Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Multifunctional Open-Framework Zinc Phosphate $|C_{12}H_{14}N_2|[Zn_6(PO_4)_4(HPO_4)(H_2O)_2]$: Photochromic, Photoelectric and Fluorescent Properties

Junbiao Wu, Yan Yan, Bingkun Liu, Xuelei Wang, Jiyang Li* and Jihong Yu

1. Synthesis of JU98

The reagents and solvents employed were commercially available and used as received without further purification. In the typical synthesis of JU98, the mixture of $Zn(OAc)_2 \cdot 2H_2O$ (0.22g, 1.0 mmol), H_3PO_3 (0.205g, 2.5 mmol) and 4,4′-bipyridine (0.192g, 1.0 mmol) was dissolved in 2 mL water with stirring, and then 5 mL methanol was added. The resulting mixture was stirred for half an hour and then sealed in a 15 mL Teflon-lined stainless steel autoclave for heating at 170 °C for 7 days under static conditions in an oven. The resulting colorless single crystals of JU98 were collected and washed with deionized water, and then dried at 353 K. Compositional Anal. Calc. (%) for $C_{12}H_{19}N_2O_{22}P_5Zn_6$ (1090.60): Zn 35.98, P 14.20, C 13.21, H 1.76, N 2.57; found (%): Zn 35.31, P 14.30, C 12.94, H 1.87, N 2.48.

2. Experimental characterization

Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Powder X-ray diffraction (XRD) and *in-situ* temperature dependent X-ray diffraction data were both collected on a Rigaku D-Max 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The *in-situ* temperature dependent XRD of JU98 was performed at a heating rate of 10 ºC min^{-1}, and the data were collected at a rate of 6° min^{-1}. The UV/Vis absorption spectra were recorded at room temperature on a shimadzu UV-2450 spectrophotometer. Photoluminescence spectra of the samples were detected by a Fluoromax-4 spectrofluorometer (Horiba). The electron paramagnetic resonance (EPR) spectroscopy was obtained on a JES-FA200 EPR spectrometer. A 500 W high-pressure mercury lamp was used as an irradiation light source for in situ ESR measurements. The surface photovoltage (SPV) measurement system was composed of a

monochromatic light source, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a sample cell, and a computer. A 500-W xenon lamp and a double-prism monochromator provided the monochromatic light. In the photovoltaic cell, the powder sheet was directly sandwiched between two blank indium tin oxide (ITO) electrodes. The field-induced surface photovoltage spectroscopy (FISPS) is a supplement to the SPV spectroscopy method. In FISPS, the external electric fields were applied between the two electrodes.

3. Single-crystal X-ray diffraction

Suitable single crystal with dimensions of 0.21 × 0.16 × 0.09 mm^3 for JU98 was selected for single-crystal X-ray diffraction analysis. The intensity data were collected on a Bruker SMART APEX Ⅱ CCD diffractometer by oscillation scans using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at temperature of 23±2°C. Cell refinement and data reduction were accomplished with the SAINT processing program. The structure was solved in monoclinic space group $P2_1/c$ (No.14) by direct methods and refined by full matrix least-squares technique with the SHELXTL crystallographic software package. All framework atoms Zn, P and O could be unambiguously located, and the C and N atoms were subsequently located in the difference Fourier maps. It should be noted that P(5), O(21) and O(22) atoms, and one of MV cations were disordered over two positions with the same occupancy. The positions of H atoms were not added in the structure. All non-hydrogen atoms were refined anisotropically. CCDC 927994 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.uk/data_request/cif.

