Supporting information

Substituent group-tunable hydrogen evolution activity observed in isostructural Cu(II)-based coordination polymer photocatalysts

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Table S1 Crystal and structure refinement data for **Cu-CP-R**.[a]

	Cu-CP-NH_2	**Cu-CP-NO_2**	**Cu-CP-H**	**Cu-CP-OH**	**Cu-CP-Br**
Temperature	293	127	118.6	293	296
empirical formula	$C_{50}H_{35}CuN_7O_6$	$C_{50}H_{33}CuN_7O_8$	$C_{50}H_{34}CuN_6O_6$	$C_{50}H_{34}CuN_6O_7$	$C_{50}H_{32}CuN_6O_6Br$
F_w	893.39	923.37	878.37	894.37	956.26
cryst size (mm)	0.25 × 0.22 × 0.20	0.22 × 0.21 × 0.20	0.25 × 0.22 × 0.20	0.25 × 0.22 × 0.20	0.22 × 0.21 × 0.18
cryst syst	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
space group	*P*–1	*P*–1	*P*–1	*P*–1	*P*–1
a (Å)	7.1100(5)	7.1161(8)	7.0631(4)	7.1213(3)	7.2467(13)
b (Å)	10.9172(8)	10.8134(14)	10.9098(7)	10.9493(5)	10.935(2)
c (Å)	13.7599(10)	13.898(2)	13.8073(8)	13.8046(6)	13.919(3)
α (°)	82.193(6)	81.988(12)	82.556(5)	81.707(4)	82.290(4)
β (°)	87.050(6)	86.064(10)	89.225(5)	88.055(4)	87.182(4)
γ (°)	72.875(6)	74.160(10)	73.069(6)	72.596(4)	72.275(4)
V (Å^3)	1011.16(13)	1018.3(2)	1008.93(11)	1016.33(8)	1041.1(3)
Z, D_c (g cm^{-3})	1, 1.467	1, 1.506	1, 1.446	1, 1.461	1,1.525
h / *k* / *l*	– 8, 8 / – 12, 13 / – 16, 16	– 8, 8 / – 12, 12 / – 16, 16	– 8, 8 / – 8, 12 / – 16, 16	– 8, 8 / – 13, 11 / – 16, 16	– 8, 8 / – 12, 12 / – 16, 13
F(000)	461	475	453	461	486
μ (mm^{-1})	1.288	0.606	0.603	1.294	1.545
reflections collected / unique	7041 / 3601	6857 / 3584	6646 / 3554	6457 / 3633	6040 / 3663
R_{int}	0.2331	0.0582	0.0505	0.0345	0.0451
data / restraints / params	3601 / 54 / 297	3585 / 54 / 314	3554 / 0 / 287	3633 / 7 / 296	3663 / 12 / 304
R_1 [a], wR_2 [b] ($I > 2\sigma(I)$)	0.1637, 0.3632	0.0998, 0.1954	0.0481, 0.0989	0.0430, 0.1074	0.0911, 0.2312
R_1, wR_2 (all data)	0.2252, 0.4191	0.1388, 0.2115	0.0635, 0.1064	0.0508, 0.1144	0.1339, 0.2565

GOF on F^2	1.029	1.183	1.045	1.059	1.073
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å^{-3})	1.84, – 2.02	0.97, – 0.56	0.45, – 0.70	0.73, – 0.47	0.58, – 1.45

