Electronic Supporting Information

Room Temperature Phosphorescence of Mn(II) and Zn(II) Coordination Polymers for Photoelectron Response Applications

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A. Experimental Section.

1. Materials and general procedures. All of the chemicals and reagents are commercially available and can be used directly without secondary treatment. Single-crystal X-ray diffraction data for $[Mn_{0.5}(NH_3IPA)(H_2O)]$ (Mn-CP) and $[Zn(NH_2IPA)(H_2O)]$ (Zn-CP) were collected at room temperature on an Oxford Diffraction SuperNova area-detector diffractometer using mirror optics monochromated Mo Kα radiation (λ = 0.71073 Å). The data collection, data reduction and empirical absorption correction were obtained by using CrysAlisPro.[1] The crystal structure was solved by using SHELXS-2014 and least-squares refined with SHELXL-2014,[2] and using anisotropic thermal displacement parameters for all non-hydrogen atoms. The crystallographic data for Mn-CP and Zn-CP are listed in Table S1. The crystallographic data for Mn-CP and Zn-CP are listed in Table S1. CCDC Nos. 1917025 and 1917026 contain the supplementary crystallographic data for Mn-CP and Zn-CP, respectively. This material can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

The powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8-ADVANCE X-ray diffractometer with Cu *Kα* radiation (λ = 1.5418 Å). Measurements were made in a 2θ range of 5−50° at room temperature with a step of 0.02° (2θ), a counting time of 0.2 s/ step and 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 ^{o}C under a nitrogen atmosphere at a heating rate of 10 ^{o}C min^{-1}. The C, H, N analyses were carried out using a Perkin–Elmer Elementarvario elemental analysis instrument.

Photographs of $NH_3IPA \cdot 0.5H_2O$, NH_2IPA, Mn-CP and Zn-CP under UV excitation (365 nm) and day light were captured using a Canon digital camera (EOS 700D: the ISO value was 400, time of exposure was set to an automatic mode). 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) accessary in FLS1000 fluorescence spectrometer.

Optoelectronic measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China) in a standard three-electrode system using Mn/Zn-CP powder modified indium tin oxide (ITO) as the working electrode with a working area of 1.0 cm^2, a platinum wire electrode as a counter electrode, Ag/AgCl as a reference electrode, and 0.5 M Na_2SO_4 aqueous solution as electrolyte. The system was conducted in a quartz glass reactor ca. 50 cm^3, and irradiated by a 300 W xenon lamp. The cyclic voltammograms (CV) was measured with a scan rate of 50 mV/s. Transient current density–time characteristics was tested at bias potential of 0 and -0.6 V vs. Ag/AgCl, respectively.

2. Synthesis of Mn-CP and Zn-CP crystals

2.1 Synthesis of Mn-CP crystals

A mixture of $NH_3IPA \cdot 0.5H_2O$ (0.5 mmol, 90.5 mg), $MnSO_4 \cdot H_2O$ (1 mmol, 169.0 mg), acetonitrile (2mL) and H_2O (6 mL) was placed in a Teflon-lined stainless steel vessel, heated to 120 °C for three days, and then cooled to room temperature naturally. Light pink block crystals of Mn-CP were obtained, which were filtered, washed with water and ethanol several times, then dried under room temperature. Elemental analysis: Calc. (%) for $C_8H_8Mn_{0.5}NO_5$: C, 42.59; H, 3.57; N, 6.21; found (%): C, 43.11; H, 3.99; N, 6.79.

2.1 Synthesis of Zn-CP crystals

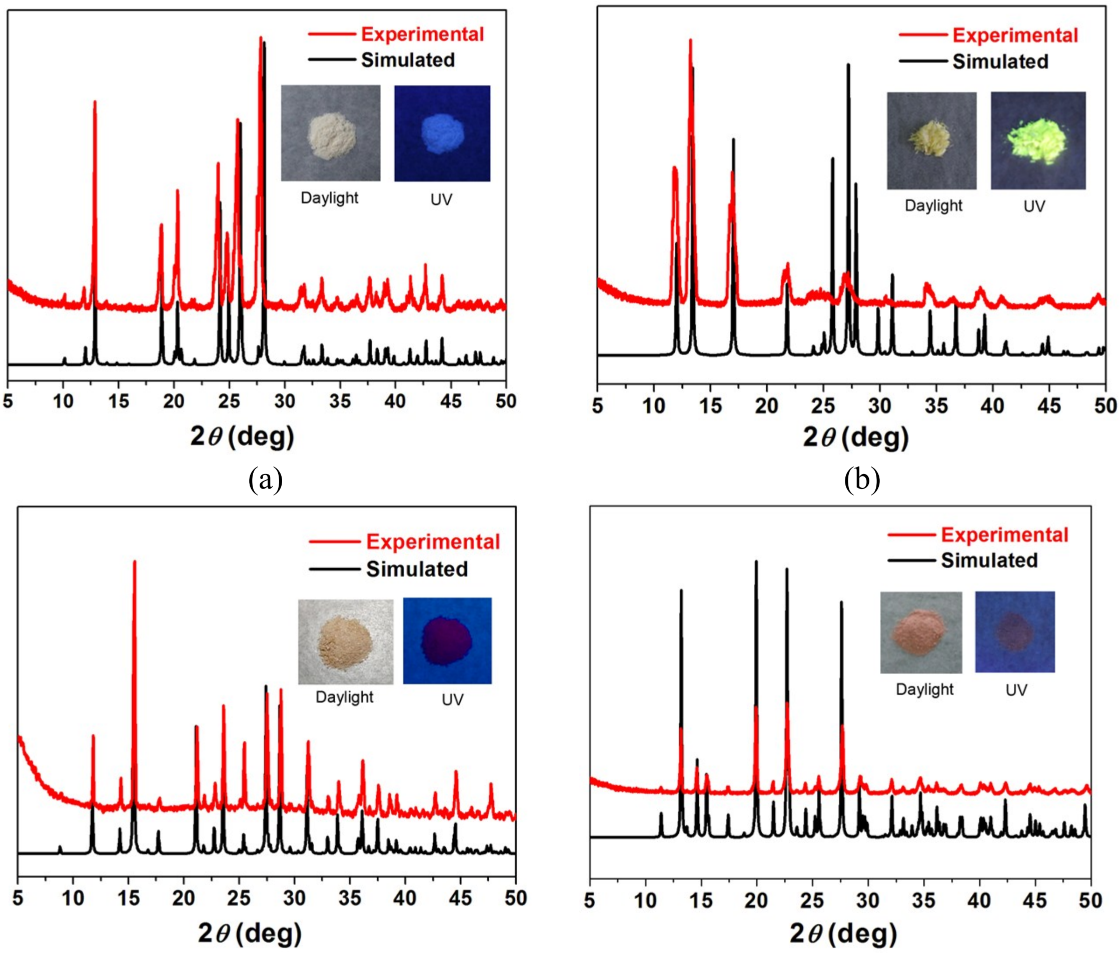
A mixture of $NH_3IPA \cdot 0.5H_2O$ (0.5 mmol, 90.5 mg), $ZnSO_4 \cdot 7H_2O$ (1 mmol, 287.5 mg), acetonitrile (2mL) and H_2O (6 mL) was placed in a Teflon-lined stainless steel vessel, heated to 120 °C for three days, and then cooled to room temperature naturally. Light brown block crystals of Zn-CP were obtained, which were filtered, washed with water and ethanol several times, then dried under room temperature. Elemental analysis: Calc. (%) for $C_8H_7ZnNO_5$: C, 36.59; H, 2.69; N, 5.34; found (%): C, 37.02; H, 2.09; N, 6.03.

