Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Novel Photo- and/or Thermochromism MOFs Derived from Bipyridinium Carboxylate Ligands

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Table S1 Crystal Data and Structure Refinement for **1** and **2.**

compound	**1**	**2**
formula	$C_{18}H_{15}N_3O_9Zn$	$C_{18}H_{17}N_3O_{10}Zn$
fw	482.70	500.72
temp (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
cryst syst	Orthorhombic,*Pbcn*	Triclinic, P-1
a (Å)	a = 27.841(6)	a = 9.6695(19)
b (Å)	b = 7.5266(15)	b = 10.135(3)
c (Å)	c = 17.413(3)	c = 10.898(2)
V (Å^3)	3648.9(12)	944.9(4)
Z	8	2
F(000)	1968	512
θ range (deg)	3.04 - 27.48	3.00 - 27.49
reflns collected / unique	31201 / 4171	9325 / 4291
R_{int}	0.0632	0.0219
data / restraints /params	4171/0/280	4291 / 0 / 284
GOF on F^2	1.058	1.085
R_1, wR_2 [a] [$I>2\sigma(I)$]	0.0577, 0.1470	0.0375, 0.1055
R_1, wR_2 (all data)	0.0810, 0.1598	0.0453, 0.1144

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $wR_2 = [\sum[w (F_o^2-F_c^2)^2] / \sum[w (F_o^2)^2]]^{1/2}$

Table S2 Selected bond lengths [Å] and angles [°] for **1**.

Zn(1)-O(2)	1.949(3)	O(4)-C(14)	1.227(5)
Zn(1)-O(3)	1.960(3)	O(5)-C(16)	1.224(5)

Zn(1)-O(1)	1.985(3)	O(6)-N(3)	1.200(7)
Zn(1)-N(1)	2.041(3)	O(7)-N(3)	1.120(7)
O(2)-C(16)	1.281(5)	O(8)-N(3)	1.158(8)
O(3)-C(14)	1.276(5)		
O(2)-Zn(1)-O(3)	105.37(12)	O(3)-C(14)-C(15)	114.6(3)
O(2)-Zn(1)-O(1)	106.60(12)	O(5)-C(16)-O(2)	123.6(4)
O(3)-Zn(1)-O(1)	113.93(13)	O(5)-C(16)-C(12)#4	120.0(3)
O(2)-Zn(1)-N(1)	124.61(14)	O(2)-C(16)-C(12)#4	116.2(3)
O(3)-Zn(1)-N(1)	96.24(13)	C(2)-N(1)-Zn(1)	125.3(3)
O(1)-Zn(1)-N(1)	109.86(13)	C(18)-N(1)-Zn(1)	117.4(3)
C(16)-O(2)-Zn(1)	109.4(2)	O(7)-N(3)-O(8)	125.0(9)
C(14)-O(3)-Zn(1)	122.6(3)	O(7)-N(3)-O(6)	115.5(7)
O(4)-C(14)-O(3)	125.0(4)	O(8)-N(3)-O(6)	118.4(9)
O(4)-C(14)-C(15)	120.5(3)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,-z #2 x+1/2,y-1/2,-z+1/2

#3 x-1/2,-y+1/2,-z #4 x-1/2,y+1/2,-z+1/2

Table S3 Selected bond lengths [Å] and angles [°] for **2**.

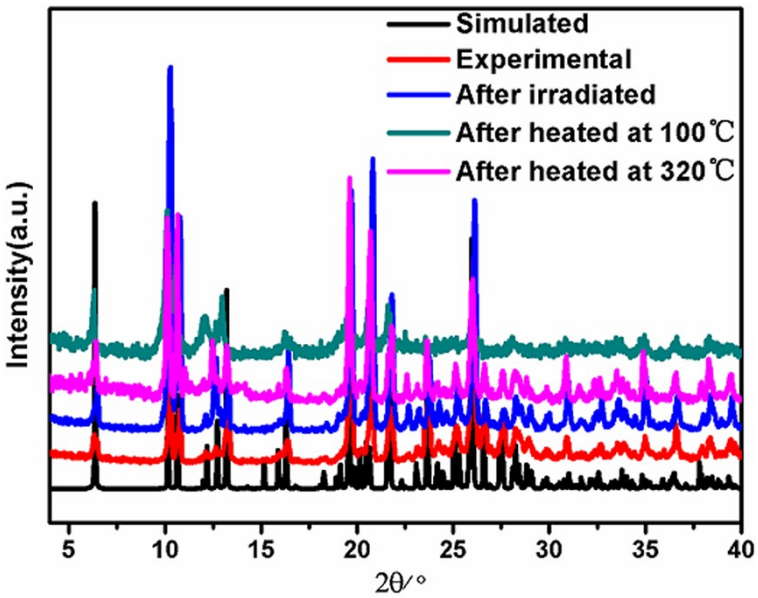
Zn(1)-O(4)	1.986(2)	O(2)-C(15)	1.248(3)
Zn(1)-O(1)	1.9983(19)	O(3)-C(14)	1.240(4)
Zn(1)-N(1)	2.079(2)	O(4)-C(14)#2	1.261(3)
Zn(1)-O(5)	2.156(2)	N(3)-O(9)	1.220(4)

