Electronic Supporting Information (ESI) for

A dual-functional Mg-CP exhibits white-emitting after modification with CuI and photochromic behavior

Zhao-Feng Wu,[a,b] Bin Tan,[c] Zai-Lai Xie,[c] Jing-Jing Fu[a] and Xiao-Ying Huang*,[a]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China

[b] University of the Chinese Academy of Sciences, Beijing 100049, P.R. China.

[c] College of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, P.R. China

1. More structural details

Single-crystal X-ray diffraction data of **1** were collected on a Xcalibur E Oxford diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at 293 K. The absorption correction was applied using a multi-scan technique. The structure was solved by direct method and refined by full-matrix least-squares on F^2 using the SHELX-97 program.[1] Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bonded to C atoms were positioned with idealized geometry and those attached to O were located from difference-Fourier maps and their postions were refined with DFIX/DANG restraints. The empirical formula was confirmed by the elemental analysis. A summary of the crystal data and structural refinement details is given in Tables S1.

Table S1 Summary of crystal data and structural refinement details for **1**.

Empirical formula	$C_{34}H_{32}Mg_2N_2O_{14}$
Formula weight	741.24
Crystal system	monoclinic
Space group	$C2/c$
T/K	293(2)
λ/ Å	0.71073

a/ Å	16.469(2)
b/ Å	15.5386(12)
c/ Å	14.540(3)
β/º	117.500(19)
V/ Å^3	3300.4(8)
Z	4
D_c/ Mg·m^{-3}	1.492
μ/mm^{-1}	0.150
F(000)	1544
Measured refls.	6976
Independent refls.	3578
R_{int}	0.0262
No. of parameters	255
GOF	1.017
$^aR_1$, wR_2 [$I > 2\sigma(I)$]	0.0587, 0.1588
R_1, wR_2 (all data)	0.0768, 0.1727

$^aR_1 = \sum||Fo|-|Fc||/\sum|Fo|$, $wR_2 = \{\sum w[(Fo)^2 - (Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$

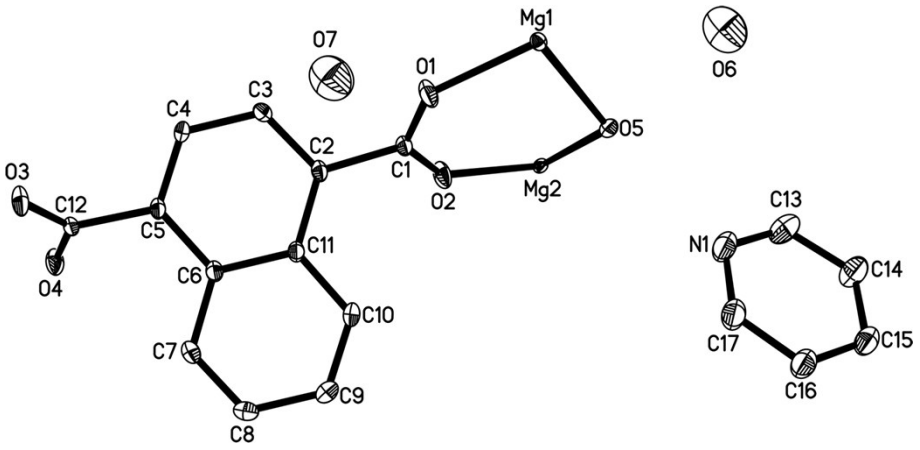


Fig. S1 *Ortep* drawing of the crystallographically asymmetric unit of **1**. Hydrogen atoms are omitted for clarity.