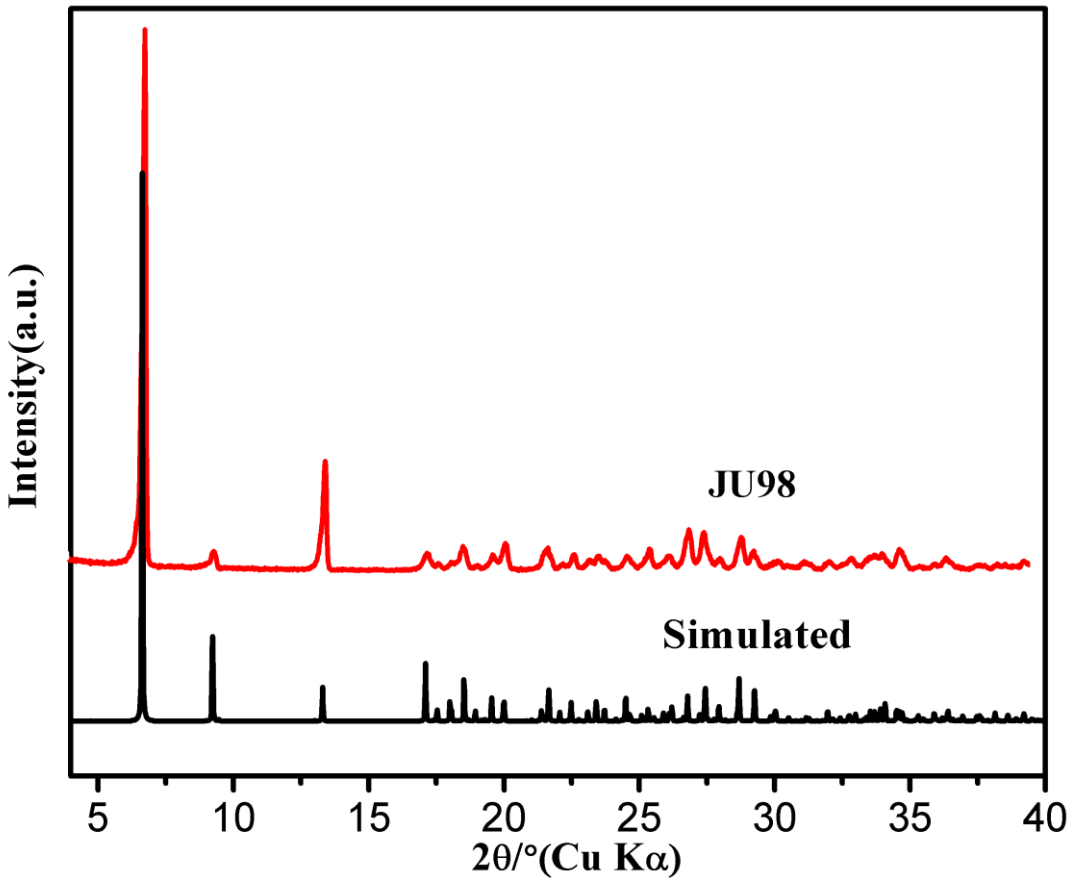

Figure S1 Experimental and simulated powder XRD patterns of JU98

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