Zn(1)-O(6)	2.167(2)	N(3)-O(8)	1.237(4)
O(1)-C(15)#1	1.260(3)	N(3)-O(7)	1.249(4)
O(4)-Zn(1)-O(1)	121.69(8)	C(14)#2-O(4)-Zn(1)	114.54(18)
O(4)-Zn(1)-N(1)	100.52(9)	O(3)-C(14)-O(4)#3	125.2(2)
O(1)-Zn(1)-N(1)	137.73(9)	O(3)-C(14)-C(18)	117.8(2)
O(4)-Zn(1)-O(5)	91.77(9)	O(4)#3-C(14)-C(18)	117.0(2)
O(1)-Zn(1)-O(5)	88.14(9)	O(2)-C(15)-O(1)#4	123.8(2)
N(1)-Zn(1)-O(5)	88.38(9)	O(2)-C(15)-C(16)	119.2(2)
O(4)-Zn(1)-O(6)	95.12(9)	O(1)#4-C(15)-C(16)	117.0(2)
O(1)-Zn(1)-O(6)	88.68(9)	O(9)-N(3)-O(8)	119.1(3)
N(1)-Zn(1)-O(6)	89.83(9)	O(9)-N(3)-O(7)	120.4(3)
O(5)-Zn(1)-O(6)	173.08(8)	O(8)-N(3)-O(7)	120.4(3)
C(15)#1-O(1)-Zn(1)	113.78(16)		

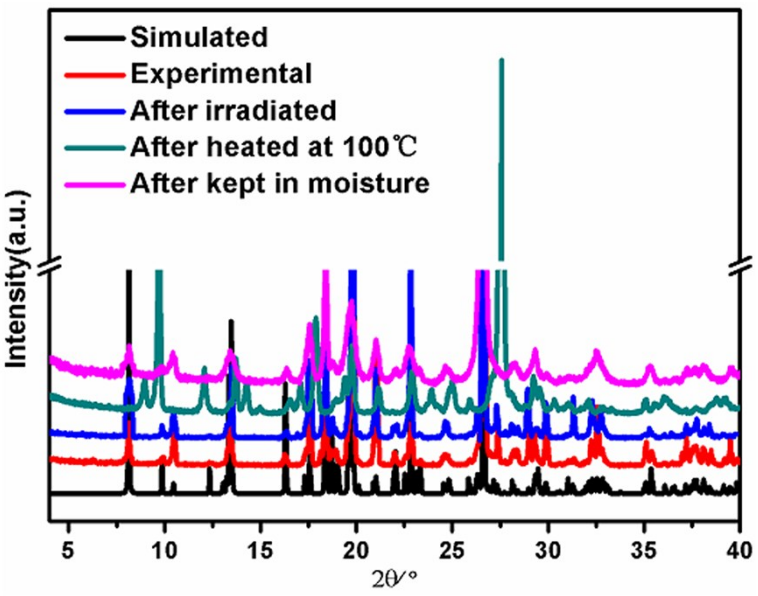
Symmetry transformations used to generate equivalent atoms:

#1 x+1,y-1,z-1 #2 x,y-1,z-1

#3 x,y+1,z+1 #4 x-1,y+1,z+1



(a)



(b)

Fig. S1 (a) Experimental, simulated , irradiation and heated powder XRD patterns of compound **1;** (b) Experimental, simulated, irradiation and heated powder XRD patterns of compound **2**.

