

Electronic Supplementary Information (SI) for

**π -Type halogen bonding enhanced long-last room temperature
phosphorescence of Zn(II) coordination polymers for photoelectron
response applications**

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A. Experimental Section.

1. Materials and general procedures.

Analytically pure $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1,10-phenanthroline, 5-bromoisophthalic acid and 4-bromoisophthalic acid were purchased from commercial vendors and used without further purification. Single-crystal X-ray diffraction data for **1** and **2** were collected at room temperature (293K) on an Oxford Diffraction SuperNova area-detector diffractometer using mirror optics monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). CrysAlisPro¹ was used for the data collection, data reduction and empirical absorption correction. The crystal structure were solved by direct methods, using SHELXS-2014 and least-squares refined with SHELXL-2014 using anisotropic thermal displacement parameters for all non-hydrogen atoms.^{2,3} The crystallographic data for **1** and **2** are listed in Table S1. The CIF file of **1** and **2** (CCDC Nos. 1983256 and 1983257) can be downloaded free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

PXRD patterns were collected on a Bruker D8-ADVANCE X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Measurements were made in a 2θ range of $5\text{--}50^\circ$ at room temperature with a step of 0.02° (2θ) and a counting time of 0.2 s/ step. The operating power was 40 KV, 40 mA. Thermogravimetric analysis (TGA) experiments were carried out using SII EXSTAR6000 TG/DTA6300 thermal analyzer from room temperature to $800 \text{ }^\circ\text{C}$ under a nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The infrared spectra ($4000\text{--}400\text{cm}^{-1}$) were recorded on a NICOLET 6700

FT-IR spectrometer by incorporating the samples in KBr disks. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Vario EL III elemental analyzer. Room temperature photoluminescence (PL) spectra and time-resolved lifetime were conducted on an Edinburgh FLS1000 fluorescence spectrometer. The fluorescence spectra were measured by a continuous radiation of xenon arc lamp (Xe900). While the phosphorescence spectra and phosphorescence decay curves were tested by a pulsing radiation of microsecond flash lamp with time-resolved single photon counting–multi-channel scaling (MCS) mode. The phosphorescence quantum yields (QY) at room temperature were estimated using an integrating sphere (F-M101, Edinburgh) accessory in FLS1000 fluorescence spectrometer.

Optoelectronic properties were conducted by a Chenhua CHI 660E electrochemical workstation. Using **1** and **2** powder modified indium tin oxide (ITO) electrode (with a working area of 1.0 cm²), Ag/AgCl, and platinum wire as working, reference, and counter electrodes, respectively. The electrolyte is 0.5 M sodium sulfate aqueous solution. The system was conducted in a quartz glass reactor ca. 50 cm³ and irradiated by a 300 W xenon lamp. Transient photocurrent responses with the on–off cycle's illumination were tested in three-electrode system at ambient pressure and room temperature.

2. Synthesis of 1 and 2

Synthesis of [Zn(5-BIPA)(phen)] (1).

A mixture of 5-bromoisophthalic acid (0.5 mmol, 122.50 mg), 1,10-phenanthroline (0.5 mmol, 99.10 mg), Zn(NO₃)₂·6H₂O (1 mmol, 290.81 mg), and H₂O (10 mL) was

sealed in a 25 mL Teflon-lined stainless steel vessel reactor. The mixture was heated at 120 °C for 72 hours, and then cooled to room temperature over 24 hours. Colorless block crystals of **1** were obtained, which were washed with water and ethanol several times, then dried in natural environment. Elemental analysis: Calc. (%) for $C_{40}H_{22}Zn_2N_4O_8Br_2$: C, 49.16; H, 2.27; N, 5.73; found (%): C, 49.47; H, 2.73; N, 5.33.

Synthesis of [Zn(4-BIPA)(phen)] (2)

The synthesis of **2** was similar to that of **1** except that 5-bromoisophthalic acid was replaced by 4-bromoisophthalic acid (0.5 mmol, 122.50 mg). Colorless block crystals of **2** were obtained, which were washed with water and ethanol several times, then dried in natural environment. Elemental analysis: Calc. (%) for $C_{20}H_{11}ZnN_2O_4Br$: C, 49.16; H, 2.27; N, 5.73; found (%): C, 49.88; H, 2.69; N, 5.98.

3. Preparation of working electrode

The ITO ($1 \times 4 \text{ cm}^2$) substrate was washed by ethanol, and water under ultrasonic processing for about 30 min then dried in natural environment. The complex powders (10 mg) were added into 10 μL Nafion and 1 mL anhydrous ethanol mixed solution and ultrasonicated for 30 min to form suspension liquid. The working electrodes were prepared by dropping the above suspension (0.2 mL) onto the surface of the pre-treated ITO by controlling the coating area about 1 cm^2 , and allowing it to dry at room temperature.

4. Electronic structure calculations

All calculations were performed with the periodic density functional theory (DFT) method using Dmol³ module in Material Studio software package.⁴ The initial

configuration was fully optimized by Perdew-Wang (PW91) generalized gradient approximation (GGA) method with the double numerical basis sets plus polarization function (DNP).⁵⁻⁷ The core electrons for metals were treated by effective core potentials (ECP). The self-consistent field (SCF) converged criterion was within 1.0×10^{-5} hartree atom⁻¹ and the converging criterion of the structure optimization was 1.0×10^{-3} hartree bohr⁻¹. The Brillouin zone is sampled by $1 \times 1 \times 1$ k-points, and test calculations reveal that the increase of k-points does not affect the results.

