Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Reversible mechanochromic and thermochromic luminescent switching via the hydrogen-bond-directed assemblies in a zinc coordination complex

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General methods and materials

All of the reagents were purchased from commercial channels and used without further purification. 4’-(4-pyridyl)-2,2’:6’,2’’-terpyridine (PYTPY) was synthesized according to a reported method.[S1]ATA Instrument Q600 SDT thermogravimetric analyser was used to obtain the thermogravimetric analysis (TGA) curve in N_2 100 ml•min^{-1} at a rate of 10 °Cmin^{-1}. The X-ray powder diffraction (XRD) data were collected in the angular range of 2θ= 5°-50 with a Bruker D8 Advance X-ray diffractometer using CuKα radiation (λ= 1.5406 Å). UV-Vis diffuse reflectance spectra were carried out using a HITACHIU-3010 spectrometer, and a $BaSO_4$ plate was used as a 100% reflectance standard. Photoluminescence spectra were obtained using a F-7000 FL Spectrophotometer. The excited-state lifetimes were acquired using a Hamamatsu time-resolved spectrometer C11367-11 Quantaurus-Tau. IR spectra were characterized by a Bruker Tensor 27 FTIR spectrometer in the range of 4000-400 cm^{-1} using KBr pellets. The C, H and N elemental analyses (EA) were performed on a Vario EL III elemental analyzer.

[S1] L. Hou, D. Li, W. J. Shi, Y. G. Yin and S. W. Ng, *Inorg. Chem.*, 2005, **44**, 7825.

Synthesis of compound 1

A mixture of $ZnCl_2$ (0.0136 g, 0.1mmol), PYTPY (0.0310 g, 0.1 mmol), H_2BDC (0.0166 g, 0.1 mmol) and H_2O (10 mL) was stirred for 30 min in air, and then transfered and sealed in a 25mL Teflon-lined steel bomb, which was heated at 160 °C for 48 h and then cooled to room temperature at a rate of 5 °C h^{-1}, Finally, pink crystals were collected by filtration, washed with DMF and distilled water for 3 times and then dried at room temperature for 12 h (12.3mg，20.71 % based on PYTPY). Elemental Anal. Calc. (%) for $C_{28}H_{24}N_4O_7Zn$ (593.88): C 56.58, H 4.04, N 9.43; found: C 57.97, H 4.08, N 9.43. IR data :3452(m), 3103(w), 3069(w), 3033(w), 1615(s), 1598(s), 1541(s), 1473(m), 1405(s), 1350(vs), 1243(m), 1154(m), 1079(m), 1011(m), 936(w), 896(w), 794(s), 746(s), 719(s), 638(m), 563(w), 509(m), 413(m).

X-ray single crystal diffraction

The data were measured on a Agilent Gemini E X-ray single crystal diffractometer with graphite monochromated Mo/Kα radiation ($\lambda = 0.71073$ Å). Data were collected at 173K, using the ω- and φ-scans to amaximum θ value of 25.02°. Absorption corrections were performed using a multi-scan method. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-square technique on F^2 with SHELXL-97.

CCDC 1562985 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.ukf/data_request/cif.

Table S1. Crystal data for 1.

Empirical formula	$C_{28}H_{24}N_4O_7Zn$	
Formula weight	593.88 g /mol	
Crystal system	Triclinic	
Space group	*P -1*	
Unit cell dimensions	a = 8.7484(7) Å	α = 80.673(8)°
	b = 10.2091(13) Å	β =89.866(6)°
	c = 14.7961(11) Å	γ = 70.745(9)°
Volume	1229.2(2) $Å^3$	
F (000)	612	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2σ (I)]	R1 = 0.0510, wR2 = 0.1237	
R indices (all data)	R1 = 0.0643, wR2 = 0.1363	

$^aR_1 = \sum || F_o| - |F_c||/\sum|F_o|$. $^bwR_2 = [\sum [w (F2\ o - F2\ c)^2] /\sum [w (F2\ o)^2]]^{1/2}$.