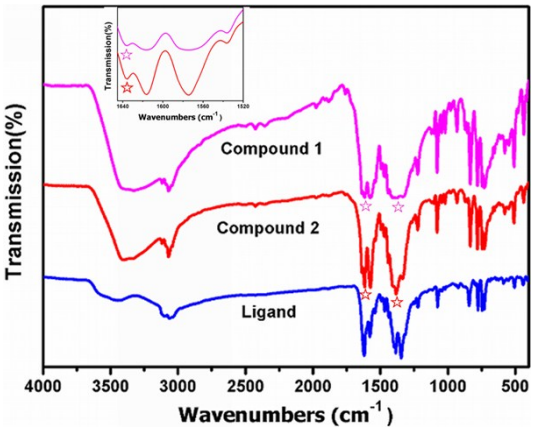
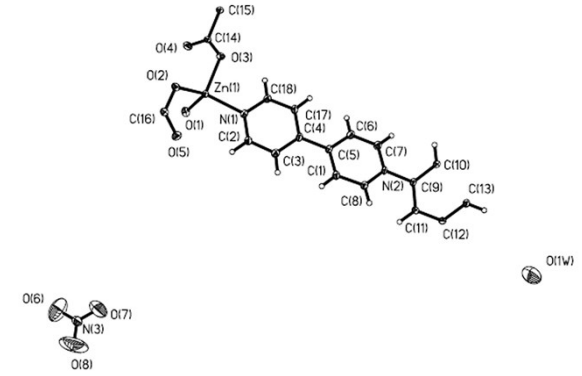
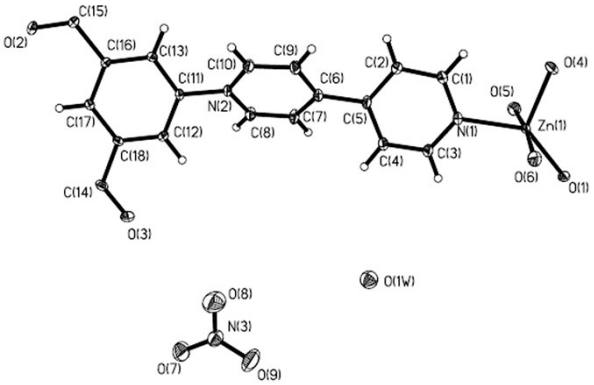


Fig. S2 IR spectra of **H_2ipbp** ligand, **1** and **2**. Besides the C=O stretch vibrations of the carboxylic groups around 1615 cm^{-1}, 1382cm^{-1}, the characteristic absorption around 1636 cm^{-1} of these two compounds confirms the exist of the C=N and C=C stretching vibrations of the pyridinium group.[1]



(a)



(b)

Fig. S3 The asymmetric unit of **1** (a) and **2** (b) showing ellipsoid at the 30% probability level.

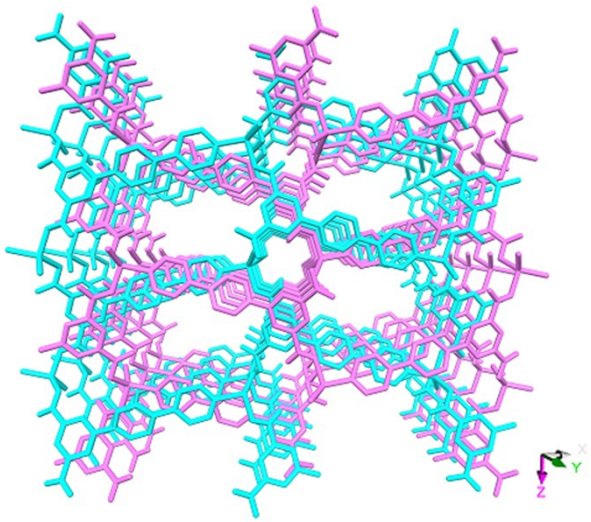


Fig. S4 The perspective view of 3D framework for compound **1**.