B. Supporting Figures

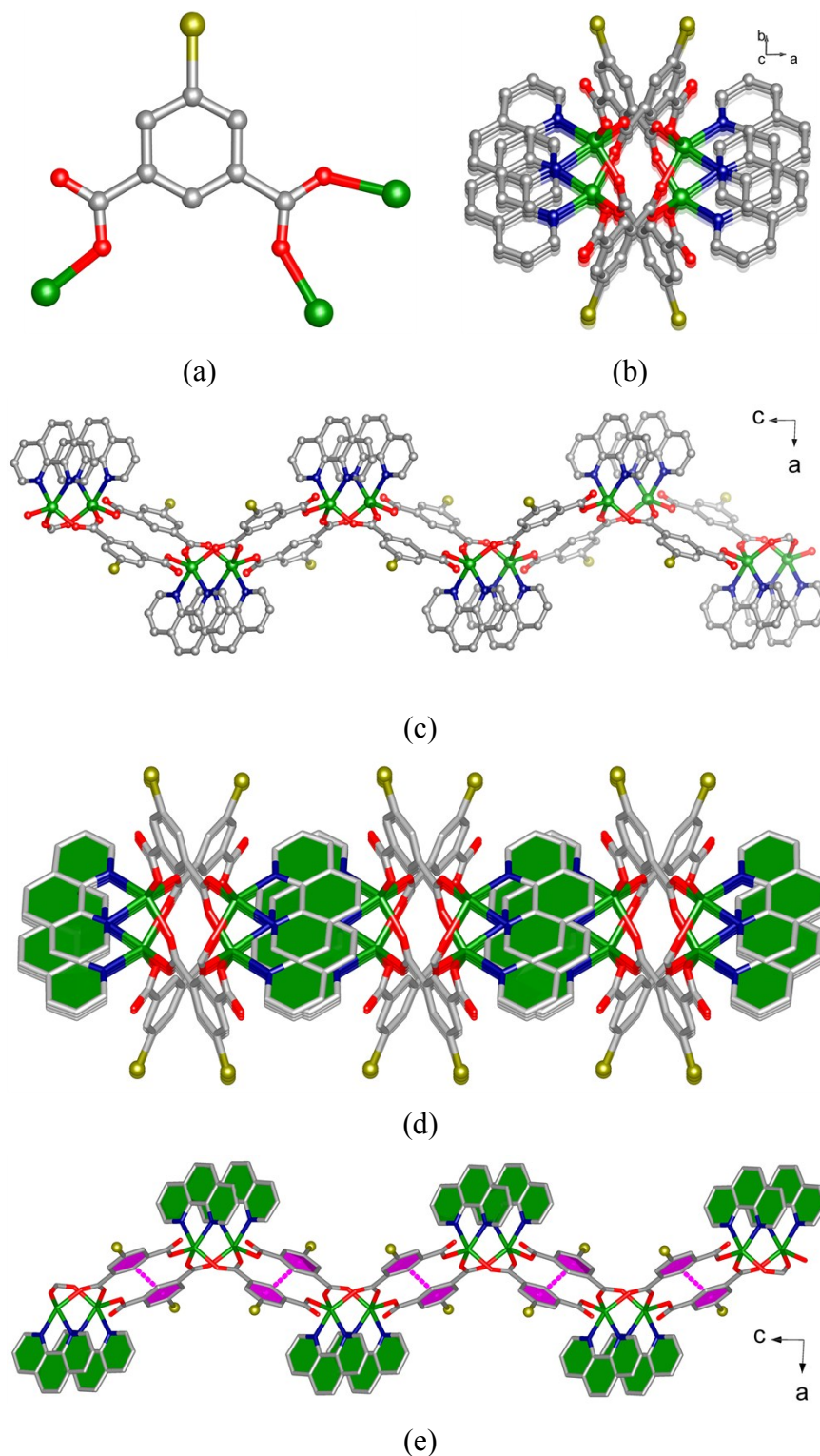


Figure S1. (a) View of the coordination mode of 5-BIPA in **1**. View of 1D chain along *c* (b) and *b* (c) direction. (d) View of 2D layer along *c* direction extended by $\pi \cdots \pi$ stacking between phen. (e) $\pi \cdots \pi$ stacking between benzene rings of 5-BIPA from different chains.

