

Supporting Information

Photomechanical behavior triggered by [2 + 2] cycloaddition and photochromism of pyridinium-functionalized coordination complex

Yun-Rui Chen, Meng-Ze Jia, Jia-Qi Pan, Bin Tan and Jie Zhang*

MOE Key Laboratory of Cluster Science, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, P. R. China, E-mail: zhangjie68@bit.edu.cn

Section 1. Experimental

1.1 Materials and instruments

All chemicals and reagents used in the experiment were purchased directly from suppliers, and were of AR/GR grade without further purification. Infrared (IR) spectra were measured using a KBr pellet on a Nicolet iS10 FT-IR spectrometer. Thermogravimetric analysis (TGA) was collected on a Mettler Toledo TGA/DSC 1/1100 analyzer in a flowing air atmosphere at a heating rate of 10 °C min⁻¹ from 25 to 1000 °C. UV-Vis spectra measurements were carried out at room temperature by using a PE Lambda 750 spectrometer. Elemental analysis (C, H, N) was performed using a Vario EL III CHNOS elemental analyzer. ¹H NMR spectrum was recorded on a Bruker AV-400 NMR spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.54056$ Å). The electron spin resonance (ESR) signal was collected with a JES-FA200 spectrometer at air environment (25 °C). Luminescence spectra were recorded on an Edinburgh Instruments FLS980 spectrophotometer at air environment (25 °C). LED light source (MLED4-1) was from Zolix Instruments CO., LTD, the light intensity of 365 nm light was 214 mW cm⁻², while that of 550 nm light is 127 mW cm⁻².

1.2 Preparation and characterization of crystals

HBCbpeCl: The synthetic method of HBCbpeCl is the same as previously reported (J.-K. Sun, W. Li, C. Chen, C.-X. Ren, D.-M. Pan and J. Zhang, *Angew. Chem. Int. Ed.*, 2013, **52**, 6653).

Preparation of Zn-Bpe: HBCbpeCl (6.0 mg, 0.017 mmol) was dissolved in a mixture of water and DMSO (v/v = 9 : 1, 2 mL) and the pH value was adjusted to 7 with 0.5 mol/L NaOH solution, then mixed with 2 mL ZnSO₄ solution (0.05 mol/L). After stirring, the mixture was filtered and volatilized about a day, pale yellow transparent block crystals of 3.4 mg were obtained. Yield: 18.3%. Elemental analysis (%): calculated for ZnSC₄₀N₄O_{24.5}H₆₅ (1091.43): C 44.02, N 5.13, H 6.00; found: C 44.12, N 5.02, H 5.73.

Preparation of Zn-Bpe-rod: HBCbpeCl (8.8 mg, 0.025 mmol) was dissolved in water (3 mL) and the pH value was adjusted to 7 with 0.5 mol/L NaOH solution, then mixed with 1 mL ZnSO₄ solution (0.1 mol/L). The mixture was poured into a 20 mL glass bottle, stirred, and heated at 110 °C for 5h. After cooling to room temperature gradually, orange yellow rod-shaped crystals of 10.7 mg were obtained. Yield: 39.2%. Elemental analysis (%): calculated for ZnSC₄₀N₄O_{24.5}H₆₅ (1091.43): C 44.02, N 5.13, H 6.00; found: C 44.16, N 4.99, H 5.81.

Preparation of composite film PVA+Zn-Bpe: 1.0 g Poly (vinyl alcohol) (PVA) was dissolved in 20 mL water

and heated at 98 °C for 1h. When it was cooled to 70 °C, 8mL PVA aqueous solution is blended with 20 mg **Zn-Bpe** and stirred evenly. The composite film **PVA+Zn-Bpe** was obtained by coating the mixture on the glass plate and drying it in an oven at 40 °C.

1.3 X-ray crystallography

The X-ray diffraction data of **Zn-Bpe** and **Zn-Bpe-rod** were collected on a Gemini A Ultra diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXL-2018/3 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms except those attached to coordinated water molecules were calculated in ideal positions and refined by riding on their respective carbon atoms, while the hydrogen atoms of coordinated water molecules were first determined by the difference Fourier map and then fixed at the calculated positions. The solvent molecules were disordered in the structure and could not be modelled satisfactorily, therefore was removed using Solvent Mask in Olex2. Their formulas are derived from the crystallographic data combined with thermogravimetric analysis (TGA) and elemental analysis.

Table S1. Crystal Data and Structural Refinement Parameters of **Zn-Bpe** and **Zn-Bpe-rod**

Compound name	Zn-Bpe	Zn-Bpe-rod
Structural formula	$[\text{Zn}(\text{BCbpe})_2(\text{H}_2\text{O})_4] \cdot \text{SO}_4 \cdot 12.5\text{H}_2\text{O}$	$[\text{Zn}(\text{BCbpe})_2(\text{H}_2\text{O})_4] \cdot \text{SO}_4 \cdot 12.5\text{H}_2\text{O}$
Empirical formula	$\text{ZnSC}_{40}\text{N}_4\text{O}_{24.5}\text{H}_{65}$	$\text{ZnSC}_{40}\text{N}_4\text{O}_{24.5}\text{H}_{65}$
Formula weight	1091.43	1091.43
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
a (Å)	14.710(8)	14.611(3)
b (Å)	27.961(2)	28.055(3)
c (Å)	13.589(2)	13.583(3)
α (°)	90	90
β (°)	116.57(6)	116.71(2)
γ (°)	90	90
Volume (Å ³)	4999.1(10)	4973.7(17)
Z	4	4
D_{calcd} (g/cm ³)	1.151	1.157
Absorption coefficient (mm ⁻¹)	0.588	0.591
$F(000)$	1800	1800
Reflections collected/unique	24513/5144 ($R_{\text{int}} = 0.0336$)	26130/4372 ($R_{\text{int}} = 0.0785$)
GOOF on F^2	1.023	1.048
R_1, wR_2 ($I > 2\sigma(I)$)	0.0439, 0.1240	0.0530, 0.1366
R_1, wR_2 (all data)	0.0588, 0.1374	0.0847, 0.1537

