Electronic Supplementary Information

Improved electrical conductivity of Co(II) and Cu(II) ladder polymers in the fabrication of photoresponsive Schottky device

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Experimental Section

Materials

All of the chemicals were purchased from different chemical company and used as was. High purity cobalt(II) nitrate hexahydrate and copper(II) nitrate trihydrate were collected in their pure state for the crystallization process. All other chemicals and solvents were collected as AR grade. It is also stated that above chemicals were utilized in this analysis without any further purification.

General methods

Elemental analyses (carbon, hydrogen, and nitrogen) of all the compounds were performed using a Perkin−Elmer 240C elemental analyzer. Thermal analysis (TGA) was carried out on a Perkin-Elmer Pyris Diamond TG/DTA thermal analyzer under a nitrogen atmosphere (flow rate: 50 cm^3 min^{-1}) at the temperature range of 30−810 °C with a heating rate of 10 °C/ min. X-ray powder diffraction (PXRD) patterns in different states of the sample were recorded on a Bruker D8 Discover instrument using Cu−Kα radiation. UV-Vis spectra were collected using a Perkin-Elmer Lambda 25 spectrophotometer.

Synthesis of compound Co-CP

A solution of bpd (0.042 g, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered onto a solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.058 g, 0.2 mmol), in H_2O (2 mL) using a 2 mL 1 : 1 (= v/v) buffer solution of MeOH and H_2O followed by layering of Hnac (0.023 g, 0.2 mmol) neutralized with Et_3N (0.021 g, 0.2 mmol) in 2 mL EtOH. The brown colour block shaped crystals of $[Co_2(bpd)_2(nac)_2] \cdot 2CH_3OH \cdot H_2O$, (**Co-CP**) were obtained after three days (0.196 g, yield 70%). Elemental analysis (%) calcd for $C_{78}H_{68}Co_2N_8O_{11}$: C 66.38, H 4.86, N7.94; found: C 66.39, H 4.58, N 7.93.

Synthesis of compound Cu-CP

A solution of bpd (0.042 g, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered onto a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.048 g, 0.2 mmol), in H_2O (2 mL) using a 2 mL 1 : 1 (= v/v) buffer solution of CH_3CN and H_2O followed by layering of Hnac (0.023 g, 0.2 mmol) neutralized with Et_3N (0.021 g, 0.2 mmol) in 2 mL EtOH. The green colour Block shaped crystals of $[Cu_2(bpd)_2(nac)_2] \cdot 2CH_3CN \cdot 2H_2O$, (**Cu-CP**) were obtained after five days (0.275 g, yield 65%). Elemental analysis (%) calcd for $C_{118}H_{94}Cu_3N_{14}O_{14}$: C 66.77, H 4.46, N9.24; found: C 66.69, H 4.48, N 9.89.

General X-ray Crystallography

Suitable shaped single crystals of CPs (**Co-CP** and **Cu-CP**) having suitable dimensions, were used for single crystal X-ray diffraction (SCXRD) and data collection using a Bruker SMART APEX II diffractometer furnished with graphite-monochromatedMoKα radiation (λ = 0.71073 Å). The molecular arrangement of the single crystal was solved using the SHELXL-2016/6 package.[1] Non-hydrogen atoms of the diffracted compound were refined with anisotropic thermal parameters. The unit cell parameters and crystal-orientation matrices of the compound were determined by least-squares refinement of all reflections within hkl range -19<h<19, -31<k<31, -20<l<20 (for **Co-CP**) and -16<h<16, -18<k<18, -18<l<18. All the hydrogen atoms were placed in their geometrically perfect positions and constrained to ride on their parent atoms. Collected data ($I>2\sigma(I)$) of crystal was integrated by employing the SAINT program and the absorption correction was performed through SADABS. The crystallographic data for CPs are summarized and depicted in Table S1 and S3. The selected bond lengths and bond angles around the coordination atmosphere of the metal ion are also given in Table S2 and S4.