Table S2 The hydrogen bonding data in the structure of 1。

	Donor---H....Acceptor	D...A	D - H...A
1	O5 --H....N1	2.927(5)	151(6)
2	O5--H....O1	2.892(5)	157(7)
3	O6--H....O5	2.860(6)	178(6)
4	O6--H....O5	2.947(6)	157(4)
5	O7--H....O6	2.787(8)	150
6	O7--H....O3	2.942(7)	137

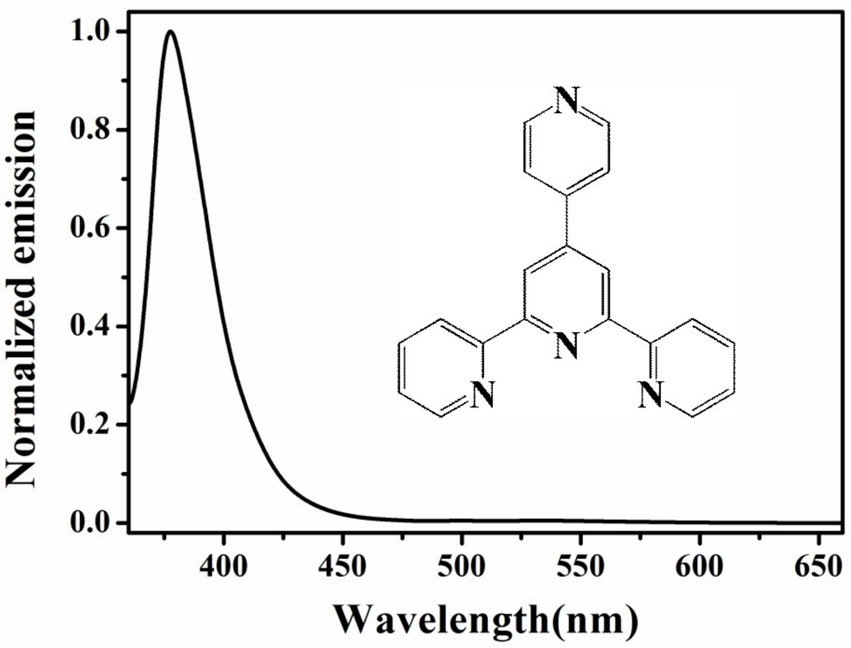

Fig. S1 PL spectrum of **PYTPY**, upon excitation at 345nm.

