Electronic Supplementary Information

Polyoxometalates–viologen photochromic hybrids for rapid solar ultraviolet light detection, photoluminescence and inkless and erasable prints

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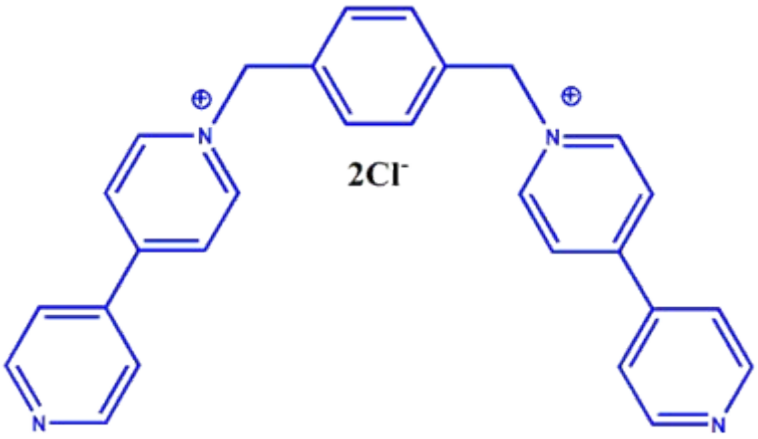

Scheme 1. The molecular structure of $PbpyCl_2$.

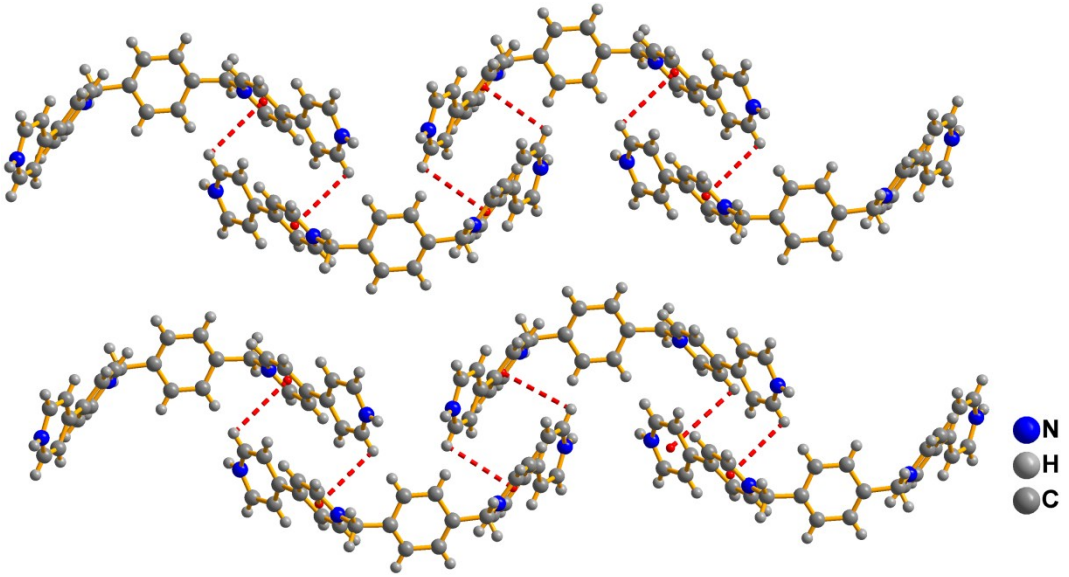

Fig. S1 C−H···π interactions in neighboring viologen cations. The distance of C−H···Cg (π–ring) is 3.3974(1) Å.

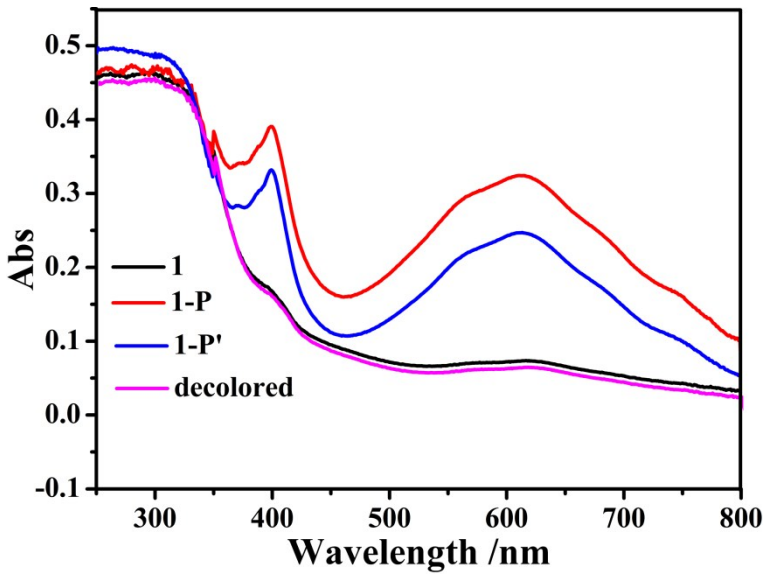

Fig. S2 UV–Vis absorption spectra of **1** in the photochromic process. **1**: before photo irradiation; **1-P**: after exposure in a 300 W UV Xe lamp; **decolored**: heating in 130 °C for 2 h; **1-P′**: decolored sample immediately photo irradiation.