Section 2. Additional Data and Figures

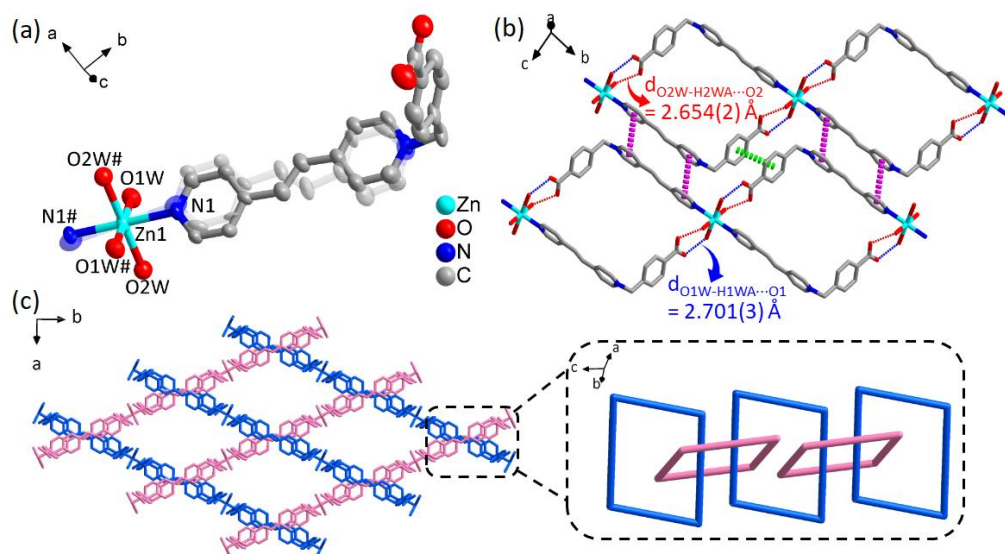


Fig. S1 (a) The coordination environment of Zn(II) ion in **Zn-Bpe**, in which the shading indicates the structure of the split part. #: 1.5-x, 0.5-y, 2-z. (b) The 2D supramolecular layer stabilized by the π - π and cation- π interactions in **Zn-Bpe**. (c) The interpenetrated 3D framework of **Zn-Bpe**. The split part of the crystal is not shown for the brevity of the structure.

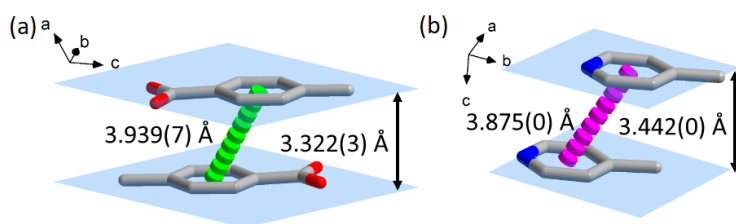


Fig. S2 The centroid...centroid distances and the interplanar distances of π - π (a) and cation- π (b) interactions. The split part of the crystal is not shown for the brevity of the structure, and the distance in the figure is determined by the atoms with higher occupancy.

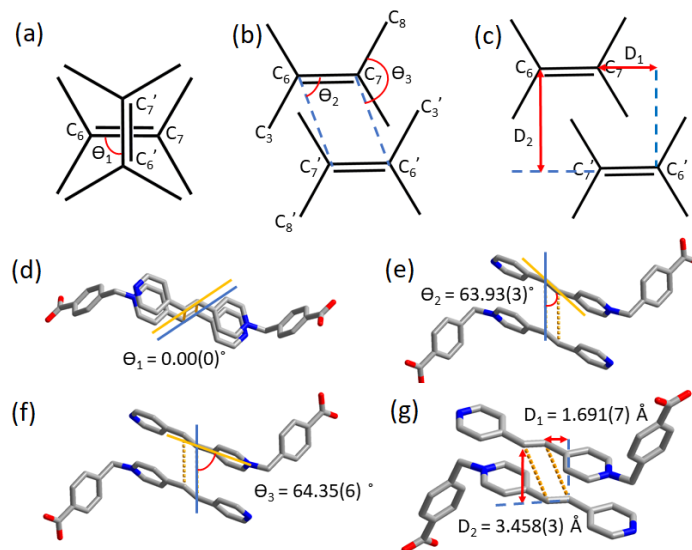


Fig. S3 Some geometric parameters of the olefinic groups in the BCbpe pair in **Zn-Bpe**. The split part of the crystal is not shown for the brevity of the structure, and the distance in the figure is determined by the atoms with higher occupancy.

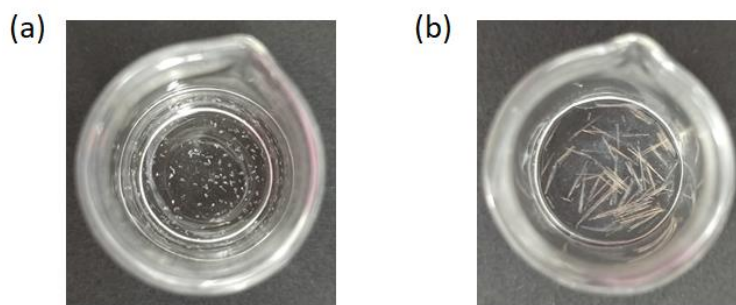


Fig. S4 Macroscopic crystal morphologies of **Zn-Bpe**(a) and **Zn-Bpe-rod**(b).