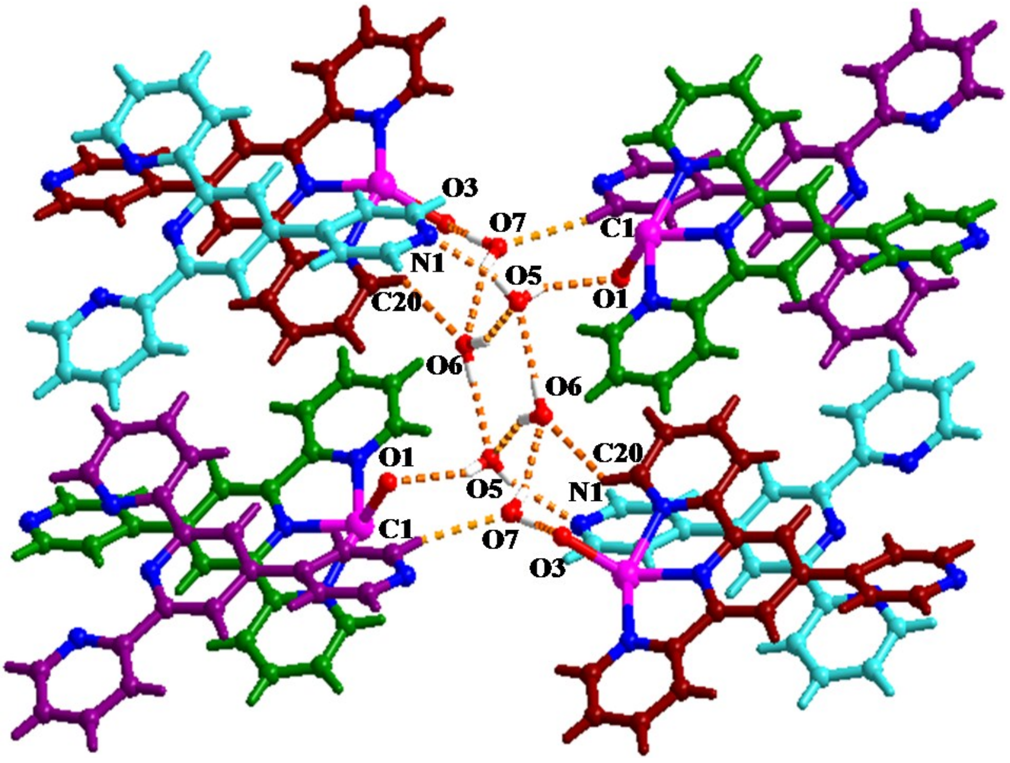

Fig. S2 The hydrogen bonding network in **1.**

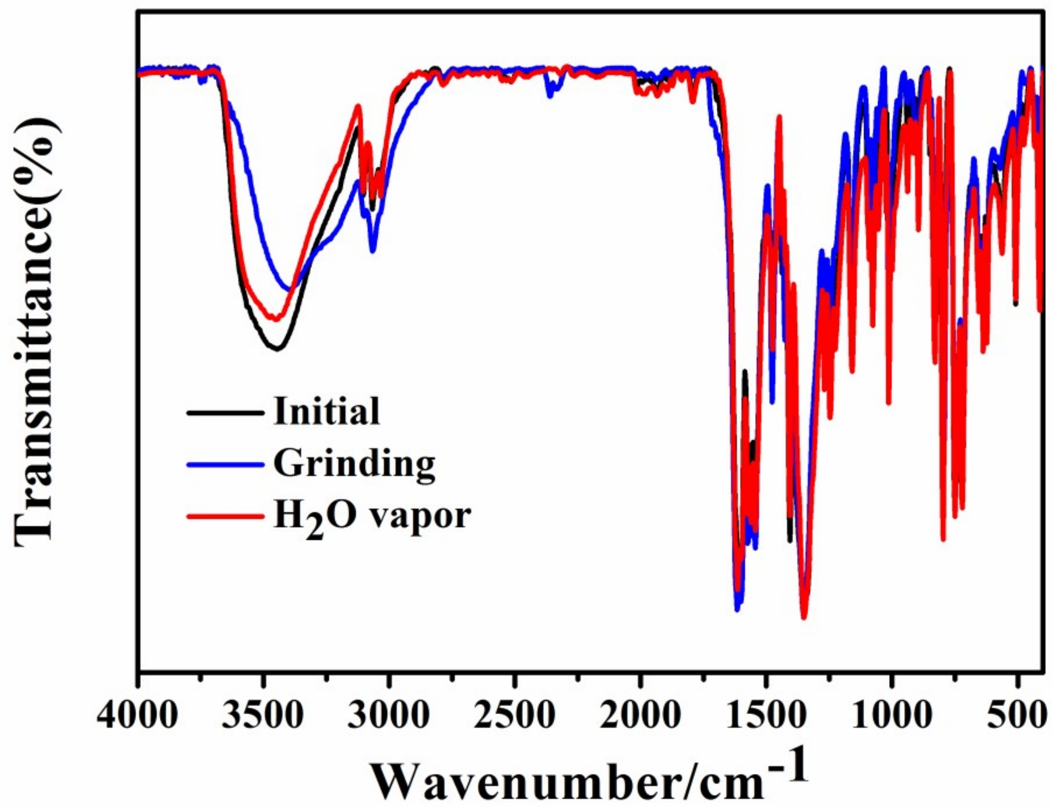

Fig. S3 IR spectra of **1** before and after grinding, and being treated by water vapor.