Table S1. Crystal data and refinement parameters of **Co-CP**

Formula	$C_{78}H_{66}Co_2N_8O_{11}$
fw	1411.26
cryst syst	Monoclinic
space group	*C*2/*c*
a (Å)	16.4018(15)
b (Å)	26.468(3)
c (Å)	16.8967(16)
α (deg)	90
β (deg)	105.290(3)
γ (deg)	90
V (Å^3)	7075.7(12)
Z	4
D_{calcd} (g/cm^3)	1.325
μ (mm^{-1})	0.536
λ (Å)	0.71073
total reflections	6341
refine parameters	452
GOF on F^2	1.144
final *R* indices [$I > 2\sigma(I)$][a,b]	*R*1 = 0.0536 *wR*2 = 0.1309

[a]$R1 = \Sigma||F_o| \quad |F_c||/ \Sigma|F_o|$, [b]$wR2 = [\Sigma w(F_o^2 \quad F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths and bond angles in **Co-CP**

Co01-O1	2.209(2)	N1 -Co1 -O2	88.24(9)

Co01-O2	2.170(2)	N4 -Co1 -O2	92.13(9)
Co01-O3	2.012(2)	O3 -Co1 -O1	91.52(9)
Co01-O4	2.037(2)	O4 -Co1- O1	146.72(9)
Co01-N1	2.146(2)	N1- Co1- O1	94.60(9)
Co01-N4	2.152(2)	N4- Co1- O1	87.29(9)
O1 - C1	1.261(4)	O2 -Co1- O1	59.52(8)
O2 - C2	1.257(4)	C24- N1- C23	117.5(3)
O3 -Co1 -O4	121.76(10)	C24- N1- Co1	124.0(2)
O3 -Co1 -N1	87.94(9)	C23- N1- Co1	118.5(2)
O4 -Co1- N1	86.61(9)	C14- N4- C18	117.1(3)
O3- Co1- N4	92.71(9)	C14- N4- Co1	121.4(2)
O4 -Co1 -N4	91.42(9)	C18- N4- Co1	121.4(2)
N1 -Co1 -N4	177.98(10)	C1- O1- Co1	89.6(2)
O3 -Co1- O2	150.35(10)	C1- O2- Co1	91.5(2)
O4 -Co1- O2	87.32(9)	C26- O4- Co1	131.9(2)

Table S3. Crystal data and refinement parameters of **Cu-CP**

Formula	$C_{118}H_{94}Cu_3N_{14}O_{14}$

fw	2122.69
crystsyst	Triclinic
space group	*P*-1
a (Å)	13.7133(12)
b (Å)	15.3391(13)
c (Å)	15.7844(13)
α (deg)	64.399(2)
β (deg)	76.000(3)
γ (deg)	63.866(2)
V (Å^3)	2682.7(4)
Z	1
D_{calcd} (g/cm^3)	1.314
μ (mm^{-1})	0.659
λ (Å)	0.71073
total reflections	9443
refine parameters	680
GOF on F^2	1.090
final *R* indices [$I > 2\sigma(I)$][a,b]	*R*1 = 0.0599 *wR*2 = 0.1739

[a]$R1 = \Sigma||F_o| \quad |F_c||/ \Sigma|F_o|$, [b]$wR2 = [\Sigma w(F_o^2 \quad F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S4. Selected bond lengths and bond angles in **Cu-CP**

Cu(1) - O(4)	1.980(3)	O(4) - Cu(1) - O(5)	126.43(12)

Cu(1) - O(5)	2.534(4)	O(4) - Cu(1) - O(6)	176.27(11)
Cu(1) - O(6)	1.990(3)	O(4)- Cu(1) - N(1)	90.32(15)
Cu(1) - N(1)	2.017(3)	O(4) - Cu(1) - C(12)	154.21(13)
Cu(1) - N(4)d	2.027(3)	O(4)- Cu(1) - N(4)d	91.91(12)
Cu(1) - O(4)e	2.439(3)	O(4) - Cu(1) - O(4)e	76.40(10)
O(3) - C(25)	1.231(5)	O(5) - Cu(1) - O(6)	57.24(12)
O(4) - C(25)	1.288(5)	O(5) - Cu(1) - N(1)	89.77(14)
O(5) - C(12)	1.232(6)	O(5) - Cu(1) - C(12)	27.82(14)
O(6) - C(12)	1.298(5)	O(5)- Cu(1) - N(4)d	85.10(13)
N(1) - C(1)	1.332(5)	O(5) - Cu(1) - O(4)e	157.16(12)
N(1) - C(5)	1.342(5)	O(6) - Cu(1) - N(1)	88.98(15)
N(1) - Cu(1) - C(12)	88.64(16)	O(6) - Cu(1) - C(12)	29.43(13)
N(1) - Cu(1) - N(4)d	174.77(12)	O(6)- Cu(1) - N(4)d	89.09(12)
N(1) - Cu(1) - O(4)e	90.93(11)	O(6) - Cu(1) - O(4)e	99.94(11)
C(12) - Cu(1) - N(4)d	87.29(14)	C(12) - Cu(1) - O(4)e	129.38(13)
N(4)d - Cu(1) - O(4)e	94.20(11)	Cu(1) - O(4) - C(25)	118.5(3)
Cu(1) - O(4) - Cu(1)e	103.60(11)	C(25) -O(4) - Cu(1)e	137.1(3)
Cu(1) - O(5) - C(12)	78.5(3)	Cu(1) - O(6) - C(12)	101.7(3)
Cu(1) - N(1) - C(1)	122.0(3)	C(7)- N(3)- N(2)	111.2(3)