Crystalline state of $NH_3IPA \cdot 0.5H_2O$ sample was commercially available from Tokyo Chemical Industry Co. Ltd. A mixture of $NH_3IPA \cdot 0.5H_2O$ (1 mmol, 181.0 mg) and EtOH (8 mL) was placed in a Teflon-lined stainless steel vessel, heated to 120 °C for 4 h, and then cooled to room temperature naturally. Light yellow block crystals of NH_2IPA can obtained from the clear liquid.

3. Electronic structure calculations

All calculations were performed with the density functional theory (DFT) method using Dmol^3 module in Material Studio software package.[3] Herein, the structure mode were directly used from the “cif” files of $NH_3IPA\cdot 0.5H_2O$, NH_2IPA and Mn/Zn-CP. 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).

B. Supporting Figures



(a) (b) (c) (d)

Figure S1. PXRD patterns of $NH_3IPA \cdot 0.5H_2O$ (a) NH_2IPA (b) and Mn-CP (c) and Zn-CP (d) crystal samples.

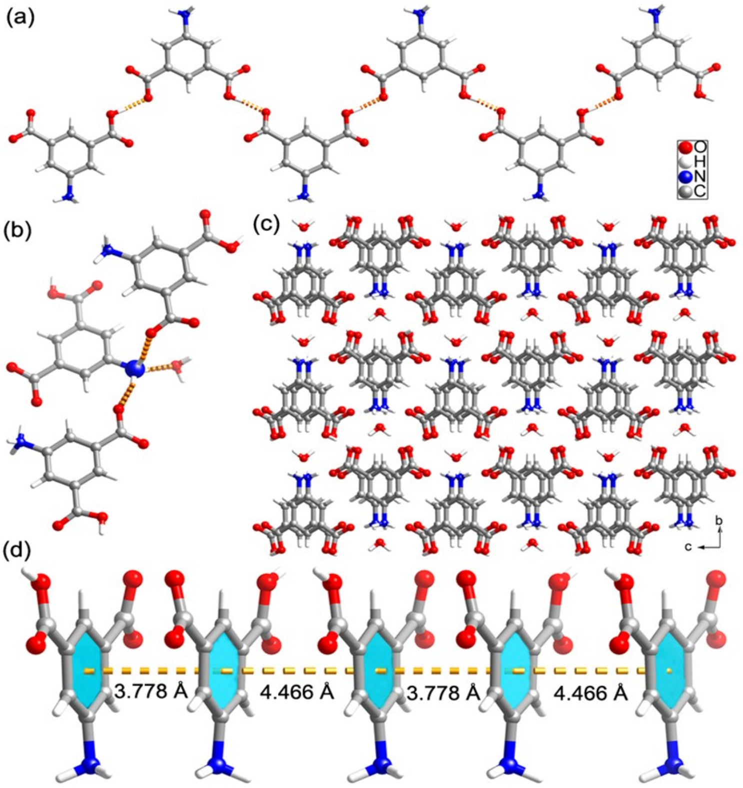


Figure S2. View of 1D zig-zag chain (a) and N/O–H···O hydrogen bonding between adjacent NH_3IPA molecules (b). (c) 3D supramolecular network of $NH_3IPA \cdot 0.5H_2O$. (d) Alternating arrangement of π···π stacking between NH_3IPA molecules.