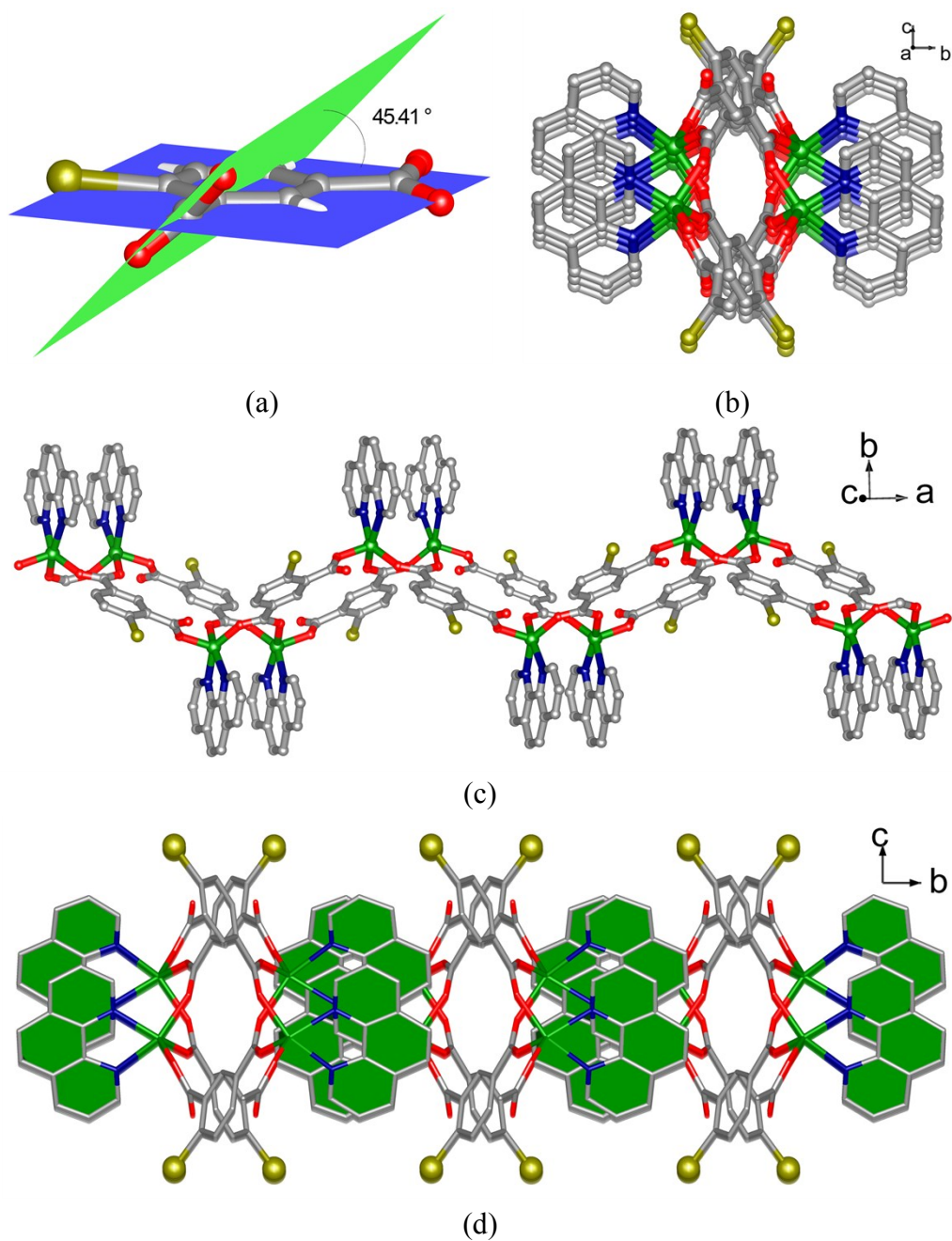
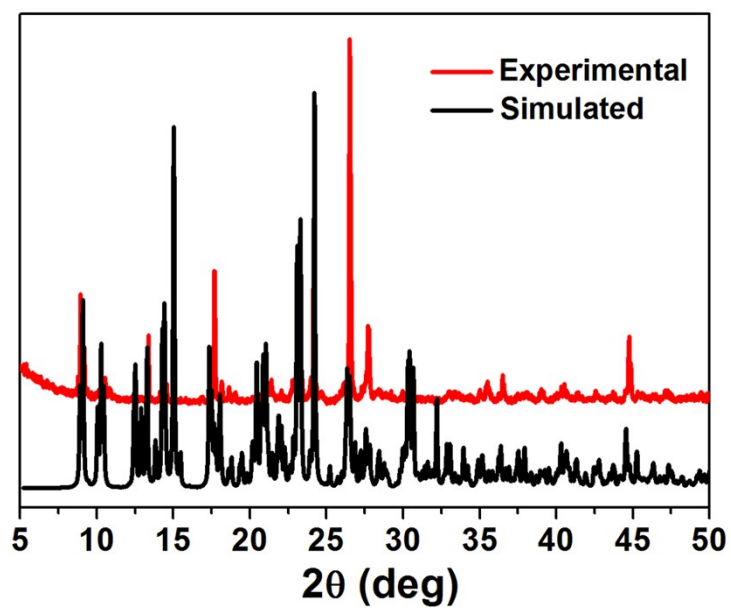
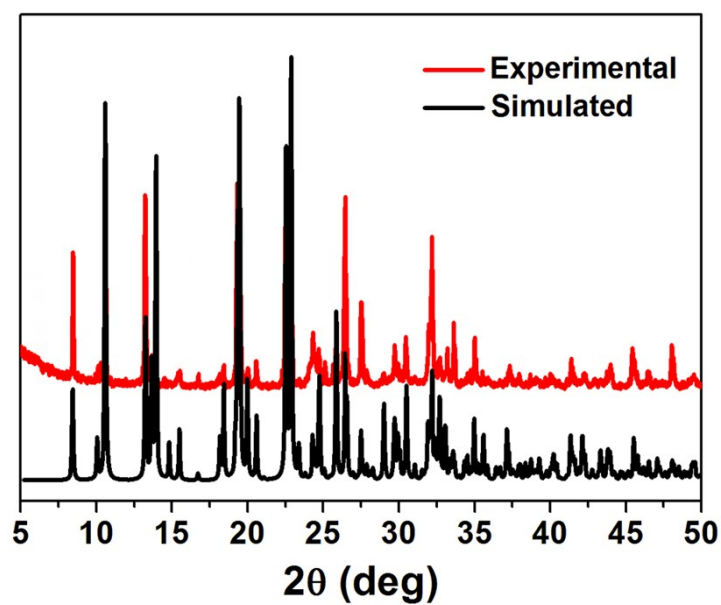


Figure S2. (a) The torsion angle between carboxylic group and benzene ring of 5-BIPA in **2**. View of 1D chain along *a* (b) and *c* (c) direction. (d) View of 2D layer along *a* direction extended by $\pi \cdots \pi$ stacking between phen.

