Supporting Information

Trinuclear Cationic Silver Nanoclusters Based-on Bis-(phosphine) Ligands and Stabilized by $CF_3SO_3^-$ Anions

Chu-Xia Han,[a] Zi-Mo Shao,[a] Li Li,[a] Kun Zhou,*[a] Chun-Hui Xue,[a] Bao-Kuan Chen,[a] Jiu-Yu Ji[a] and Yan-Feng Bi*[a]

School of Chemistry and Materials Science, Liaoning Shihua University, Fushun, Liaoning 113001, China. Tel/Fax: (+86) -24-56861709; E-mail: zhouk800@aliyun.com; biyanfeng@lnpu.edu.cn

Table of contents

1. Crystallographic data.....S2-S6

2. Physical Measurements.....S7-S13

1. Crystallographic data

Table S1. Crystal data, data collection and structure refinement details for compounds 1-3

Compound	1	2	3
Empirical formula	$C_{83}H_{75}Ag_3F_6O_6P_6S_2$	$C_{78}H_{72}Ag_3F_3O_8P_6S_1$	$C_{85}H_{87}Ag_3Cl_2F_3N_3O_6P_6S_1$
Formula weight	1855.98	1735.84	1915.96
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pnma	$P2_1/m$	$P2_1/c$
a (Å)	19.9123(18)	13.0670(6)	19.7589(14)
b (Å)	20.9620(18)	22.5859(11)	23.1840(16)
c (Å)	19.6197(17)	14.0988(6)	18.9443(15)
α (Å)	90	90	90
β (Å)	90	114.9290(10)	94.853(2)
γ (Å)	90	90	90
V (Å3)	8189.3(12)	3773.3 (3)	8647.1(11)
Z	4	2	4
D/g cm^{-3}	1.505	1.528	1.472
μ/mm^{-1}	0.943	0.987	0.928
F(000)	3752	1756	3896
Reflection collected	58162	32189	75082
Unique reflections	6635	6853	15350
Parameters	562	509	988
*R*int	0.0696	0.0269	0.0583
GOF	1.045	1.094	1.008
R_1 [a] [$I>2\sigma(I)$]	0.0540	0.0366	0.0388
wR_2 [b](all data)	0.1383	0.0882	0.1026

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

Table S2. Selected bond distances (Å) data for 1

Bond	Bond distance (Å)	Bond	Bond distance (Å)
Ag(1)-C(1)	2.243(9)	Ag(1)-P(1)	2.4922(17)
Ag(2)-C(1)	2.325(7)	Ag(2)-P(2)	2.4559(16)
C(1)-Ag(2)#1	2.325(7)	Ag(2)-P(3)	2.4722(15)
Ag(1)-P(1)#1	2.4922(17)		

Symmetry transformations used to generate equivalent atoms: #1 x, -y+3/2, z.

Table S3. Ag···Ag interactions (Å) data for 1

Bond	Bond distance (Å)	Bond	Bond distance (Å)
Ag(1)-Ag(2)#1	3.1442(7)	Ag(2)-Ag(2)#1	3.1669(9)
Ag(1)-Ag(2)	3.1441(8)		

Symmetry transformations used to generate equivalent atoms: #1 x, -y+3/2, z.

Table S4. Selected bond angle (°) data for 1

Bond	Bond angle (°)	Bond	Bond angle (°)
C(1)-Ag(1)-P(1)#1	120.90(6)	C(7)-P(1)-Ag(1)	117.5(2)
C(1)-Ag(1)-P(1)	120.89(6)	C(13)-P(1)-Ag(1)	115.2(3)
P(1)#1-Ag(1)-P(1)	115.54(8)	C(31)-P(1)-Ag(1)	113.3(2)
C(1)-Ag(2)-P(2)	118.39(18)	C(25)-P(2)-Ag(2)	115.3(3)
C(1)-Ag(2)-P(3)	109.9(2)	C(19)-P(2)-Ag(2)	113.3(2)
P(2)-Ag(2)-P(3)	123.19(5)	C(31)-P(2)-Ag(2)	115.8(2)
C(2)-C(1)-Ag(1)	141.7(8)	C(38)-P(3)-Ag(2)	117.4(2)
C(2)-C(1)-Ag(2)	119.6(5)	C(32)-P(3)-Ag(2)	111.2(2)
C(2)-C(1)-Ag(2)#1	119.6(5)	C(44)-P(3)-Ag(2)	113.8(3)

Symmetry transformations used to generate equivalent atoms: #1 x, -y+3/2, z.