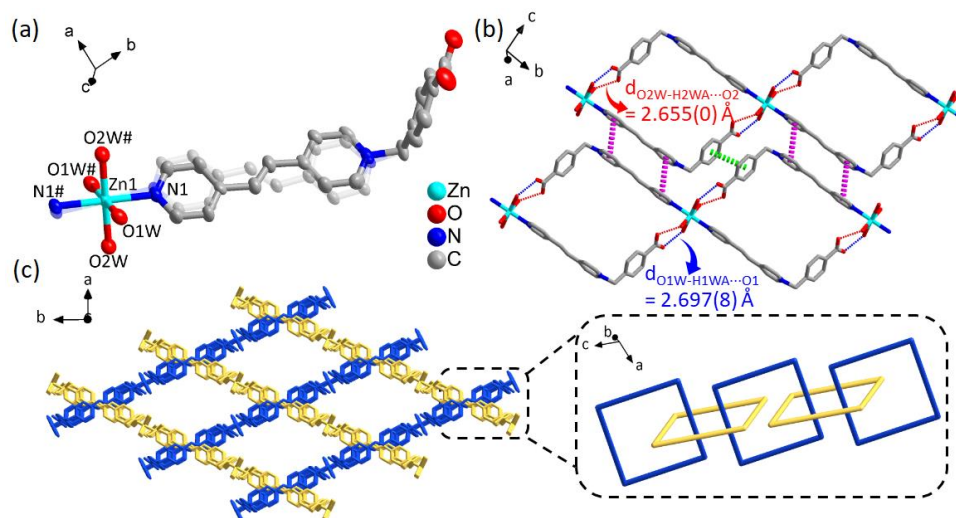


Fig. S5 (a) The coordination environment of Zn(II) ion in **Zn-Bpe-rod**, in which the shading indicates the structure of the split part. #: 1.5-x, 0.5-y, 2-z. (b) The 2D supramolecular layer stabilized by the π - π and cation- π interactions in **Zn-Bpe-rod**. (c) The interpenetrated 3D framework of **Zn-Bpe-rod**. The split part of the crystal is not shown for the brevity of the structure.

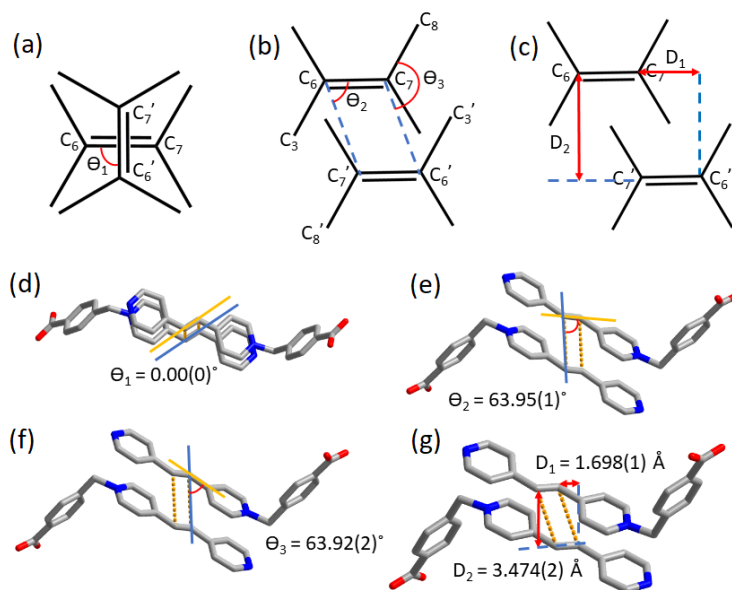


Fig. S6 Some geometric parameters of the olefinic groups in the BCbpe pair in **Zn-Bpe-rod**. The split part of the crystal is not shown for the brevity of the structure, and the distance in the figure is determined by the atoms with higher occupancy.

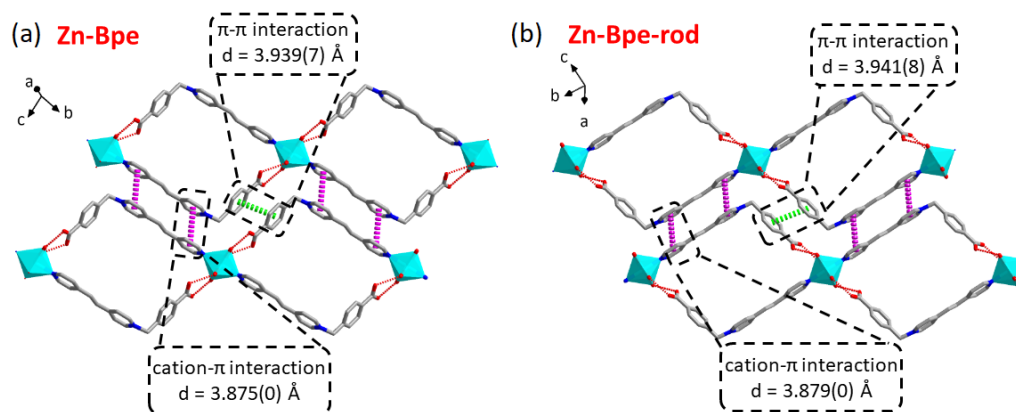


Fig. S7 Comparisons of interactions between two-dimensional supramolecular layers of **Zn-Bpe** and **Zn-Bpe-rod**. The split part of the crystal is not shown for the brevity of the structure, and the distance in the figure is determined by the atoms with higher occupancy.