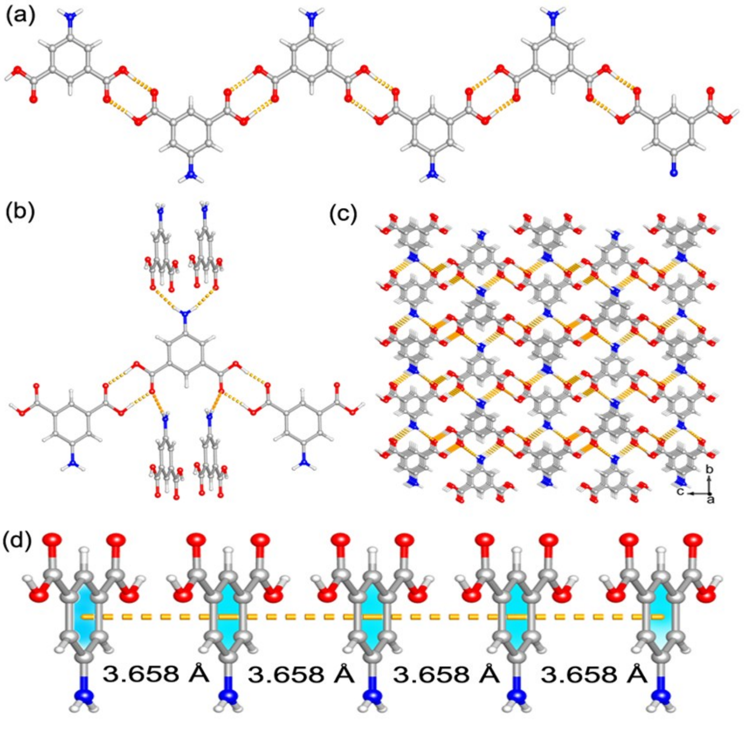
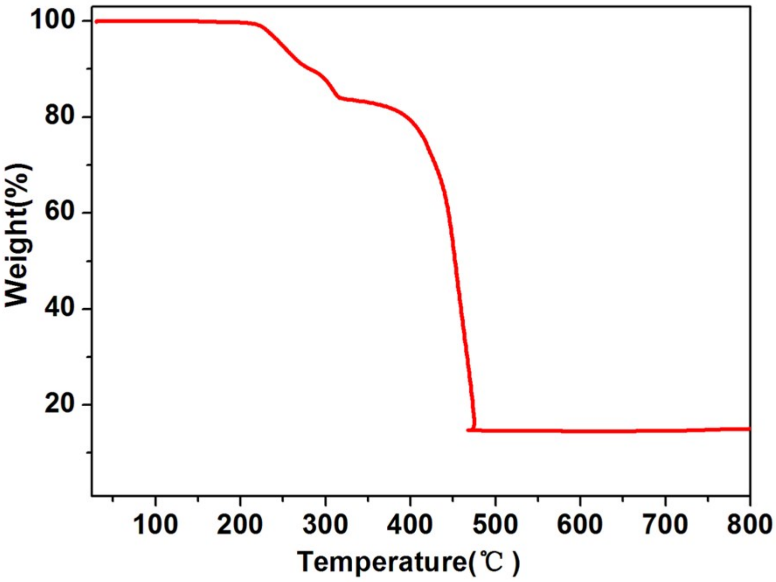
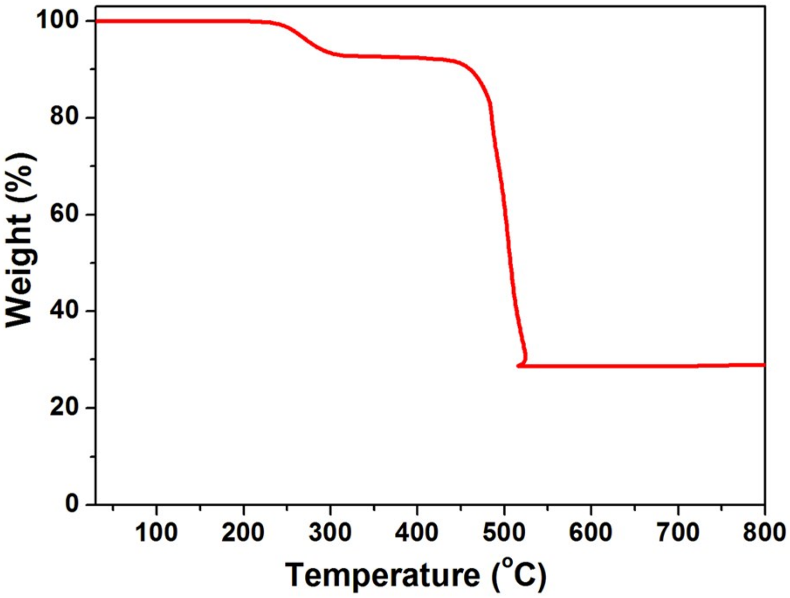


Figure S3. View of 1D zig-zag chain (a) and N/O–H···O hydrogen bonding between adjacent NH_2IPA molecules (b). (c) 3D supramolecular network of NH_2IPA. (d) Arrangement of π···π stacking between NH_2IPA molecules.