Table S5. Selected bond distances (Å) data for 2

Bond	Bond distance (Å)	Bond	Bond distance (Å)
Ag(1)-P(2)#1	2.4392(8)	Ag(2)-P(3)	2.4673(9)
Ag(1)-P(2)	2.4392(9)	Ag(2)-P(1)	2.4697(9)
Ag(1)-O(1)	2.58(2)		

Symmetry transformations used to generate equivalent atoms: #1 x, -y+1/2.

Table S6. Ag···Ag interactions (Å) data for 2

Bond	Bond distance (Å)	Bond	Bond distance (Å)
Ag(1)-Ag(2)#1	2.9572(4)	Ag(2)-Ag(2)#1	3.1466(5)
Ag(1)-Ag(2)	2.9572(4)		

Symmetry transformations used to generate equivalent atoms: #1 x, -y+1/2, z.

Table S7. Selected bond angle (°) data for 2

Bond	Bond angle (°)	Bond	Bond angle (°)
P(2)#1-Ag(1)-P(2)	124.74(4)	P(2)-Ag(1)-O(1)	94.10(17)
P(3)-Ag(2)-P(1)	124.37(3)	C(14)-P(2)-Ag(1)	118.34(12)
C(1)-P(1)-Ag(2)	112.10(12)	C(26)-P(2)-Ag(1)	110.66(11)
C(7)-P(1)-Ag(2)	113.12(12)	C(27)-P(3)-Ag(2)	115.19(11)
C(13)-P(1)-Ag(2)	115.38(14)	C(33)-P(3)-Ag(2)	114.17(11)
C(20)-P(2)-Ag(1)	114.54(13)	C(26)-P(3)-Ag(2)	112.86(11)
P(2)#1-Ag(1)-O(1)	94.10(17)		

Symmetry transformations used to generate equivalent atoms: #1 x, -y+1/2, z.

Table S8. Selected bond distances (Å) data for 3

Bond	Bond distance (Å)	Bond	Bond distance (Å)
Ag(1)-P(1)	2.4600(9)	Ag(2)-Cl(2)	2.7243(9)
Ag(1)-P(6)	2.4705(9)	Ag(2)-Cl(1)	2.8118(10)
Ag(1)-Cl(1)	2.7385(10)	Ag(3)-P(4)	2.4433(9)
Ag(1)-Cl(2)	2.7617(10)	Ag(3)-P(5)	2.4540(9)
Ag(2)-P(3)	2.4361(9)	Ag(3)-Cl(1)	2.7040(10)
Ag(2)-P(2)	2.4487(9)	Ag(3)-Cl(2)	2.7095(10)

Table S9. Ag···Ag interactions (Å) data for 3

Bond	Bond distance (Å)	Bond	Bond distance (Å)
Ag(2)-Ag(3)	3.2462(4)	Ag(1)-Ag(3)	3.5552(7)
Ag(1)-Ag(2)	3.3923(6)		

Table S10. Selected bond angle (°) data for 3

Bond	Bond angle (°)	Bond	Bond angle (°)
P(1)-Ag(1)-P(6)	137.60(3)	C(8)-P(1)-Ag(1)	116.82(13)
P(1)-Ag(1)-Cl(1)	111.41(3)	C(2)-P(1)-Ag(1)	115.17(12)
P(6)-Ag(1)-Cl(1)	103.42(3)	C(1)-P(1)-Ag(1)	112.38(12)
P(1)-Ag(1)-Cl(2)	103.39(3)	C(14)-P(2)-Ag(2)	119.06(12)
P(6)-Ag(1)-Cl(2)	101.23(3)	C(1)-P(2)-Ag(2)	114.31(12)
Cl(1)-Ag(1)-Cl(2)	87.94(3)	C(20)-P(2)-Ag(2)	109.03(12)
P(3)-Ag(2)-P(2)	122.25(3)	C(33)-P(3)-Ag(2)	117.80(13)
P(3)-Ag(2)-Cl(2)	129.17(3)	C(26)-P(3)-Ag(2)	115.68(11)
P(2)-Ag(2)-Cl(2)	96.02(3)	C(27)-P(3)-Ag(2)	109.19(12)
P(3)-Ag(2)-Cl(1)	95.07(3)	C(39)-P(4)-Ag(3)	116.27(13)
P(2)-Ag(2)-Cl(1)	124.73(3)	C(45)-P(4)-Ag(3)	113.61(12)
Cl(2)-Ag(2)-Cl(1)	87.21(3)	C(26)-P(4)-Ag(3)	113.68(12)
P(4)-Ag(3)-P(5)	130.44(3)	C(52)-P(5)-Ag(3)	111.72(12)
P(4)-Ag(3)-Cl(1)	103.87(3)	C(58)-P(5)-Ag(3)	113.07(13)
P(5)-Ag(3)-Cl(1)	111.81(3)	C(51)-P(5)-Ag(3)	117.36(11)
P(4)-Ag(3)-Cl(2)	117.17(3)	C(64)-P(6)-Ag(1)	117.79(13)
P(5)-Ag(3)-Cl(2)	96.68(3)	C(70)-P(6)-Ag(1)	111.93(12)
Cl(1)-Ag(3)-Cl(2)	89.72(3)	C(51)-P(6)-Ag(1)	115.32(11)

