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Metal-Organic Frameworks Based on Bipyridinium Carboxylate: Photochromism and Selective Vapochromism

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

compounds	**1**	**2**
formula	$C_{42}H_{36}N_8O_{16}Cd_2$	$C_{72}H_{58}Br_4Cd_4N_8O_{23}$
*f*w	1133.59	2158.39
temp (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
space group	$Pna2_1$	$P2_1/c$
a (Å)	19.575(4)	15.3906(10)
b (Å)	15.170(3)	7.7582(5)
c (Å)	14.240(3)	17.3185(12)
V (Å^3)	4228.6(15)	1951.3(2)
Z	4	1
F(000)	2272	1048
θ range (deg)	3.22 - 27.48	2.42- 26.14
reflections collected/unique	37091/9601	11810/3901
R_{int}	0.1043	0.0422
data / restraints /params	9601/1/548	3901/12/269
GOF on F^2	1.017	1.018
R_1, wR_2 [a] [$I>2\sigma(I)$]	0.0644, 0.1425	0.0377, 0.0908
R_1, wR_2 (all data)	0.1098, 0.1588	0.0578, 0.0991

[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**.

Cd(1)-O(7)	2.246(5)	Cd(2)-O(3)	2.273(6)
Cd(1)-N(1)	2.327(6)	Cd(2)-O(1)	2.278(6)
Cd(1)-O(5)	2.343(8)	Cd(2)-N(7)	2.377(8)
Cd(1)-O(9)	2.400(10)	Cd(2)-O(4)	2.454(9)
Cd(1)-O(8)	2.460(7)	Cd(2)-O(10)	2.476(14)
Cd(1)-O(4)	2.572(8)	Cd(2)-O(2)	2.602(6)
Cd(1)-O(6)	2.635(6)	Cd(2)-O(11)	2.636(12)
O(7)-Cd(1)-N(1)	129.8(2)	O(4)-Cd(2)-O(11)	150.1(4)
O(7)-Cd(1)-O(5)	143.0(3)	O(10)-Cd(2)-O(11)	48.4(4)
N(1)-Cd(1)-O(5)	83.2(3)	O(2)-Cd(2)-O(11)	119.1(4)
O(7)-Cd(1)-O(9)	85.7(3)	O(3)-Cd(2)-O(2)	98.1(2)
N(1)-Cd(1)-O(9)	81.6(3)	O(1)-Cd(2)-O(2)	52.8(2)
O(5)-Cd(1)-O(9)	83.2(4)	N(7)-Cd(2)-O(2)	133.1(2)
O(7)-Cd(1)-O(8)	80.4(3)	O(4)-Cd(2)-O(2)	85.5(3)
N(1)-Cd(1)-O(8)	99.4(3)	O(10)-Cd(2)-O(2)	71.2(3)
O(5)-Cd(1)-O(8)	114.1(4)	O(3)-Cd(2)-O(11)	79.7(4)
O(9)-Cd(1)-O(8)	162.7(3)	O(1)-Cd(2)-O(11)	114.9(4)
O(7)-Cd(1)-O(4)	105.4(3)	N(7)-Cd(2)-O(11)	78.8(3)
N(1)-Cd(1)-O(4)	123.5(3)	O(3)-Cd(2)-O(10)	78.8(3)
O(5)-Cd(1)-O(4)	51.7(3)	O(1)-Cd(2)-O(10)	92.2(3)
O(9)-Cd(1)-O(4)	118.2(3)	N(7)-Cd(2)-O(10)	117.1(4)
O(8)-Cd(1)-O(4)	75.8(2)	O(4)-Cd(2)-O(10)	145.7(4)
O(7)-Cd(1)-O(6)	52.3(2)	O(3)-Cd(2)-O(1)	150.7(2)
N(1)-Cd(1)-O(6)	77.6(2)	O(3)-Cd(2)-N(7)	128.6(2)
O(5)-Cd(1)-O(6)	155.8(3)	O(1)-Cd(2)-N(7)	80.3(2)
O(9)-Cd(1)-O(6)	79.6(3)	O(3)-Cd(2)-O(4)	80.1(3)
O(8)-Cd(1)-O(6)	83.8(3)	O(1)-Cd(2)-O(4)	93.2(3)
O(4)-Cd(1)-O(6)	152.5(3)	N(7)-Cd(2)-O(4)	97.1(3)

Symmetry transformations used to generate equivalent atoms:

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

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

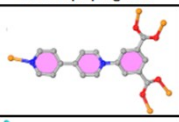
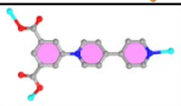
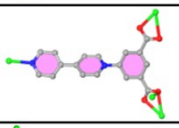
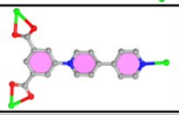
#5 x, y-1, z #6 x, y+1, z