Symmetry Code: d = x, 1+y, z; e = 1-x, 1-y, 2-z

Table S5. Comparison of conductivity with the reported works

Sl.	**Compounds**	**Electrical**	**Reference**

No		Conductivity (S cm^{-1})	
1.	$[Zn(ADC)(PBT)_2(H_2O)_2]_n$ $[Zn(Succ)(PBT)_2(H_2O)_2]_n$ (H_2ADC = acetylenedicarboxylic acid, H_2Succ = succinic acid and PBT = 2-pyridin-4-ylbenzothiazole)	1.31×10^{-4} 1.80×10^{-7}	2
2.	$[Zn(cis\text{-}1,4\text{-}chdc)(4\text{-}phpy)]_n$ $[Zn(cis\text{-}1,4\text{-}chdc)(py)]_n$ (1,4-H_2chdc = 1,4-cyclohexanedicarboxylic acid, 4-phpy = 4-phenylpyridine and py = pyridine)	1.09×10^{-5} 6.01×10^{-7}	3
3.	[Cd(2,2′-dsb)(4-nvp)(DMF)(H_2O)] (H2,2′-dsba = 2,2′-disulfanediyldibenzoic acid and 4-nvp = 4-(1-naphthylvinyl)-pyridine)	6.60×10^{-6} (Dark) 10.71×10^{-6} (Light)	4
4.	$[Fe^{II}(pc)(\mu\text{-}pyz)]$ and $[Fe(pc)(\mu\text{-}pyz)I_{2.54}]$ [μ-pyz = pyrazine and pc = porphyrin ring]	1×10^{-6} 2×10^{-1}	5
5.	$Cu[Ni(pdt)_2]$ (pdt = 2,3-pyrazinedithiolate)	1×10^{-4}	6
6.	$[Co_3(NDC)_3]$ (H_2NDC = 2,6-napthalenedicarboxylic acid)	1.8×10^{-6}	7
7.	$[Cu(fum)(4\text{-}phpy)_2(H_2O)]$ (H_2fum = fumaric acid and 4-phpy = 4-phenyl pyridine)	6.13×10^{-6}	8
8.	$[Co(C_9H_6NS)_2]$ (C_9H_6NS = 8-mercaptoquinoline)	1.7×10^{-7}	9
9.	$[Co_2(bpd)_2(nac)_2]\cdot 2CH_3OH\cdot H_2O$ and $[Cu_2(bpd)_2(nac)_2]\cdot 2CH_3CN\cdot 2H_2O$ (bpd = *N,N*′-bis(1-pyridine-4-yl-ethylidene and Hnac = 3-(1-naphthyl)acrylic acid)	4.78×10^{-8} (Dark) 6.15×10^{-8} (Light) and 19.97×10^{-8}(Dark) 70.61×10^{-8}(Light)	**This work**

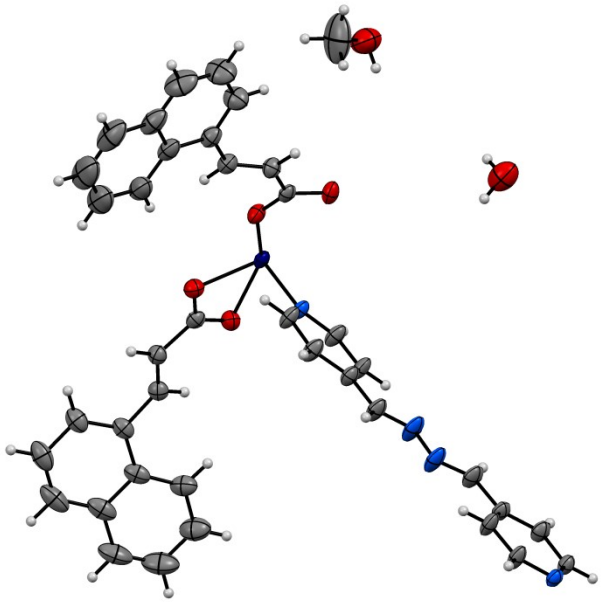


Fig. S1 Asymmetric unit of **Co-CP** with 30% ellipsoid plot.