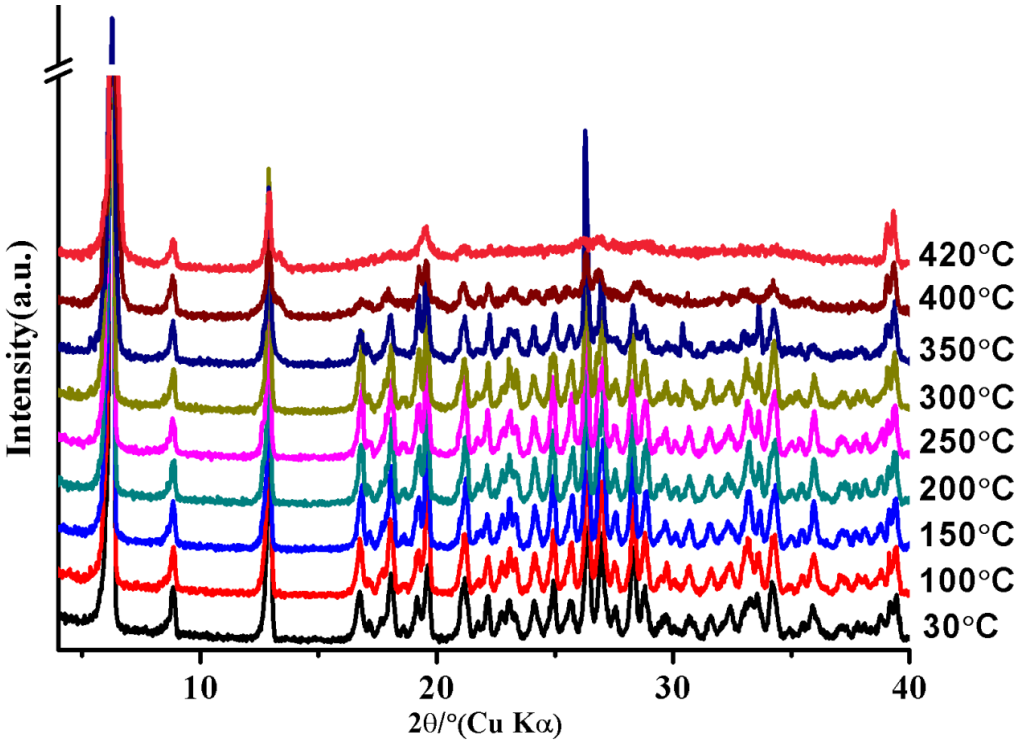

Figure S2 *In-situ* temperature dependent X-ray diffraction patterns of JU98, showing the structure of JU98 can be stable up to 400 °C