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

Cd(1)-N(1)	2.3250(13)	Cd(1)-O(3)	2.3748(13)
Cd(1)-O(4)	2.3663(14)	Cd(1)-O(1)	2.4077(14)
Cd(1)-O(2)	2.3686(14)	Cd(1)-Br(1)	2.5768(3)
N(1)-Cd(1)-O(4)	85.51(5)	O(3)-Cd(1)-O(1)	135.49(4)
N(1)-Cd(1)-O(2)	136.00(5)	N(1)-Cd(1)-Br(1)	98.41(4)
O(4)-Cd(1)-O(2)	93.11(5)	O(4)-Cd(1)-Br(1)	144.46(4)
N(1)-Cd(1)-O(3)	129.78(4)	O(2)-Cd(1)-Br(1)	107.22(4)
O(4)-Cd(1)-O(3)	55.18(4)	O(3)-Cd(1)-Br(1)	98.57(3)
O(2)-Cd(1)-O(3)	81.43(5)	O(1)-Cd(1)-Br(1)	95.51(3)
N(1)-Cd(1)-O(1)	88.99(5)	O(2)-Cd(1)-O(1)	54.06(5)
O(4)-Cd(1)-O(1)	119.94(5)	N(1)-Cd(1)-C(17)	114.31(6)

Symmetry transformations used to generate equivalent atoms:
#1 x-1, y, z #2 x-1, -y+1/2, z-1/2
#3 x+1, -y+1/2, z+1/2 #4 x+1, y, z

Table S4 Summary of diverse coordination modes of ipbq ligands in the synthesized MOFs, A: central pyridine; B: isophthalic moieties; C: edge pyridine (colour modes: Cu, orange; Zn, cyan; Cd, green; oxygen, red; N, blue; carbon, gray).

Compound	Coordination modes of the ipbp ligand	Dihedral angles between			Framework	Note
		A-B	A-C	B-C		
Cu-MOF		44.46°	11.49°	32.98°	3D	Ref 35
Zn-MOF1		44.96°	13.11°	31.96°	3D	Ref 30
Zn-MOF2		38.37°	23.19°	4.45°	2D	
Cd-MOF1		47.71°	26.48°	24.02°	2D	This work
		43.47°	32.16°	11.79°		
Cd-MOF2		49.02°	39.87°	11.73°	2D	

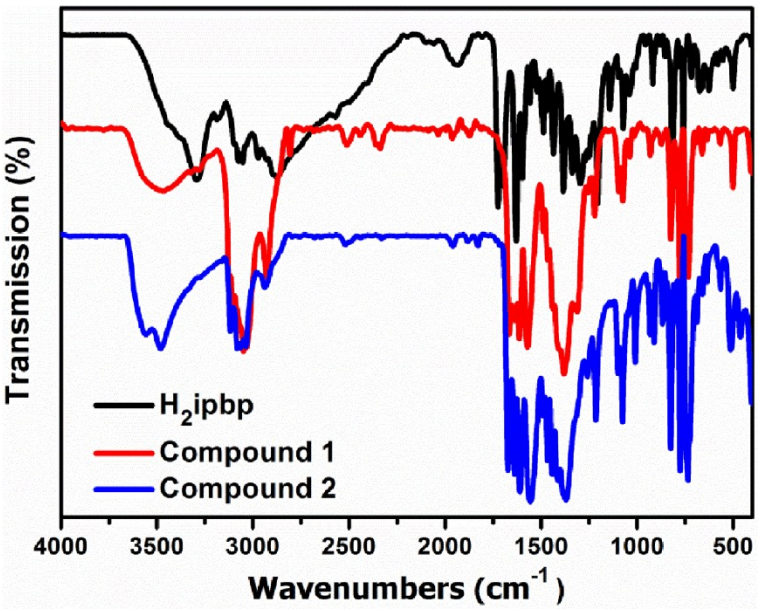


Fig. S1 IR spectra of **H_2ipbp** ligand, **1** and **2**. Besides the C=O stretch vibrations of the carboxylic groups around 1612 cm^{-1} and 1380 cm^{-1}, the characteristic absorption around 1638 cm^{-1} of these two compounds confirms the existence of the C=N and C=C stretching vibrations of the pyridinium group.