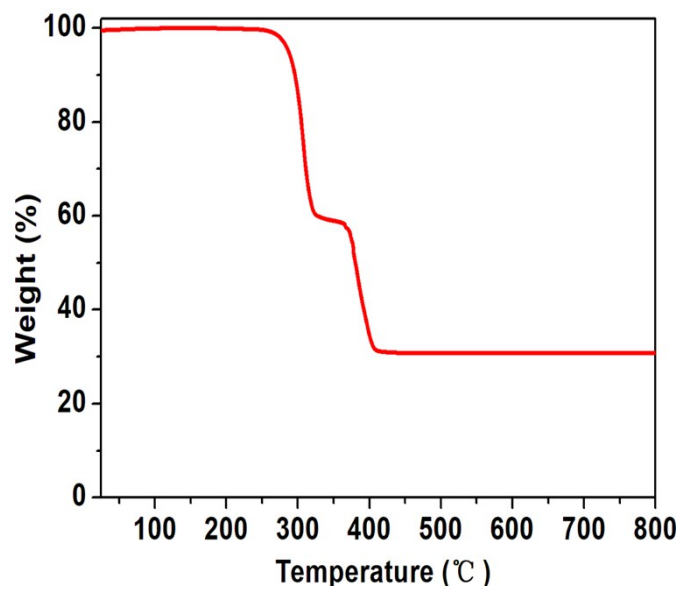


(a)

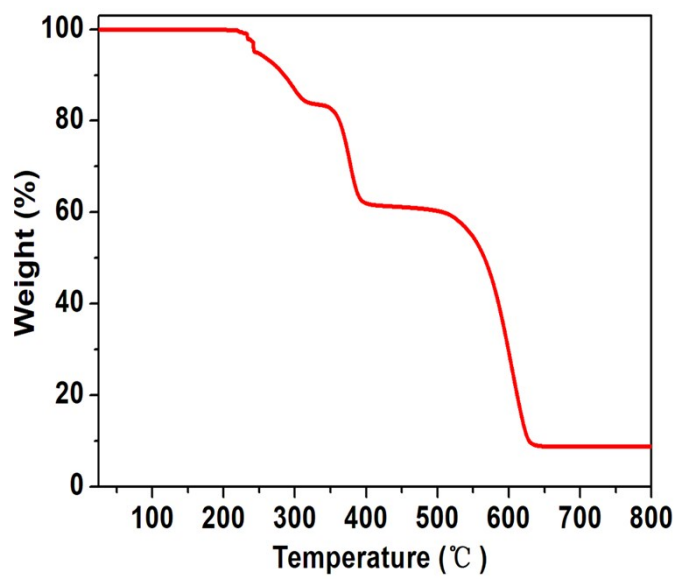


(b)

Figure S3. PXRD patterns of 1 (a) and 2 (b) crystal samples.

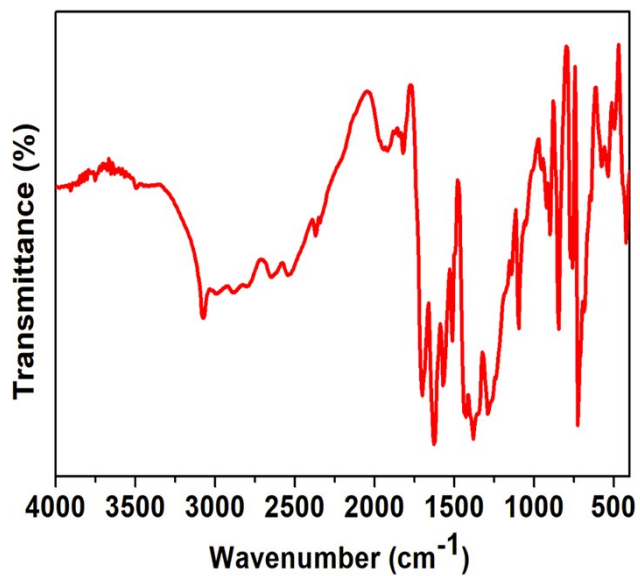


(a)

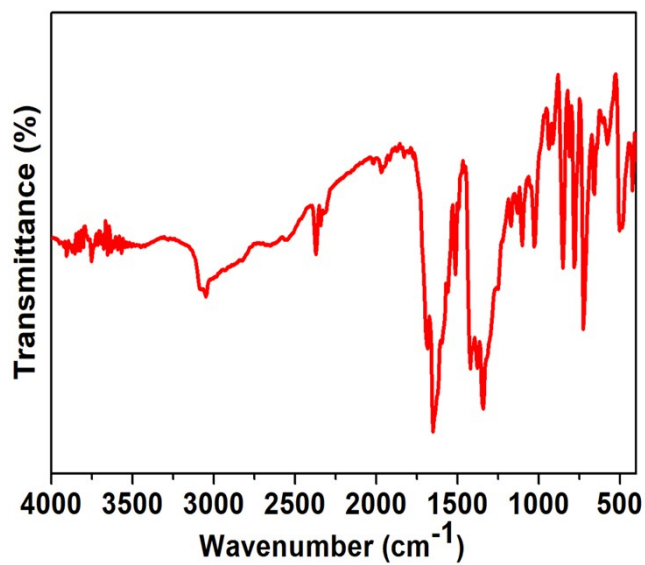


(b)

Figure S4. Thermogravimetric analysis (TGA) curves for **1** (a) and **2** (b) crystal samples.