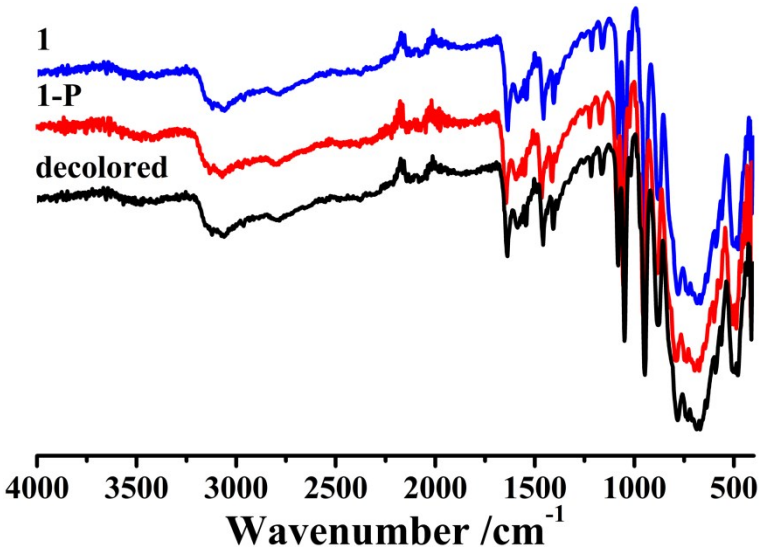

Fig. S3 FT-IR spectra of **1**. Labels: **1**: before irradiation; **1-P**: after photo irradiation; **decolored**: heating in 130 °C for 2 h.

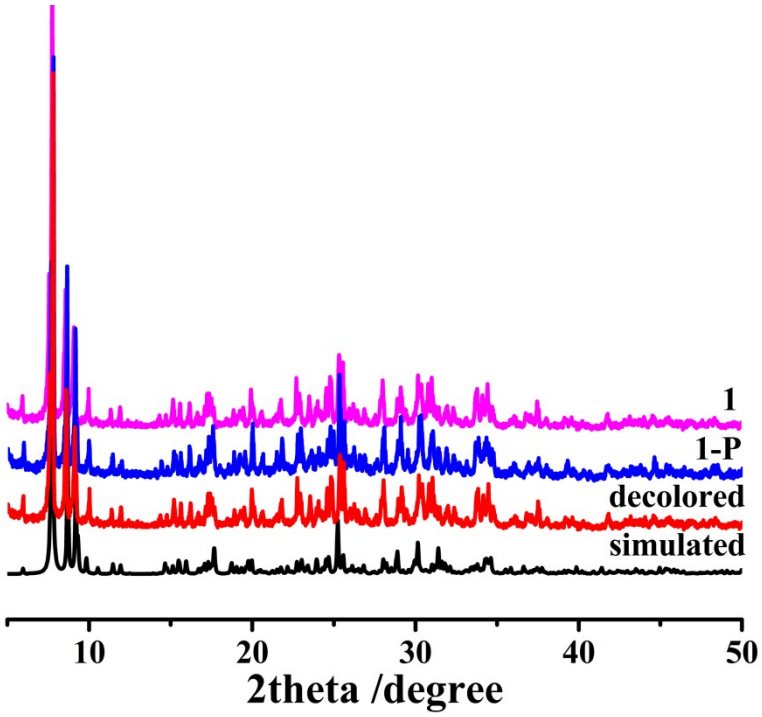

Fig. S4 PXRD patterns of **1**. Labels: **simulated**: simulated patterns from single-crystal X-ray structure data; **1**: before irradiation; **1-P**: after photo irradiation; **decolored**: heating in 130 °C for 2 h.