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

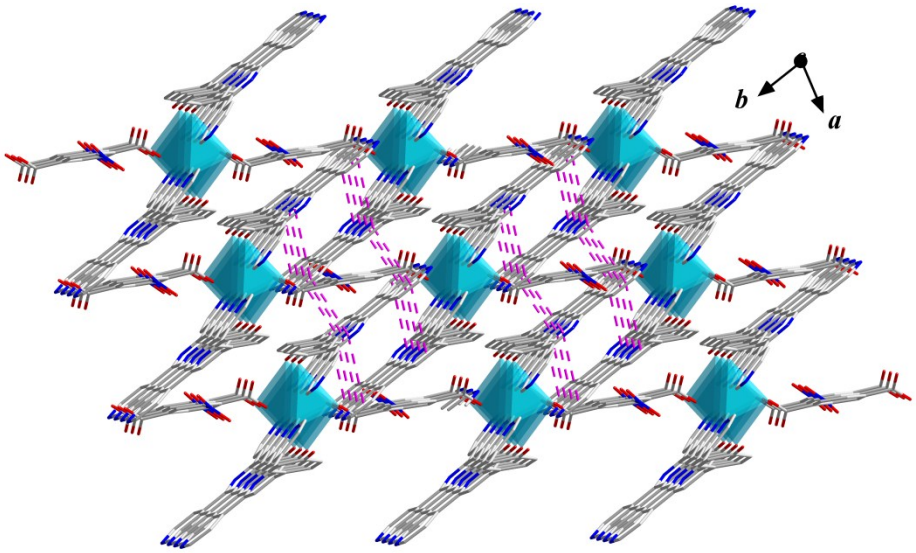

Fig. S1 3D stacking structure of **Cu-CP-NO_2**.

Table S2. Selected bond lengths (Å) and angles (deg) for Cu-CP-R [a]

Parameters	R					Average value
	NH_2	NO_2	H	OH	Br	
Cu(1)–O(1)	1.948(6)	1.977(5)	1.954(2)	1.9584(14)	1.953(4)	1.958±0.019
Cu(1)–N(2)	2.014(7)	1.992(5)	1.993(2)	1.9917(17)	1.998(6)	1.998±0.019
Cu(1)–O(3)$^{\#2}$	2.6159(76)	2.6246(56)	2.6234(56)	2.6198(22)	2.6799(70)	2.633±0.047
O(1)–Cu(1)–N(2)	89.7(3)	89.9(2)	89.54(8)	89.07(7)	90.0(2)	89.64±0.57
O(1)$^{\#1}$–Cu(1)–N(2)	90.3(3)	90.1(2)	90.46(8)	90.93(7)	90.0(2)	90.36±0.57

[a] Symmetry codes: $^{\#1}$ $1-x, 2-y, -z$; $^{\#2}$ $x, y, -1+z$.

