Supporting information

Amino group promoted photocatalytic hydrogen evolution activity observed in two copper(II)-based layered complexes

Lei Li,[†] Shuang Zhu,[‡] Rui Hao,[‡] Jia-Jun Wang,[‡] En-Cui Yang*,[‡] and Xiao-Jun Zhao*,[‡,†]

[†] *Department of Chemistry, Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071*, *People's Republic of China*

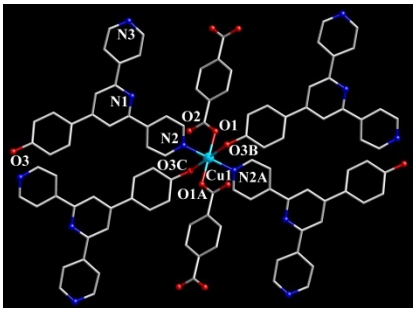
[‡] *College of Chemistry*, *Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry*, *Ministry of Education*, *Tianjin Key Laboratory of Structure and Performance for Functional Molecules*, *Tianjin Normal University*, *Tianjin 300387*, *People's Republic of China*

Table S1 Crystal data and structure refinement for **1** and **2**[a]

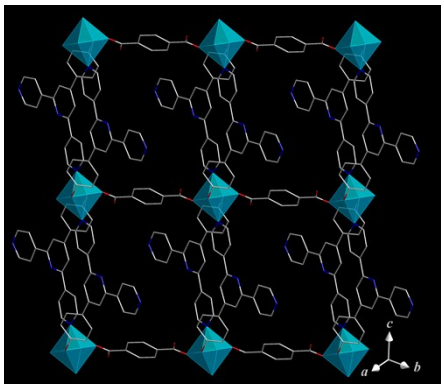
	1	**2**
empirical formula	$C_{50}H_{35}CuN_7O_6$	$C_{50}H_{34}CuN_6O_6$
F_w	893.39	878.37
cryst syst	Triclinic	Triclinic
space group	*P*–1	*P*–1
a (Å)	7.1100(5)	7.0631(4)
b (Å)	10.9172(8)	10.9098(7)
c (Å)	13.7599(10)	13.8073(8)
α (º)	82.193(6)	82.556(5)
β (º)	87.050(6)	89.225(5)
γ (º)	72.875(6)	73.069(6)
V (Å^3)	1011.16(13)	1008.93(11)
Z	1	1
D_c (g cm^{-3})	1.467	1.446
h / *k* / *l*	– 8, 8 / – 12, 13 / – 16, 16	– 8, 8 / – 8, 12 / – 16, 16
μ (mm^{-1})	1.288	0.603
reflections collected	7041	6646
Reflections unique	3601	3554
R_{int}	0.2331	0.0505
GOF on F^2	1.029	1.045

R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.1637, 0.3632	0.0481, 0.0989
R_1, wR_2 (all data)	0.2252, 0.4191	0.0635, 0.1064

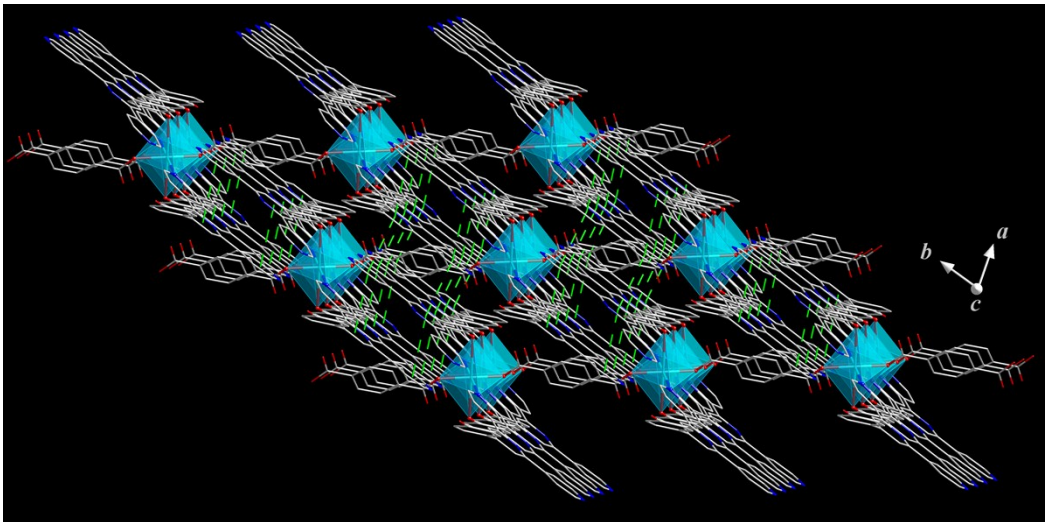
[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$