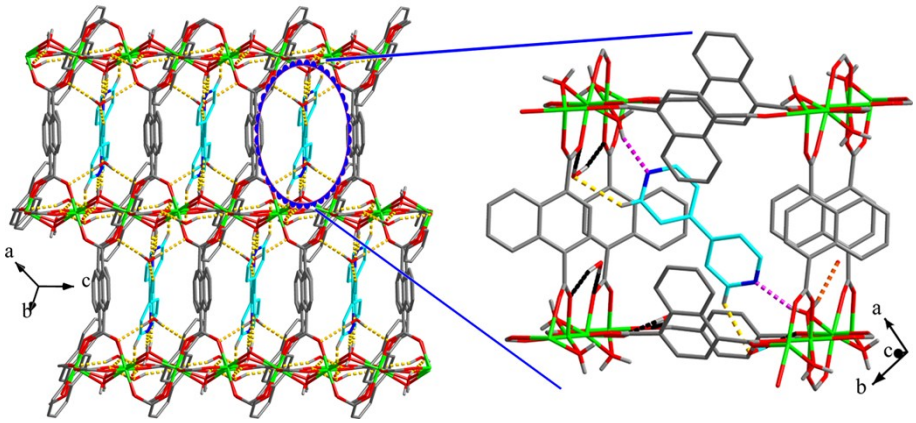


Fig. S2 The hydrogen bonding acting as the inter-molecular interactions to stabilize the host-guest system in **1**.

Table S2 Hydrogen bonds for compound **1**.

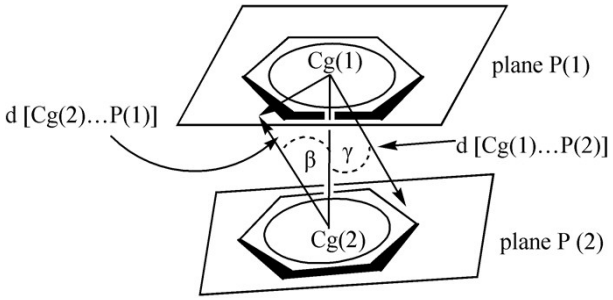
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5) -H(5A) ··N(1)	0.859	2.00	2.816	160
O(5) -H(5B) ··O(6)	0.793	1.98	2.755	167
O(7)-H(7A) ··O(1)	0.905	2.00	2.905	179
O(7)-H(7B) ··O(3) #1	0.90	2.17	3.033	161
C(17)-H(17) ··O(7) #2	0.93	2.60	3.312	134

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

Table S3 Distances (*d*/Å) and angles (°) for the ***π-π*** interactions in **1**.

ring(1)···ring(2)	*d*[Cg(1)···Cg(2)] [b]	*α* [c]	*β* [d]	*γ* [e]	*d*[Cg(1)···P(2)] [f]	*d*[Cg(2)···P(1)] [g]
C(6) ~ C(11)··· C(13)^{i}~C(17)^{i}, N1^{i}; i: 1\2+*x*,3\ 2-*y*, 1\2+*z*	3.984(2)	6.68(17)	19.4	19.8	3.7494(13)	3.7585(15)

[a] For a graphical depiction of distances and angles in the assessment of ***π-π*** interactions, see Scheme 1. [b] Centroid–centroid distance. [c] Dihedral angle between the ring planes. [d] Angle between the centroid vector Cg(1)···Cg(2) and the normal to the plane 2. [e] Angle between the centroid vector Cg(1)···Cg(2) and the normal to the plane 1. [f] Perpendicular distance of Cg(1) on ring plane 2. [g] Perpendicular distance of Cg(2) on ring plane 1.



Scheme S1 Graphical presentation of the parameters used in Table S3 for the description of ***π-π*** stacking.

Table S4 Distances (*d*/Å) and angles (°) for the C-H···π interactions in **1**.

X-H···ring(3)	*d*[H···Cg(3)]	*d*[X···Cg(3)]	°[X-H..Cg]
C(8) -H(8A)··· C(13)^{ii}~C(17)^{ii}, N1^{ii}; ii: 1\2+*x*,1\ 2+*y*, *z*	2.91	3.541	127

2. Materials and physical measurements

All chemicals were commercially purchased and used without further purification. Elemental analyses (EA) for C, H and N were performed on a German Elementary Vario EL III instrument. Energy dispersive spectroscopy (EDS) was obtained with a JEOL JSM-6700F scanning electron microscope. The UV-Vis spectra were measured at room temperature using a Perkin-Elmer Lambda 950 spectrometer, and a $BaSO_4$ plate was used as a standard (100% reflectance). The photochromic behavior was induced by irradiation with a Xe lamp (Beijing, 500 W). The absorption spectrum was calculated from reflectance spectrum by using the function: $\alpha/S = (1-R^2)/2R$,[2] where α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance. Powder X-ray diffraction (PXRD) patterns were conducted in the angular range of 2θ = 5 - 65° on a Miniflex II diffractometer using Cu$K\alpha$ radiation. Electron spin resonance (ESR) signals were recorded with a Bruker A300 spectrometer. Inductively coupled plasma (ICP) analyses were performed with an Ultima 2 unit. X-ray photoelectron spectroscopy (XPS) measurements were performed using a ESCALAB 250Xi X-ray Photoelectron Spectrometer (XPS) Microprobe. Emission, excitation spectra and the photoluminescence life-time measurements of the compounds were recorded on a Edinburgh FLS980 fluorescence spectrometer at room temperature. The quantum yields (Φ) were recorded on an Edinburgh FLS920 fluorescence spectrometer at room temperature.