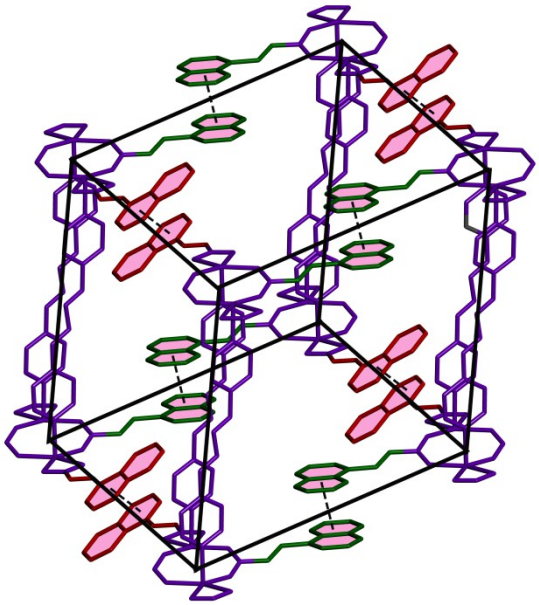


Fig. S2 3D supramolecular pillar-layered structure of **Co-CP** formed by π···π stacking interactions.

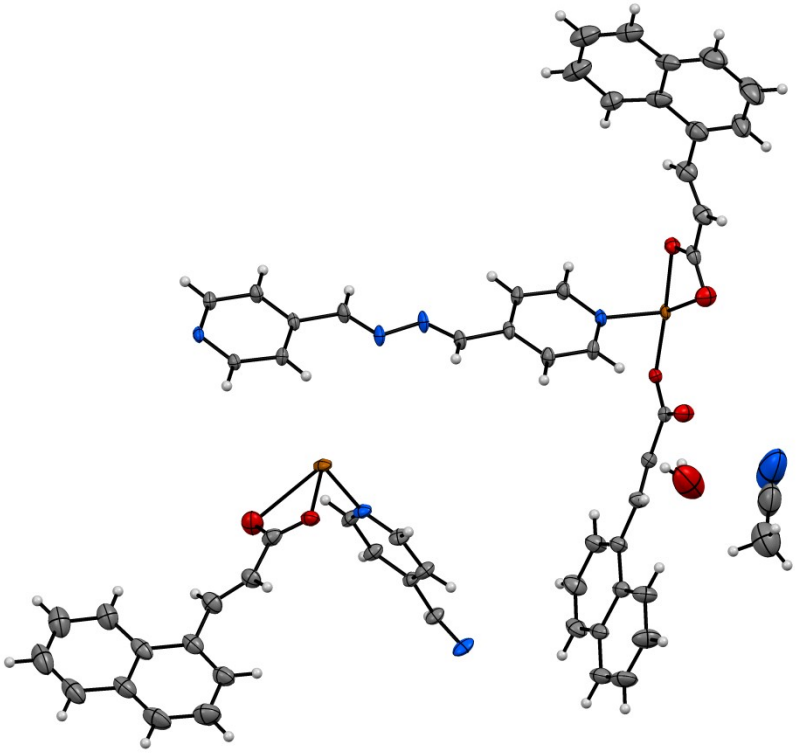


Fig. S3 Asymmetric unit of **Cu-CP** with 30% ellipsoid plot.