(a)



(b)

Figure S5. FT-IR spectra of **1** (a) and **2** (b) crystal samples.

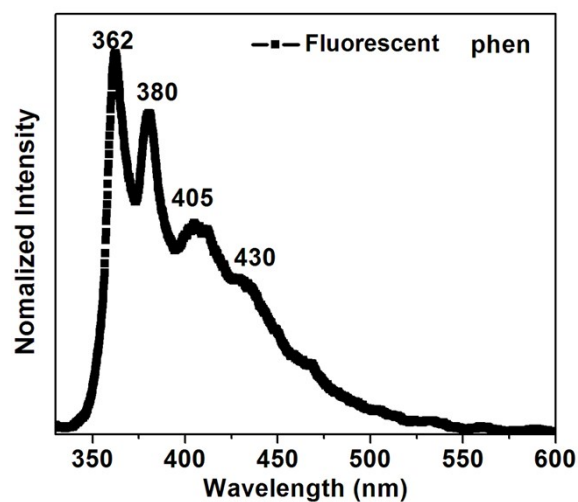


Figure S6. Fluorescence spectra of free phen in solid measured at room temperature.

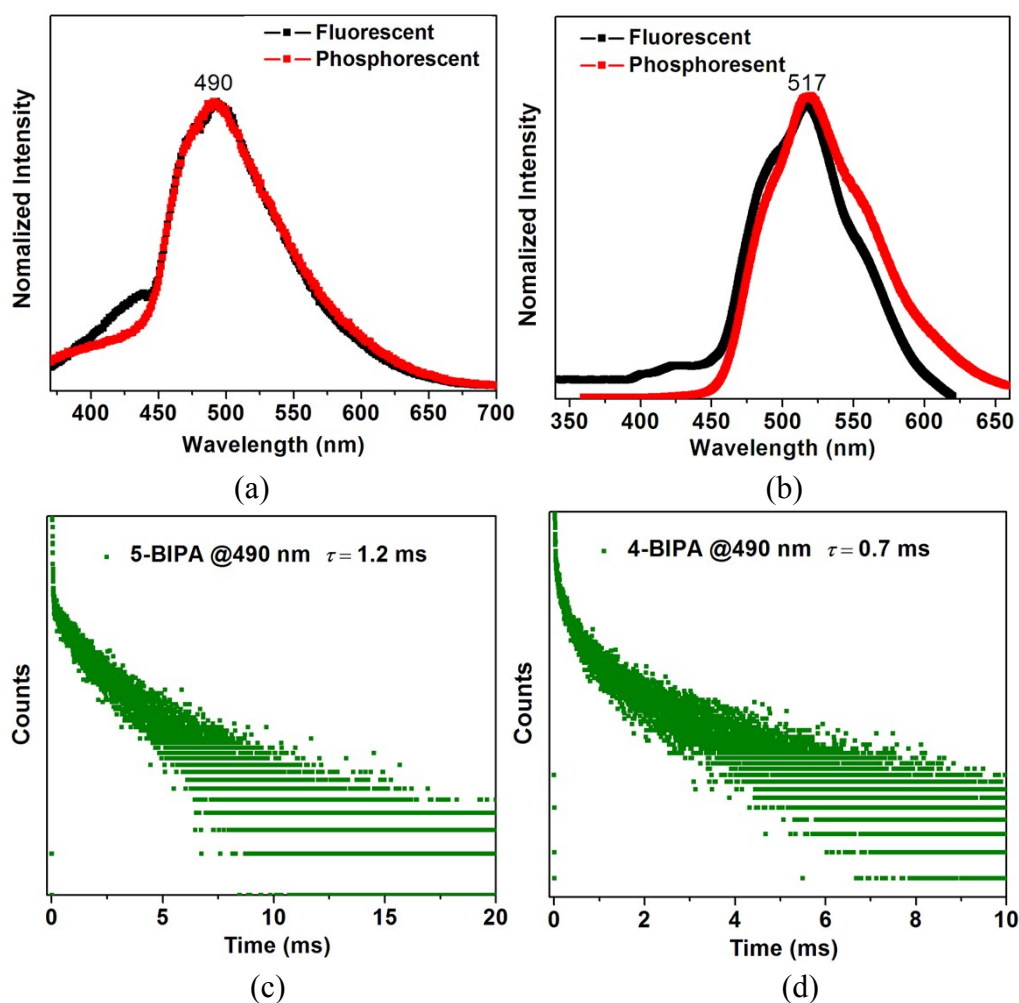


Figure S7. Normalized photoluminescence (black line) and/or phosphorescence spectra (red line) of 5-BIPA (a) and 4-BIPA (b). Phosphorescence decay curves of 5-BIPA (c) and 4-BIPA (d) measured at room temperature.