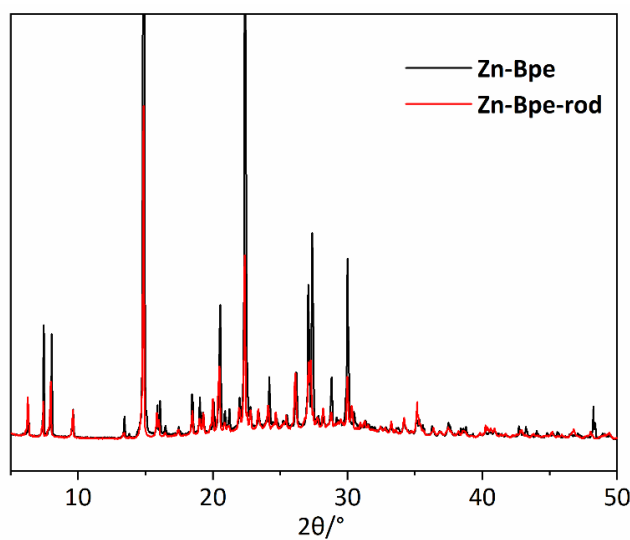


Fig. S8 PXRD patterns of **Zn-Bpe** and **Zn-Bpe-rod**.

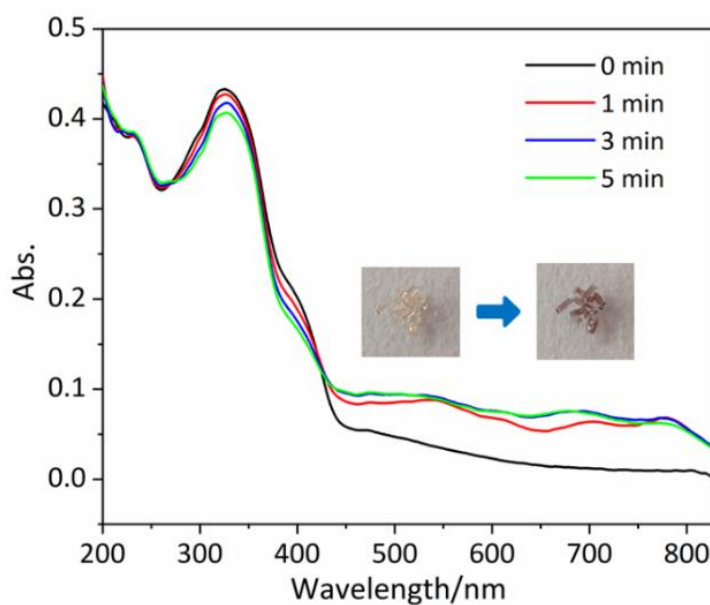


Fig. S9 UV-Vis diffuse reflectance spectral changes of **Zn-Bpe** under 425 nm light irradiation at different time scales.

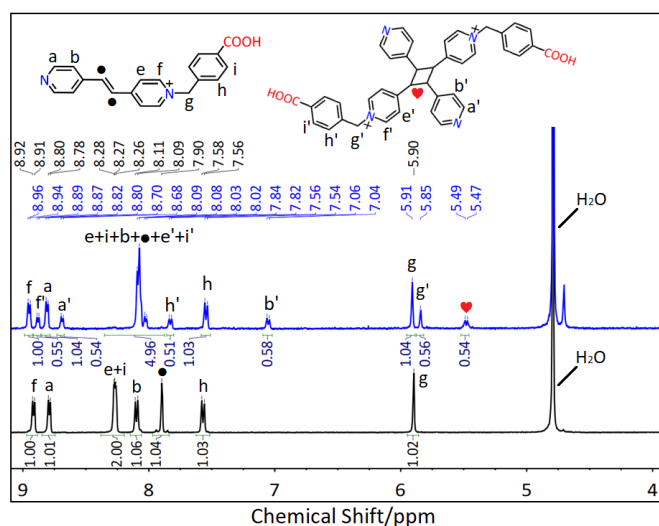


Fig. S10 ^1H NMR spectra (400 MHz, in D_2O digested by DCI) of **Zn-Bpe** (black) and **Zn-365** (blue). The difference in the amount of DCI added has a slight influence on the position of the peak. The hydrogen bond is enhanced due to the addition of DCI, which makes the water peak split more obvious in the ^1H NMR spectra of **Zn-365**.

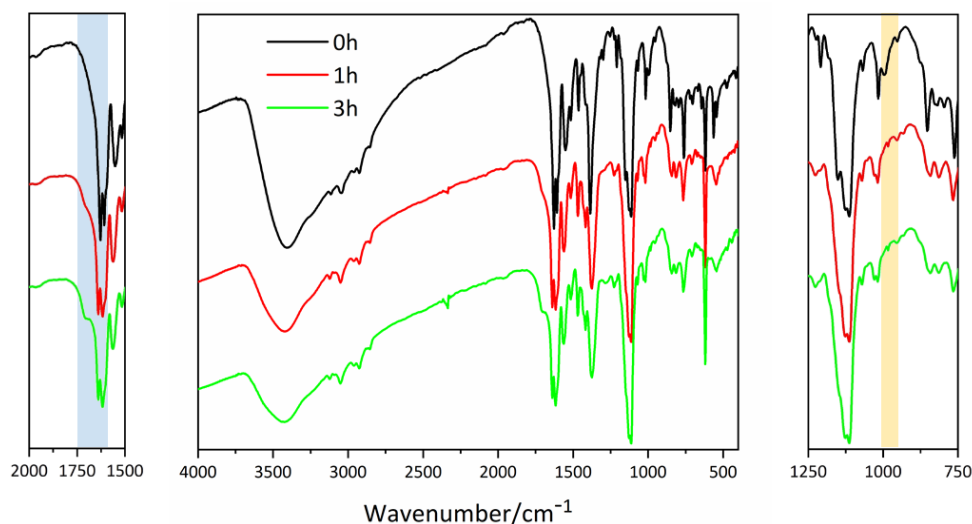


Fig. S11 IR spectra of **Zn-Bpe** under 365 nm light irradiation at different time points.