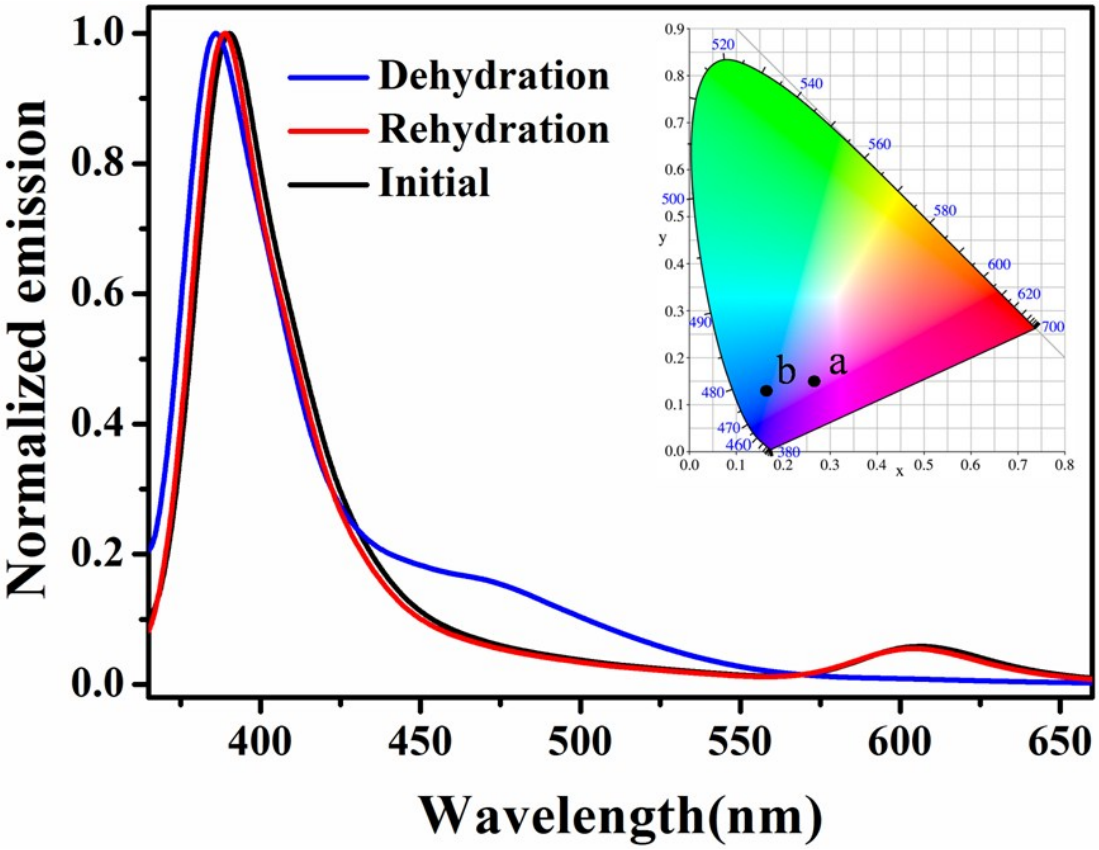

Fig. S4 PL spectra of 1 before (black) and after dehydration (blue) and being treated by water vapor (red). Inset: the CIE chromaticity coordinates: (a) initial sample (0.2645, 0.1461), (b) dehydration sample (0.1641, 0.1286).

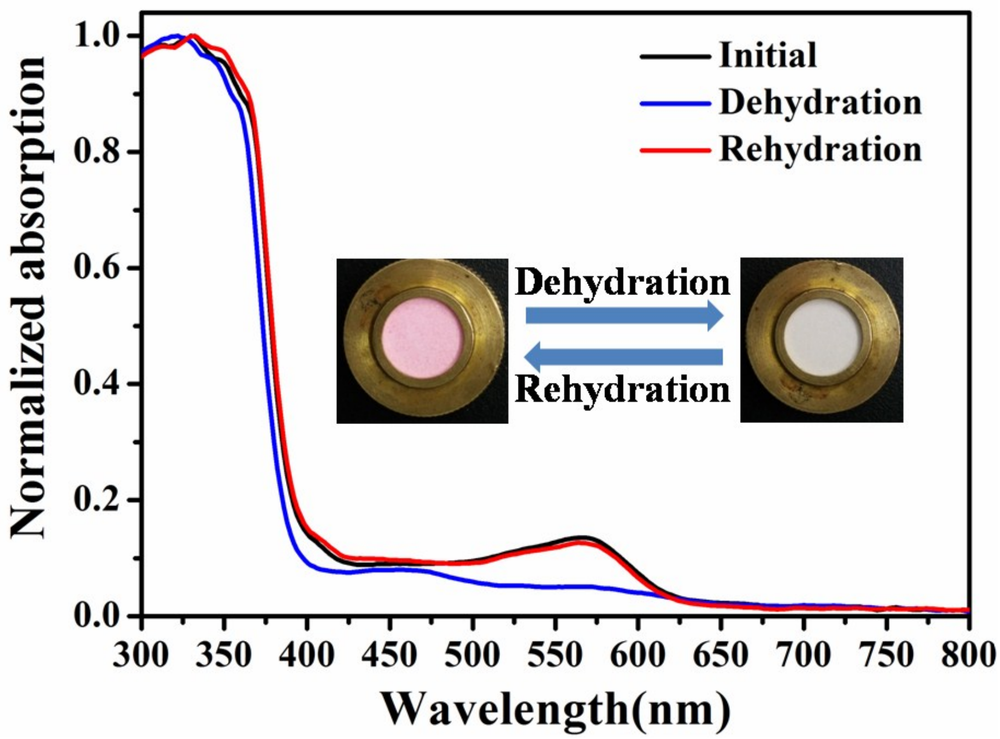

Fig. S5 UV-Vis spectrum of **1** before (black) and after dehydration (blue) and being treated by water vapor (red).