Synthesis of compound 1. A mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (0.256 g, 1 mmol), 1,4-$NDCH_2$ (0.216 g, 1 mmol), bpy (0.198 g, 1 mmol), NaOH (0.080 g, 2 mmol) in CH_3OH (2 mL) and H_2O (2 mL) was sealed in a 20 mL Teflon-lined stainless-steel autoclave at 373K for 2 days. Colorless block-like crystals of **1** (0.125 g, yield: 34% based on magnesium) were obtained. Anal. Calc. for **1**: C, 55.09%; H, 4.35%; N, 3.78%. Found: C, 55.31%; H, 4.16%; N, 3.77%.

Synthesis of 1-CuI. As-synthesized compound **1** (~75 mg, 0.2 mmol) was loaded into an agate mortar and manually ground with the pestle to afford a fine powder. After that it was immersed in 10 mL anhydrous acetonitrile with CuI (0.025 and 0.05 mmol, respectively) in a 20 mL glass bottle that was kept at 373K for about 24 h, to get complexes of **1-CuI** (1.87% and 3.15%), respectively.

Preparation for the guest-exchangeable samples. As-synthesized compound **1** (~100 mg) was immersed in 10 mL CH_3OH or CH_3CH_2OH, and kept at 373K for about 5 days, to get the guest-exchanged compounds. The EA results for the CH_3OH and CH_3CH_2OH-exchanged samples are C, 54.06/54.53%; H, 4.08/3.97% and C, 57.75/58.07%; H, 3.90/3.96%, respectively.

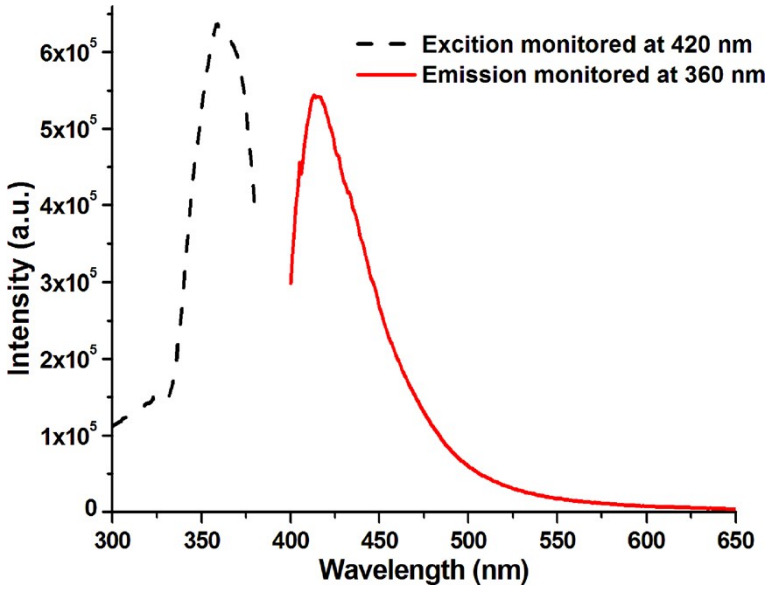


Fig. S3 The excitation and emission spectra of compound **1** in the solid state at room temperature.