(a)



(b)



(c)

Fig. S1 (a) Local coordination environments of Cu^{II} ion in **2** (H atoms were omitted for clarity, Symmetry codes: A = 1 – *x* , 2 – *y* , – *z*, B = *x*, *y*, *z*– 1, C = 1 – *x*, 2 – *y*, 1 – *z*). (b) 2D layered structure of **2**. (c) 3D structure of **2**.

Table S2 Selected bond lengths (Å) and angles (deg) for **1** and **2** [a]

	1	**2**
Cu(1)–O(1)	1.948(6)	1.954(2)
Cu(1)–N(2)	2.014(7)	1.993(2)
Cu(1)–O(3)$^{\#2}$	2.6159(76)	2.5967(23)
O(1)–Cu(1)–N(2)	89.7(3)	90.46(8)
O(1)$^{\#1}$–Cu(1)–N(2)	90.3(3)	89.54(8)

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

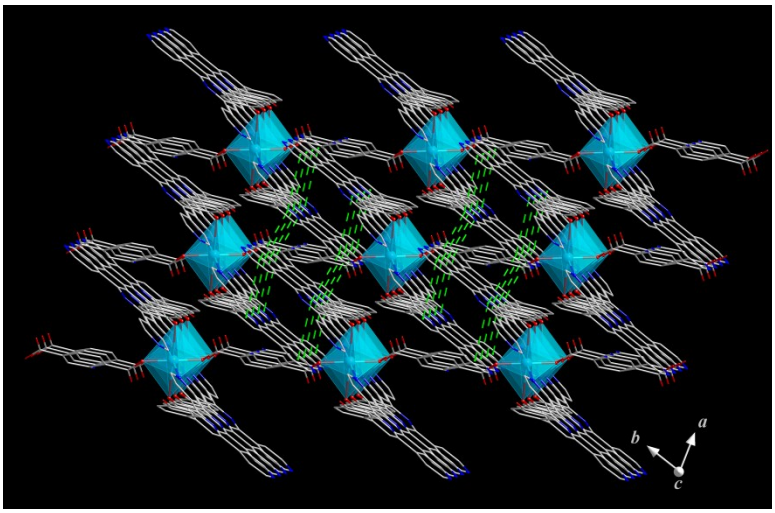


Fig. S2 3D stacking structure of **1**.

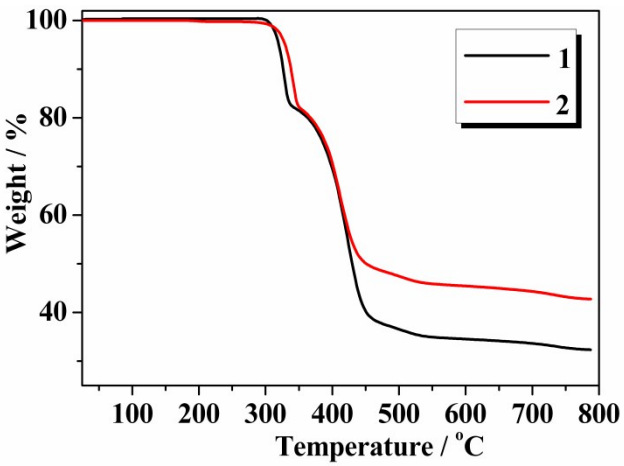


Fig. S3 TG curves for **1** and **2**.