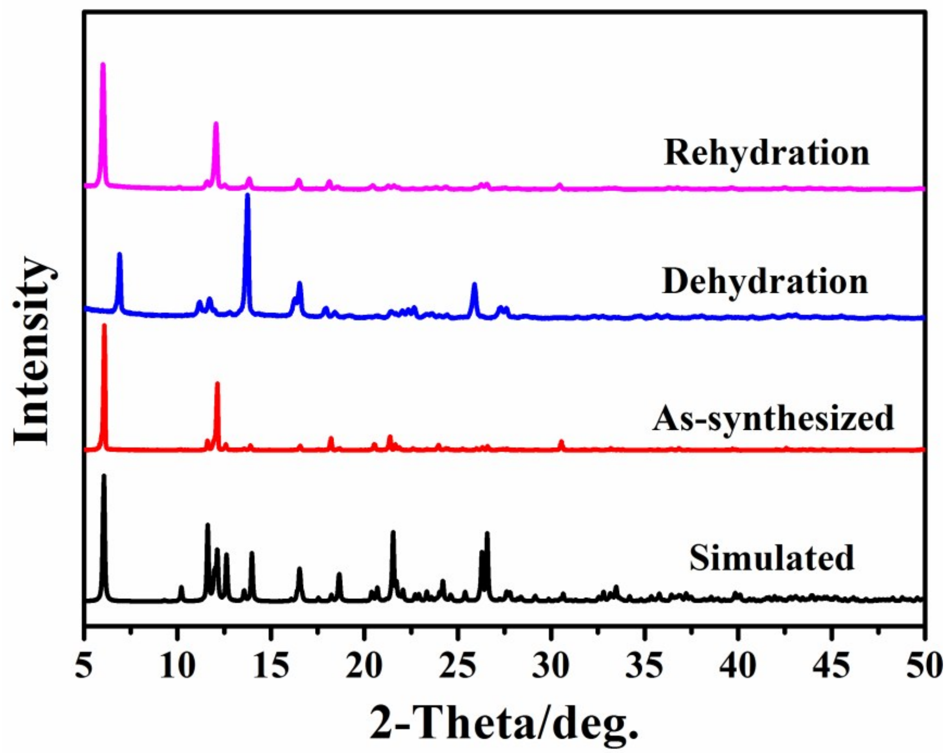

Fig. S6 PXRD data of **1** before and after dehydration, simulated and being treated by water vapor.