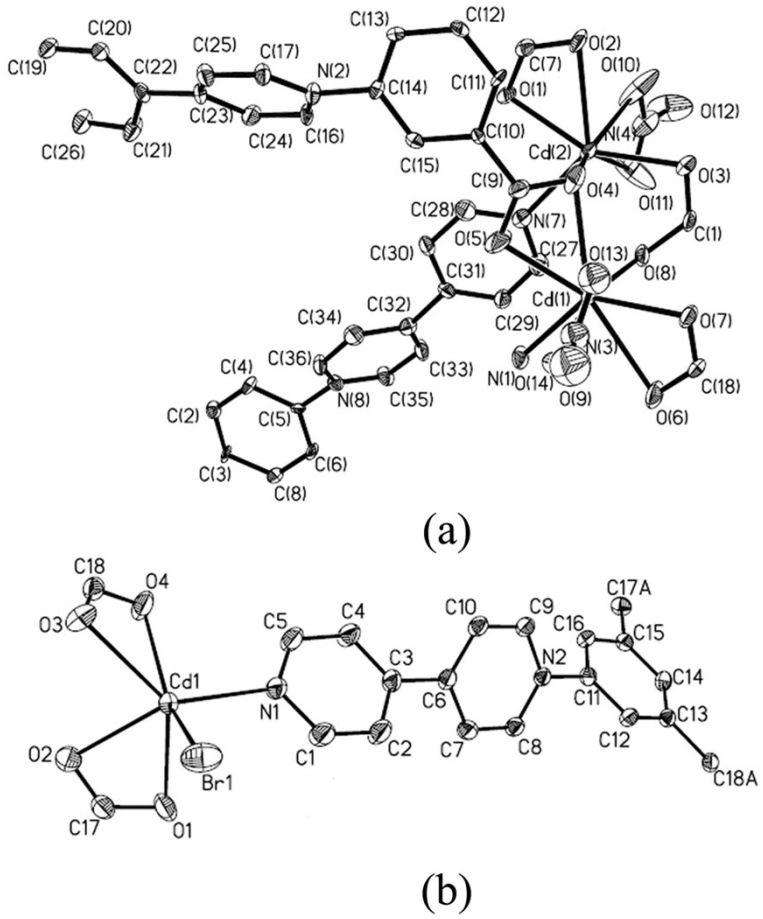


Fig. S2 The asymmetric units of **1** (a) and **2** (b) showing ellipsoid at the 30% probability level. The hydrogen atoms and guest DMF molecules for **1** and guest H_2O molecules for **2** are omitted for clarity.

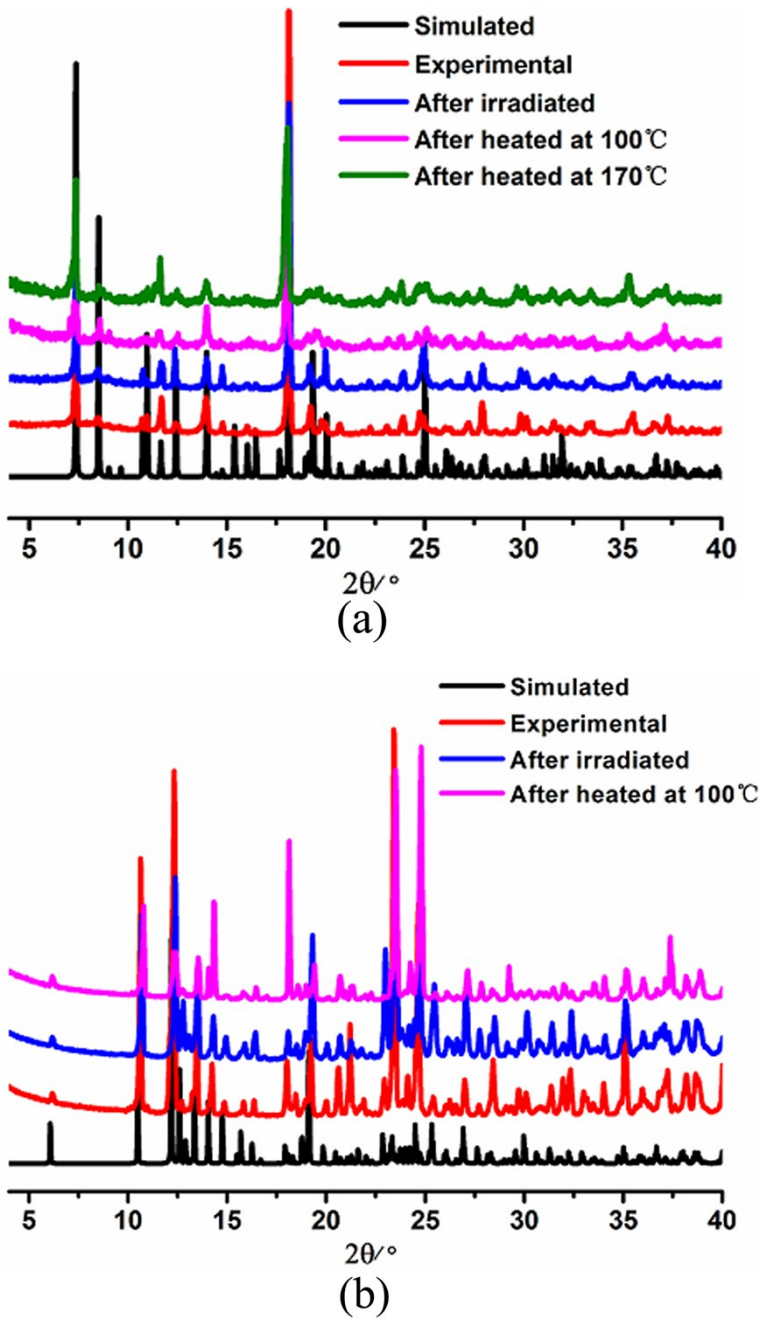


Fig. S3 Powder XRD patterns of experimental, simulated, irradiated and heated samples of compound **1** (a) and compound **2** (b).