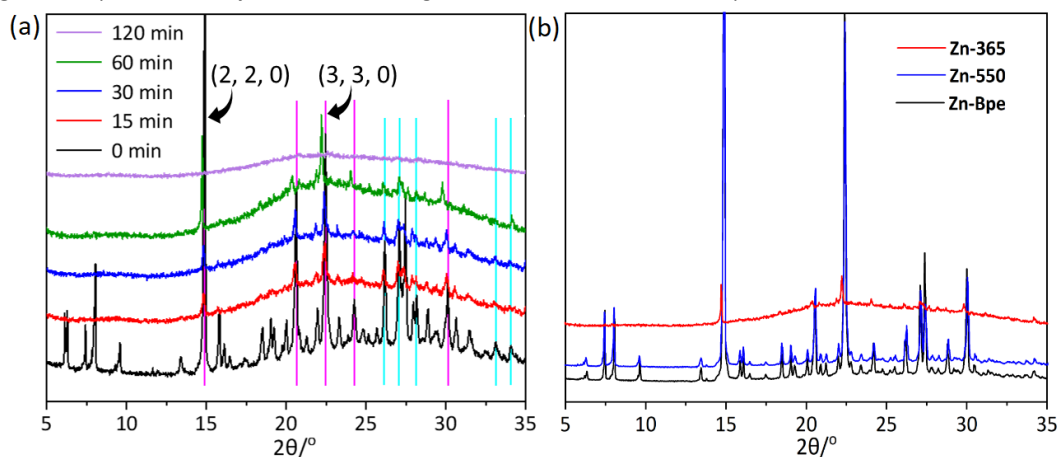


Fig. S12 (a) PXRD patterns of **Zn-Bpe** varied with irradiation times of the 365 nm light source. Cyan lines indicate that diffraction peaks are not shifted, while purple lines indicate that diffraction peaks are shifted. (b) PXRD patterns of **Zn-Bpe**, **Zn-550** and **Zn-365**.

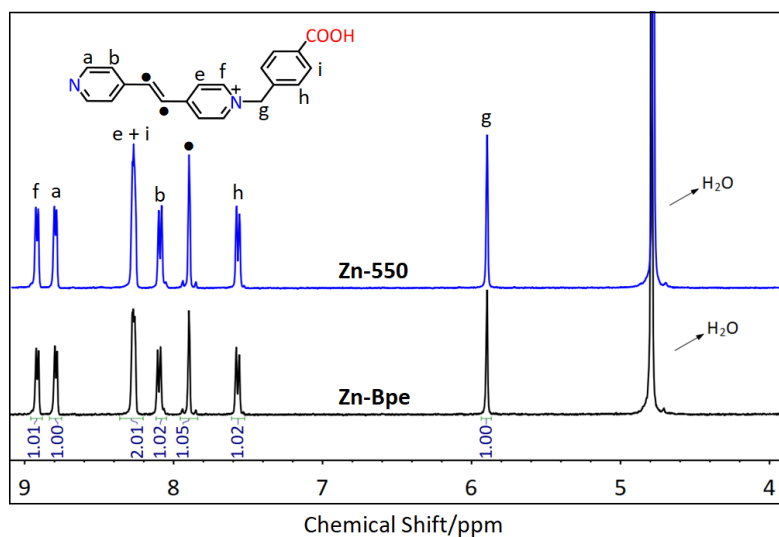


Fig. S13 ^1H NMR spectra (400 MHz, in D_2O digested by DCl) of **Zn-Bpe** and **Zn-550**.

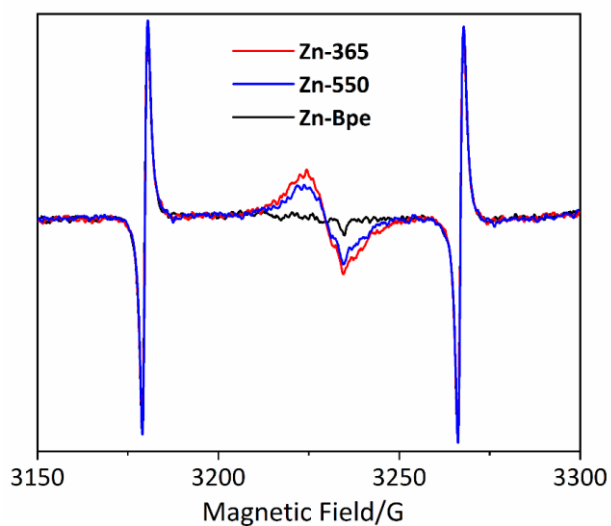


Fig. S14 ESR spectra of **Zn-Bpe**, **Zn-550** and **Zn-365**. The internal standard signals are shown on the two sides.

