Electronic Supporting Information (ESI)

Incorporation of One-Dimensional Electron-Rich Chain in Viologen-based Coordination Polymers for Super Photochromic Properties and Improved Optical Applications in Polyvinyl Alcohol Film

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Section 1. Experimental Section

1. Experimental

1.1 Materials and physical measurements

Materials and physical measurements

All reagents and solvents are commercially available and can be used directly without further purification, H_2bcbpy·2Cl was prepared according to previously reported synthetic procedures [1]. Fourier transform infrared (FT-IR) spectra were recorded on an Avatar 360 FT-IR spectrometer using KBr particles at 4000-400 cm^{-1}. C, H, and N elemental analyses were collected using a Vario EL elemental analyzer. A SHIMADZU XRD-7000 diffractometer was used to gather an X-ray powder diffraction (PXRD) pattern at 25°C using Cu-Kα radiation (=1.5418). Thermogravimetric data (TGA) were collected using a Mettler TGA instrument in the range of 25−500°C with a heating rate of 5°C min^{-1} under nitrogen flow. A Mettler DSC 1 STAR System apparatus was used to perform differential scanning calorimetry (DSC). XtaLAB Synergy-DW and Oxford Diffraction SuperNova area-detector diffractometers were used to acquire single-crystal X-ray diffraction data at low temperatures utilizing mirror optics monochromated Cu-Kα radiation (= 1.54184, 100 K). A hand-held UV lamp was used to produce the UV light (365 nm). At ambient temperature, solid-state UV-Vis diffuse reflectance spectra were recorded on a TU-1901 spectrophotometer with an integrating sphere in the 200–850 nm range. A Bruker E500 system was used to record electron paramagnetic resonance (EPR) data.

1.2 Single crystal X-ray diffraction determination

Single crystal X-ray diffraction data for **1** was acquired at 100 K using an XtaLAB Synergy-DW diffractometer with Cu-Kα (= 0.71073, powered at 4kW) radiation. The structure was solved using direct techniques in SHELXT and improved in the Olex2.solve package with SHELXL-2014 software. [2] Anisotropic displacement parameters were used to refine all non-hydrogen atoms. The riding mode was used to insert other hydrogen atoms in determined optimal places and refine them isotropically.[3,4] **Table S1** summarizes the crystallographic information and structure refinement parameters for **1**. **Tables S2,** and **S3** provides selected bond lengths and bond angles.

1.3 Theoretical calculation

Characterization of the most important electronic transitions of **1** based on calculation. Computational Details: All calculations were performed using the Gaussian 09 software. [5] Ground state geometries were optimized by the Ground state DFT density functional method and b3lyp/6-311g basis set. [6]

Section 2. Supplementary Tables, Structural Figures

2.1 Table Titles:

Table S1 Crystallographic data and refinement parameters of **1.**

Table S2 Selected Bond Lengths [Å] for the **1.**

Table S3 Selected Bond Angles [º] for the **1.**

Table S1 Crystallographic data and refinement parameters of **1.**

Compound	**1**
CCDC	2164686
Formula	$C_{60}H_{52}ClN_4O_{19}SZn_2$
$D_{calc.}$/ g cm^{-3}	1.567
μ/mm^{-1}	2.530
Formula Weight	1331.30
Colour	colorless
Shape	needle
Size/mm^3	0.20×0.15×0.10
T/K	293(2)
Crystal System	monoclinic
Space Group	$P2/_C$
a/Å	18.2457(3)
b/Å	9.46260(10)
c/Å	32.9769(5)
α/°	90
β/°	97.6890(10)
γ/°	90
V/Å^3	5642.33(14)
Z	4
Wavelength/Å	1.54184
Radiation type	CuK_a □
Measured Refl.	71848
Independent Refl.	11621
R_{int}	0.0757
Parameters	814
Restraints	64
Largest Peak	1.99
Deepest Hole	-1.22
GooF	1.049
wR_2 (all data)	0.2178
wR_2	0.1991
R_1 (all data)	0.0958
R_1	0.0715