Table S11. Synthesis methods contrasted for compounds 1-3

	Dppm	CF_3SO_3Ag	Second ligand	Na_2MoO_4/$KMnO_4$	$NaBH_4$	Solvent
Compound **1**	23.3 mg 0.0606 mmol	30.3 mg 0.118 mmol	^{t}BuC≡Cag 11.6 mg 0.0614 mmol	Na_2MoO_4 11.2 mg 0.0500 mmol	500 μL	CH_3OH-CH_2Cl_2 (V : V = 1 : 1) 5 mL
Compound **2**	47.3 mg 0.123 mmol	63.4 mg 0.247 mmol	^{t}BuSAg 24.1mg 0.122 mmol	Na_2MoO_4 23.8 mg 0.116 mmol	500 μL	CH_3OH-CH_2Cl_2 (V : V = 1 : 1) 5 mL
Compound **3**	38.3 mg 0.0996 mmol	22.6 mg, 0.0880 mmol	$MeOC_6H_4SAg$ 49.8 mg 0.202 mmol	$KMnO_4$ 2.90 mg 0.0184 mmol	-	CH_3OH-CH_2Cl_2-DMF (V : V : V = 1 : 1 : 1) 15 mL

Notes: "-" indicates it has not been involved.

Table S12. The pH values and Ag···Ag interactions (Å) data for compounds 1-3

	pH (before reaction)	pH (after reaction)	Bond (Average distance (Å))	Ag···Ag interactions (Å)
Compound **1**	5.1	6.7	Ag-C (2.298 Å)	3.1441(8)-3.1669(9) Å
Compound **2**	3.5	3.0	Ag-O (2.743 Å)	2.9572(4)-3.1466(5) Å
Compound **3**	5.0	6.0	Ag-Cl (2.742 Å)	3.2462(4)-3.5552(7) Å

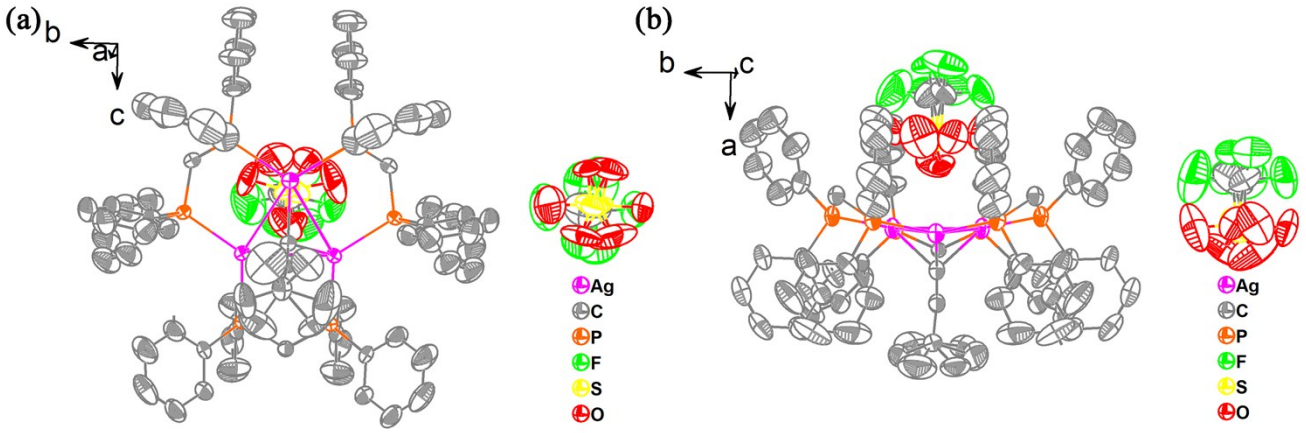


Fig. S1 Ellipsoid representations of compound **1**. All the hydrogen atoms are omitted.