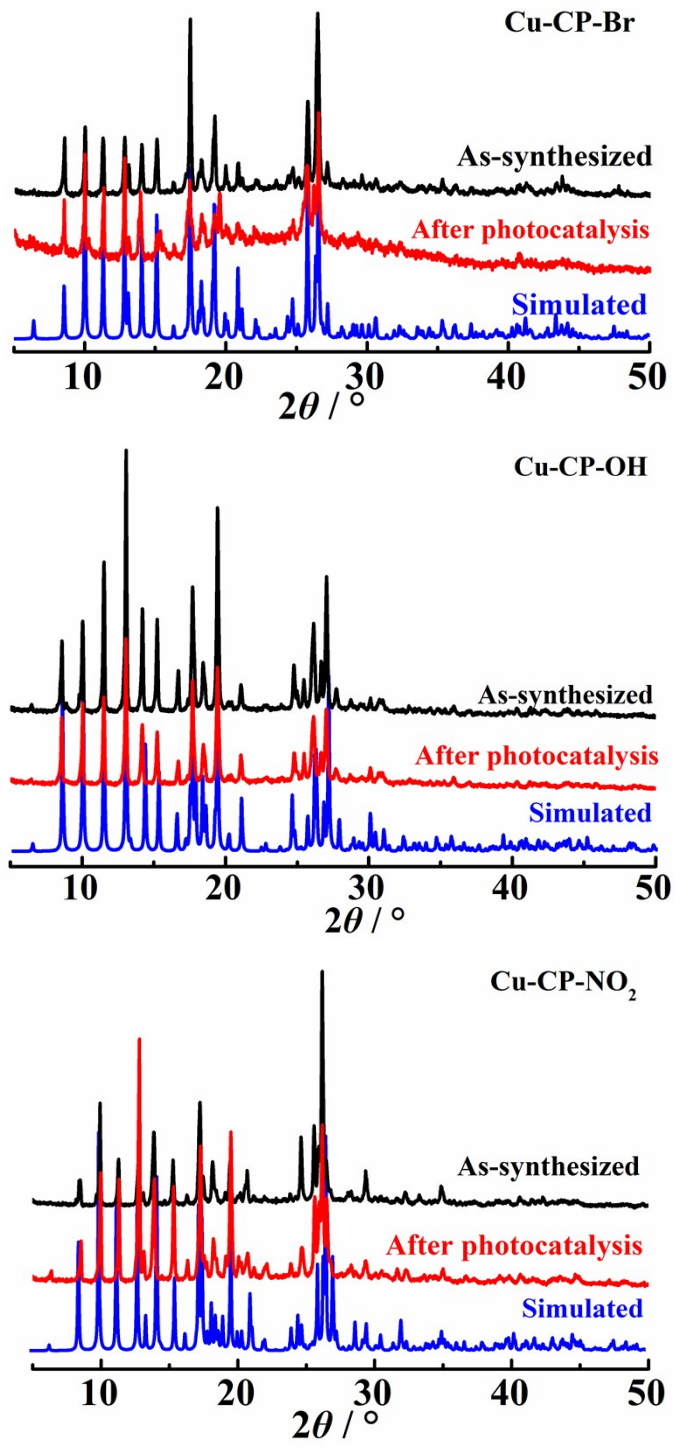

Fig. S2 PXRD patterns for the as-synthesized photocatalysts before and after photocatalysis.

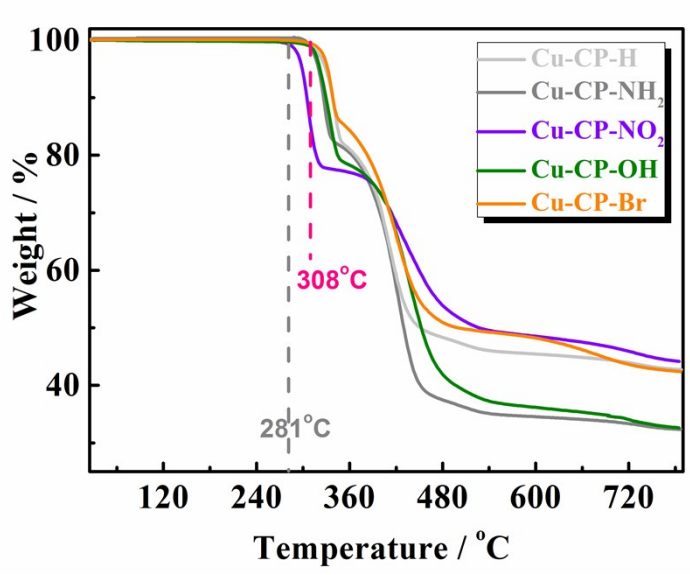

Fig. S3 TG curves of the five **Cu-CP-R** photocatalysts.