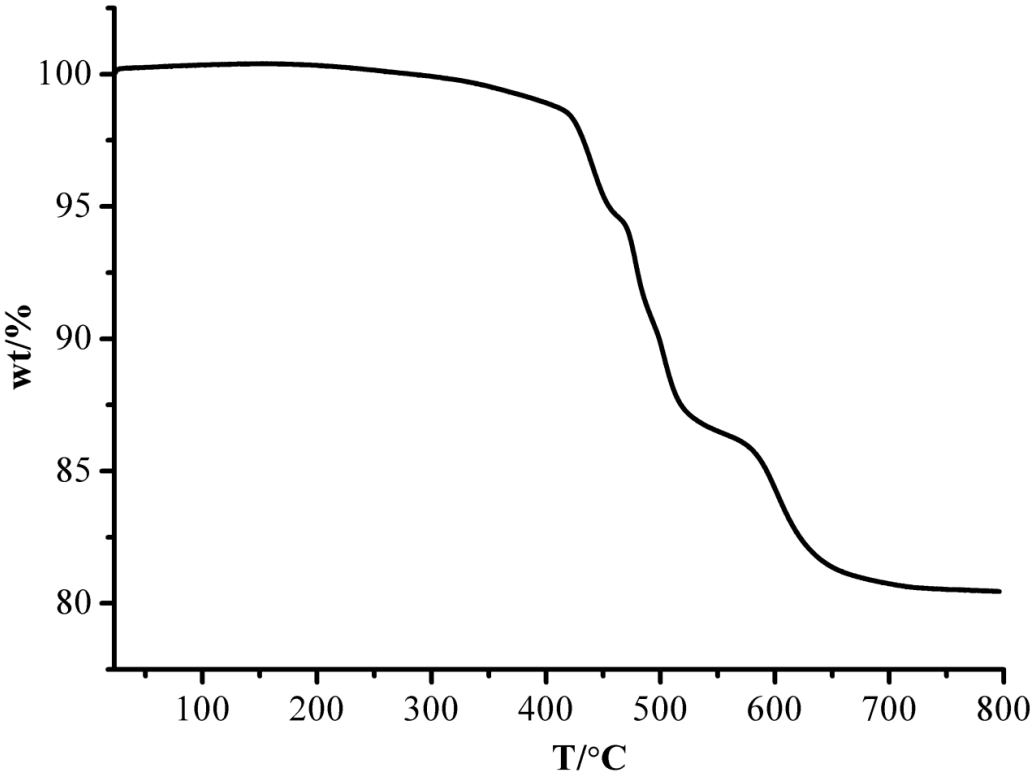

Figure S3 TG curve of JU98

The TG curve of JU98 shows a weight loss of 19.55 wt% from 420 °C to 700°C, corresponding to the loss of MV templates (calc. 20.38 wt%)

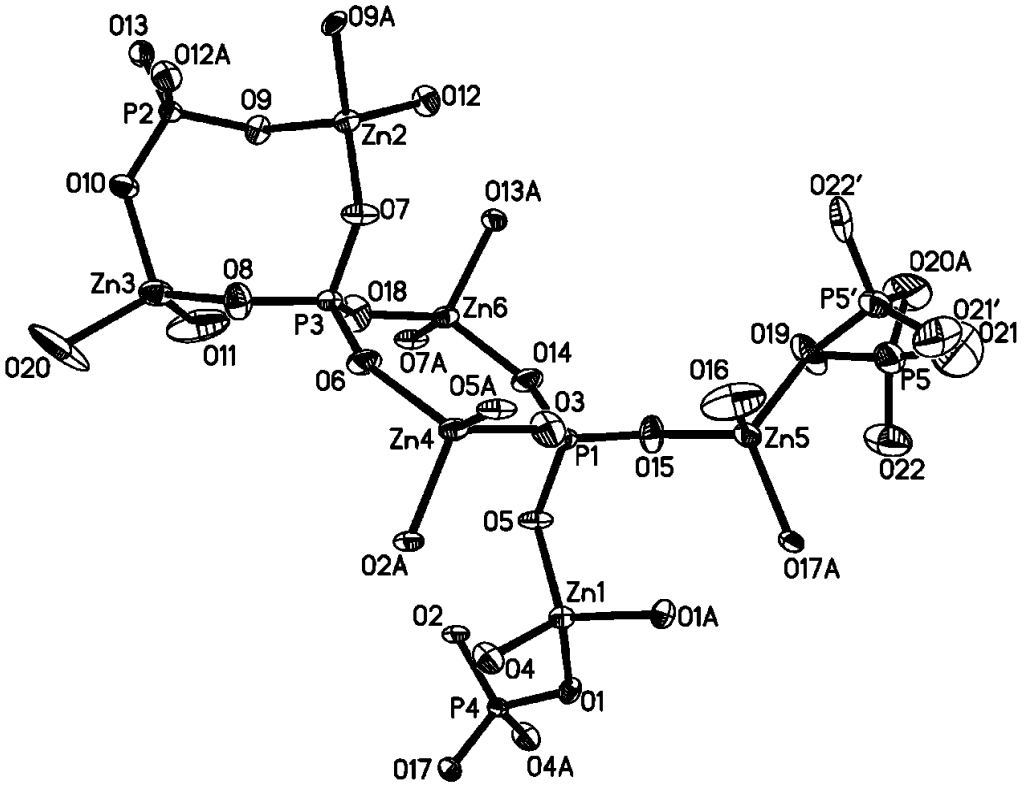

Figure S4 Thermal ellipsoid plots (50% probability) and atomic labeling schemes of JU98 (the organic MV^{2+} is omitted for clarity)