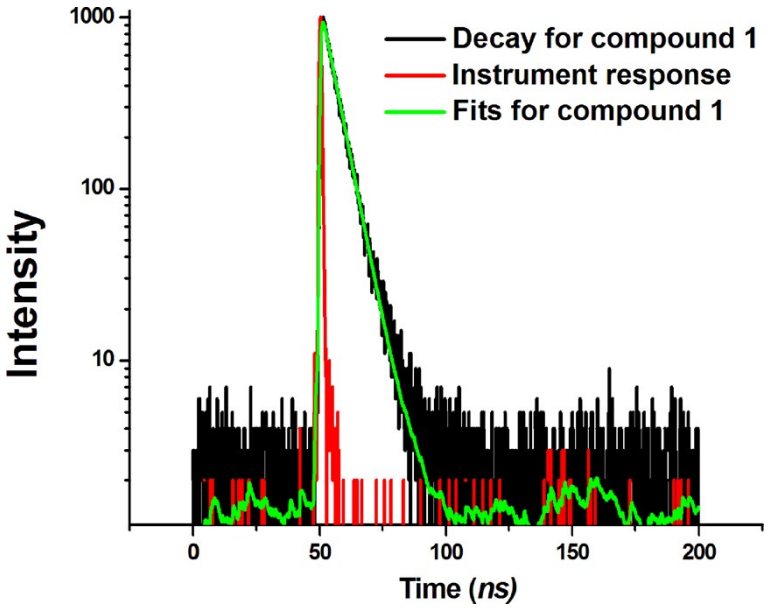


Fig. S4 The decay profile of compound **1**.

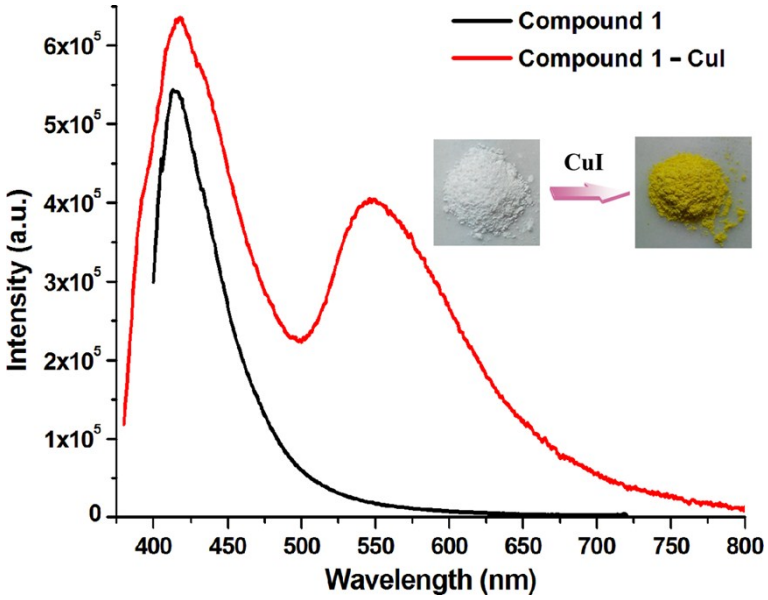


Fig. S5 Solid-state PL spectra of samples **1** and **1-CuI** monitored at 360 nm; inset: photographs of samples**1** and **1-CuI**.

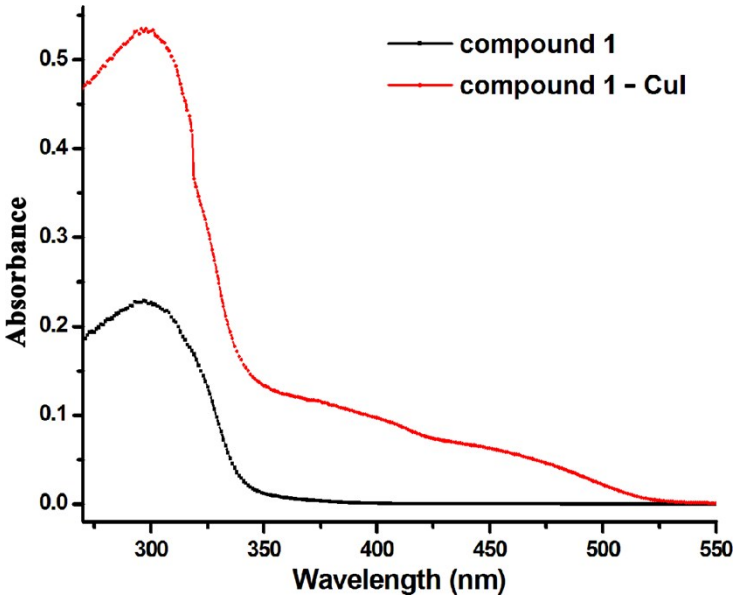


Fig. S6 Solid adsorption spectra of compounds **1** and **1-CuI**.