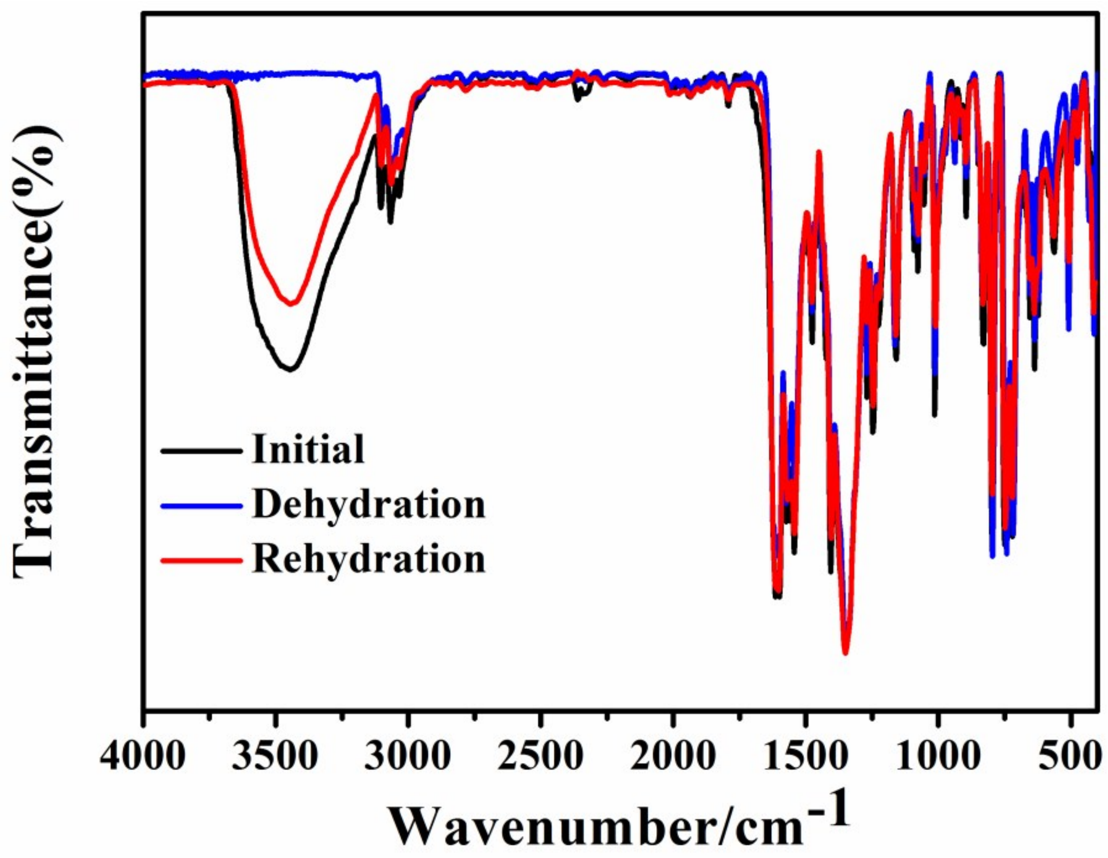

Fig. S7 IR spectra of **1** before and after dehydration, and being treated by water vapor.

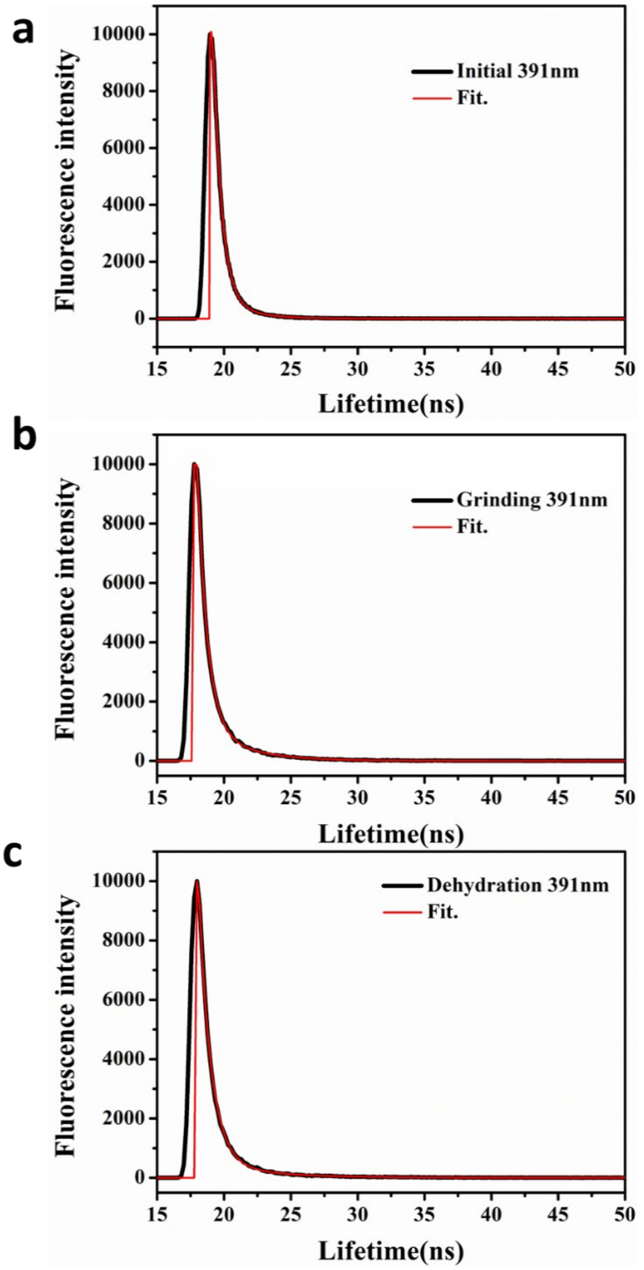

Fig. S8 Solid-state fluorescence decay profiles of initial sample (a), ground sample (b) and dehydration sample (c).