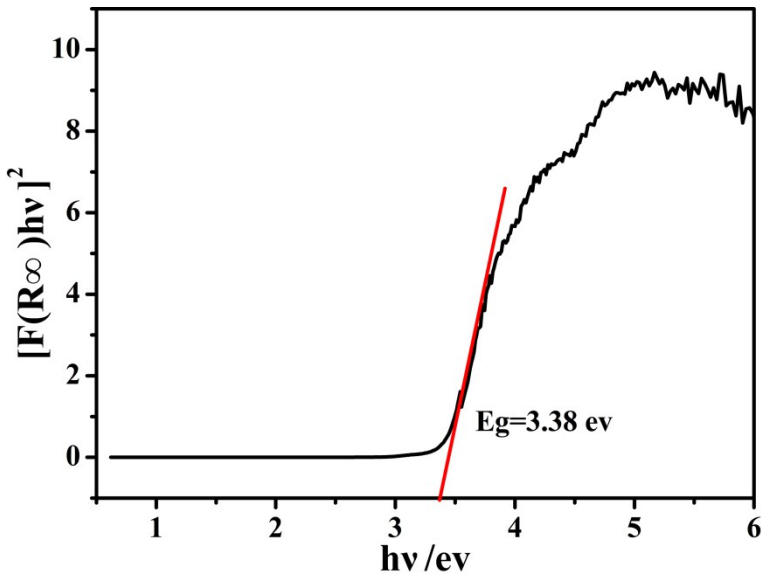

Fig. S5 Optical band gap energy of compound **1**.

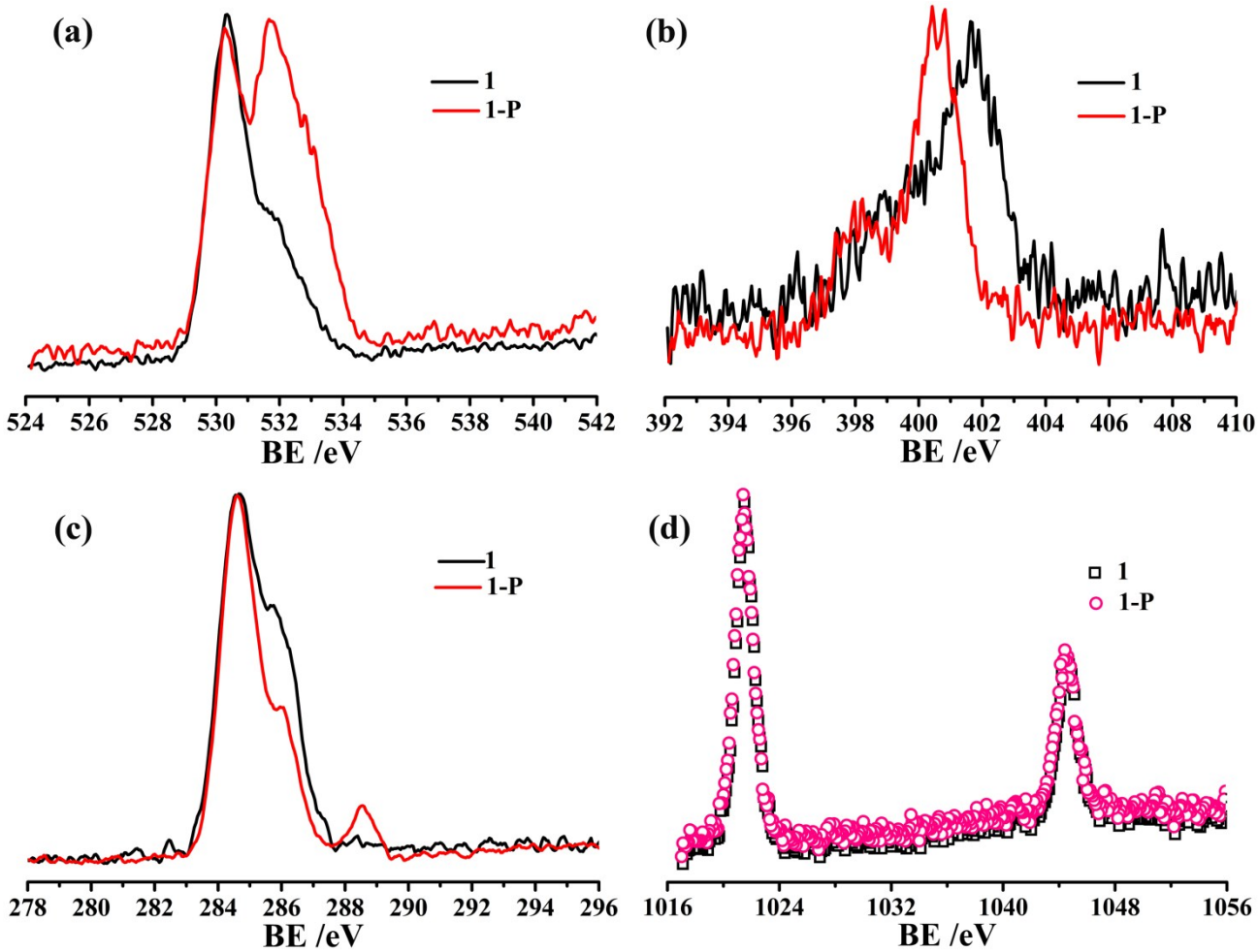

Fig. S6 XPS (Al-Kα) core-level spectra of compound **1** for O 1s (a), N 1s (b), C 1s (c) and Zn 1s (d) before and after photo irradiation. Labels: **1**, before irradiation; **1-P**, after photo irradiation; BE: Binding Energy.