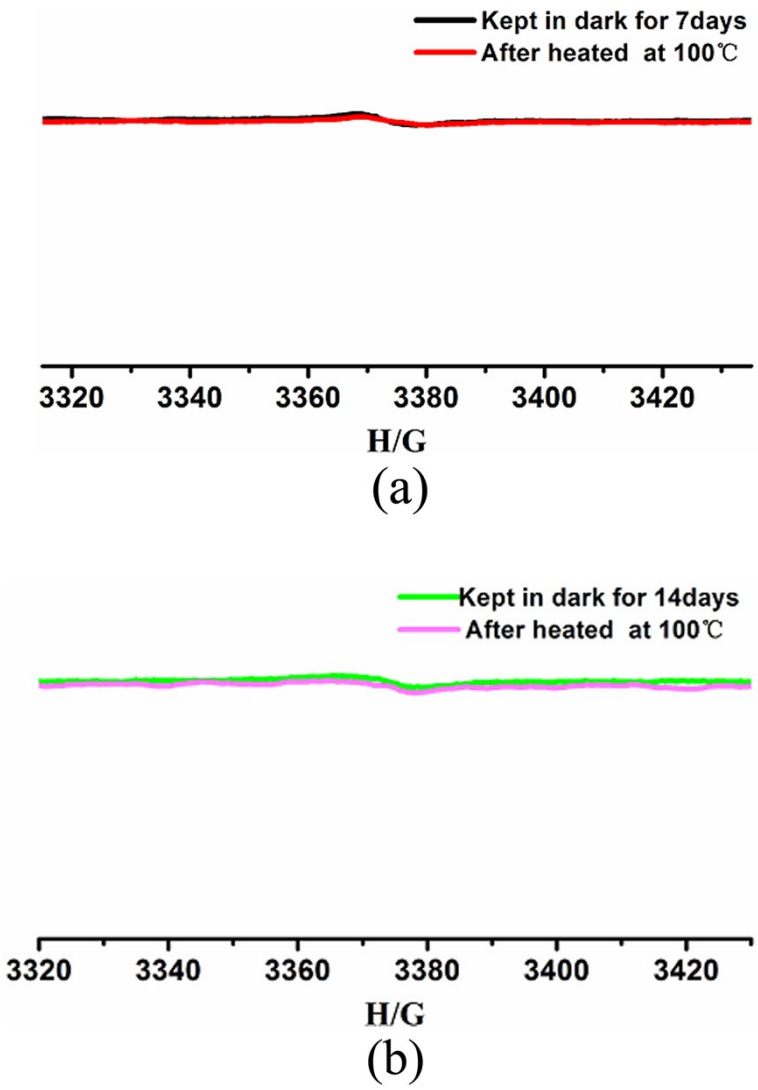


Fig. S4 (a) EPR signals of paled sample of **1**; (b) EPR signals of paled sample of **2**.

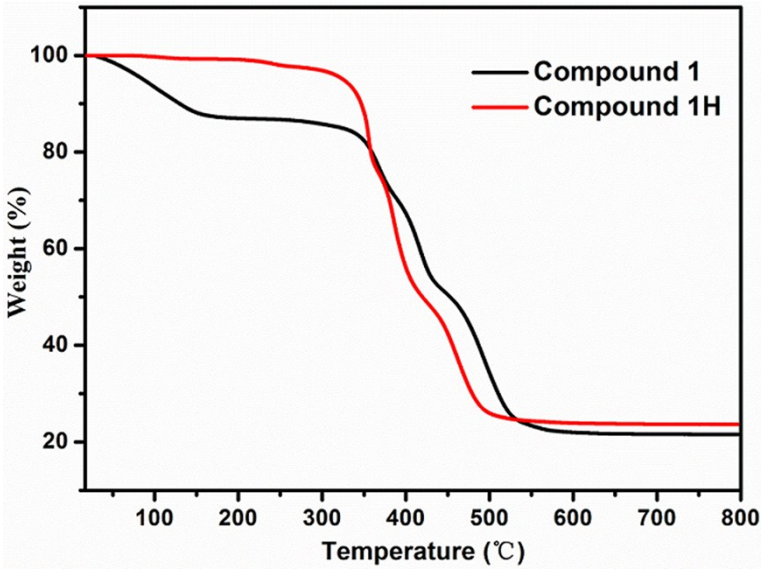


Fig. S5 TG curves of compounds **1** and **1H**. For compound **1**, the TGA curve shows two weight losses. The first weight loss of 12.55% from 25 to 173 °C is due to the removal of the guest DMF molecules (calcd 12.89%). Then, there is a platform between 173 and 310 °C, after which, the sample starts to decompose at 310 °C and ends at 570 °C with a weight loss of 63.07%. The total weight loss of **1** from room temperature to 570 °C is 75.98% (calcd 77.34%). For **1H**, no weight loss is observed before 310°C, suggesting the complete remove of guest DMF molecules after heated upon 170 °C of compound **1**.