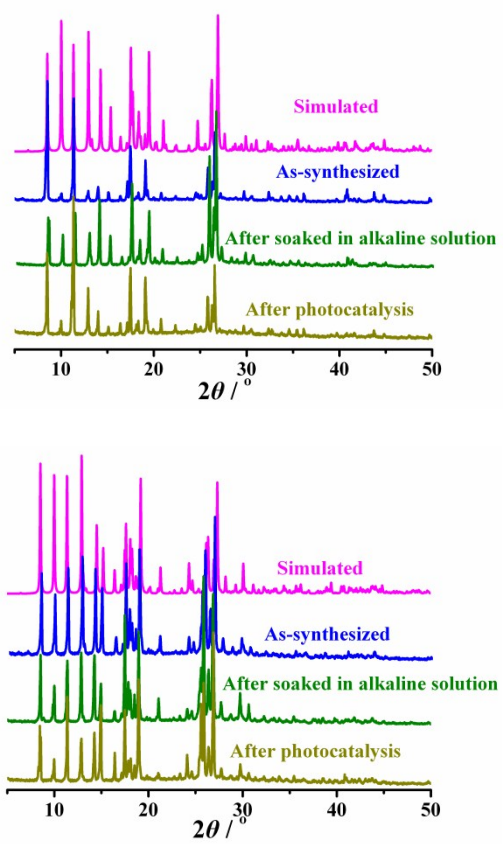


Fig. S4 PXRD patterns for **1** (upper) and **2** (bottom).

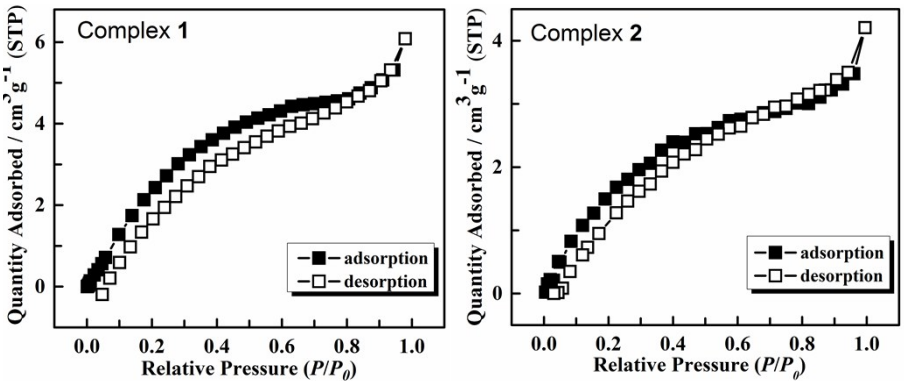


Fig. S5 N_2 adsorption-desorption isotherms at 77 K for **1** and **2**.

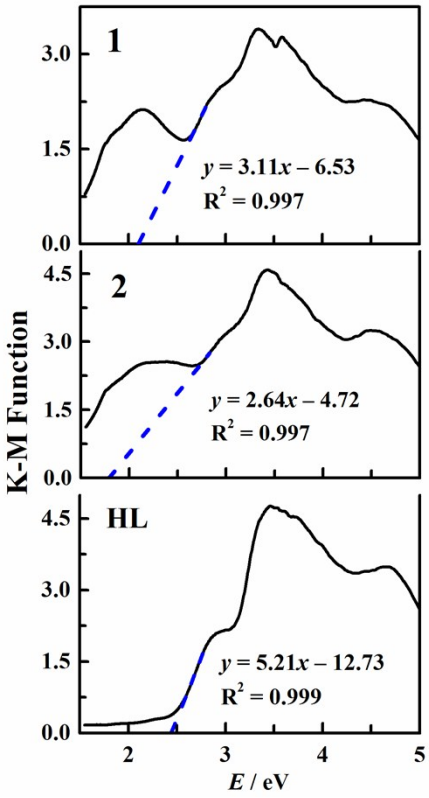


Fig. S6 Plot of K-M function vs. energy for HL, **1** and **2**.