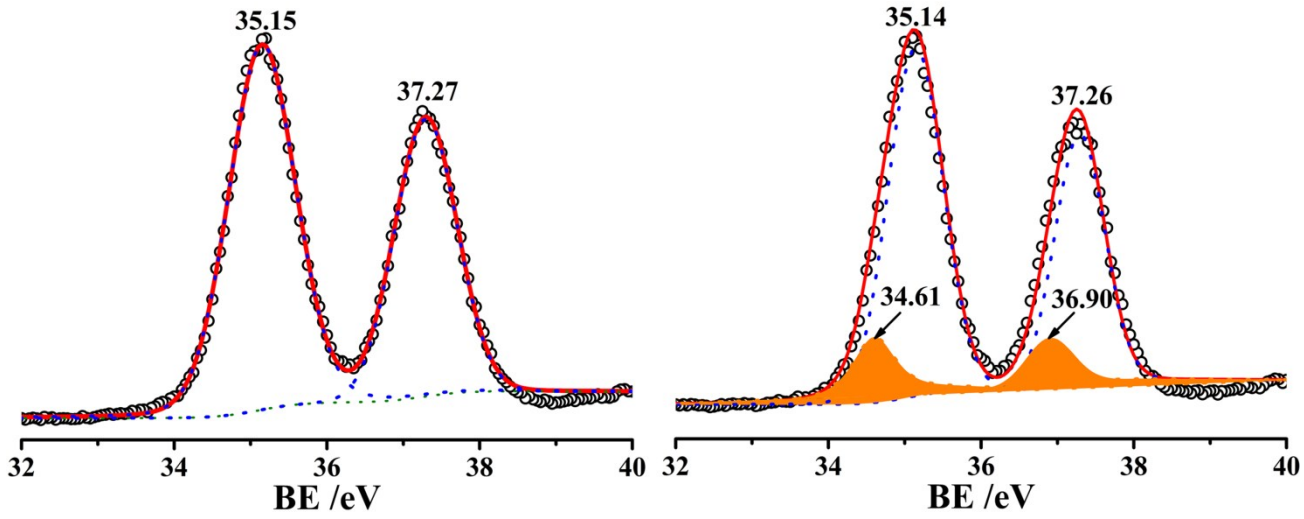

Fig. S7 XPS (Al-Kα) core-level spectra of compound **1** for Mo 3d (left: before irradiation; right: after photo irradiation), BE: Binding Energy.