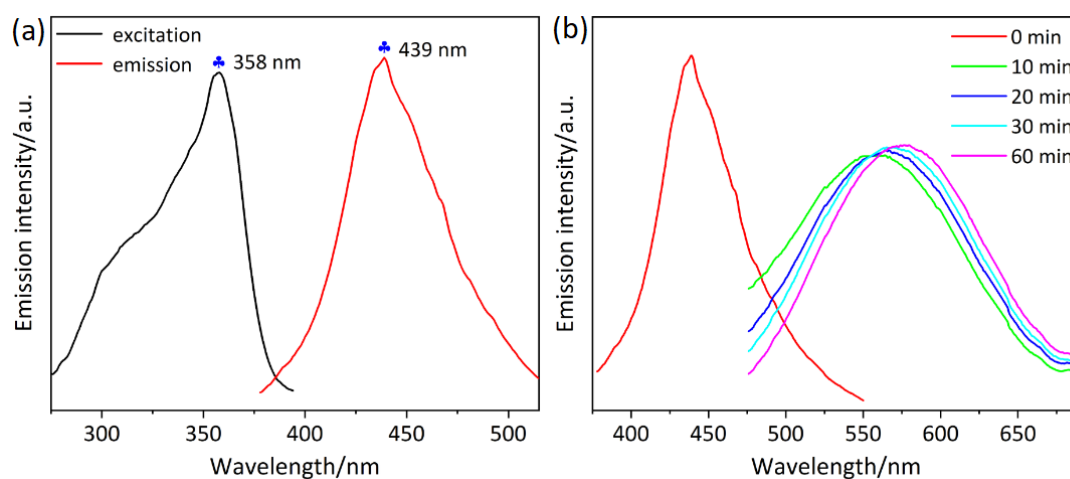


Fig. S15 (a) The excitation and emission spectra of compound **Zn-Bpe**. (b) The emission spectra of **Zn-Bpe** under 365 nm light irradiation at different time points. All emission spectra were obtained upon the excitation at 358 nm.



Fig. S16 Photographs of **Zn-Bpe-rod** (4.70 mm × 0.40 mm × 0.16 mm) before and after irradiation by 550 nm.

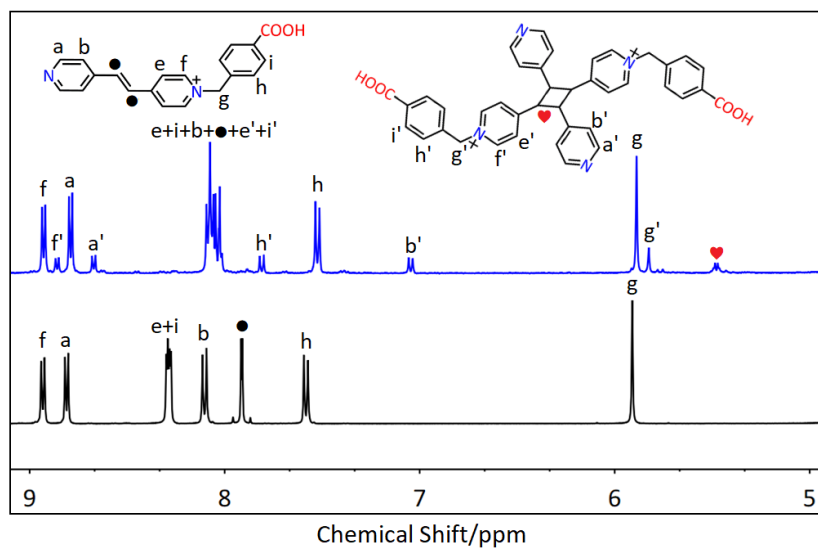


Fig. S17 ^1H NMR spectra (400 MHz, in D_2O digested by DCI) of **Zn-Bpe-rod** before (black) and after (blue) irradiation by 365 nm for 1 h.

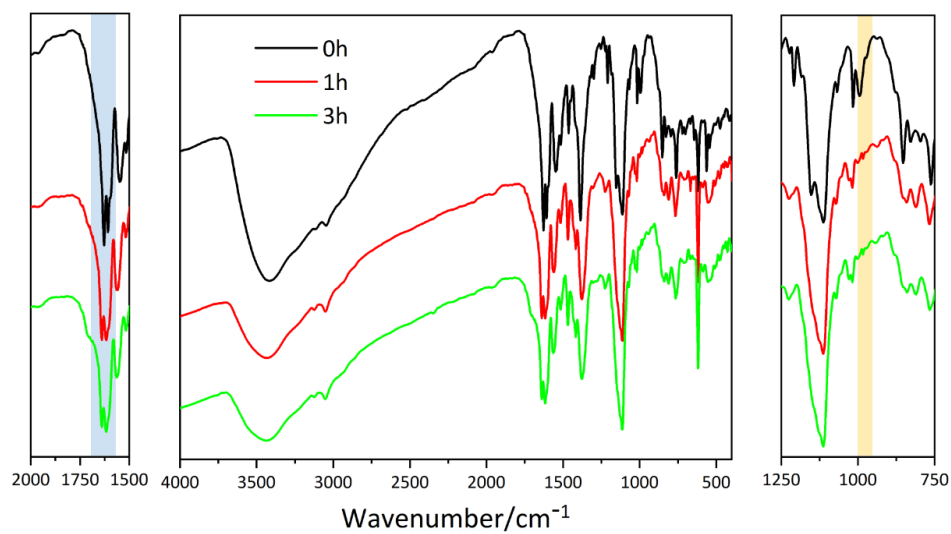


Fig. S18 IR spectral changes of **Zn-Bpe-rod** under 365 nm light irradiation at different time points.

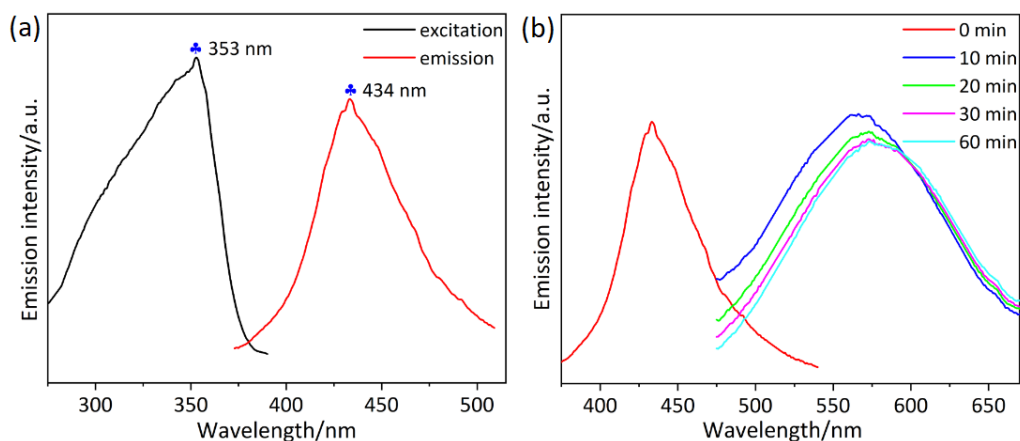


Fig. S19 (a) The excitation and emission spectra of compound **Zn-Bpe-rod**. (b) The emission spectra of **Zn-Bpe-rod** under 365 nm light irradiation at different time points. All emission spectra were obtained upon the excitation at 353 nm.