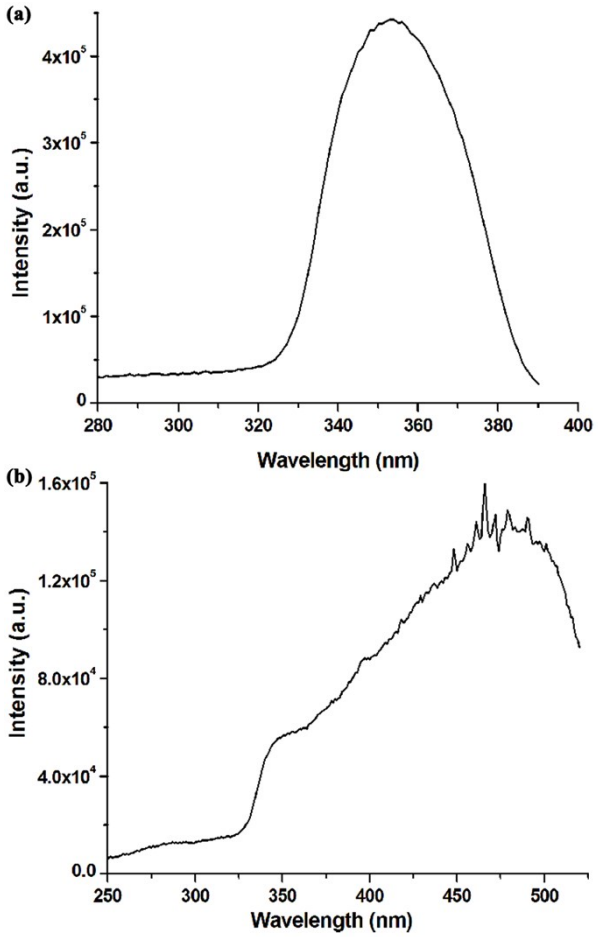


Fig. S7 Solid-state excitation spectra of **1-CuI** monitored at 410 and 550 nm, respectively.

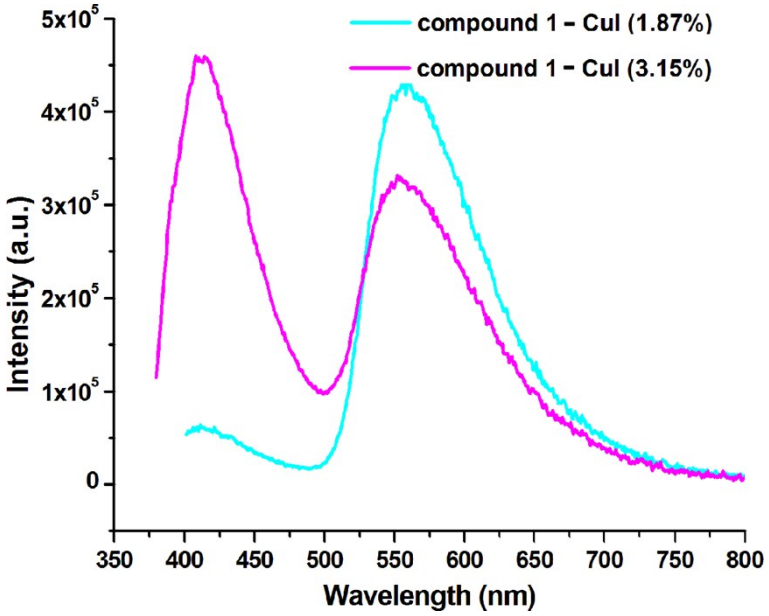


Fig. S8 Solid-state PL spectra of **1-CuI** with different Cu contents monitored at 360 nm.