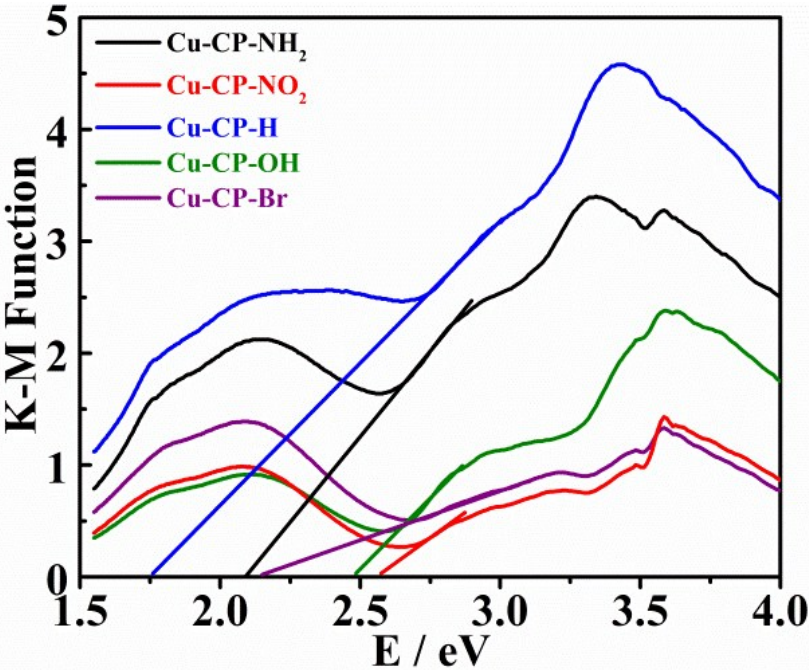

Fig. S4 Band gaps for the five Cu-CP-R photocatalysts.

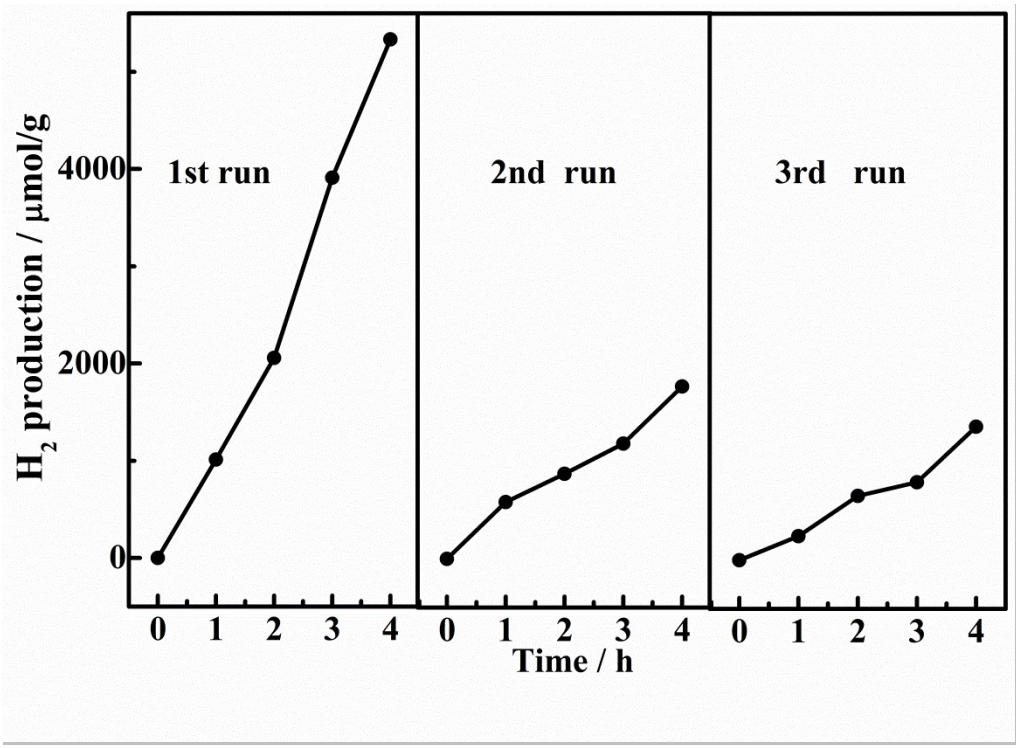

Fig. S5 Cycling tests of the photocatalytic hydrogen evolution for **Cu-CP-NO_2**.