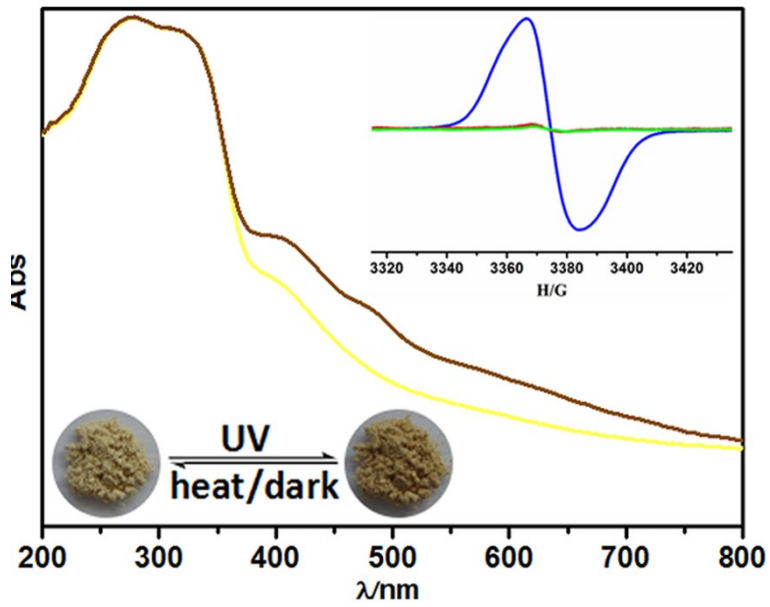
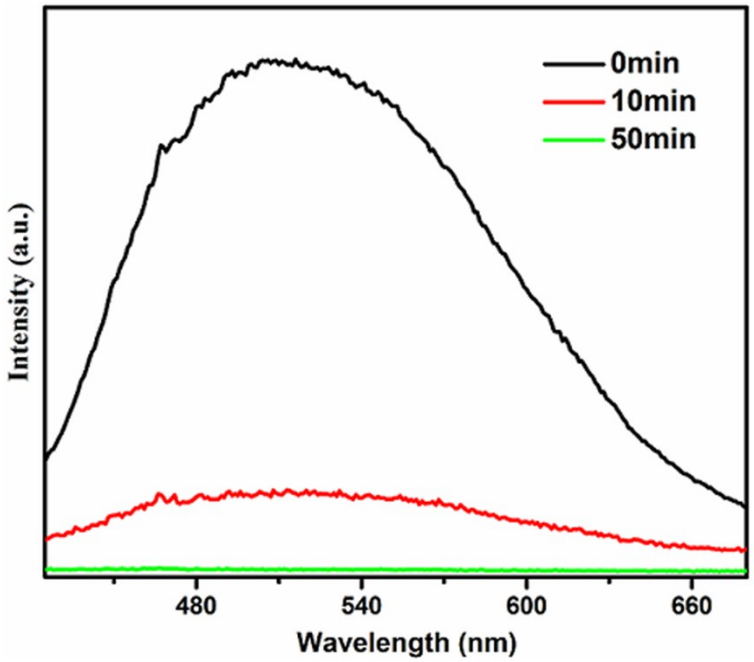
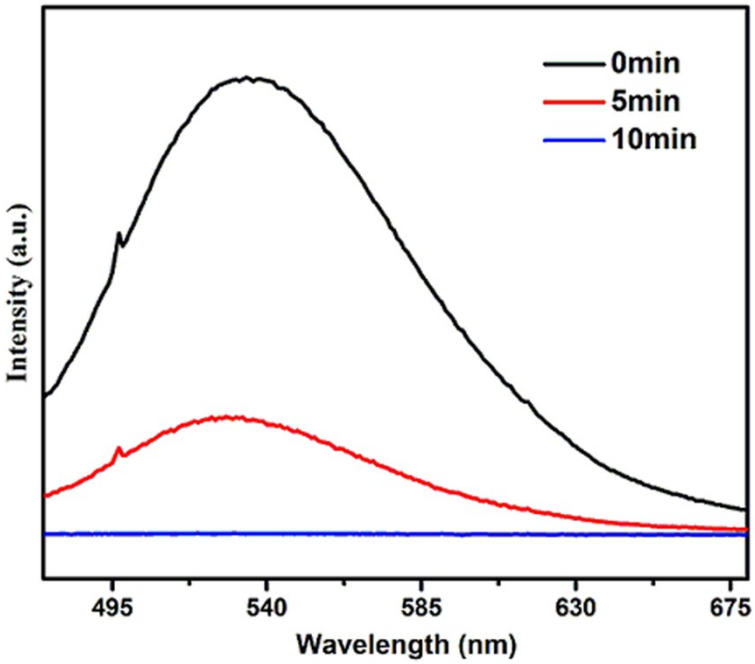


Fig. S6 UV-vis spectra and EPR signals of original and UV irradiated samples for compound **1H**.