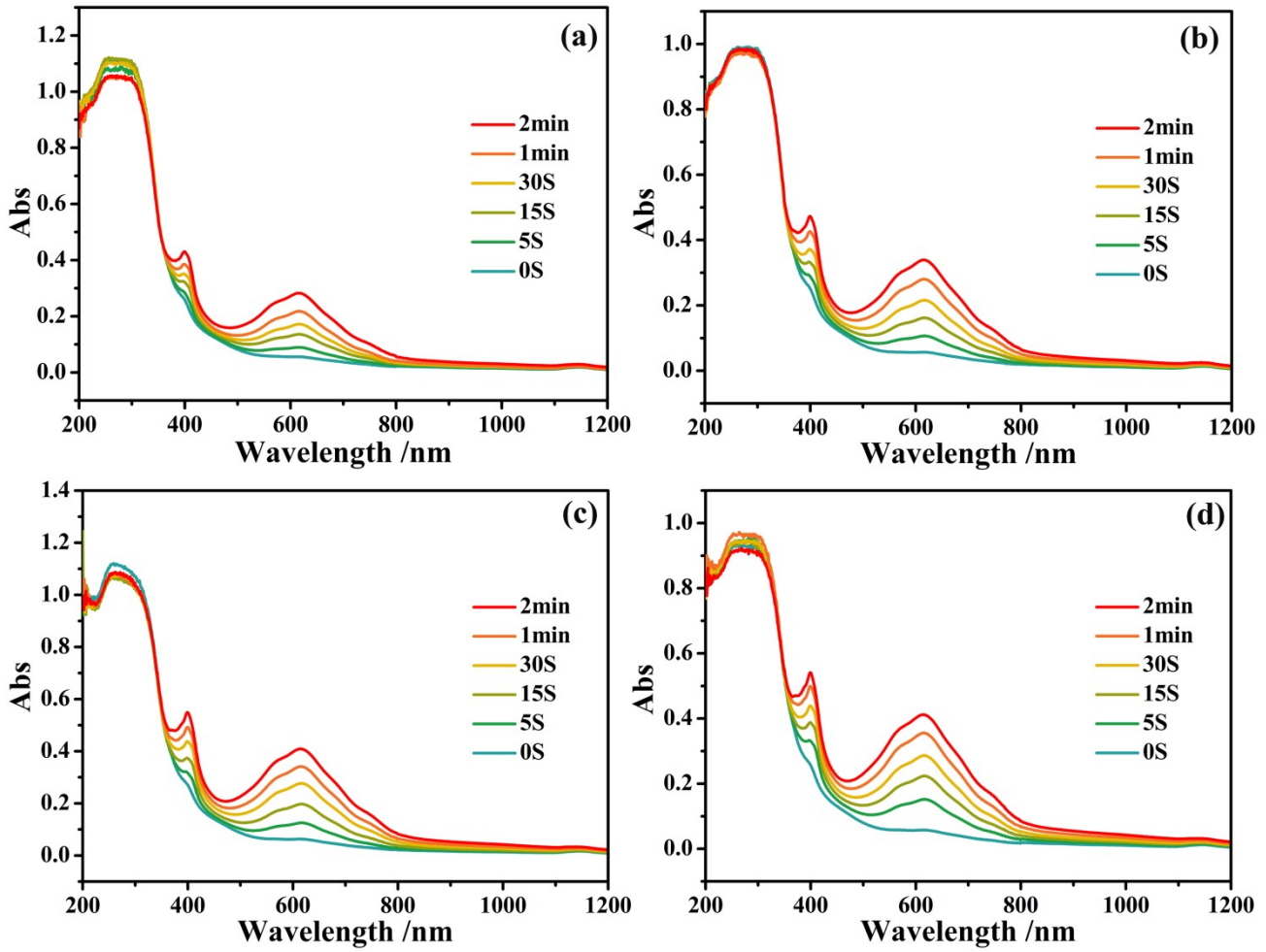

Fig. S8 UV–Vis diffuse reflectance spectra of the crystal samples upon UV light irradiation with intensity of 2 mW/cm^2 (a), 4 mW/cm^2 (b), 6 mW/cm^2 (c), 8 mW/cm^2 (d).

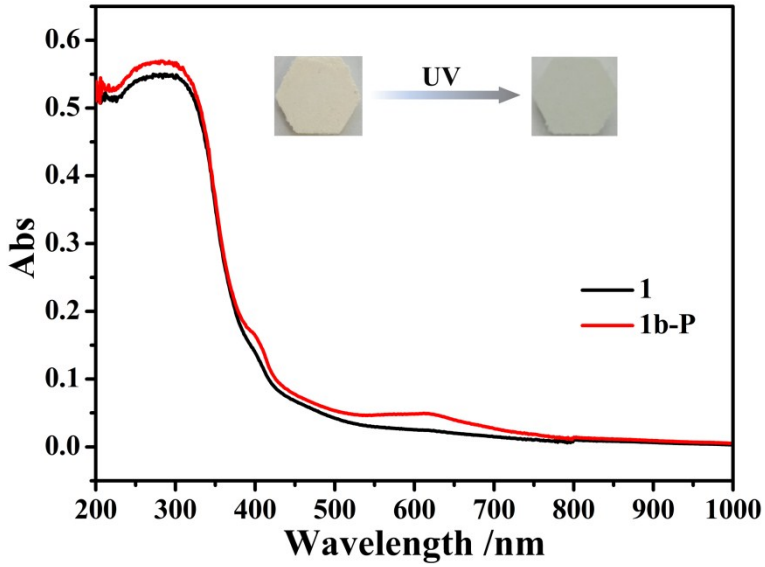

Fig. S9 UV–Vis diffuse reflectance spectra of the crystal samples upon UV light irradiation with intensity of 0.006 mW/cm^2. The colors change was shown in the inset before and after photo-irradiation.