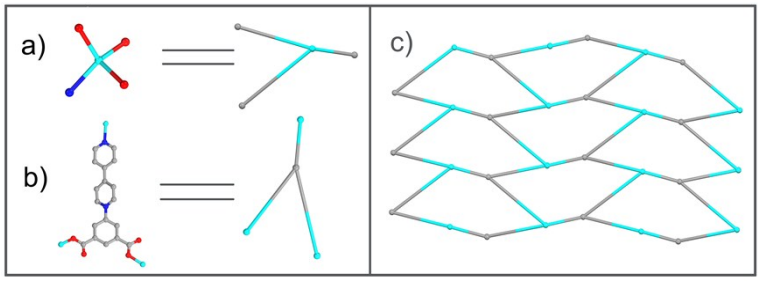


Fig. S5 a), b) Ball-and-stick and schematic representations of 3-connected znic (blue) and 3-connected ligand nodes (gray); (c) Schematic representation with 3,3-connected utp topology of **1**.

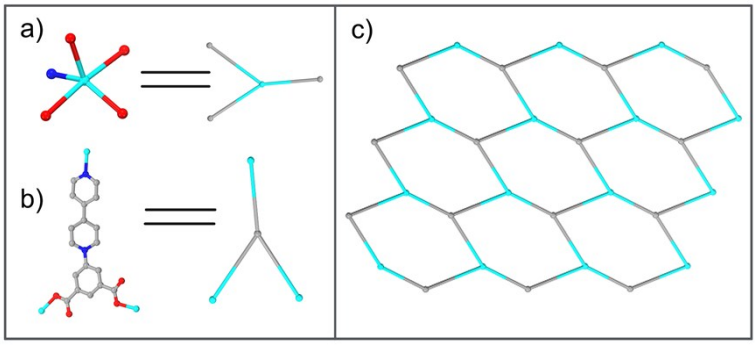


Fig. S6 a), b) Ball-and-stick and schematic representations of 3-connected znic (blue) and 3-connected ligand nodes (gray); (c) Schematic representation with 3,3-connected hcp topology of **2**.

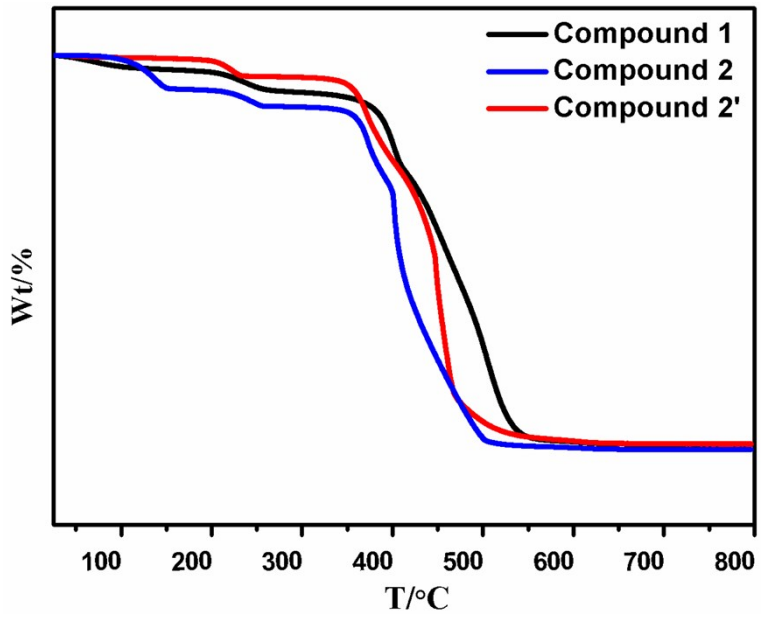


Fig. S7 TG curve of compound **1**, **2** and **2'**.