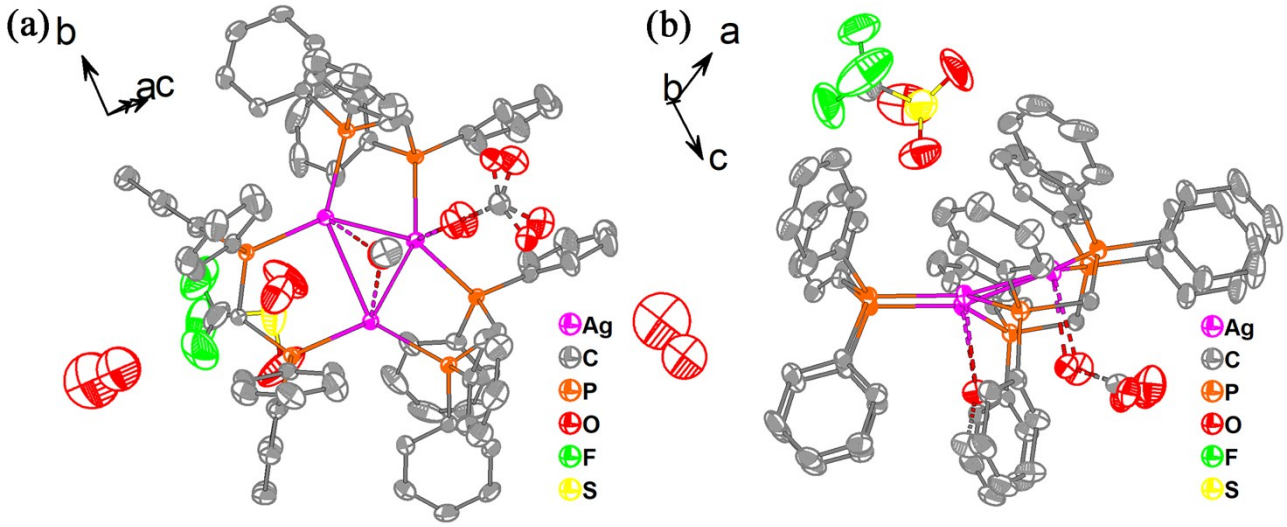


Fig. S2 Ellipsoid representations of compound **2**. All the hydrogen atoms are omitted.

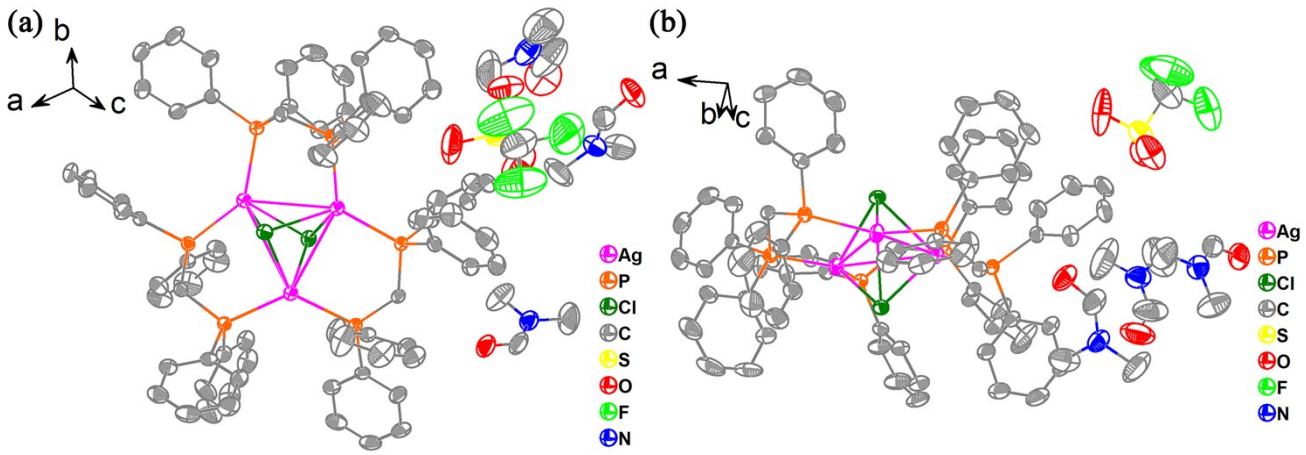


Fig. S3 Ellipsoid representations of compound **3**. All the hydrogen atoms are omitted.