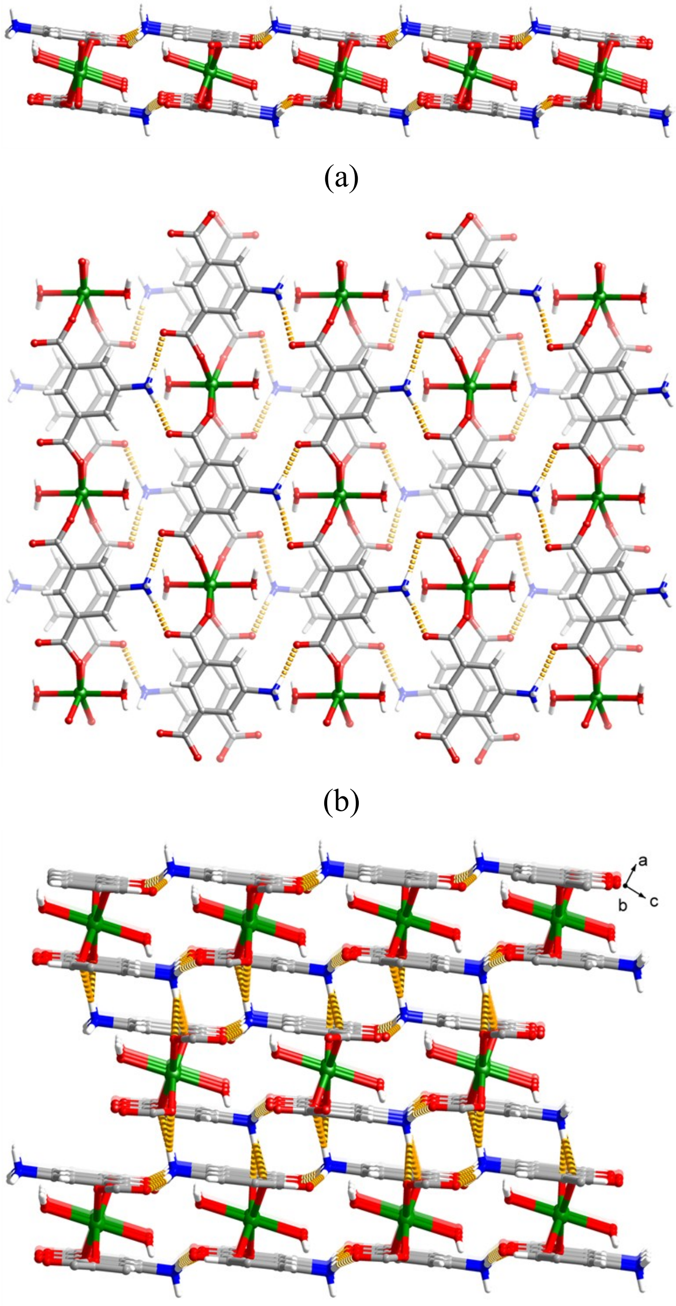


(a)



(b)

Figure S4. TGA curves for Mn-CP (a) and Zn-CP (b) crystal samples.



(a)

(b)

(c)

Figure S5. View of the 2D layer for Mn-CP along *a* (a) and *b* (b) direction. (c) View of the 3D network along *b* direction.

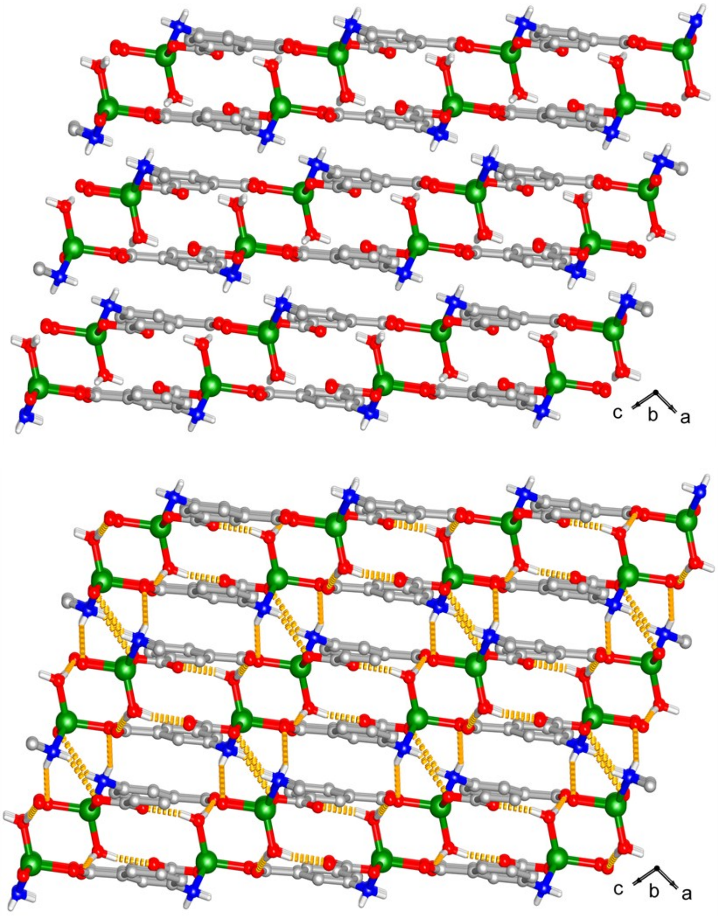


Figure S6. View of the 3D network of Zn-CP along *b* direction extended from 2D layer through N–H···O and O–H···O hydrogen bonding.

