Electronic Supporting Information (ESI) for

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

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1. More structural details

Single-crystal X-ray diffraction data of 1 were collected on a Xcalibur E Oxford diffractometer with graphite monochromated MoKα 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 positions 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.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₃₄H₃₂Mg₂N₂O₁₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>741.24</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C₂/c</td>
</tr>
<tr>
<td>T/K</td>
<td>293(2)</td>
</tr>
<tr>
<td>λ/ Å</td>
<td>0.71073</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
a / \text{Å} & \quad 16.469(2) \\
b / \text{Å} & \quad 15.5386(12) \\
c / \text{Å} & \quad 14.540(3) \\
\beta^\circ & \quad 117.500(19) \\
V / \text{Å}^3 & \quad 3300.4(8) \\
Z & \quad 4 \\
D_c / \text{Mg} \cdot \text{m}^{-3} & \quad 1.492 \\
\mu / \text{mm}^{-1} & \quad 0.150 \\
F(000) & \quad 1544 \\
\text{Measured refls.} & \quad 6976 \\
\text{Independent refls.} & \quad 3578 \\
R_{\text{int}} & \quad 0.0262 \\
\text{No. of parameters} & \quad 255 \\
GOF & \quad 1.017 \\
^a R_1, \ wR_2 \ [I > 2 \sigma(I)] & \quad 0.0587, 0.1588 \\
R_1, \ wR_2 \ (\text{all data}) & \quad 0.0768, 0.1727
\end{align*}
\]

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

**Fig. S1** *Ortep* drawing of the crystallographically asymmetric unit of 1. Hydrogen atoms are omitted for clarity.
The hydrogen bonding acting as the inter-molecular interactions to stabilize the host-guest system in 1.

Table S2 Hydrogen bonds for compound 1.

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>d(D-H)</th>
<th>d(H···A)</th>
<th>d(D···A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(5) -H(5A) ··N(1)</td>
<td>0.859</td>
<td>2.00</td>
<td>2.816</td>
<td>160</td>
</tr>
<tr>
<td>O(5) -H(5B) ··O(6)</td>
<td>0.793</td>
<td>1.98</td>
<td>2.755</td>
<td>167</td>
</tr>
<tr>
<td>O(7)-H(7A) ··O(1)</td>
<td>0.905</td>
<td>2.00</td>
<td>2.905</td>
<td>179</td>
</tr>
<tr>
<td>O(7)-H(7B) ··O(3) #1</td>
<td>0.90</td>
<td>2.17</td>
<td>3.033</td>
<td>161</td>
</tr>
<tr>
<td>C(17)-H(17) ··O(7) #2</td>
<td>0.93</td>
<td>2.60</td>
<td>3.312</td>
<td>134</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>ring(1)···ring(2)</th>
<th>d[Cg(1)···Cg(2)]</th>
<th>α°</th>
<th>β°</th>
<th>γ°</th>
<th>d[Cg(1)···P(2)]</th>
<th>d[Cg(2)···P(1)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(6) – C(11)··· C(13)–C(17); N1; i: 1/2+x,3/2-y,1/2+z</td>
<td>3.984(2)</td>
<td>6.68(17)</td>
<td>19.4</td>
<td>19.8</td>
<td>3.7494(13)</td>
<td>3.7585(15)</td>
</tr>
</tbody>
</table>

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.
Table S4 Distances ($d/\text{Å}$) and angles (º) for the C-H···π interactions in 1.

<table>
<thead>
<tr>
<th>X-H···ring(3)</th>
<th>$d[\text{H} \cdots \text{Cg}(3)]$</th>
<th>$d[\text{X} \cdots \text{Cg}(3)]$</th>
<th>$\theta[\text{X-H..Cg}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(8) -H(8A)··· C(13)º-C(17)º, N1º; ii: 1/2+x, 1/2+y, z</td>
<td>2.91</td>
<td>3.541</td>
<td>127</td>
</tr>
</tbody>
</table>

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 $\alpha$ 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 $2\theta = 5 - 65^\circ$ 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 ($\Phi$) were recorded on an Edinburgh FLS920 fluorescence spectrometer at room temperature.
Synthesis of compound 1. A mixture of Mg(NO$_3$)$_2$·6H$_2$O (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$_3$OH (2 mL) and H$_2$O (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$_3$OH or CH$_3$CH$_2$OH, and kept at 373K for about 5 days, to get the guest-exchanged compounds. The EA results for the CH$_3$OH and CH$_3$CH$_2$OH-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$_3$OH, 1-CH$_3$CH$_2$OH 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$_3$OH and 1-CH$_2$CH$_2$OH before and after the irradiation of a Xe lamp.

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

References