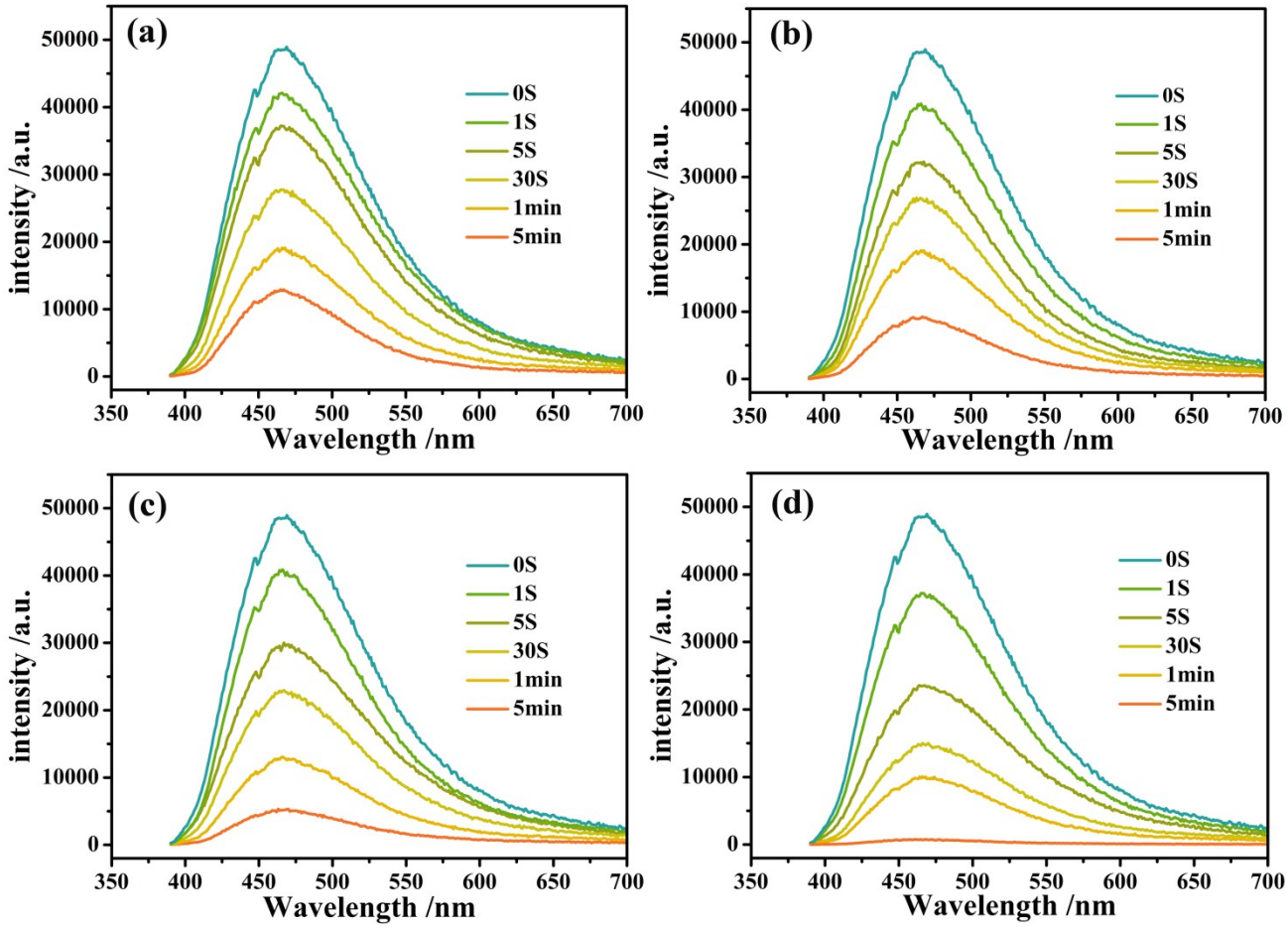

Fig. S10 Time-dependent photoluminescence spectra of **1** upon irradiation (λex = 374 nm) with different UV intensities of 2 mW/cm^2 (a), 4 mW/cm^2 (b), 6 mW/cm^2 (c), 8 mW/cm^2 (d) at room temperature in air.

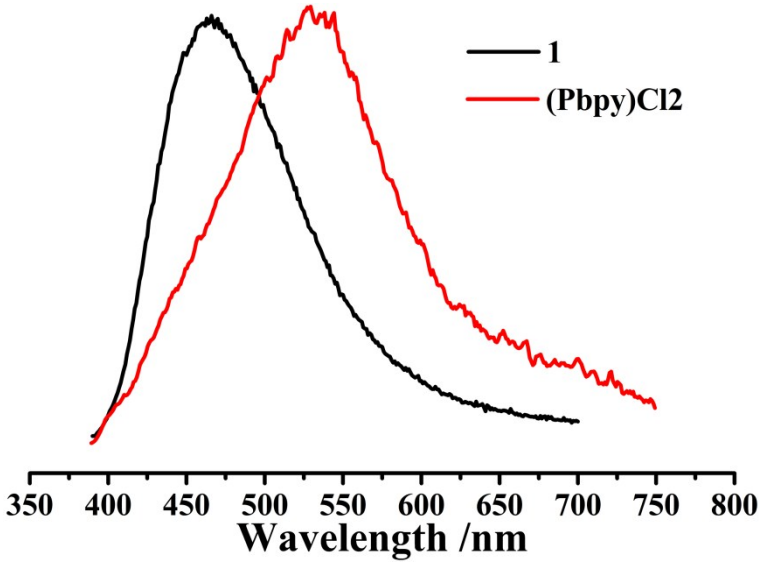

Fig. S11 Solid-state fluorescence emission spectra of $PbpyCl_2$ ligand and compound **1** at room temperature.