Table S2 Selected Bond Lengths [Å] for the **1**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
1					
Zn1	O4B	1.938(3)	Zn2	O5	1.943(3)
Zn1	O4C	1.938(3)	Zn2	O5D	1.943(3)
Zn1	O1A	1.944(4)	Zn2	O8F	1.961(4)
Zn1	O1	1.944(4)	Zn2	O8E	1.961(4)
Zn3	Cl1	2.2095(16)	Zn3	O12H	1.957(3)
Zn3	O11G	1.992(3)	Zn3	O9	1.943(4)

symmetry code: A: 1-*x*, +*y*, 1/2-*z*; B: 1+*x*, +*y*, +*z*; C: -*x*, +*y*, 1/2-*z*; D: 2-*x*, +*y*, 1/2-*z*; E: 1-*x*, +*y*, 1/2-*z*; F: 1+*x*, +*y*, +*z*; G:1-*x*, -*y*, 1-*z*; H: +*x*, 1+*y*, +*z*.

Table S3 Selected Bond Angles [º] for the **Table S2** Selected Bond Lengths [Å] for the **1.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
1-Cl							
O4B	Zn1	O4C	122.2(2)	O11G	Zn3	Cl1	105.46(10)
O4B	Zn1	O1	97.33(17)	O12H	Zn3	Cl1	120.25(12)
O4C	Zn1	O1	116.41(16)	O12H	Zn3	O11G	105.69(14)
O4C	Zn1	O1A	97.34(17)	O9	Zn3	Cl1	110.21(17)
O4B	Zn1	O1A	116.41(16)	O9	Zn3	O11G	99.27(17)
O1A	Zn1	O1	107.4(3)	O9	Zn3	O12H	113.31(17)
O5D	Zn2	O5	124.4(2)	O5D	Zn2	O8F	117.47(15)
O5D	Zn2	O8E	96.13(17)	O5	Zn2	O8E	117.47(15)
O5	Zn2	O8F	96.13(17)	O8E	Zn2	O8F	104.9(3)

symmetry code: A: 1-*x*, +*y*, 1/2-*z*; B: 1+*x*, +*y*, +*z*; C: -*x*, +*y*, 1/2-*z*; D: 2-*x*, +*y*, 1/2-*z*; E: 1-*x*, +*y*, 1/2-*z*; F: 1+*x*, +*y*, +*z*; G:1-*x*, -*y*, 1-*z*; H: +*x*, 1+*y*, +*z*.

2.2 Figure Titles:

Fig. S1 PXRD patterns of **1** simulated from the X-ray single-crystal structures (black line) and as-synthesized samples (red line).

Fig. S2 TGA (a) and DSC (b) plots for **1** under nitrogen atmosphere at a heating rate of 10°C/min.

Fig. S3 IR patterns of **1**.

Fig. S4 In **1**, the one-dimensional chain **Chain-1** formed by Zn^{2+} ions and bcbpy ligands.

Fig. S5 In **1**, the one-dimensional chain **Chain-1** formed by Zn^{2+} ions and sip ligands.

Fig. S6 PXRD patterns of **1** as-synthesized sample (black line) and sample after illumination (red line).

Fig. S7 The color contrast diagram of H_2bcbpy·2Cl ligand irradiated by 365 nm ultraviolet lamp with different time; (b) UV-visible absorption spectra of solid H_2bcbpy·2Cl ligand subjected to different irradiation time using 365 nm ultraviolet lamp.

Fig. S8 The electron transfer pathway of electron-rich **chain-2** and electron-deficient **chain-1** in **1** through hydrogen bonding.

Fig. S9 The structure of the **Chain-1** (a) and **Chian-2** (b) in **1** used in the study and the energy-minimized structures obtained using opt freq b3lyp/6-311g level of theory using Gaussian 9 suite program.

Fig. S10. XPS spectra of **1** (before irradiation, black curve) and **1-I** (after irradiation, red curve).

Fig. S11 PXRD patterns of **1** at various temperatures.

Fig. S12 PXRD patterns of **1** under different amine treatments.