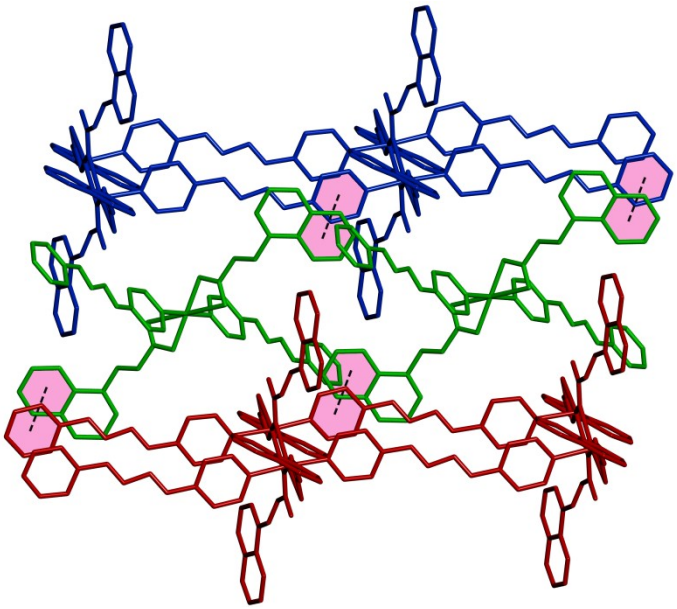


Fig. S4 3D supramolecular network of **Co-CP** formed by π···π stacking interactions.

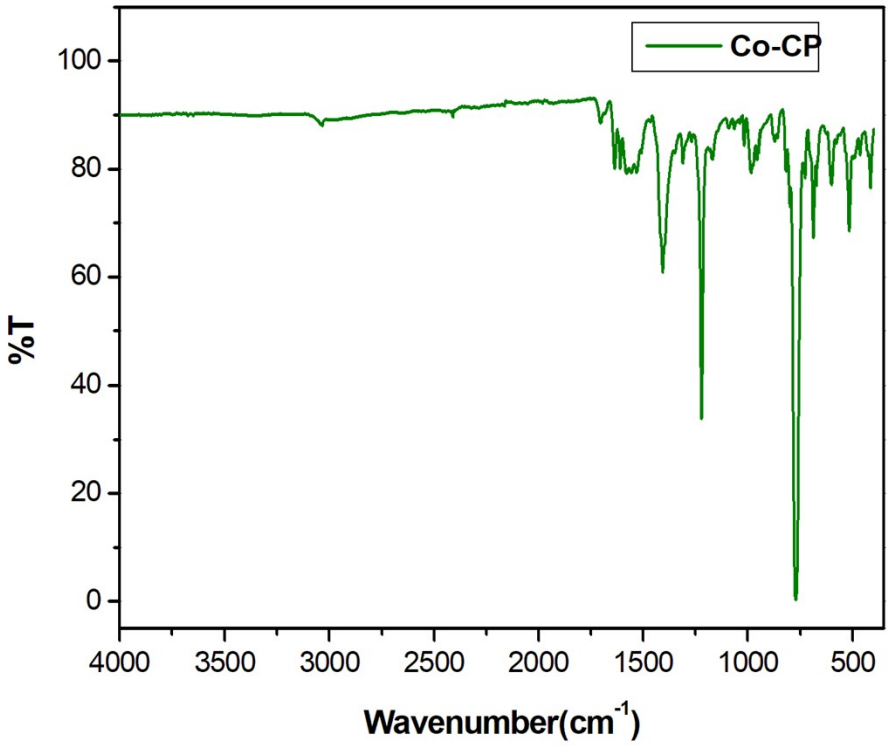


Fig. S5 IR spectrum of **Co-CP**.