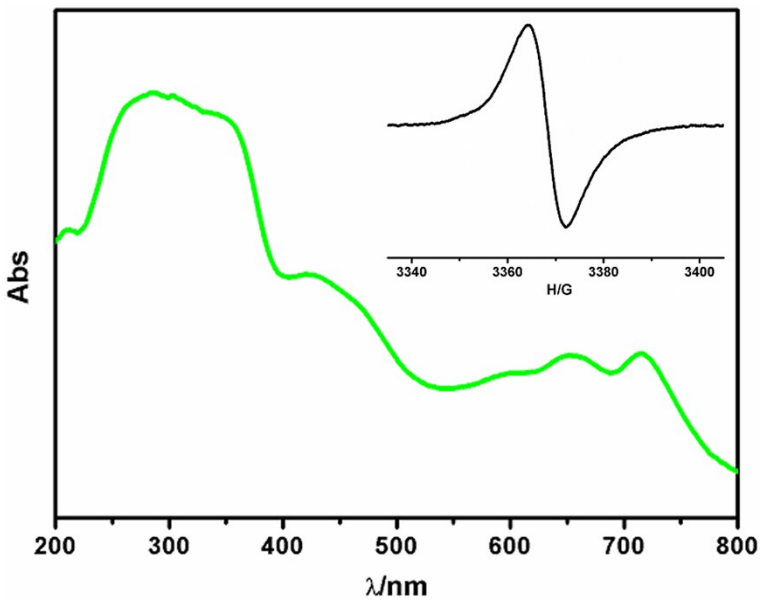


Fig. S8 UV-vis spectra and EPR signal (inserted, g=2.0023) of heated (90 °C)sample for **1**.

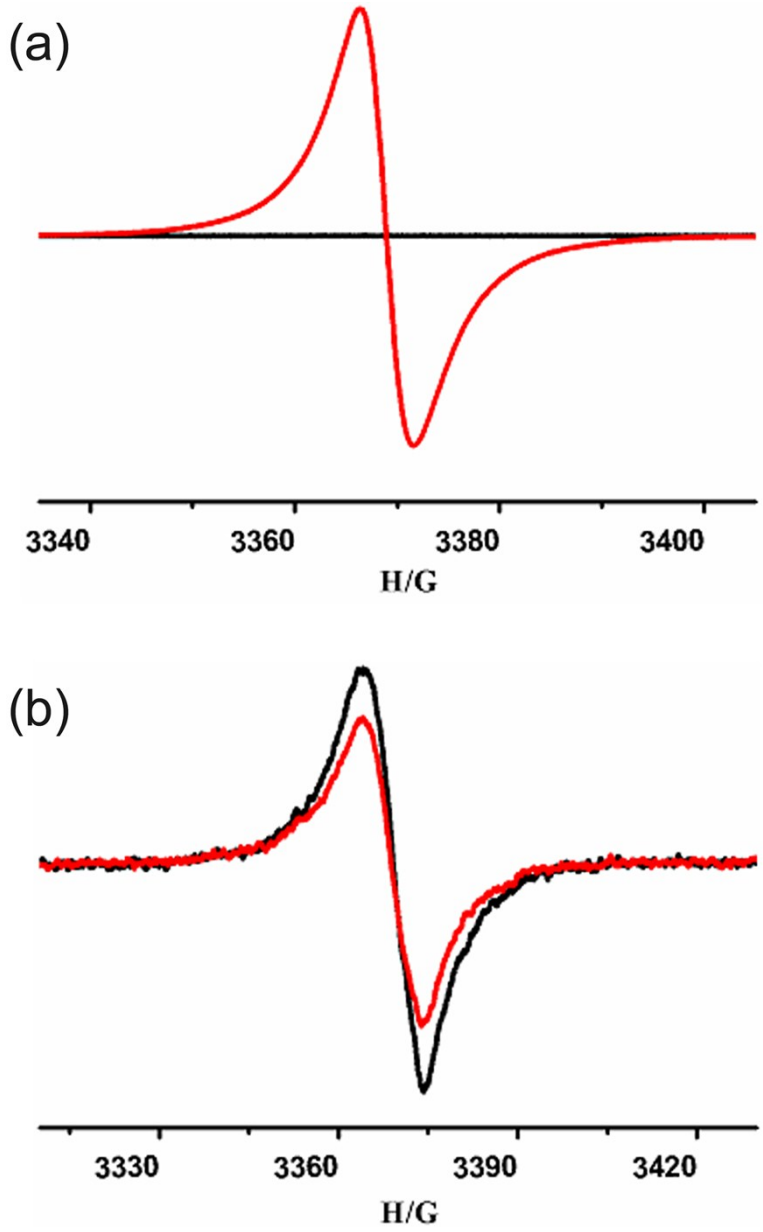


Fig. S9 (a) EPR signal of colored compound **1** (red) and paled sample of **1** (dark); (b) EPR signal of colored compound **2** (dark) and colored compound **2** kept in the dark for 21 days (red).