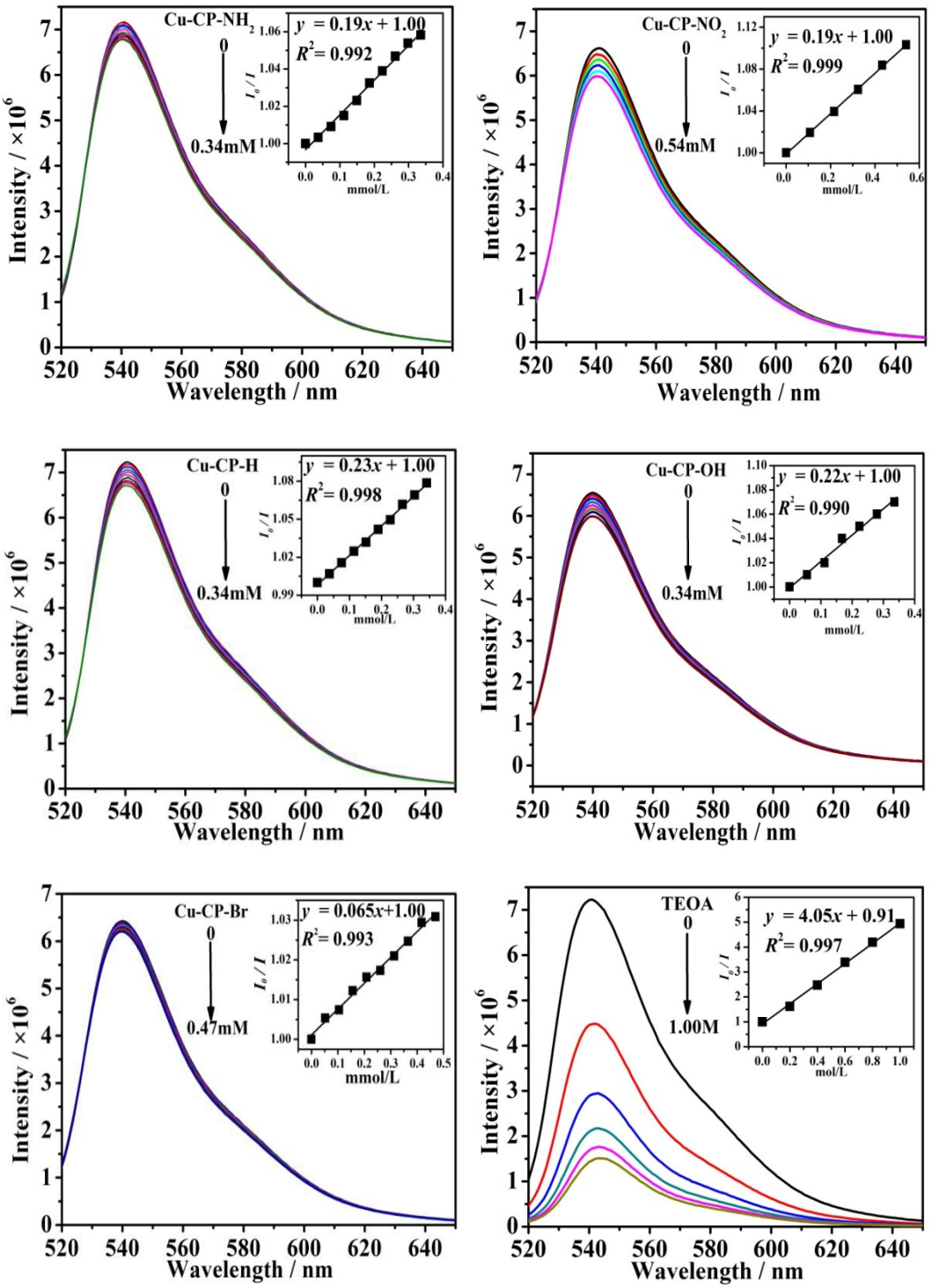

Fig. S6 Emission spectra of EY by **Cu-CP-R** samples and TEOA in an aqueous solution (Inset: Stern-Volmer plot for the photoluminescence quenching of EY by **Cu-CP-R** or TEOA).