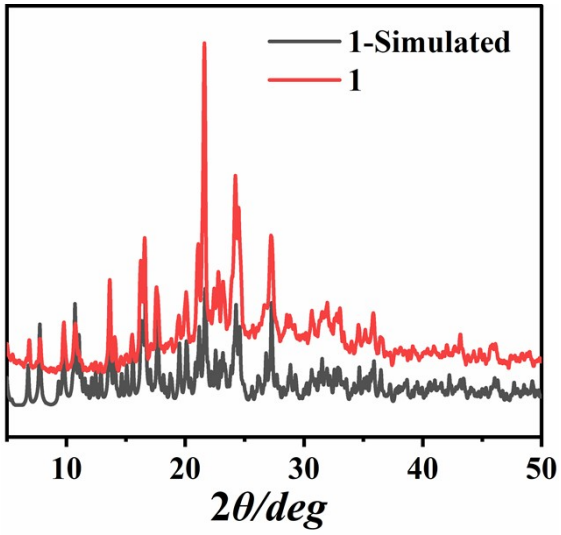
Fig. S13 The color change of 1-EA samples without EA at a specific time interval.

Fig. S14 (a) Fluorescence (λ_{em} = 530 nm) and delayed fluorescence (λ_{em} = 520 nm) excitation spectra of H_2bcbpy·2Cl ligand; (b) Fluorescence (λ_{ex} = 445 nm) and delayed fluorescence (λ_{ex} = 440 nm) emission spectra of H_2bcbpy·2Cl ligand; (c) The fluorescence decay lifetime spectra of H_2bcbpy·2Cl ligand (λ_{em} = 530 nm); (d) The decay lifetime spectrum of delayed fluorescence curve of H_2bcbpy·2Cl ligand (λ_{em} = 520 nm).

Fig. S15 (a) Fluorescence (λ_{em} = 505 nm) and delayed fluorescence (λ_{em} = 490 nm) excitation spectra of H_2sipm·Na ligand; (b) Fluorescence (λ_{ex} = 330 nm) and delayed fluorescence (λ_{ex} = 340 nm) emission spectra of NaH_2sip·ligand; (c) The fluorescence decay lifetime spectra of Na H_2sip·ligand (λ_{em} = 505 nm); (d) The decay lifetime spectrum of delayed fluorescence curve of Na H_2sip·ligand (λ_{em} = 490 nm).

Fig. S16 PXRD spectra of samples **1** and **1**-ultrasonic treatment.

Fig. S17. The **1-PVA film** printed by Mask 1 weather pattern and reused by Mask 2 QR code.



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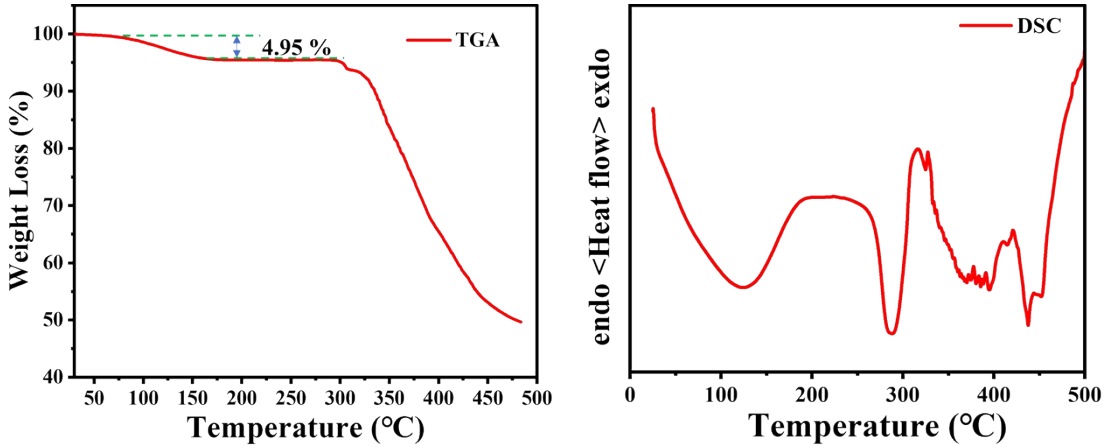