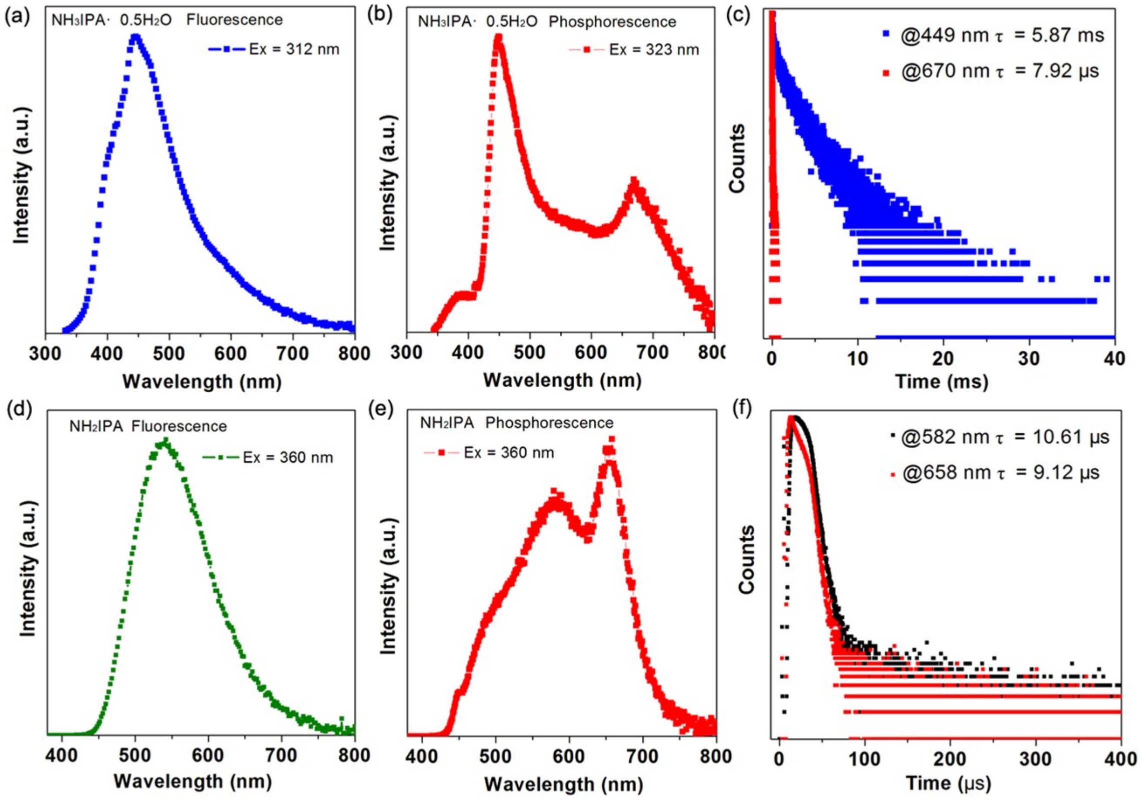
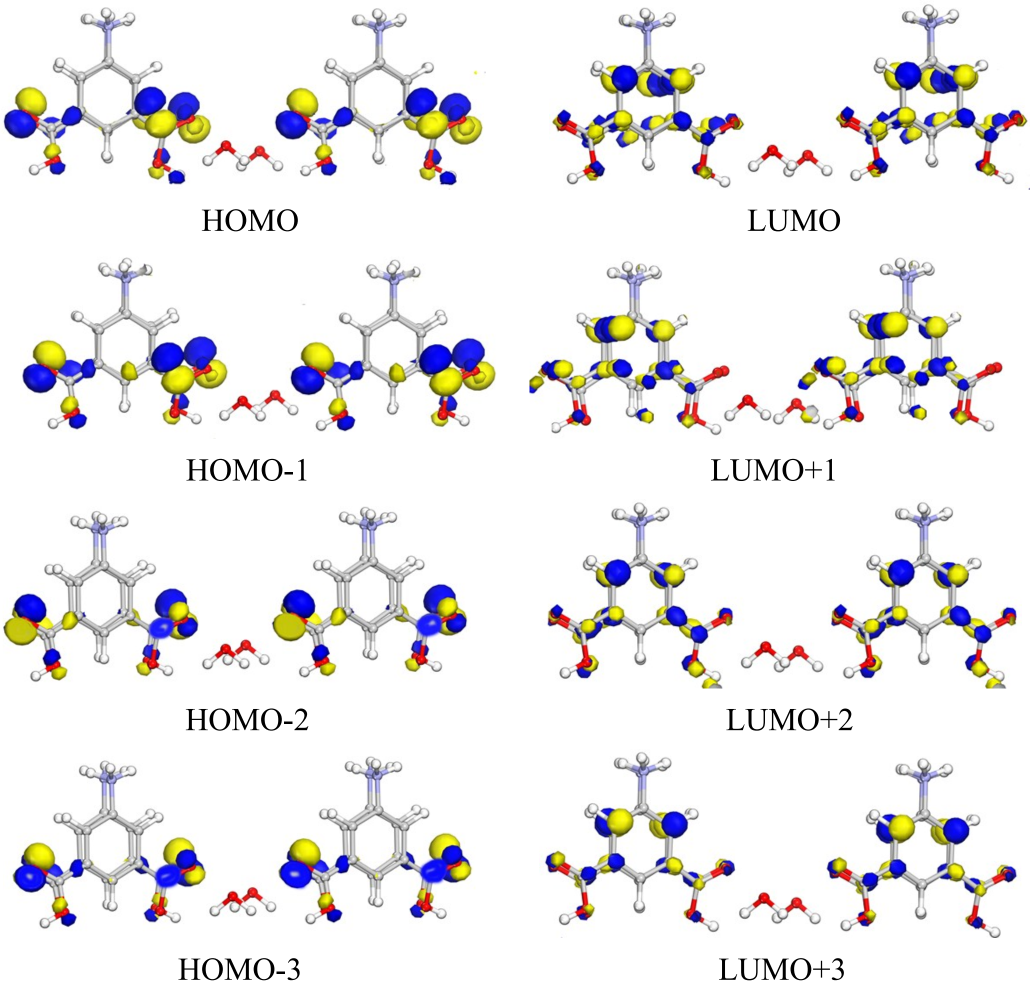


Figure S7. Fluorescence/phosphorescence spectra and phosphorescence decay curves of $NH_3IPA \cdot 0.5H_2O$ and NH_2IPA at room temperature.