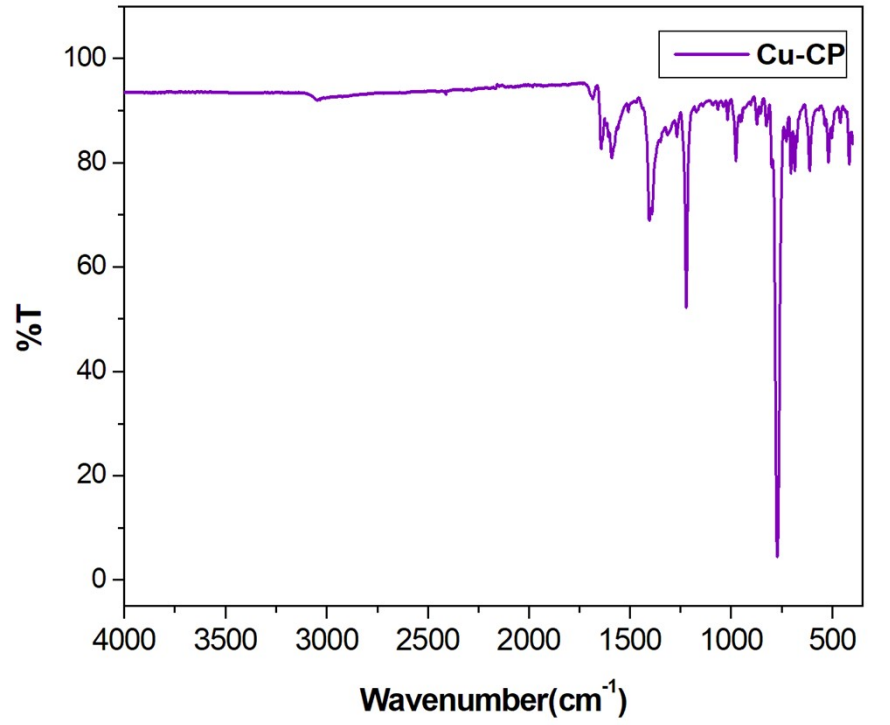


Fig. S6 IR spectrum of **Cu-CP**.

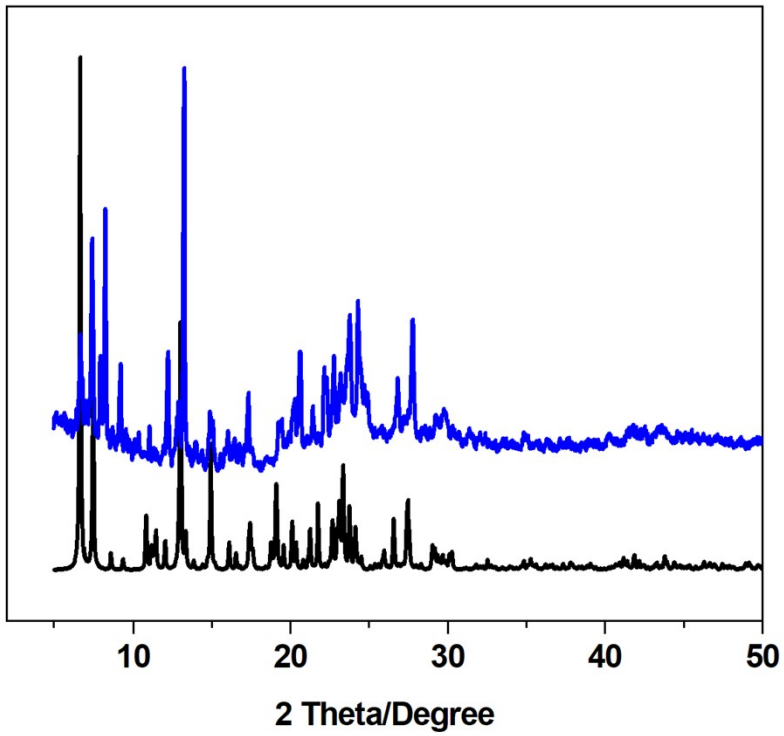


Fig. S7 PXRD patterns of simulated **Co-CP** (black), as-synthesized **Co-CP** (blue).