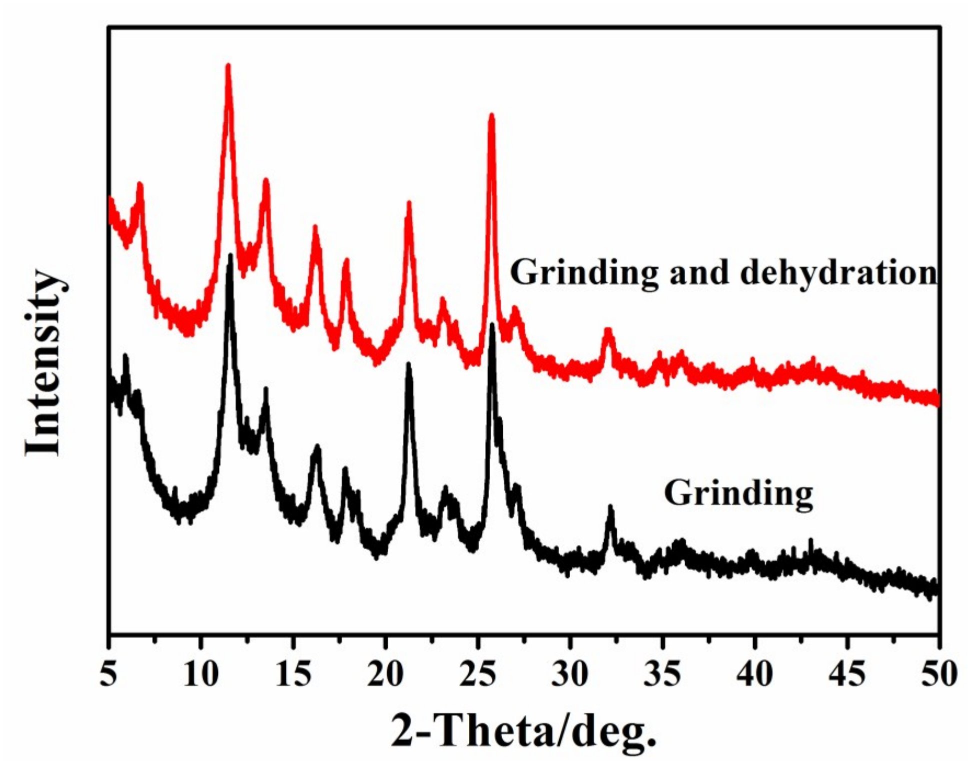

Fig. S9 PXRD patterns of the ground sample before (black) and after (red) dehydration.

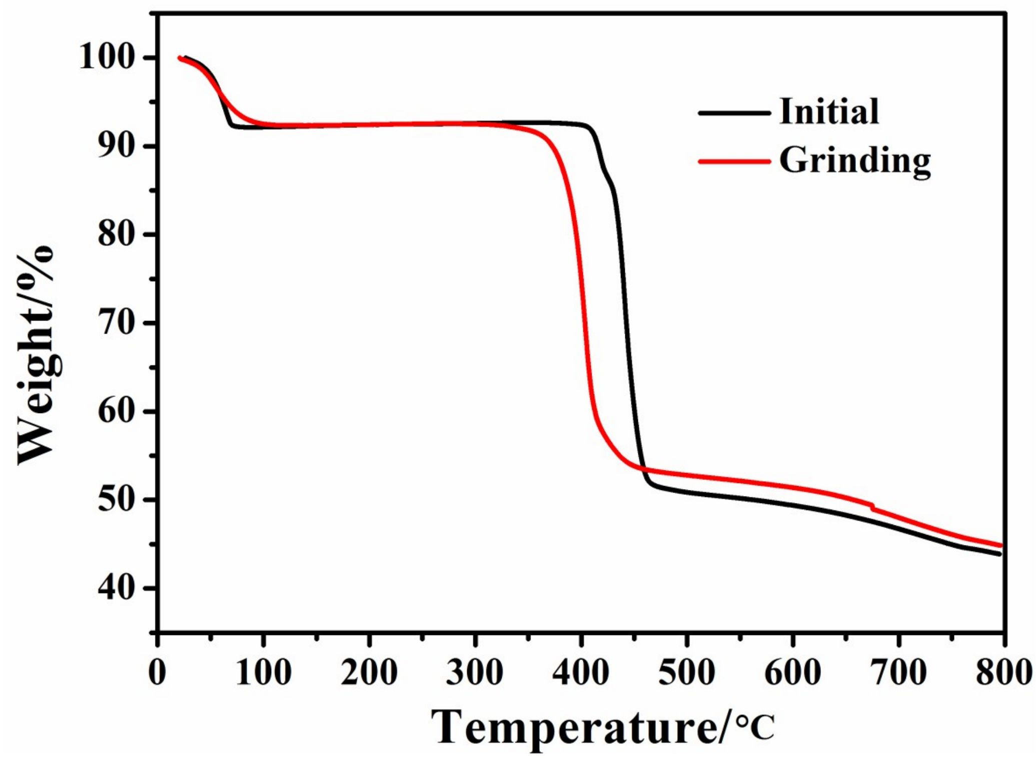

Fig. S10 Thermal gravimetric curve of compound **1:** the intact sample (black) and the ground sample (red).