(a)



(b)

Fig. S7 Solid-state fluorescent emission spectra of these two compounds before and after UV-irradiation: (a) compound **1** (λ_{ex} = 388 nm, λ_{em} = 529 nm); (b) compound **2** (λ_{ex} = 453 nm, λ_{em} = 535 nm).

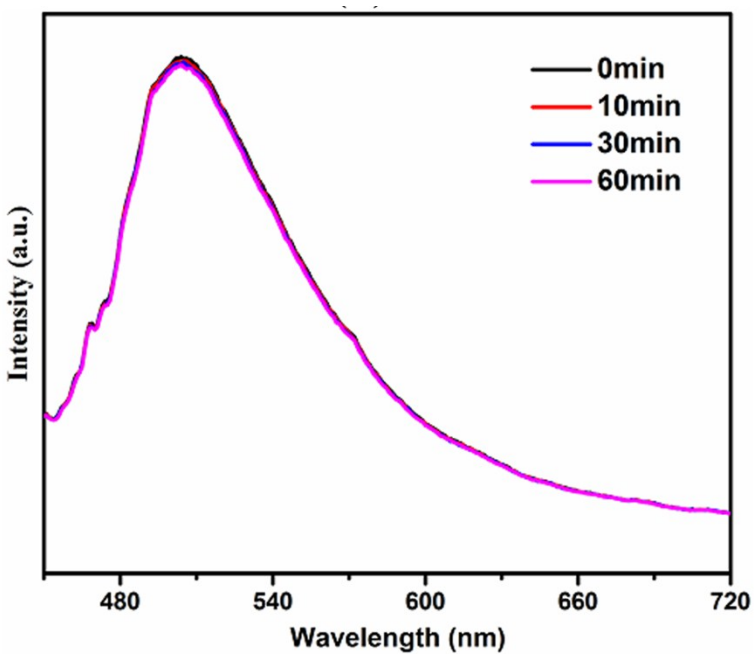
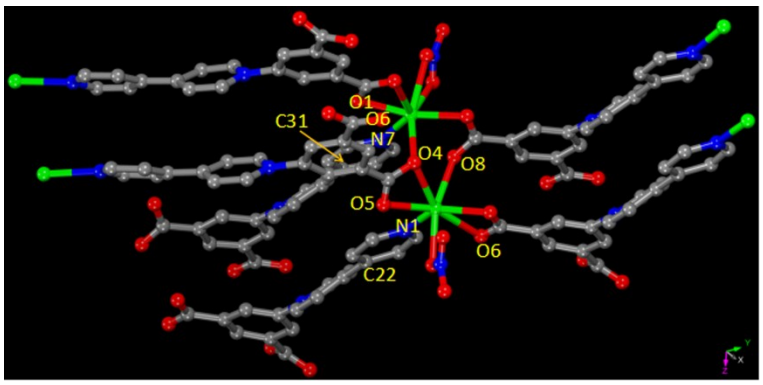
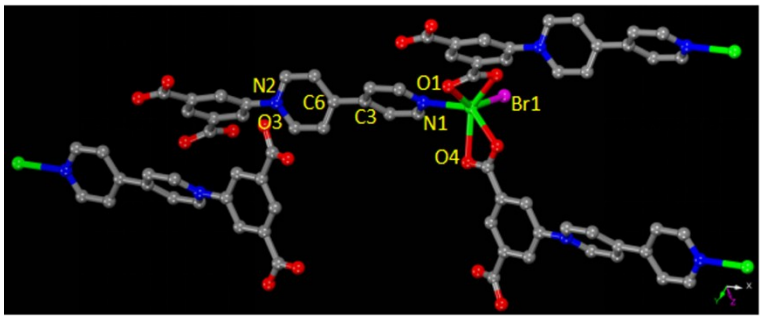


Fig. S8 Solid-state fluorescent emission spectral changes of H_2ipbp under photo-irradiation (λ_{ex} = 370 nm, λ_{em} = 503 nm).



