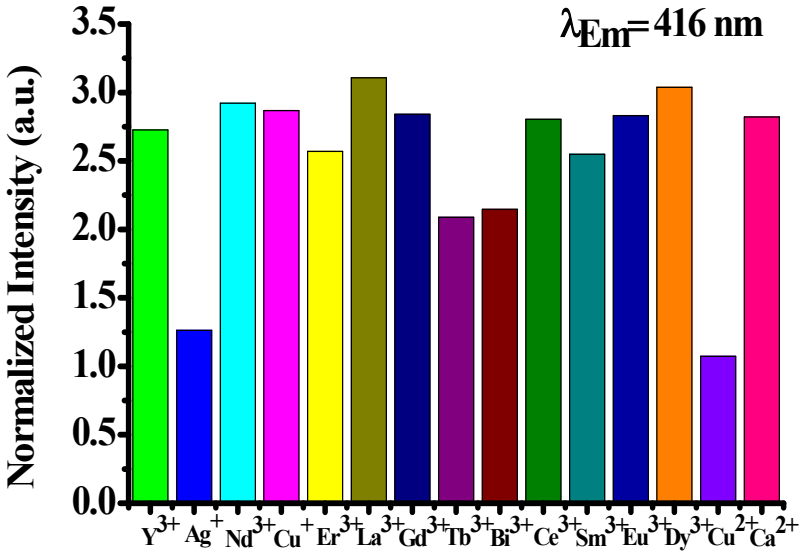

Fig. S14 Phosphorescence response of **3** to various cations.

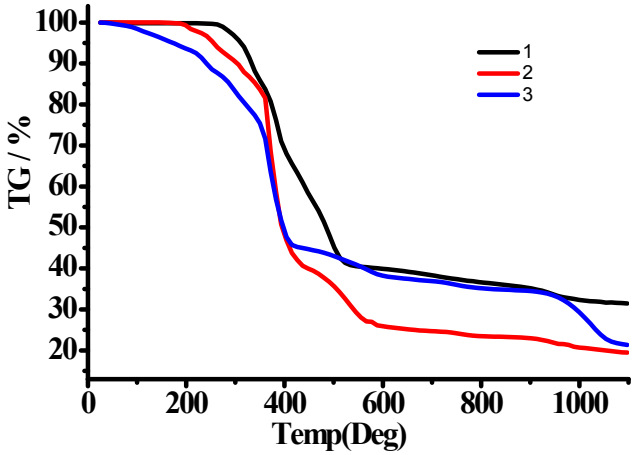

Fig. S15 TGA curve of **1**–**3** in air at the heating rate of 10 °C min^{-1}

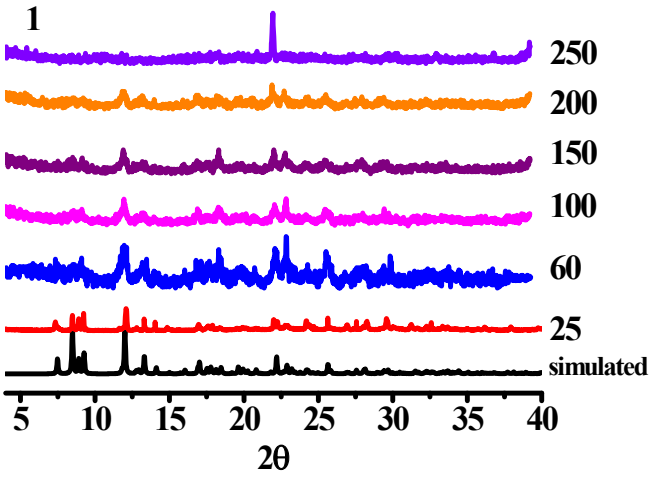

Fig. S16 Powder X-ray diffraction pattern of **1**: Experimental result (red), Simulated pattern (black)

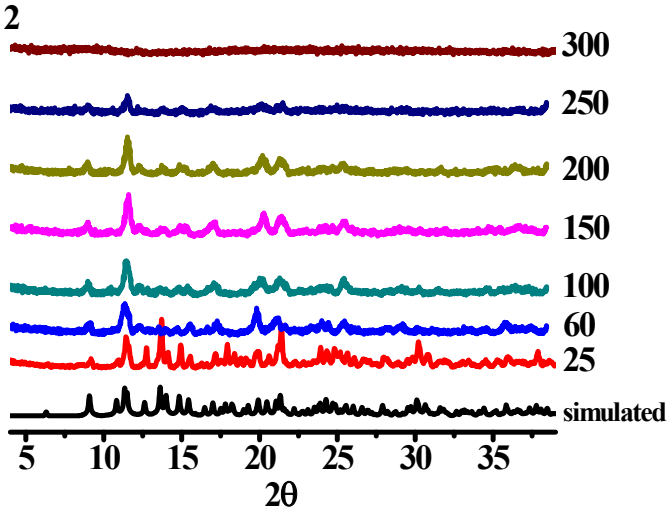

Fig. S17 Powder X-ray diffraction pattern of **2**: Experimental result (red), Simulated pattern (black)

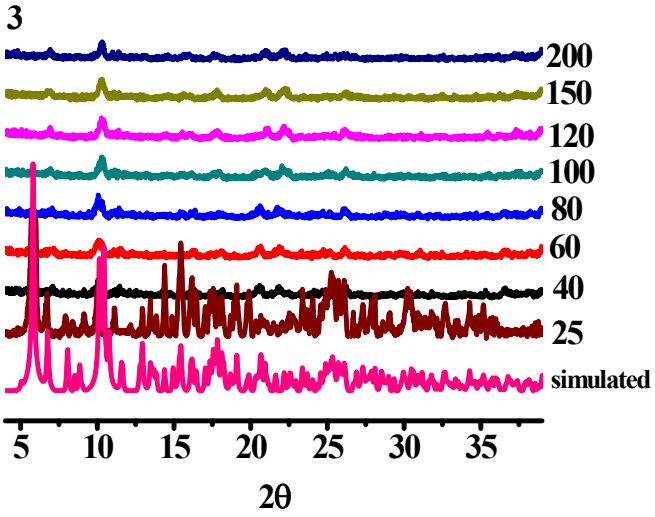

Fig. S18 Powder X-ray diffraction pattern of **3**: Experimental result (red), Simulated pattern (black)

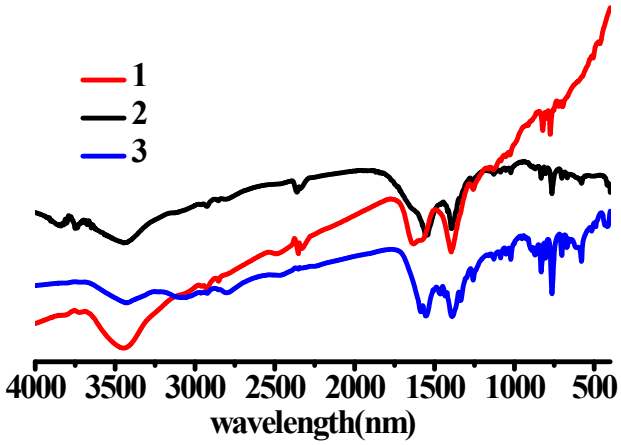

Fig. S19 IR spectra of the pristine **1**–**3**