Table S3 Selected UV-vis diffuse reflectance spectra data for the linear fit for the plot of K-M fuction versus Energy for **1**, **2** and **HL**.

Wavelength / nm	*E*/ev	Absorption/ a.u.	*R*	K-M Function /a.u.
1				
451	2.74945	0.768	0.17061	2.01599
450	2.75556	0.771	0.16943	2.03572
449	2.76169	0.774	0.16827	2.05559
448	2.76786	0.777	0.16711	2.07561
447	2.77405	0.780	0.16596	2.09578
446	2.78027	0.783	0.16482	2.11609
445	2.78652	0.786	0.16368	2.13655
444	2.79279	0.789	0.16255	2.15716
443	2.7991	0.792	0.16144	2.17792
442	2.80543	0.795	0.16032	2.19884
441	2.81179	0.798	0.15922	2.2199
440	2.81818	0.800	0.15849	2.23403
439	2.8246	0.802	0.15776	2.24823
438	2.83105	0.804	0.15704	2.2625
2				
451	2.74945	0.841	0.14421	2.53923
450	2.75556	0.843	0.14355	2.55491
449	2.76169	0.844	0.14322	2.56277
448	2.76786	0.846	0.14256	2.57856

447	2.77405	0.848	0.14191	2.59442
446	2.78027	0.850	0.14125	2.61036
445	2.78652	0.852	0.1406	2.62637
444	2.79279	0.854	0.13996	2.64246
443	2.79910	0.857	0.139	2.66674
442	2.80543	0.859	0.13836	2.68303
441	2.81179	0.861	0.13772	2.69939
440	2.81818	0.863	0.13709	2.71583
439	2.82460	0.865	0.13646	2.73235
438	2.83105	0.867	0.13583	2.74895
HL				
479	2.58873	0.507	0.31117	0.76242
478	2.59414	0.514	0.3062	0.78604
477	2.59958	0.521	0.3013	0.81012
476	2.60504	0.527	0.29717	0.83114
475	2.61053	0.534	0.29242	0.8561
474	2.61603	0.541	0.28774	0.88155
473	2.62156	0.548	0.28314	0.90749
472	2.62712	0.555	0.27861	0.93392
471	2.6327	0.562	0.27416	0.96085
470	2.6383	0.569	0.26977	0.98829
469	2.64392	0.576	0.26546	1.01625
468	2.64957	0.583	0.26122	1.04473

467	2.65525	0.591	0.25645	1.07793
466	2.66094	0.598	0.25235	1.10756
465	2.66667	0.605	0.24831	1.13774
464	2.67241	0.612	0.24434	1.16847
463	2.67819	0.619	0.24044	1.19977
462	2.68398	0.626	0.23659	1.23164
461	2.6898	0.633	0.23281	1.26409
460	2.69565	0.640	0.22909	1.29712
459	2.70153	0.647	0.22542	1.33076
458	2.70742	0.654	0.22182	1.36499
457	2.71335	0.660	0.21878	1.39483
456	2.7193	0.667	0.21528	1.43022
455	2.72527	0.673	0.21232	1.46105
454	2.73128	0.679	0.20941	1.49235
453	2.73731	0.685	0.20654	1.52413
452	2.74336	0.691	0.2037	1.55639
451	2.74945	0.697	0.20091	1.58914
450	2.75556	0.703	0.19815	1.62238
449	2.76169	0.708	0.19588	1.65047
448	2.76786	0.713	0.19364	1.6789
447	2.77405	0.718	0.19143	1.70769
446	2.78027	0.723	0.18923	1.73684
445	2.78652	0.728	0.18707	1.76636