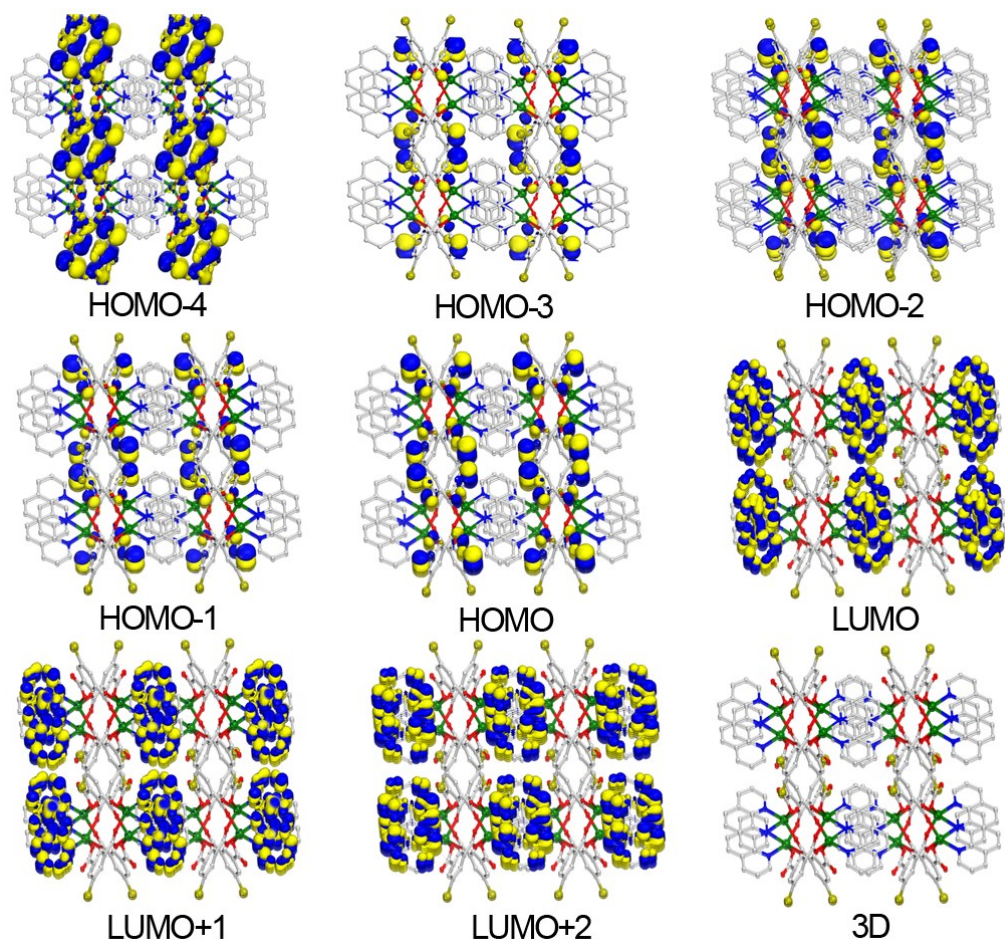


Figure S8. View of the 3D network, the distributions of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of **1** along *c* direction. It can be observed that LUMOs are mainly located on the phen ligand in **1**. HOMO, HOMO-1, HOMO-2 and HOMO-3 are occupied by $-\text{COO}^-$ groups. While HOMO-4 distributes on the whole 5-BIPA ligands including the Br atoms.

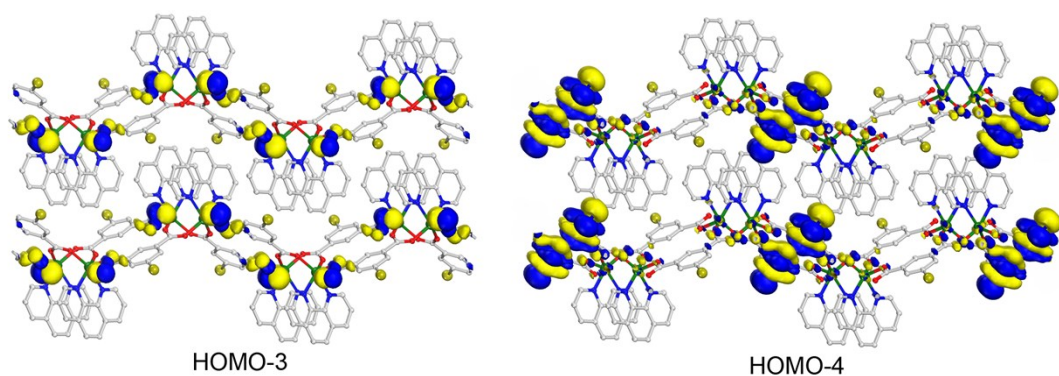


Figure S9. View of HOMO-3 and HOMO-4 of **1** along *b* direction.