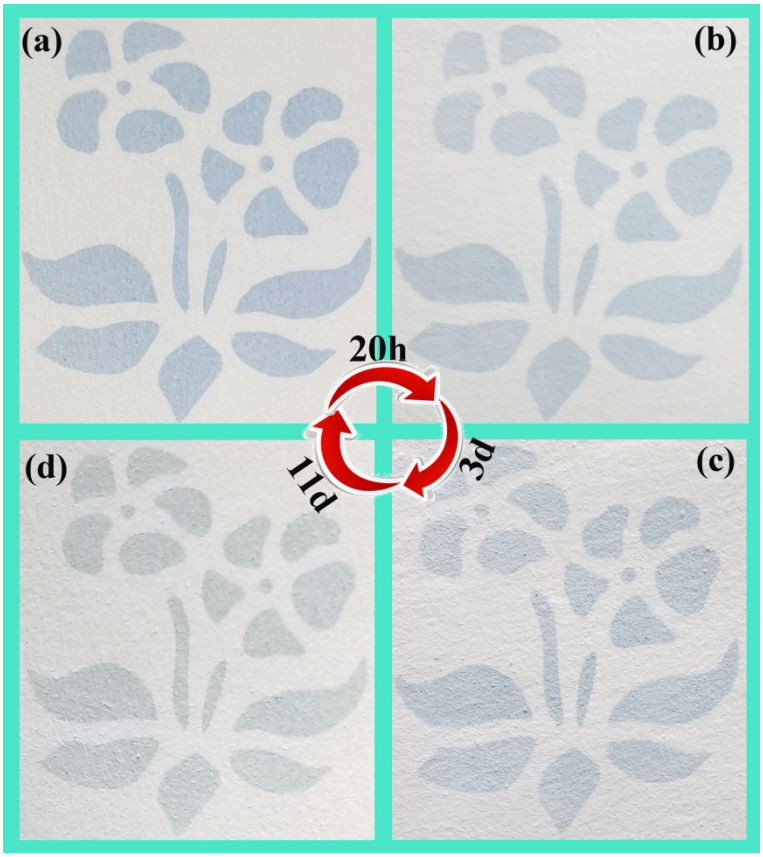

Fig. S12 (a) Photograph of content printed on one coated paper with a flower motif. (b) Printing of the content after 20 h. (c) Printing of the content after 3 days. (d) Photograph of the paper after printing for the 11 days.

Fig. S13 (left) flower motif and (right) bear motif are reusable patterns.

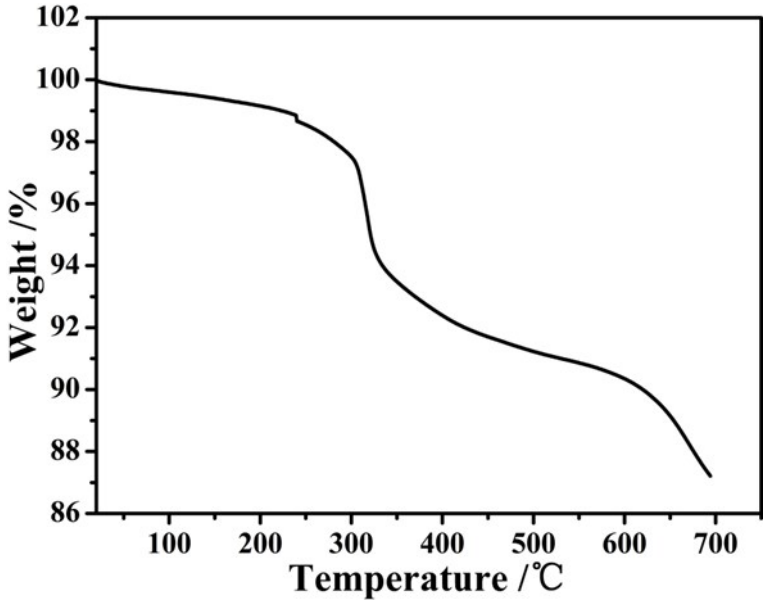

Fig. S14 TGA curve of **1** was investigated using powder samples under N_2.