444	2.79279	0.732	0.18535	1.79023
443	2.7991	0.737	0.18323	1.82041

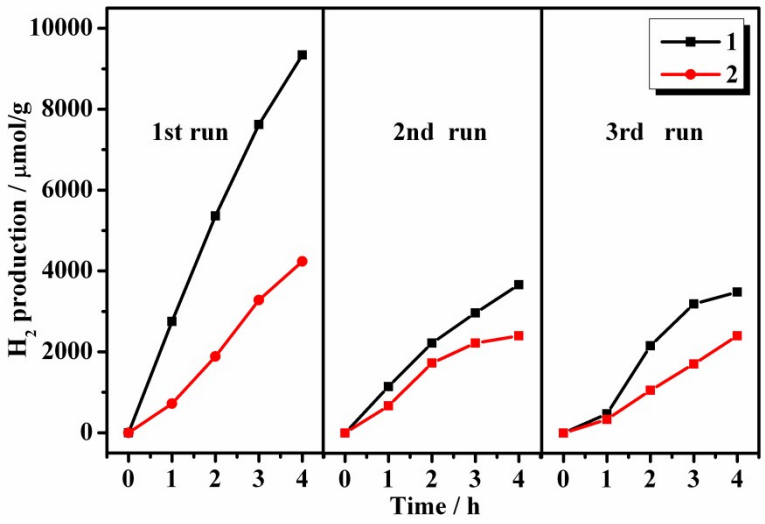


Fig. S7 Cycling tests of photocatalytic hydrogen evolution for **1** and **2** in the photocatalytic experiment period.

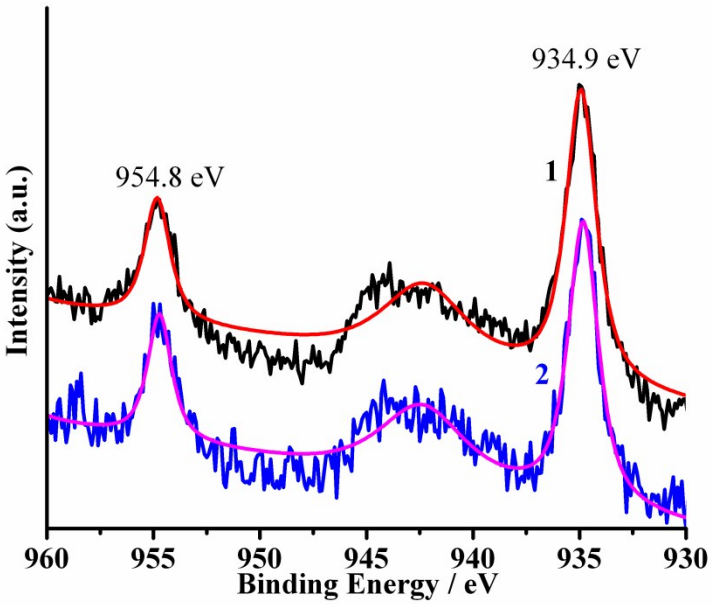
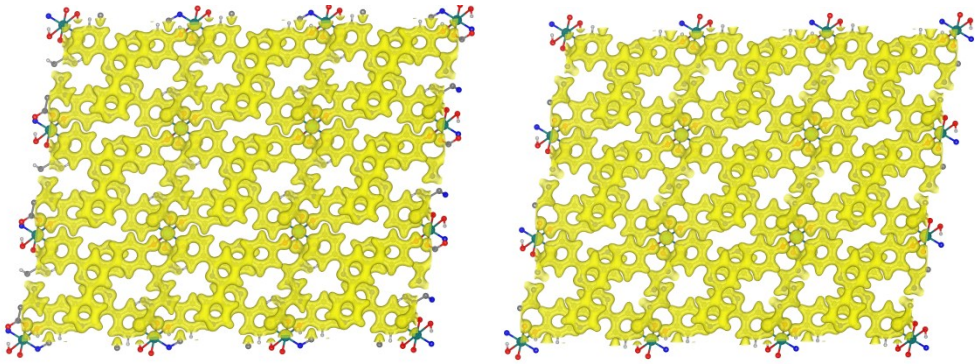
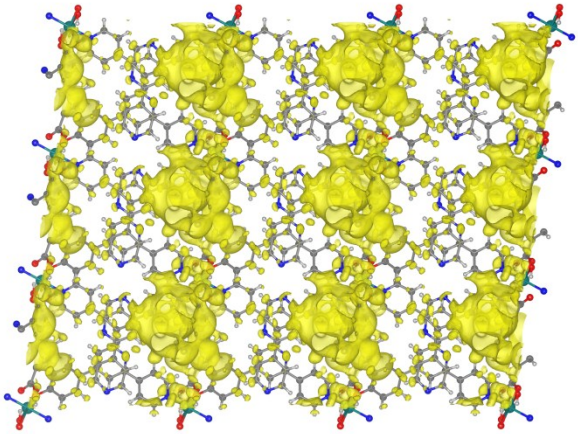