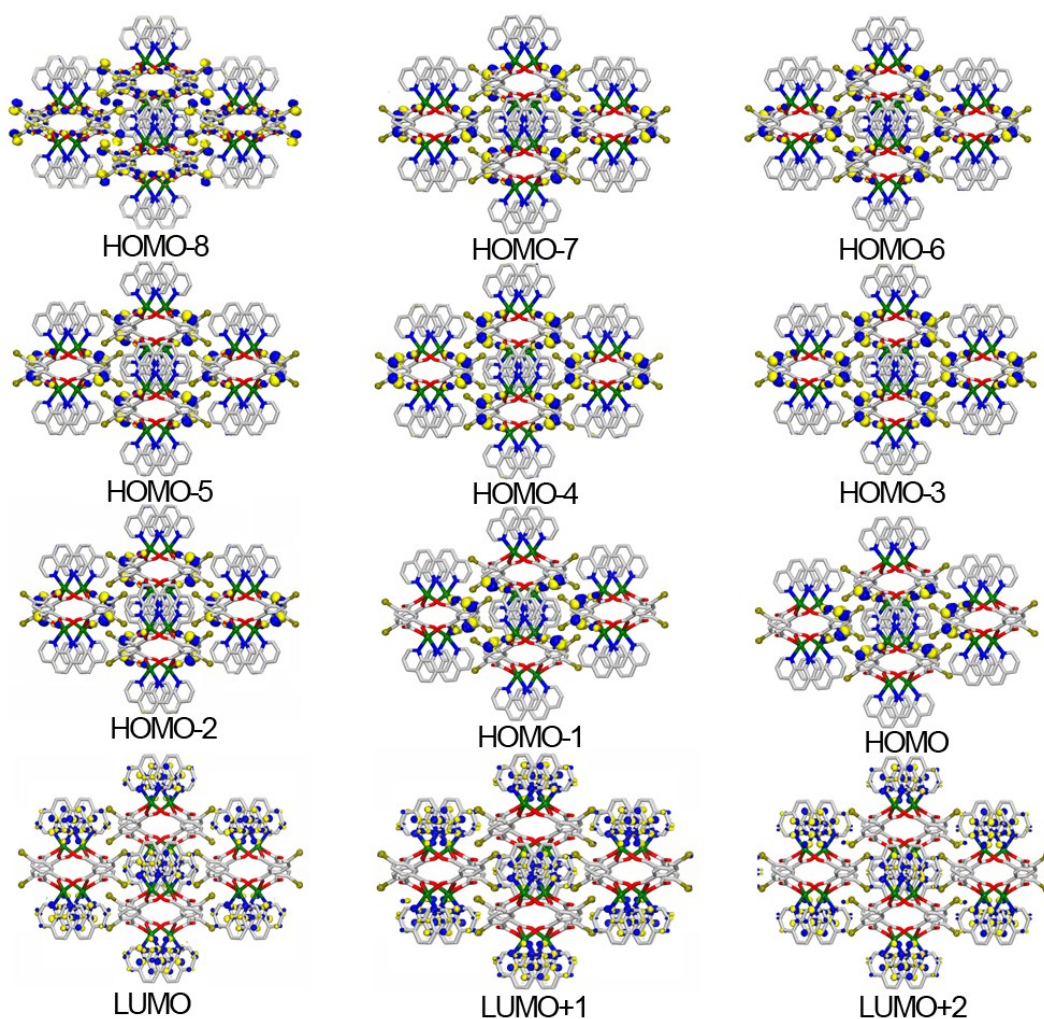


Figure S10. View of the 3D network, the distributions of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of **2** along a direction. It can be observed that LUMOs are mainly located on the phen ligand in **2**. HOMO to HOMO-7 are occupied by -COO^- groups. While HOMO-8 distributes on the Br atoms and -COO^- groups.

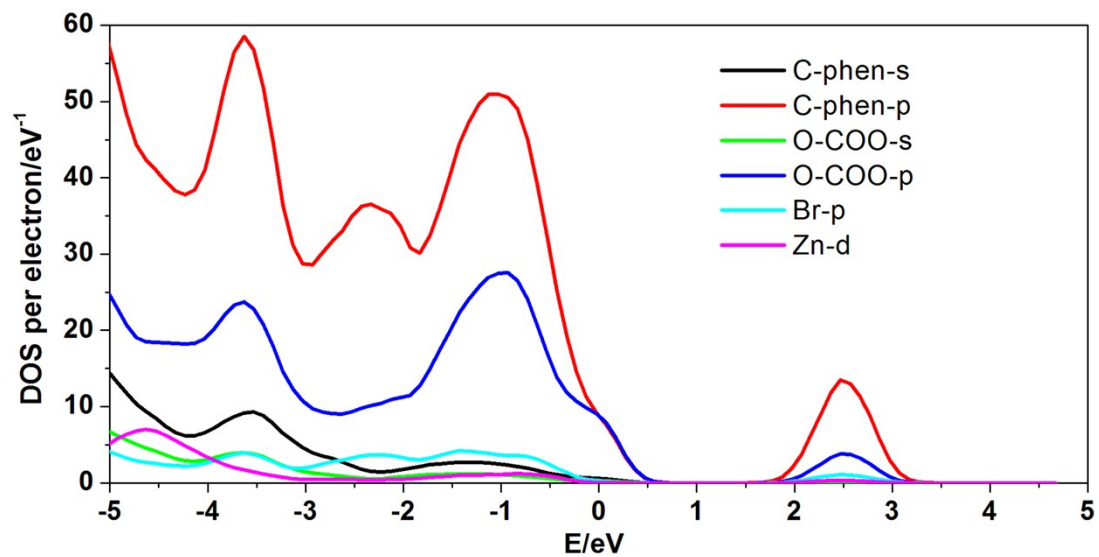


Figure S11. TDOS/PDOS for the profiles based on PDFT calculations on 2.