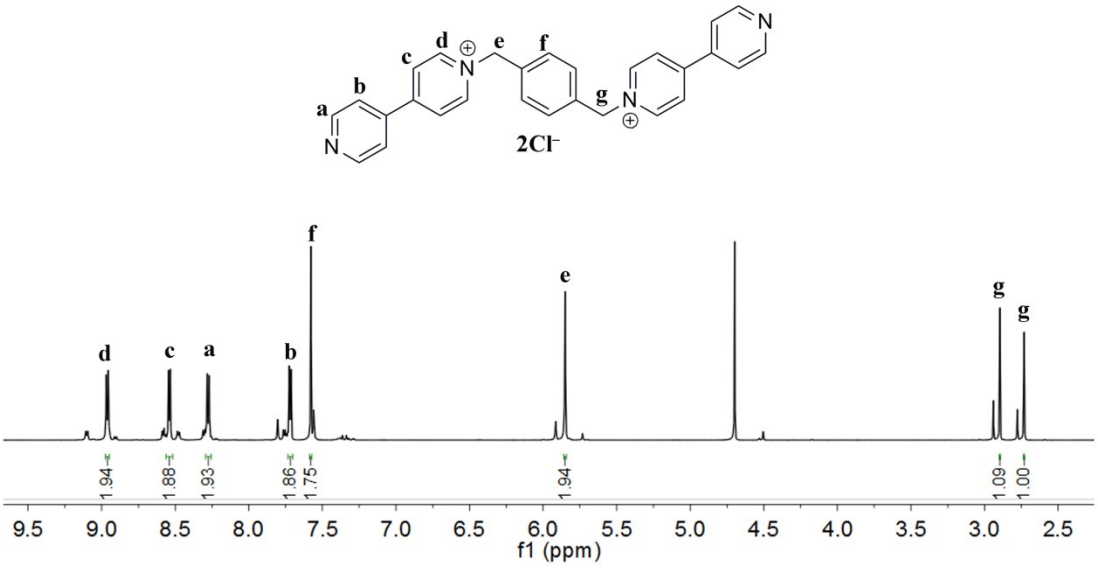

Fig. S15 ^{1}H NMR of $PbpyCl_2$ in D_2O.

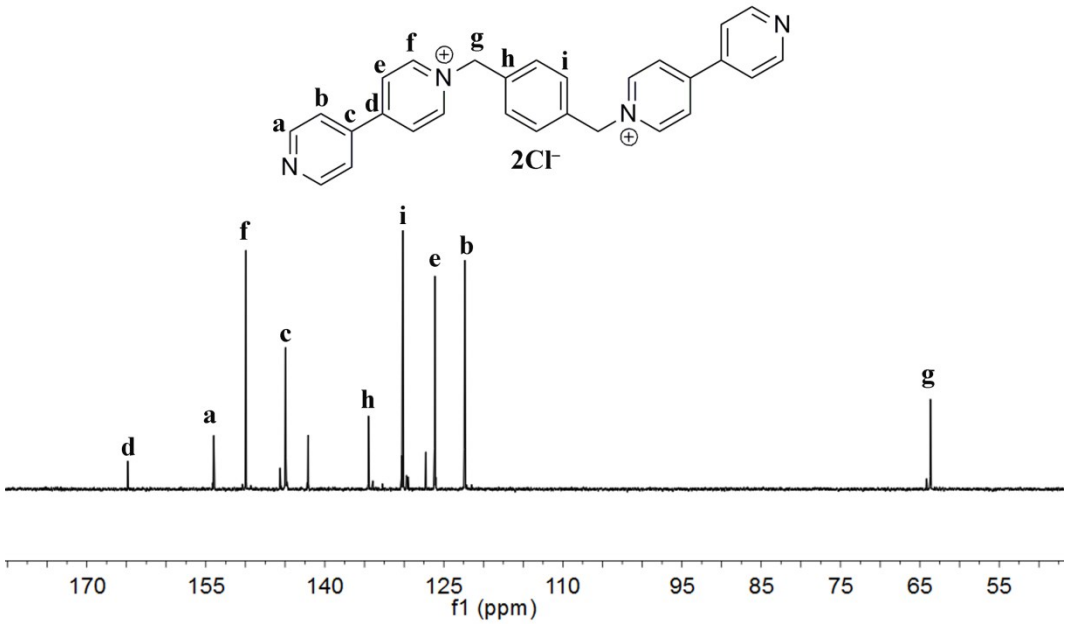

Fig. S16 ^{13}C NMR of $PbpyCl_2$ in D_2O.

Tables.

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

Empirical formula	$C_{34}\ H_{50}\ N_7\ O_{40}\ P\ W_{11}\ Zn$ **(1)**
Formula weight	3315.50
Temperature /K	286
Crystal system	Orthorhombic
Space group	*Pnma*
a /Å	*29.6331(16)*
b /Å	17.9626(9)
c /Å	*12.3339(7)*
α /deg	*90*
β /deg	*90*
γ /deg	*90*
Volume /Å^3	*6565.2(6)*
Z	*4*
D_c /g·cm^{-3}	*3.354*
Absorption coefficient /mm^{-1}	*19.663*
Goodness-of-fit on F^2	*1.024*
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0475$, $wR_2 = 0.0991$
R indices (all data)	$R_1 = 0.0921$, $wR_2 = 0.1195$

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b] $wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)_2]^2\}^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (deg) for **1**

bond lengths (Å)		**angles (deg)**	
W(1)-O(7)	1.916(12)	O(7)-W(1)-O(15)	90.3(5)
W(2)-O(6)	2.014(13)	O(2)-W(2)-O(5)	92.7(7)
W(3)-O(10)	1.926(12)	O(22)-P(1)-O(23)	109.5(8)
P(1)-O(22)	1.521(16)	C(5)-C(6)-C(8)	123(3)
C(1)-N(1)	1.46(3)	N(3)-C(9)-C(13)	129(3)
Zn(1)-O(2)	2.232(15)	W(3)-O(6)-W(2)	152.3(6)
C(6)-C(7)	1.39(3)	P(1)-O(24)-W(6)	126.7(6)