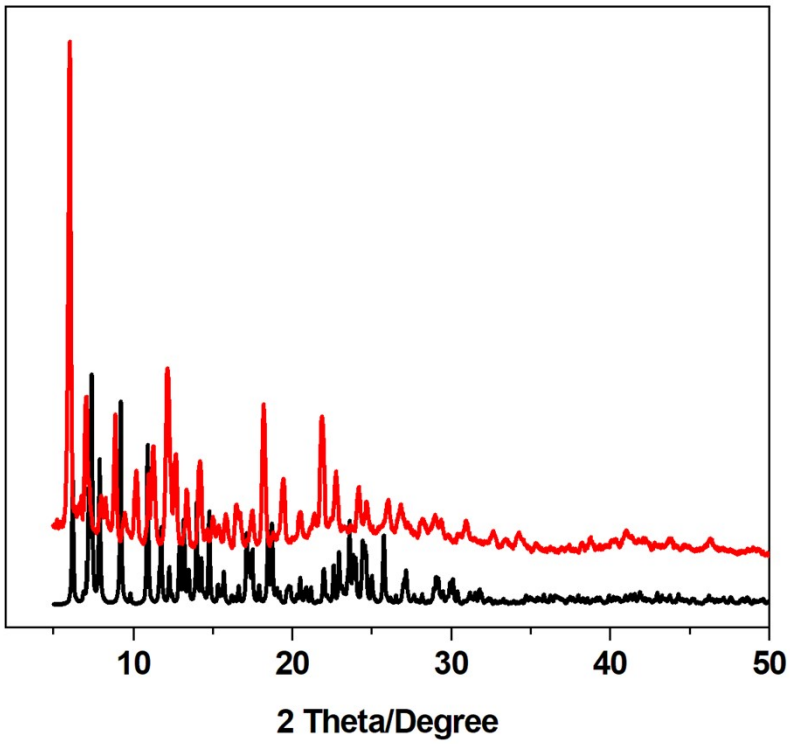


Fig. S8 PXRD patterns of simulated **Cu-CP** (black), as-synthesized **Cu-CP** (red).

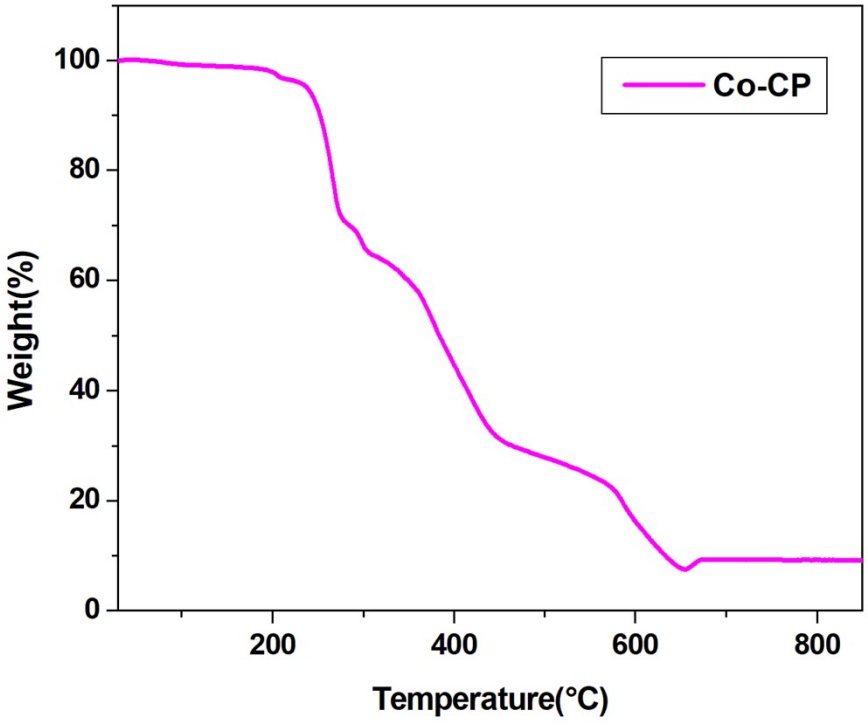


Fig. S9 TGA plot of **Co-CP**.

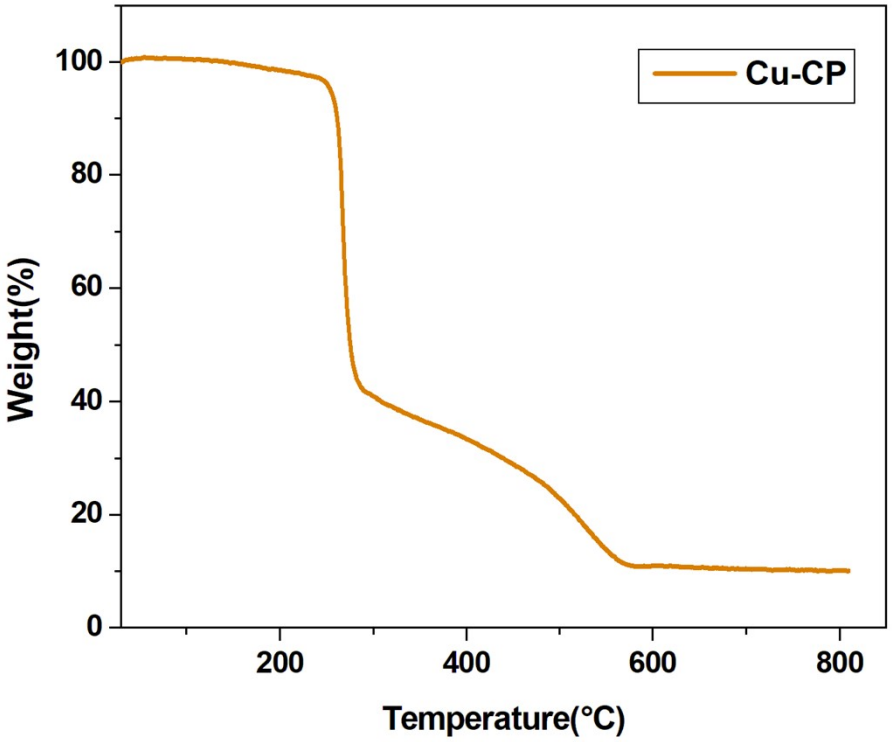


Fig. S10 TGA plot of **Cu-CP**.