Distances		Angles	
O1···N7	3.004	O1···N7···C31	130.245
O8···N7	3.114	O8···N7···C31	125.299
O5···N7	3.741	O1···N7···C31	105.422
O4···N7	3.622	O4···N7···C31	139.242
O6···N1	3.118	O6···N1···C22	125.121
O5···N1	3.100	O5···N1···C22	128.880
O8···N1	3.653	O8···N1···C22	143.986

Fig. S9 The orientations and distances of carboxylate oxygen atoms and pyridinium nitrogen atoms between adjacent ribbons of rings in compound **1**.



Distances		Angles	
O3···N2	3.106	O3···N2···C6	76.908
O1···N1	3.317	O1···N1···C3	128.765
O4···N1	3.185	O4···N1···C3	133.976
Br1···N1	3.715	Br1···N1···C3	137.420

Fig. S10 The orientations and distances of carboxylate oxygen atoms and pyridinium nitrogen atoms between adjacent ribbons of rings in compound **2**.

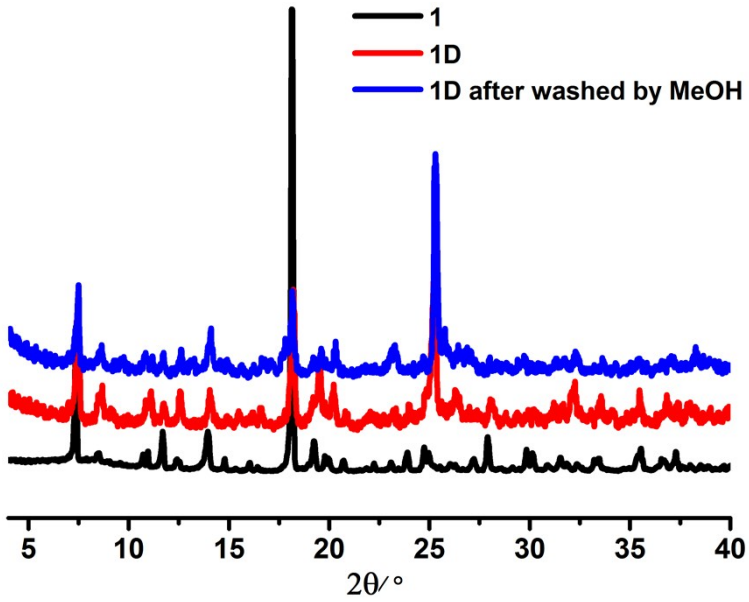


Fig. S11 Powder XRD patterns of **1**, **1D** and **1D** after washed by MeOH.

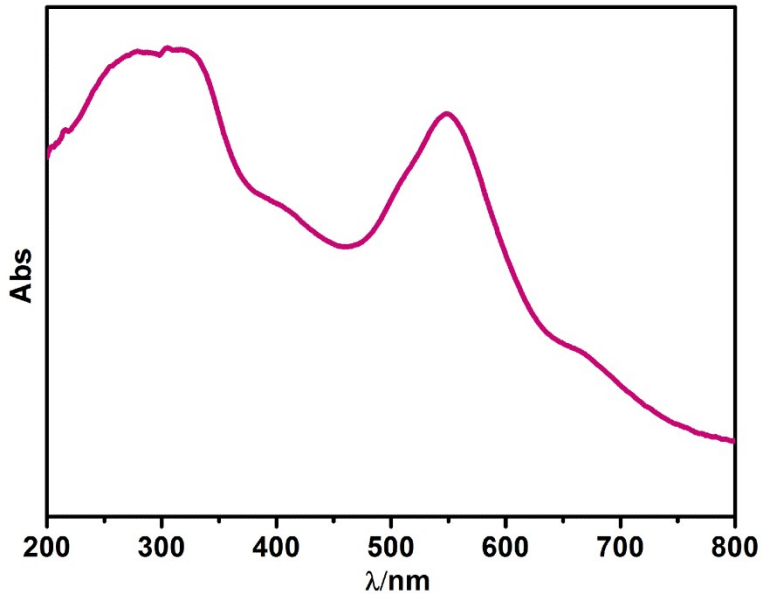


Fig. S12 The UV-vis spectrum of **1D**.

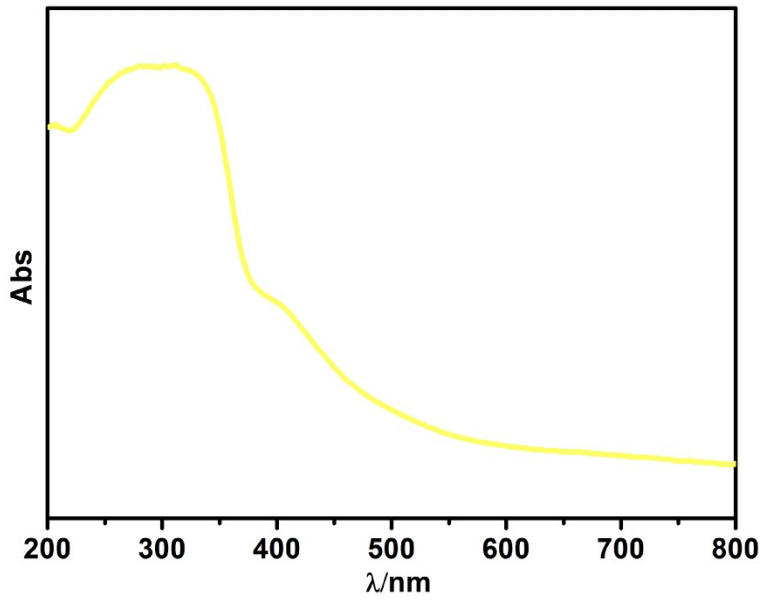


Fig. S13 The UV-vis spectrum of **1D** after washed by MeOH.