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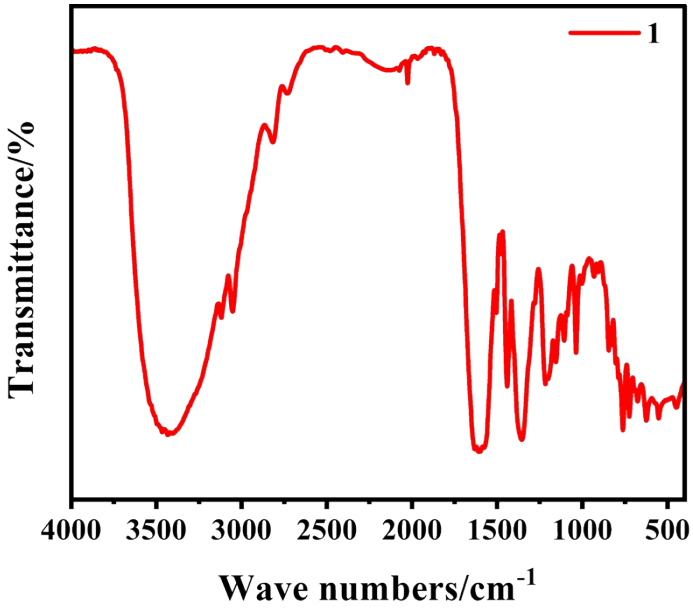

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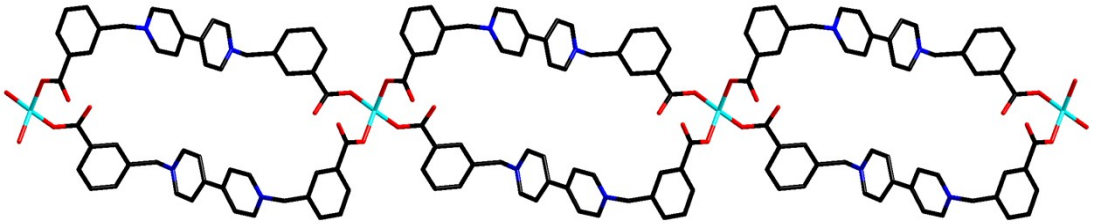

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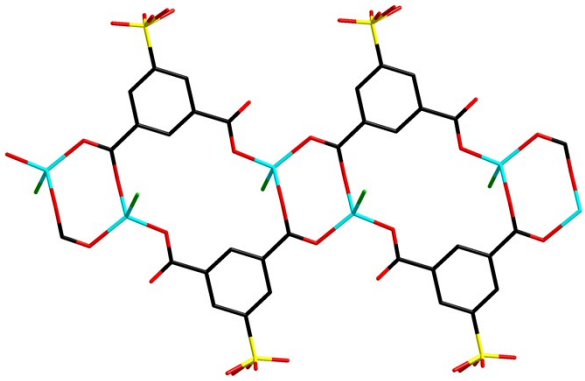
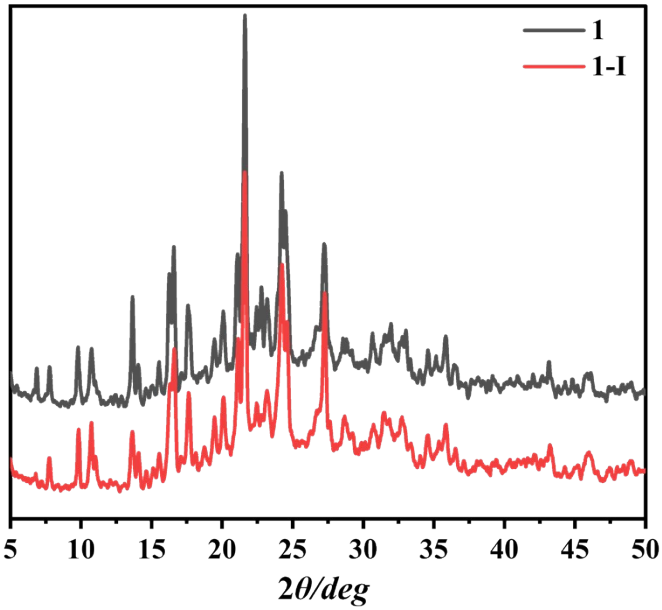


Fig. S5 In **1**, the one-dimensional chain **Chain-1** formed by Zn^{2+} ions and sip ligands.