HOMO LUMO

HOMO-1 LUMO+1

HOMO-2 LUMO+2

HOMO-3 LUMO+3

Figure S8. The distributions of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of $NH_3IPA \cdot 0.5H_2O$. It can be observed that HOMO and LUMO are separate between –COOH/-COO$^-$ groups and benzene ring owing to the large torsion angles between two carboxylic groups and benzene rings.

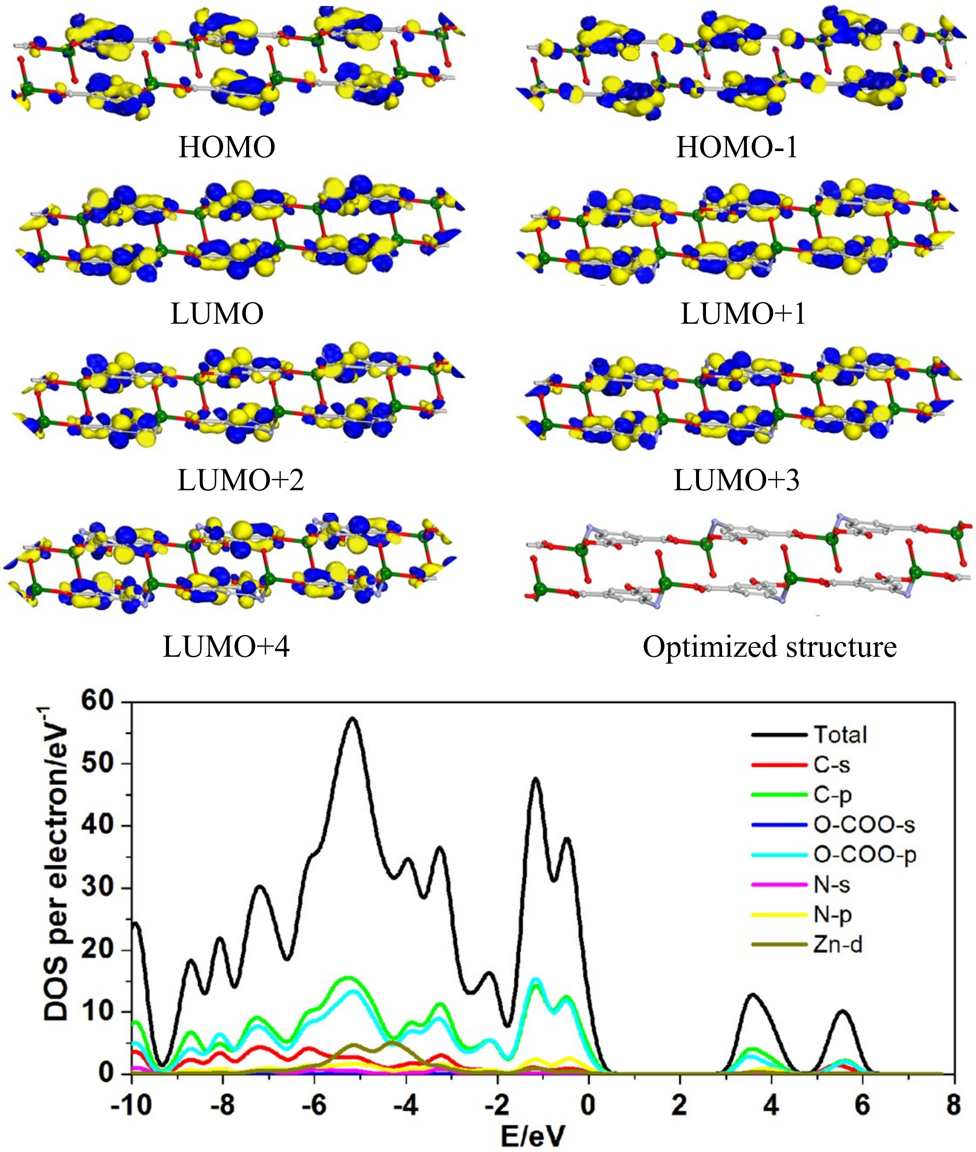
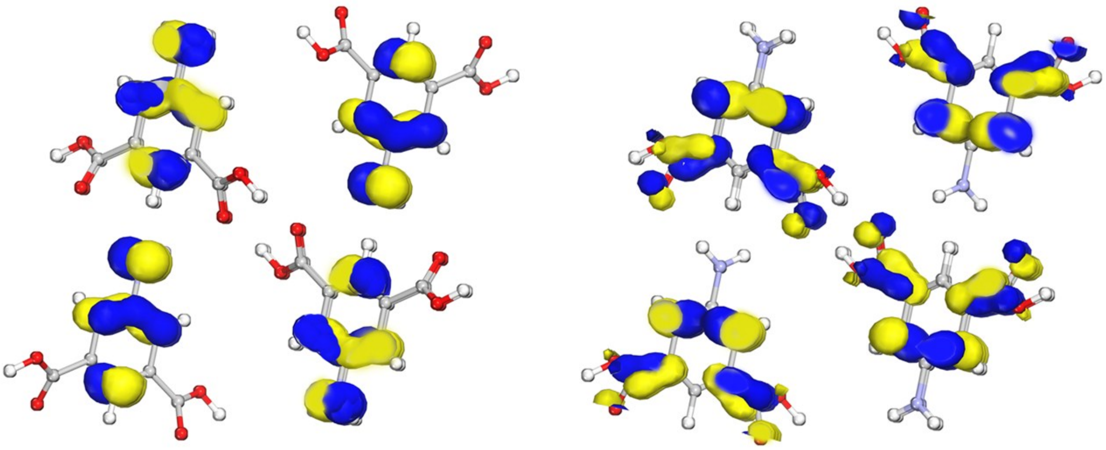
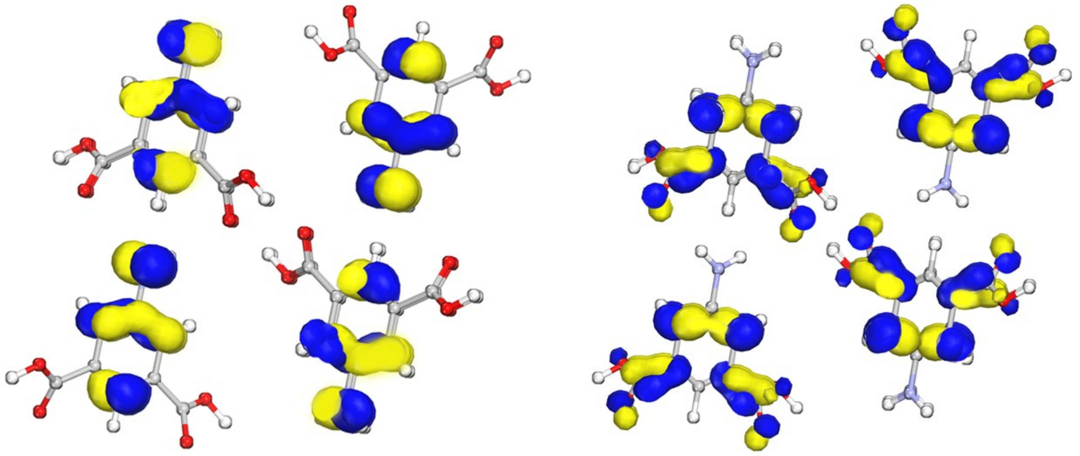