Fig. S20 Photomechanical bending photographs of **Zn-Bpe-rod** (3.50 mm × 0.20 mm × 0.10 mm) before and after irradiation by 365 nm light.



Fig. S21 Photomechanical bending photographs of **Zn-Bpe-rod** (4.50 mm × 0.30 mm × 0.20 mm) before and after irradiation by 365 nm light.



Fig. S22 Photomechanical bending photographs of **Zn-Bpe-rod** (4.10 mm × 0.35 mm × 0.34 mm) before and after irradiation by 365 nm light.

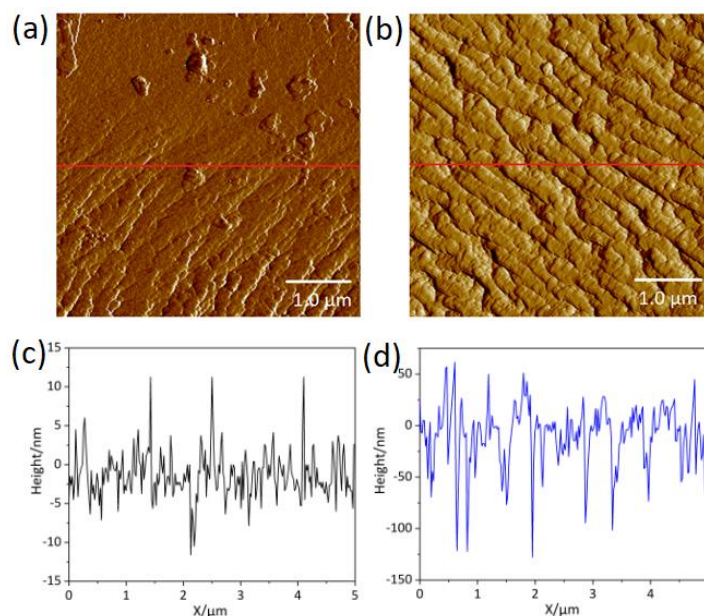


Fig. S23 Two-dimensional AFM images and the corresponding height profiles of a section of a line in **Zn-Bpe-rod** (a, c) and irradiated **Zn-Bpe-rod** (b, d).

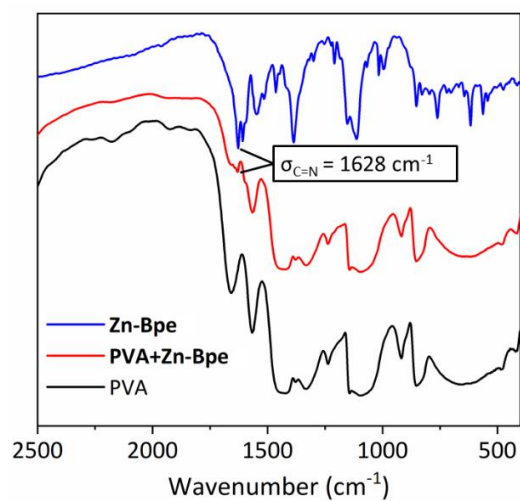


Fig. S24 IR spectra of PVA, PVA+Zn-Bpe and Zn-Bpe at 2500-400 cm^{-1} .

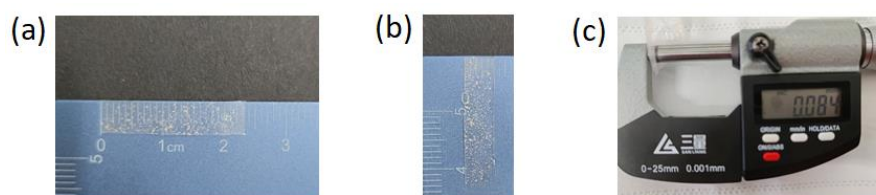


Fig. S25 The cropped length (a), the width (b) and the thickness (c) of **PVA+Zn-Bpe** film.



Fig. S26 The images showing the formation of the flexible joint under 365nm light irradiation.

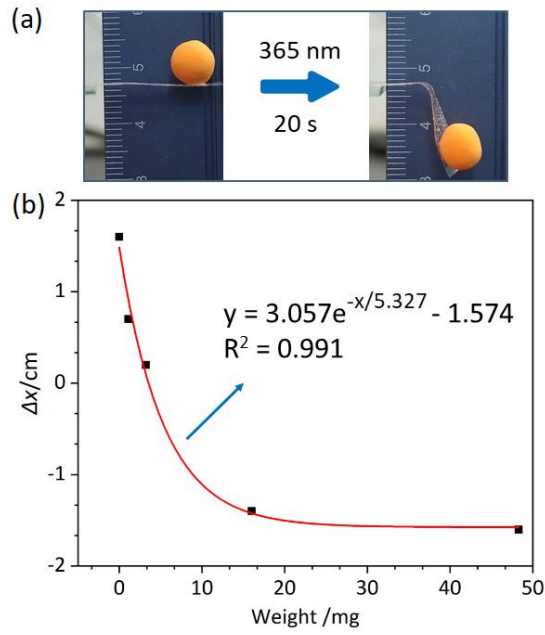


Fig. S27 (a) Photomechanical deformation of the PVA+Zn-Bpe film with 48.3 mg ball upon exposure to 365 nm light. (b) The weight-displacement curve of PVA+Zn-Bpe film.