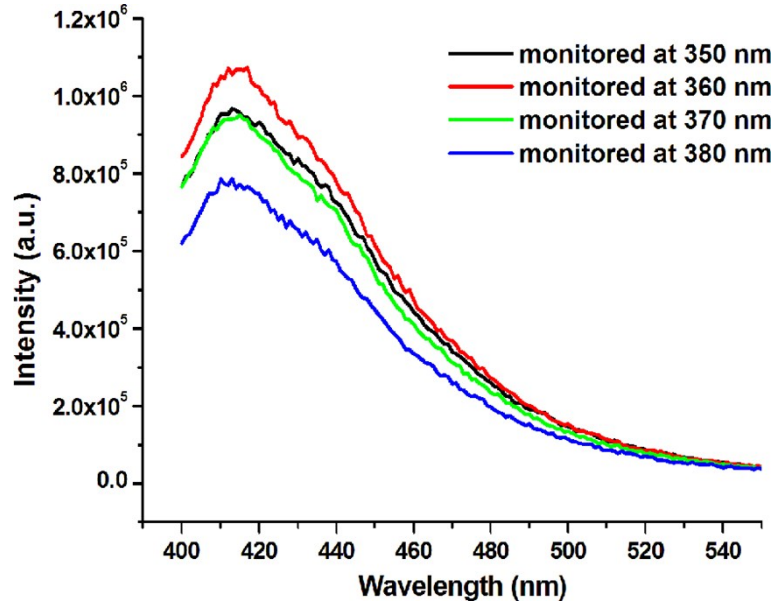


Fig. S9 Solid-state PL spectra of **1** by varying excitation wavelengths.

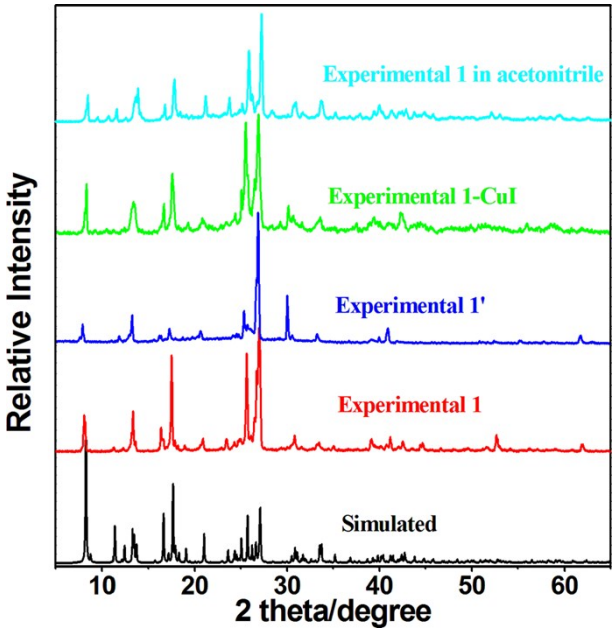


Fig. S10 PXRD patterns of **1**, **1'**, **1-CuI** and **1 in acetonitrile** at 373K for 24 hours.

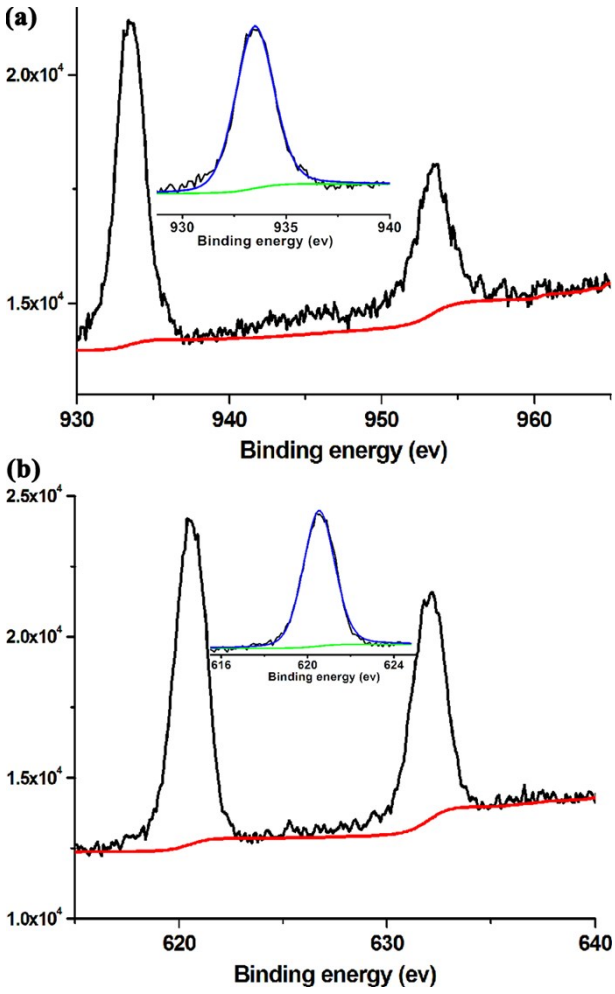


Fig. S11 XPS spectra of the Cu 2p (a) and I 3d (b) region in **1-CuI**; the inset is the fitting data of Cu 2p and I 3d.