Figure S9. The optimized structure, the distributions of HOMOs/LUMOs, and TDOS/PDOS of Zn-CP.

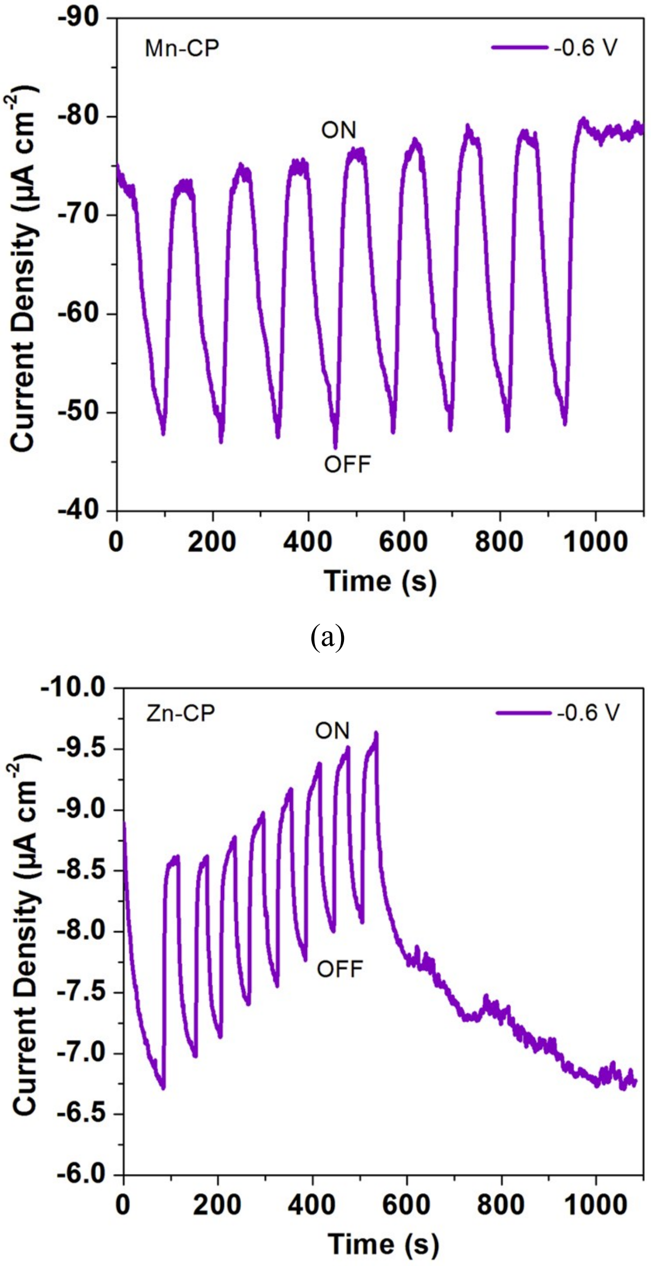


HOMO LUMO



HOMO-1 LUMO+1

Figure S10. The distributions of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of NH_2IPA. It can be observed that the electron cloud can transfer from $-NH_2IPA$ to $-COOH$ group through benzene ring.



(a)

(b)

Figure S11. Transient current–time characteristics of Mn-CP (a) and Zn-CP (b) in 0.5 M Na_2SO_4 aqueous solution at -0.6 V bias potential (vs. Ag/AgCl).