Fig. S8 XPS spectra for **1** and **2**.



(a)



(b)

Fig. S9 (a) Charge density for **1** (left) and **2** (right) with the isosurface value of 1 e/Å^3. (b) Charge density difference between **1** and **2** with the isosurface value of 0.001 e/Å^3. (The yellow region represents charge density, Green, blue, grey, light grey, and red balls represent Cu, N, C, H and O atoms, respectively).

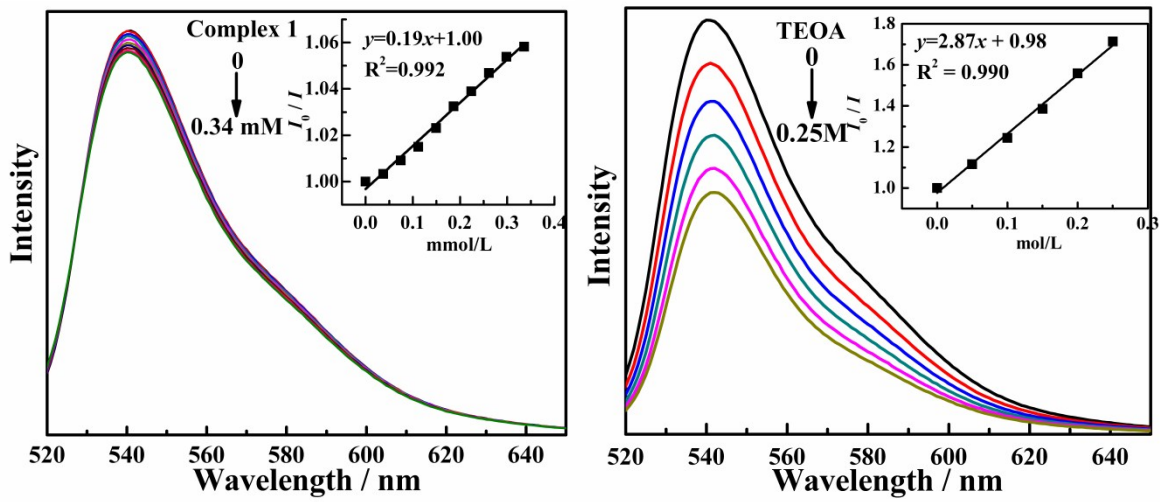


Fig. S10 Emission quenching plot of EY by **1** (left) and TEOA (right) in an aqueous solution (Inset: Stern-Volmer plot for the photoluminescence quenching of EY by **1** and TEOA).