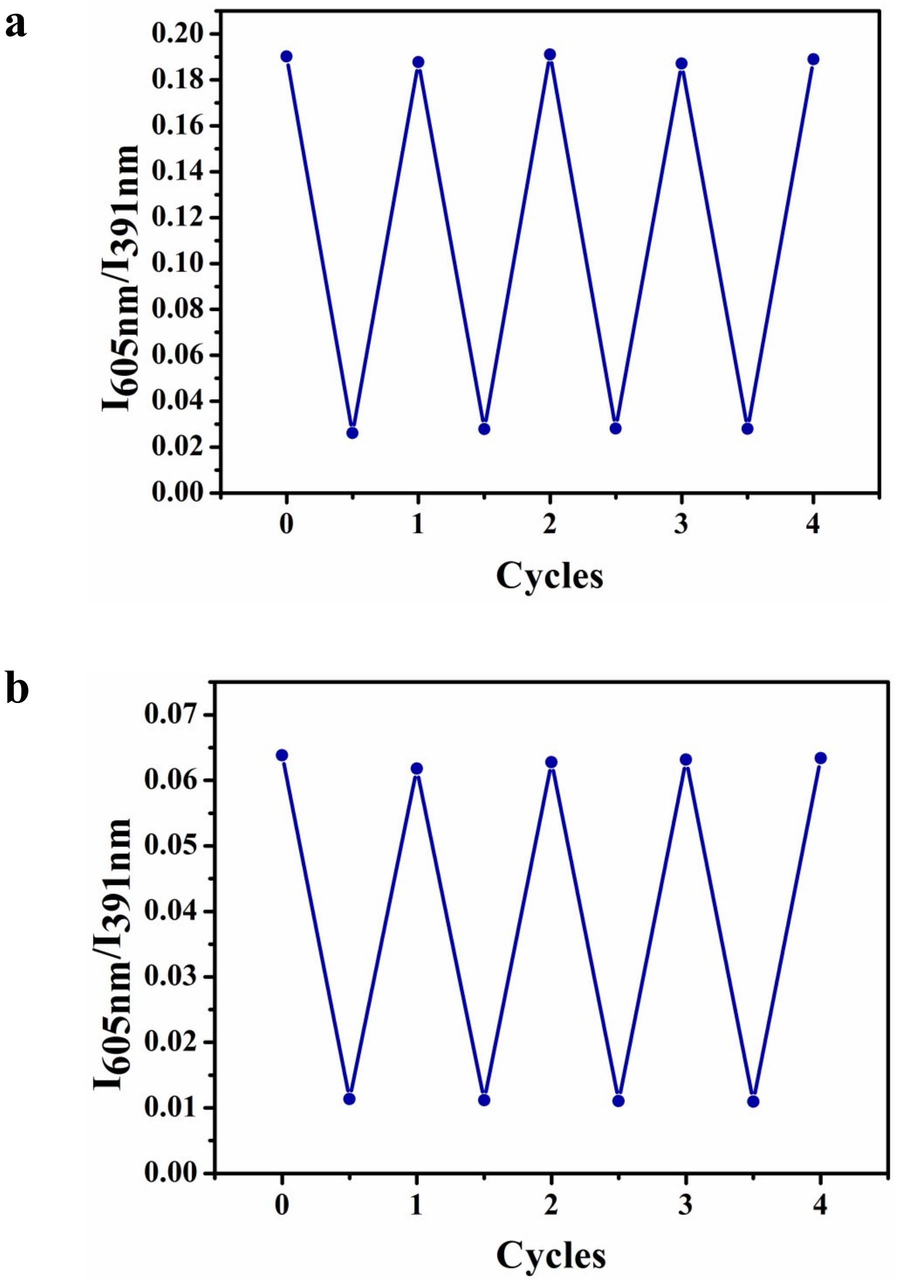

Fig. S11 (a) Mechanochromic cycles; (b) Thermochromic cycles.