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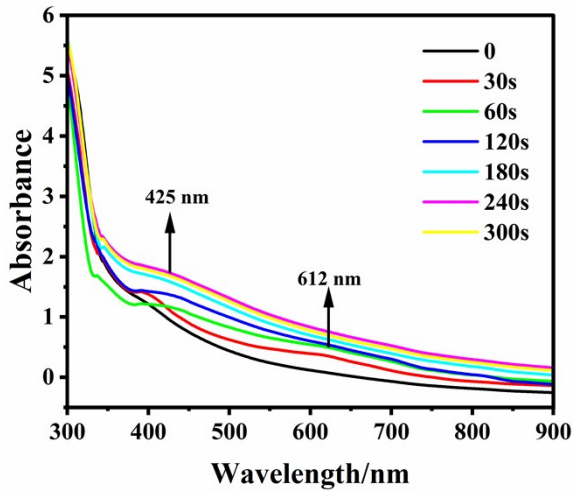

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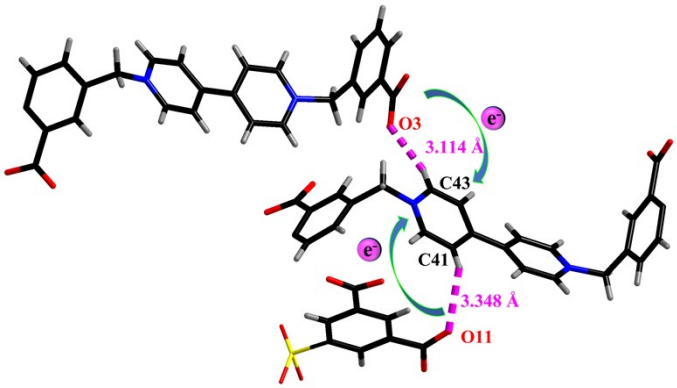

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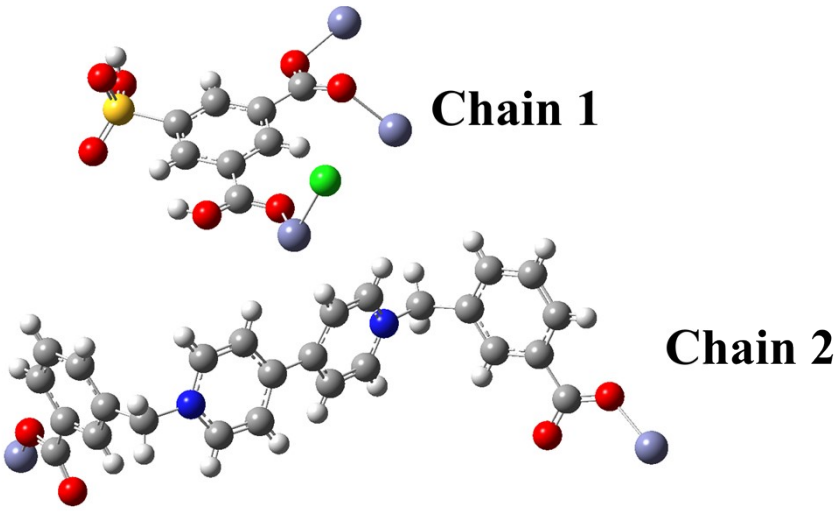