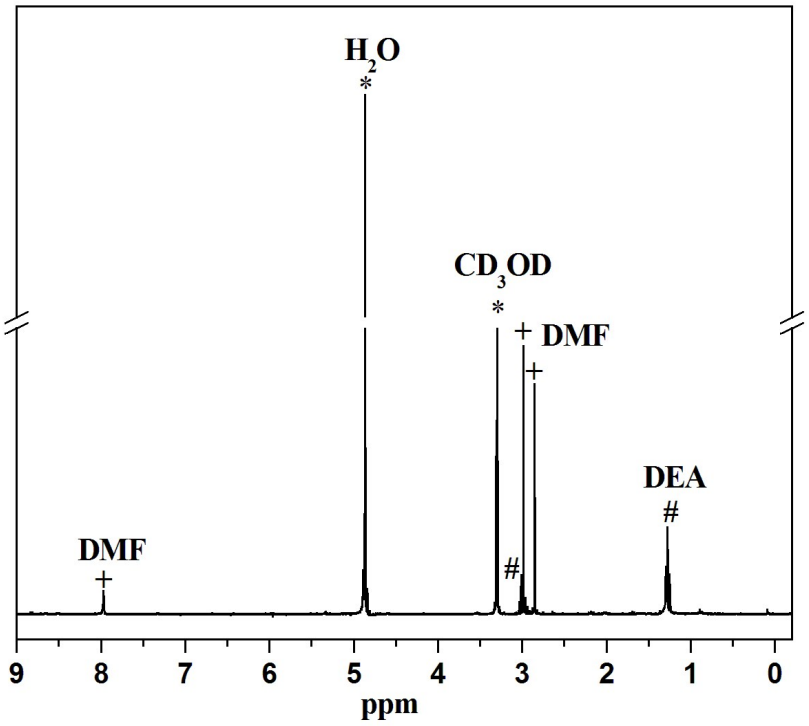


Fig. S14 ^{1}H NMR spectrum recorded for the CD_3OD extracts of **1D**.

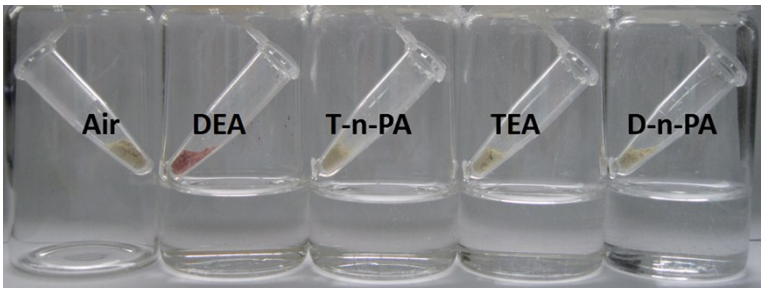


Fig. S15 The selectivity vapochromic properties of **1** for DEA (T-n-PA: tripropylamine；TEA: triethylamine；D-n-PA：di-n-propylamine).

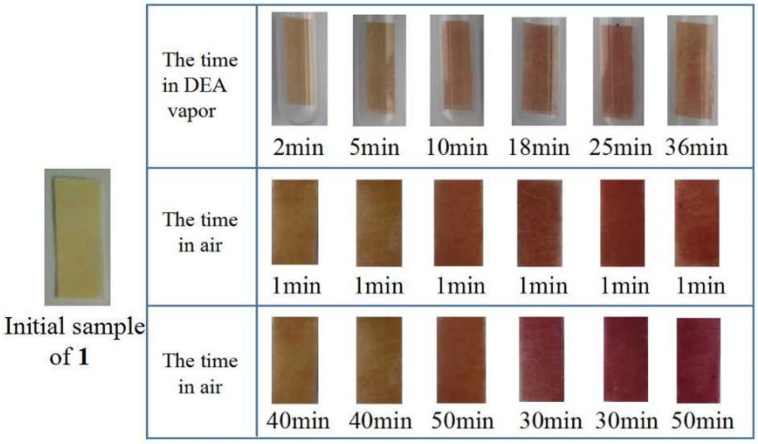


Fig. S16 The vapochromic photographs of **1** under the DEA vapor and then kept in air within different times.