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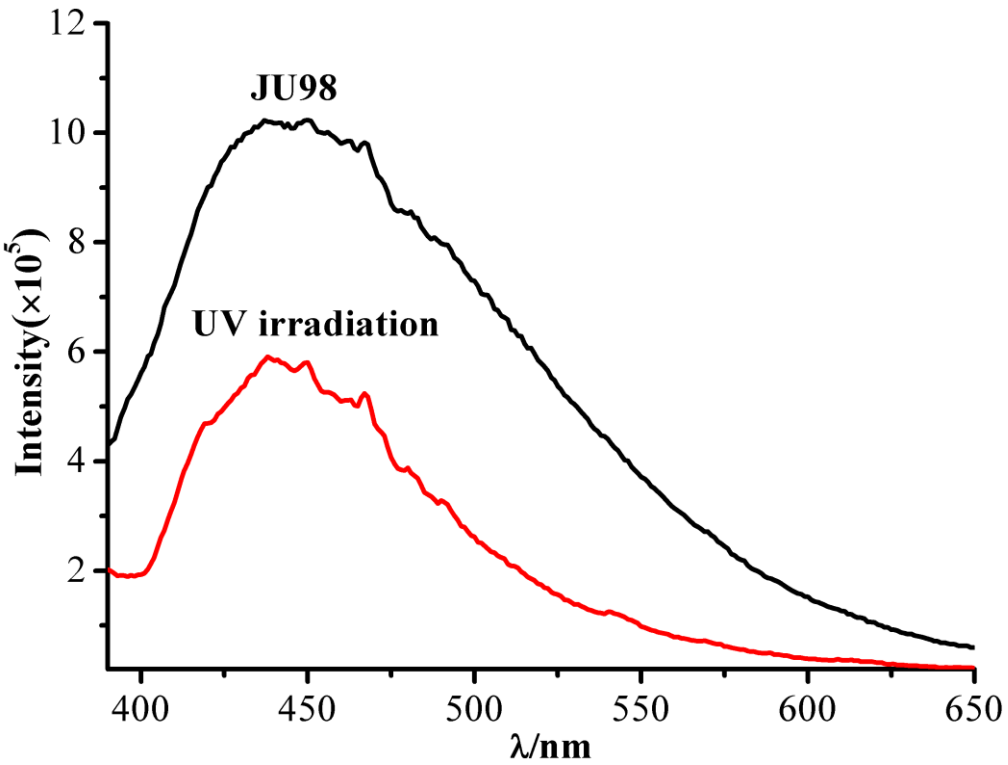

Figure S5 The emission spectra of **JU98** in the solid state at room temperature.

Table 1 Crystal data and structure refinement for JU98[a]

Empirical formula	$C_{12}H_{19}N_2O_{22}P_5Zn_6$
Formula weight	1083.31
Temperature	293(2) K
Wavelength(Å)	0.71073
Crystal system, space group	Monoclinic, *P2(1)/c*
Unit cell dimensions	
a (Å)	20.238(5)
b (Å)	5.2827(13)
c (Å)	28.859(6)
α(deg)	90
β(deg)	112.663(13)
γ (deg)	90
Volume(Å^3)	2847.1(12)
Z, calculated density(mg m^{-3})	4, 2.527
Absorption coefficient(mm^{-1})	5.354
F(000)	2116
Crystal size(mm^3)	0.21 x 0.16 x 0.09
θ range(°) for data collection	1.09–28.31
Limiting indices	$-25 \le h \le 26$, $-6 \le k \le 7$, $-38 \le l \le 29$
Reflections collected/unique	19767/7034, [*R*(int) = 0.0704]
Completeness to *θ* (%)	28.31, 99.6
Absorption correction	semi-empirical from equivalents
Max and min transmission	0.745 and 0.672
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	7034/80/465
Goodness-of-fit on F^2	1.047
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0533$, $wR_2 = 0.1214$
R indices (all data)	$R_1 = 0.1009$, $wR_2 = 0.1435$
Largest diff. peak and hole (eÅ^{-3})	1.708 and -0.968

[a] $R_1 = \sum(\Delta F/\sum(F_o))$, $wR_2 = (\sum[w(F_o^2 - F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$ and $w = 1/\sigma^2(F_o^2)$.

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