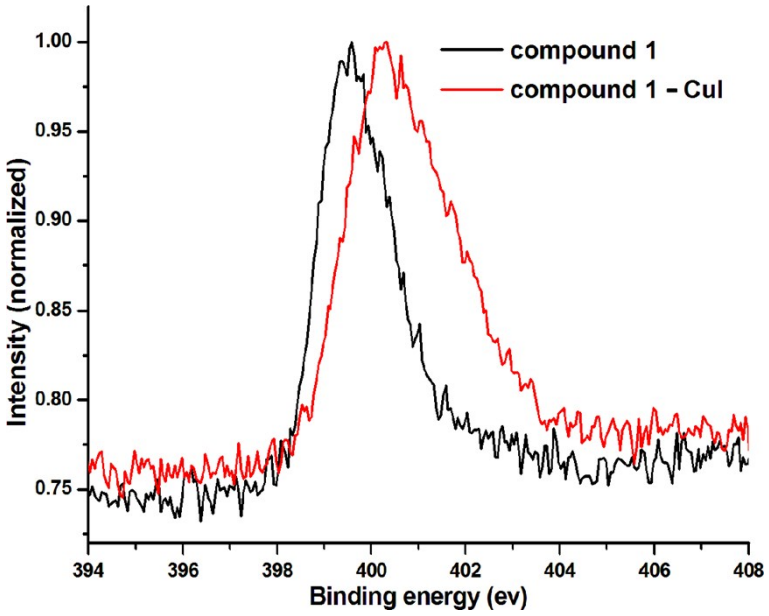


Fig. S12 XPS spectra of the N 1s region for compounds **1** and **1-CuI**.

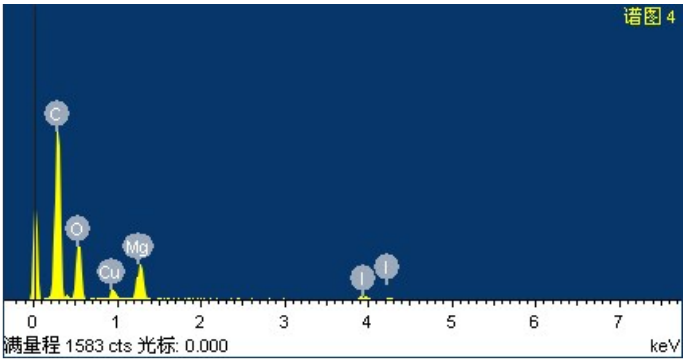


Fig. S13 Energy dispersive spectroscopy (EDS) of **1-CuI**.

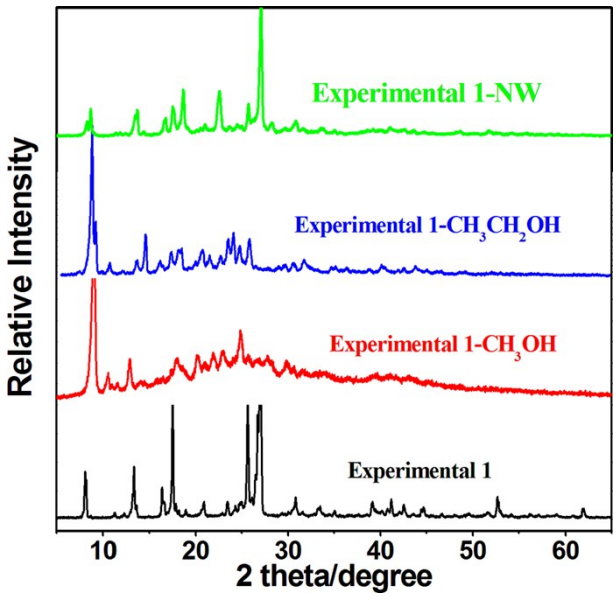


Fig. S14 PXRD patterns of compounds **1**, **1-CH_3OH**, **1-CH_3CH_2OH** and **1-NW**.