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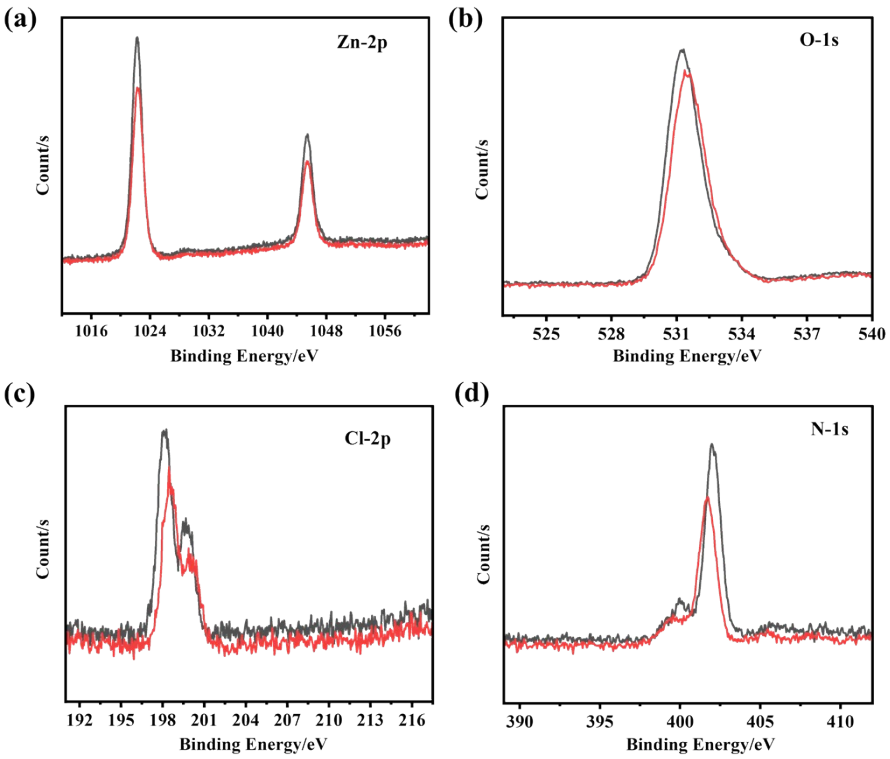

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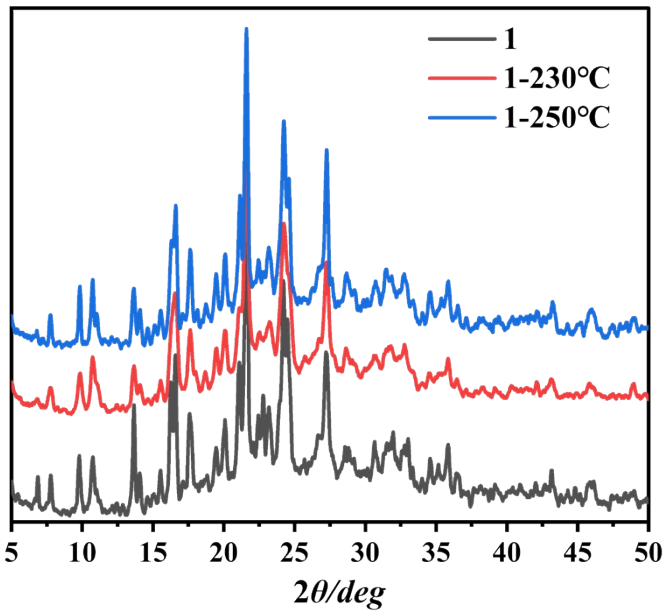

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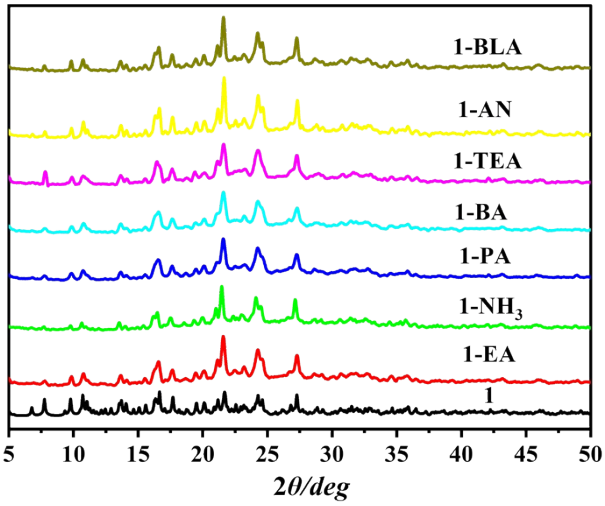