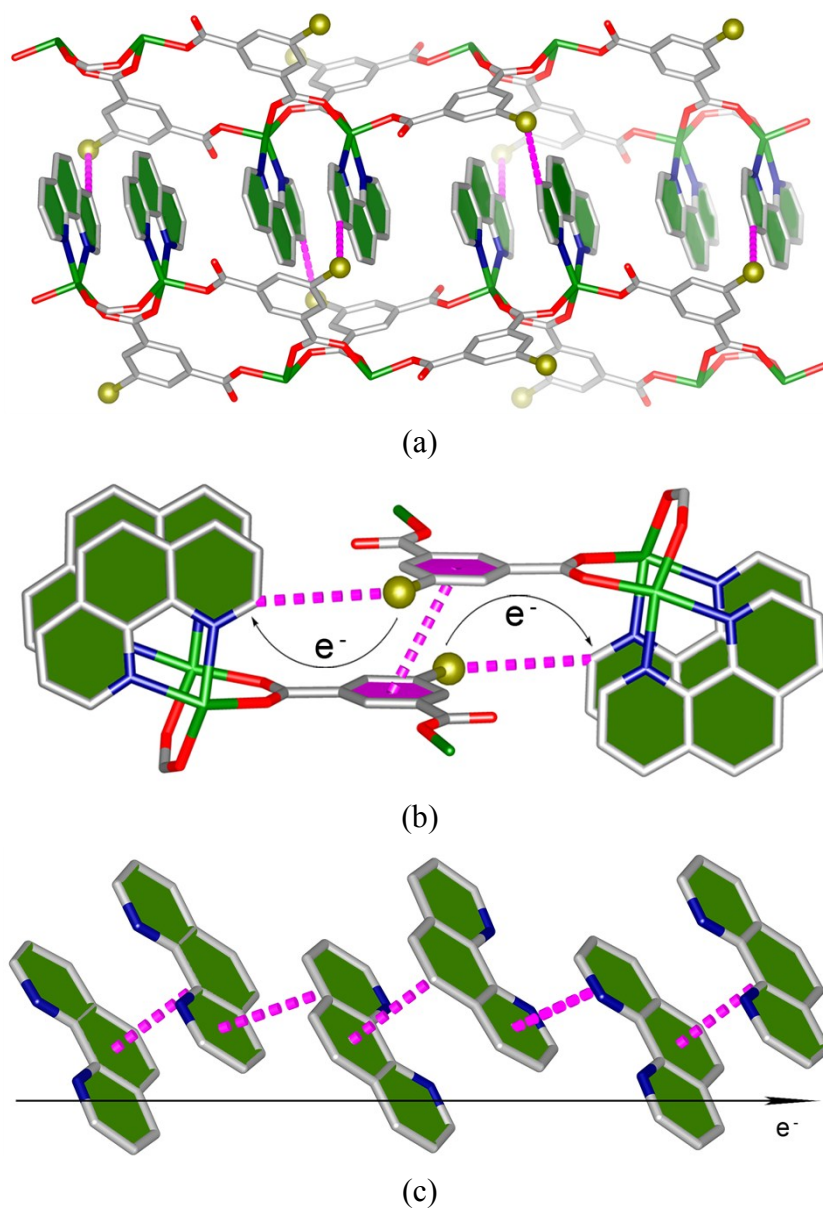


Figure S12. (a) View of the electronic transmission channel in **1**. Delivery of photoexcited electrons from the delocalized 5-BIPA dimer to phen π -conjugated chains (b) then along the phen π -conjugated chains (c) .

C. Supporting Table

Table S1. Crystallographic data for **1** and **2**

Samples	1	2
Chemical formula	C ₄₀ H ₂₂ Zn ₂ N ₄ O ₈ Br ₂	C ₂₀ H ₁₁ ZnN ₂ O ₄ Br
Formula weight	977.24	488.62
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>I</i> 2/ <i>a</i>
<i>a</i> (Å)	10.1741(10)	16.7940(9)
<i>b</i> (Å)	10.1742(10)	9.8691(6)
<i>c</i> (Å)	17.9893(13)	21.4927(11)
α (°)	77.504(7)	90
β (°)	86.836(7)	93.085(4)
γ (°)	87.221(8)	90
<i>V</i> (Å ³)	1814.0(3)	3557.1(3)
<i>Z</i>	2	8
<i>D</i> (g cm ⁻³)	1.7890	1.8427
μ (mm ⁻¹)	30587	3.658
<i>R</i> _{int}	0.0471	0.0297
Goof	1.070	1.040
<i>R</i> ₁ ^a (<i>I</i> > 2σ(<i>I</i>))	0.0860	0.0416
<i>wR</i> ₂ ^a (<i>I</i> > 2σ(<i>I</i>))	0.2075	0.0757

^a $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; ^b $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

D. Supporting References

- 1 CrysAlisPro, Rigaku Oxford Diffraction, Version 1.171.39.6a.
- 2 G. M. Sheldrick, A short history of SHELX. *Acta Crystallogr. Sect. A.*, 2008, **A64**, 112–122.
- 3 G. M. Sheldrick, SHELXT–Integrated space-group and crystal-structure determination. *Acta Cryst.*, 2015, **A71**, 3–8.
- 4 B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys.*, 1990, **92**, 508–517.
- 5 Dmol³ Module, MS Modeling, Version 2.2; Accelrys Inc.: San, Diego, 2003.
- 6 B. Delley, From molecules to solids with the DMol³ approach. *J. Chem. Phys.*, 2000, **113**, 7756–7764.
- 7 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B.*, 1992, **46**, 6671–6687.