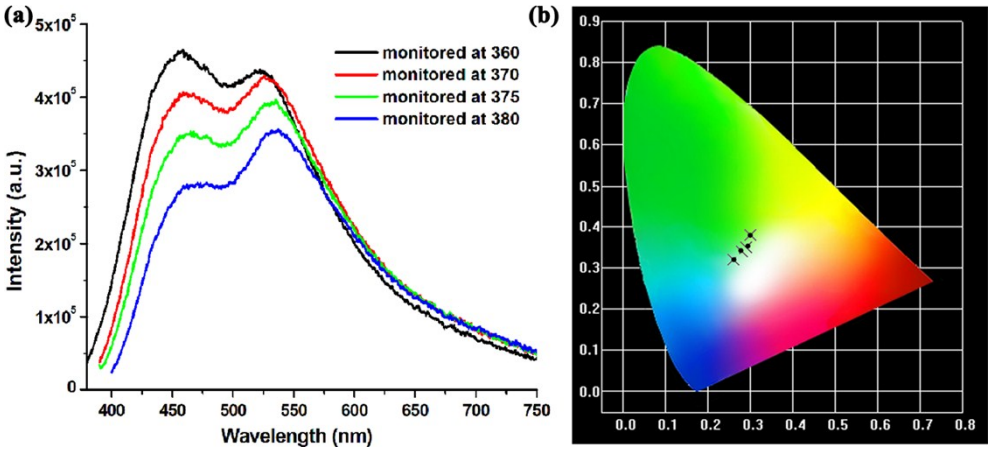


Fig. S15 Solid-state PL spectra of **1-CuI-NW** by varying excitation lights and the photograph of the CIE chromaticity diagram.

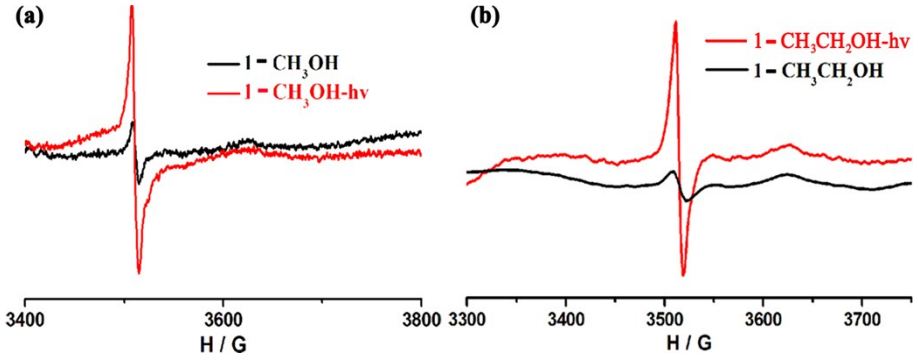


Fig. S16 The ESR profiles of samples **1-CH_3OH** and **1-CH_3CH_2OH** before and after the irradiation of a Xe lamp.

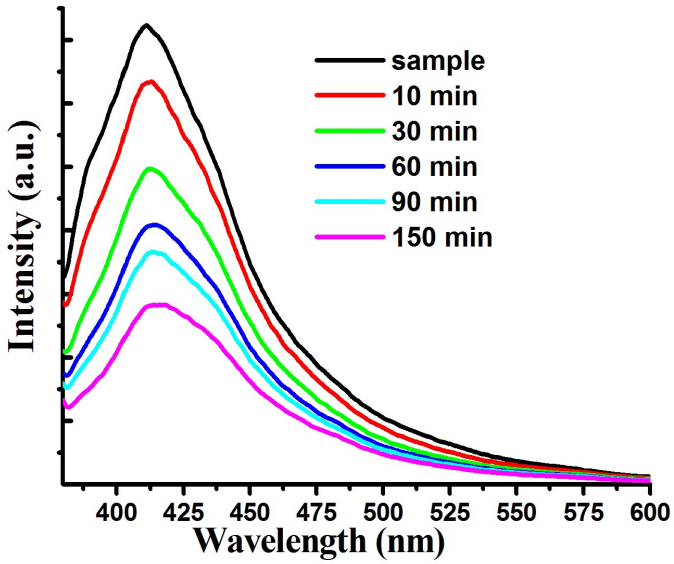


Fig. S17 The emission profiles of compound **1** under different irradiated time.

References

1. G. M. Sheldrick, *SHELXS97 and SHELXL97*, University of Göttingen, Germany, **1997**.
2. W. M. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*, Interscience, New York, **1966**.