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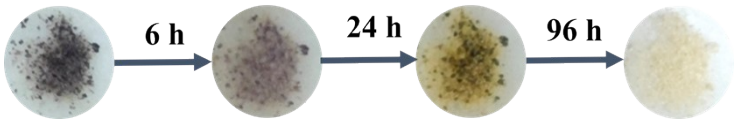

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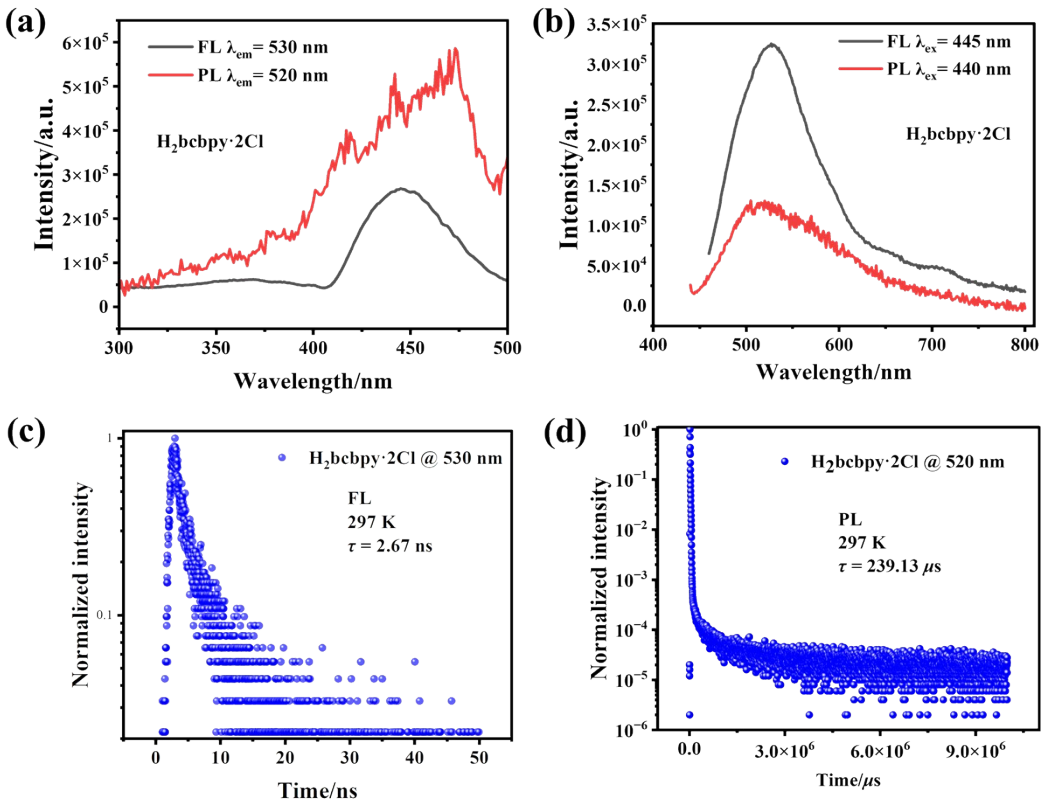