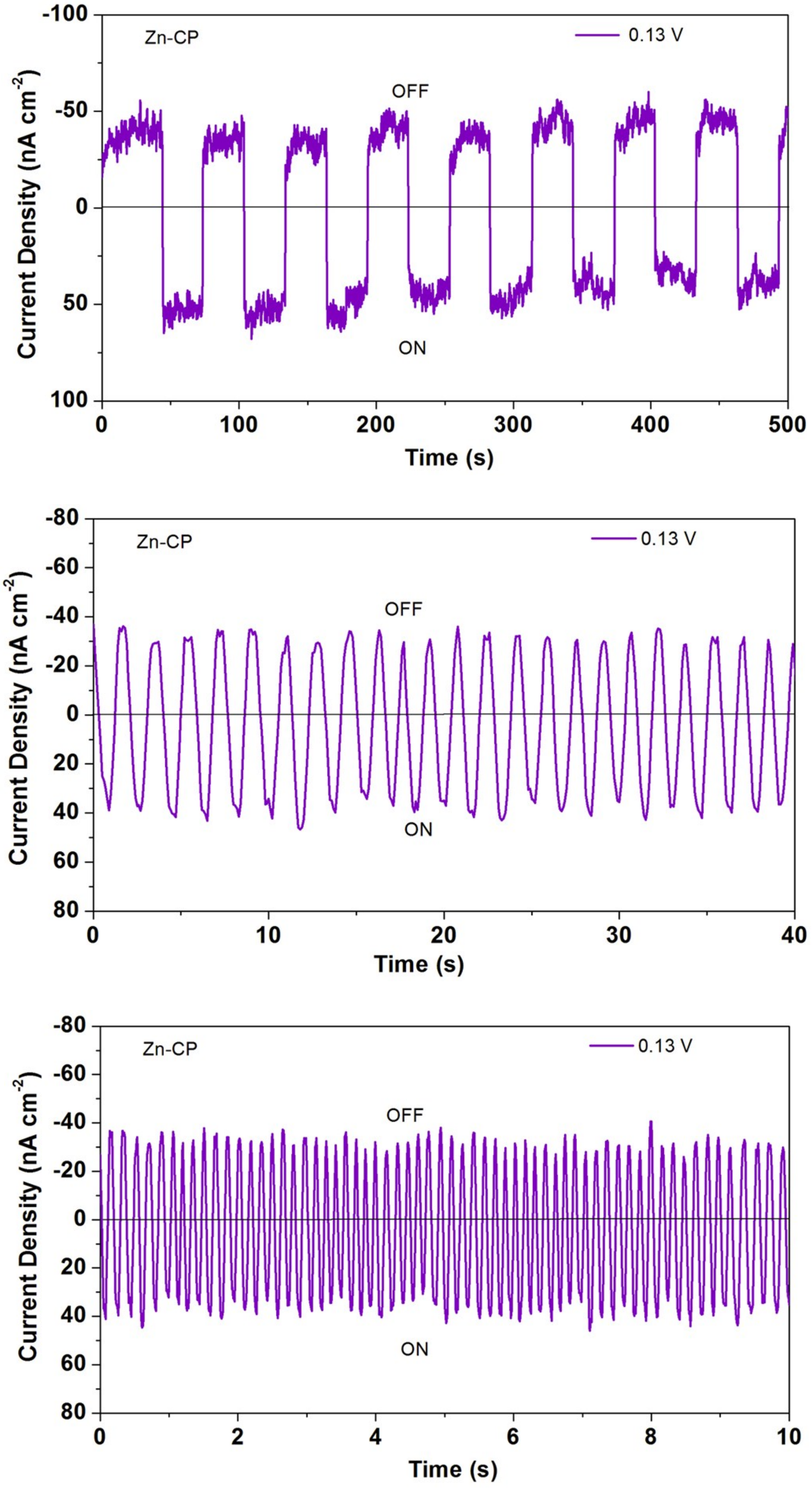


Figure S12. Alternating current with frequency tunable of Zn-CP at bias potential of 0.13 V by changing the period of on–off illumination.

Table S1. Crystallographic data for [Mn(NH_3IPA)$_2$(H_2O)$_2$] and [Zn(NH_2IPA)(H_2O)].

Samples	[$Mn_{0.5}$(NH_3IPA)(H_2O)] (Mn-CP)	[Zn(NH_2IPA)(H_2O)] (Zn-CP)
Chemical formula	$C_8H_8Mn_{0.5}NO_5$	$C_8H_7ZnNO_5$
Formula weight	225.63	262.54
CCDC NO.	1917025	1917026
Crystal system	Monoclinic	Monoclinic
Space group	$P2/n$	$P2_1/n$
a (Å)	7.0170(6)	9.0595(9)
b (Å)	10.0069(8)	8.2813(7)
c (Å)	11.4671(9)	11.6454(13)
α (°)	90	90.00
β (°)	94.909(7)	100.894(10)
γ (°)	90	90.00
V (Å^3)	802.25(11)	857.94(15)
Z	4	4
D (g cm^{-3})	1.8679	2.0324
μ (mm^{-1})	0.892	2.863
R_{int}	0.0327	0.0675
Goof	1.012	0.911
$R_1{}^a$ ($I>2\sigma(I)$)	0.0531	0.0599
$wR_2{}^a$ ($I>2\sigma(I)$)	0.1393	0.0969

^{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] (*a*) G. M. Sheldrick, *Acta Crystallogr. Sect. A*. 2008, **A64**, 112–122; (*b*) G. M. Sheldrick, *Acta Cryst*. 2015, **A71**, 3–8.

[3] (*a*) B. Delley, *J. Chem. Phys*. 1990, **92**, 508–517; (*b*) B. Delley, *J. Chem. Phys*. 2000, **113**, 7756–7764; (*c*) Dmol^3 Module, MS Modeling, Version 2.2; Accelrys Inc.: San, Diego, 2003; (*d*) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B*. 1992, **46**, 6671–6687.