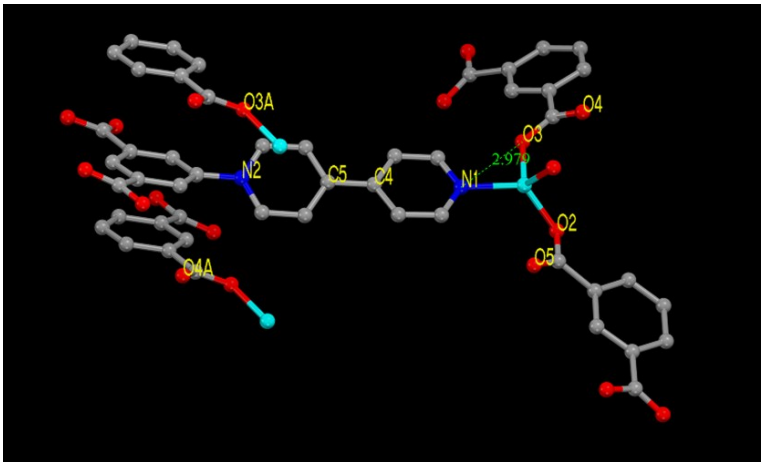


Fig. S10 The distances and orientations of carboxylate oxygen atoms and pyridinium nitrogen atoms between adjacent ribbons of rings in compound **1**.

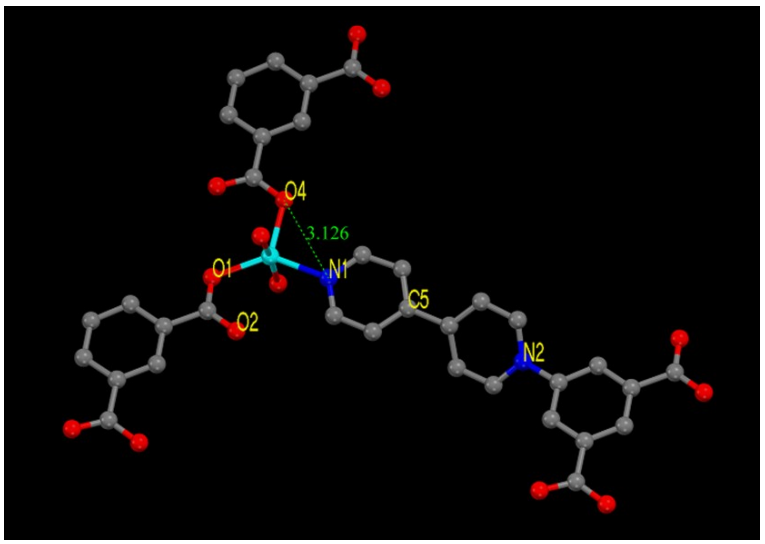


Fig. S11 The distances and orientations of carboxylate oxygen atoms and pyridinium nitrogen atoms between adjacent ribbons of rings in compound **2**.

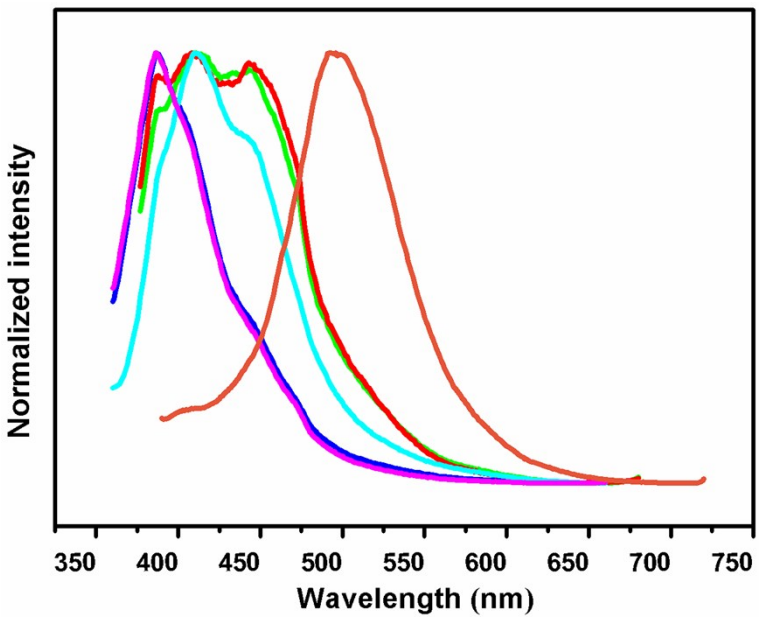


Fig. S12 Solid state luminescence emission spectra of H_2ipbp (orange, λ_{ex} = 331 nm), compound **1** (green, λ_{ex} = 344 nm) after UV irradiation, compound **1** after heated at 90 °C (red, λ_{ex} = 344 nm), compound **2** (blue, λ_{ex} = 331 nm), compound **2'** (cyan, λ_{ex} = 356 nm), compound **2'** after kept in moisture (magent, λ_{ex} = 356 nm).