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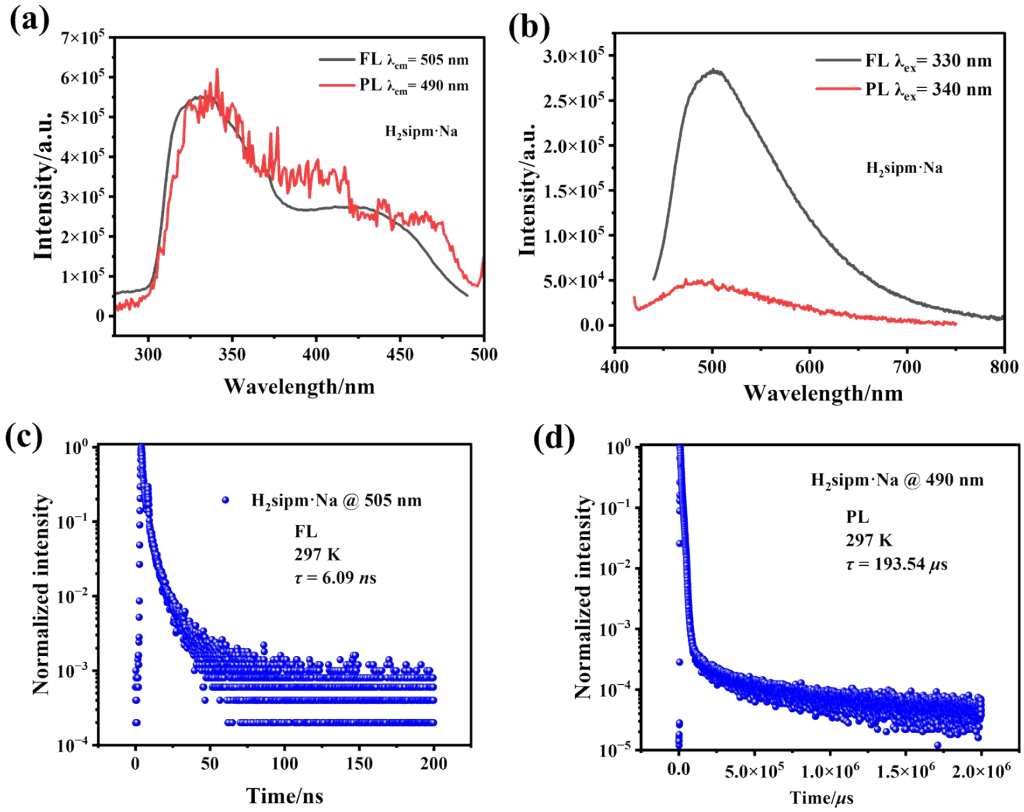

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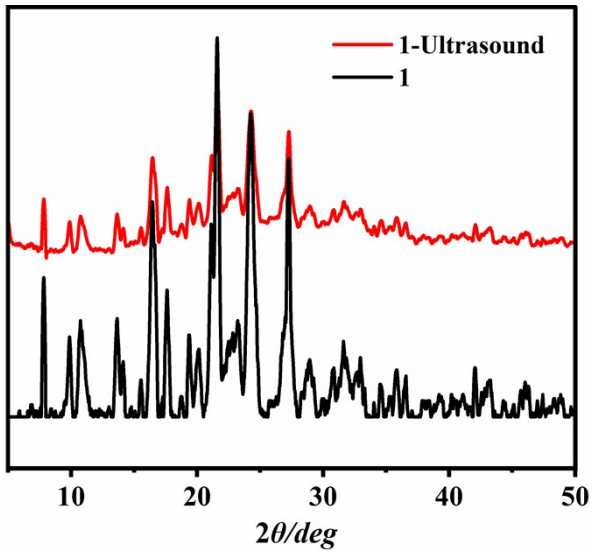

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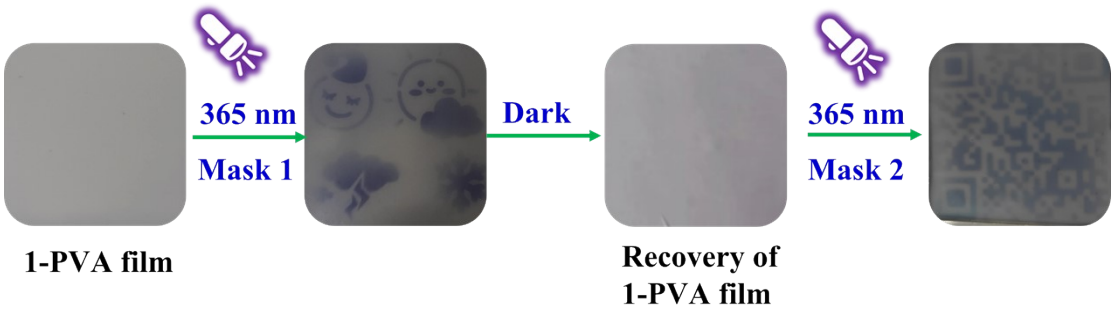

Fig. S17. The **1-PVA film** printed by Mask **1** weather pattern and reused by Mask 2 QR code.

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