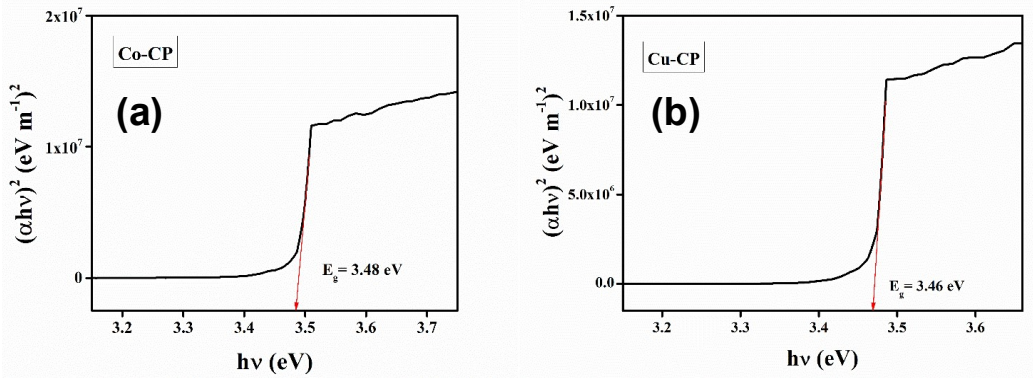


Fig. S11 Tauc's plots of (a) **Co-CP** and (b) **Cu-CP**.

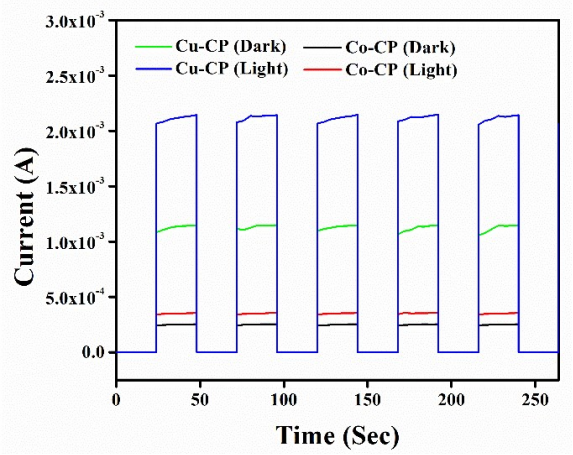
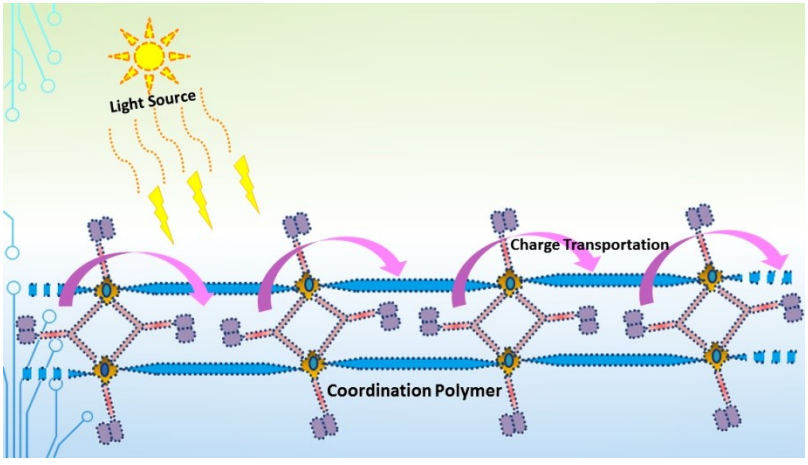


Fig. S12 Plots of photocurrent vs. time of **Co-CP** and **Cu-CP**.



Scheme S1 Schematic representation of charge transportation mechanism in CP.

Reference

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