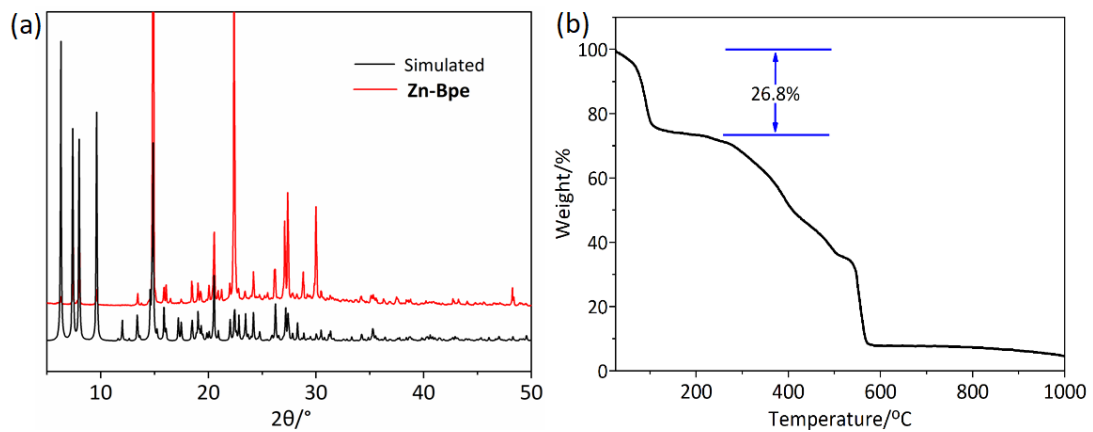


Fig. S28 (a) PXRD patterns of Zn-Bpe. (b) TGA curve of Zn-Bpe.

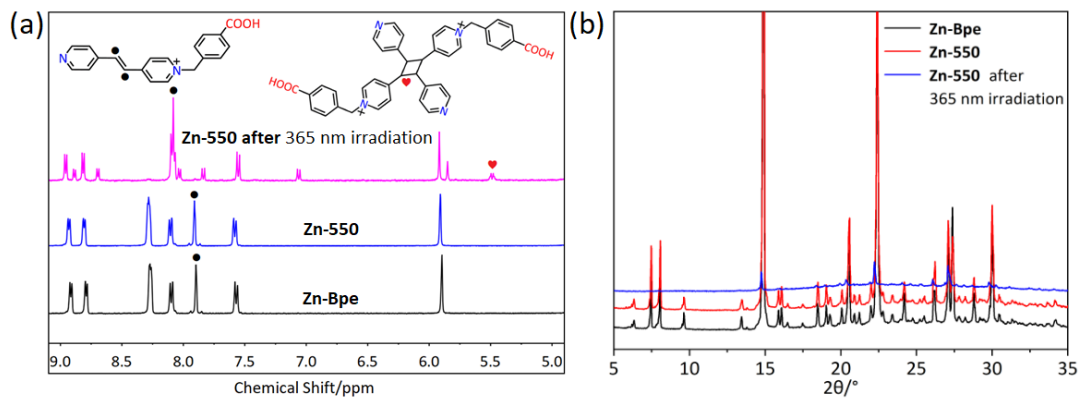


Fig. S29 ^1H NMR spectra (400 MHz, in D_2O digested by DCI) (a) and PXRD patterns (b) of Zn-Bpe, Zn-550 and Zn-550 after 365 nm light irradiation for 1 h.

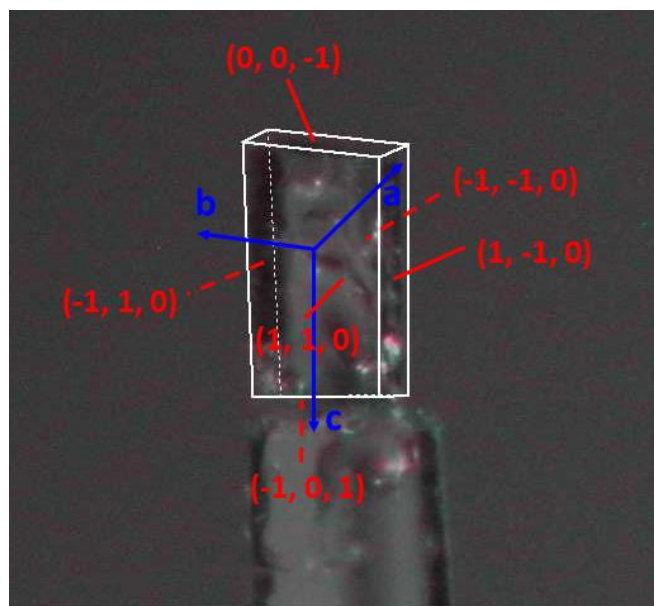


Fig. S30 Face indexing images of Zn-Bpe-rod.

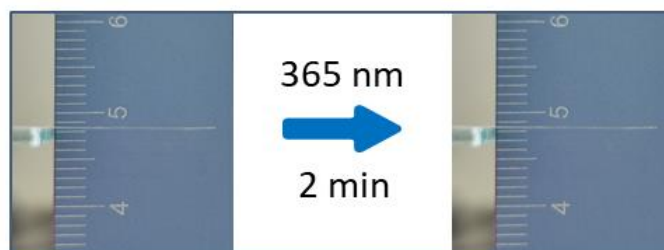


Fig. S31 Photomechanical deformation observation of a PVA film upon exposure to 365 nm light.