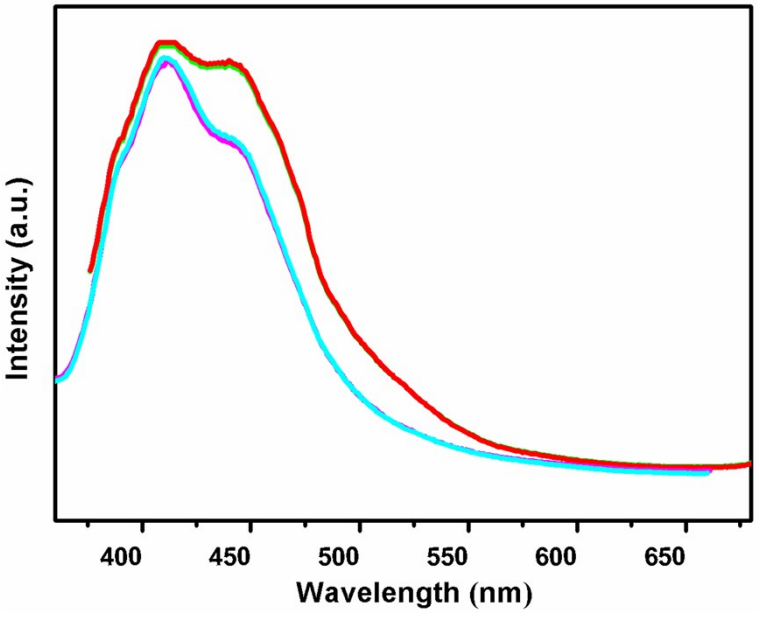


Fig. S13 Solid-state luminescence emission spectra of initial compound **1** (red) and paled sample of **1** (green) in dark, initial compound **2'** (cyan) and paled sample of **2'**(magenta) after heated at 100 °C.

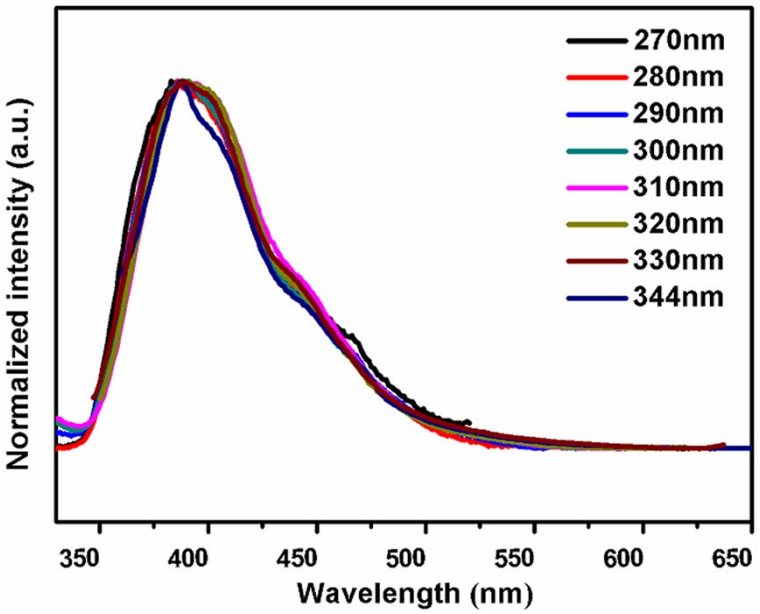


Fig. S14 Solid-state luminescence emission spectra of compound **2** with several excitation wavelengths.

Reference

1. J.-K. Sun, P. Wang, C. Chen, X.-J. Zhou, L.-M. Wu, Y.-F. Zhang and J. Zhang, *Dalton Trans.*, 2012, **41**, 13441.