2. Physical Measurements

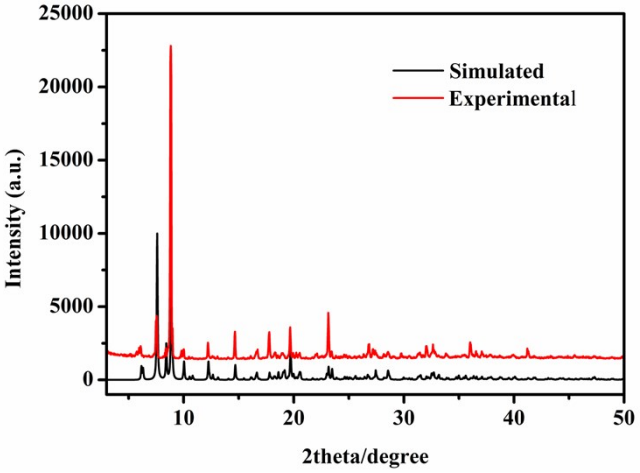


Fig. S4 Experimental and simulated powder X-ray diffraction patterns of compound **1**.

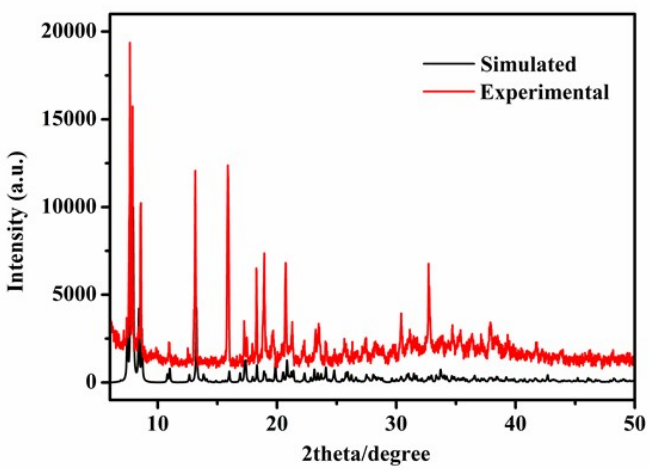


Fig. S5 Experimental and simulated powder X-ray diffraction patterns of compound **2**.

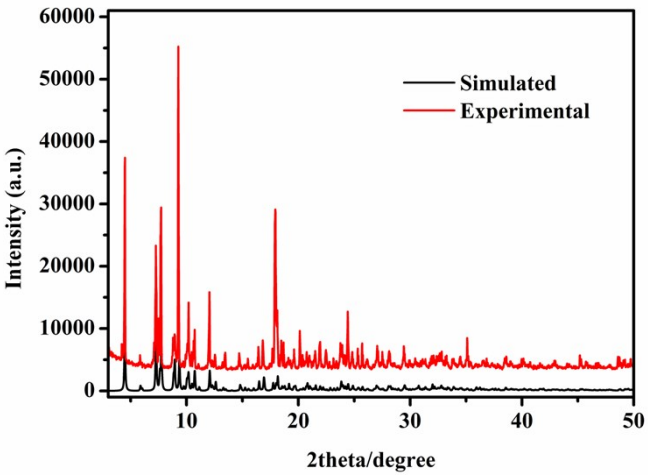


Fig. S6 Experimental and simulated powder X-ray diffraction patterns of compound **3**.

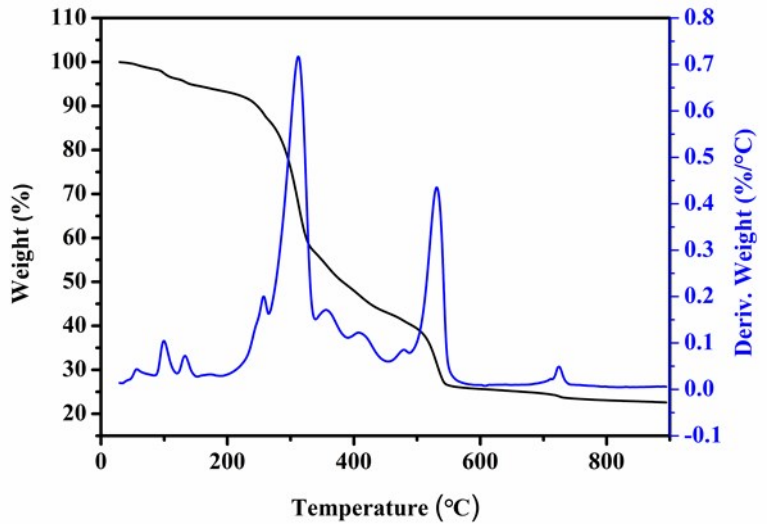


Fig. S7 TGA/DSC curve of compound **1** (in N_2).

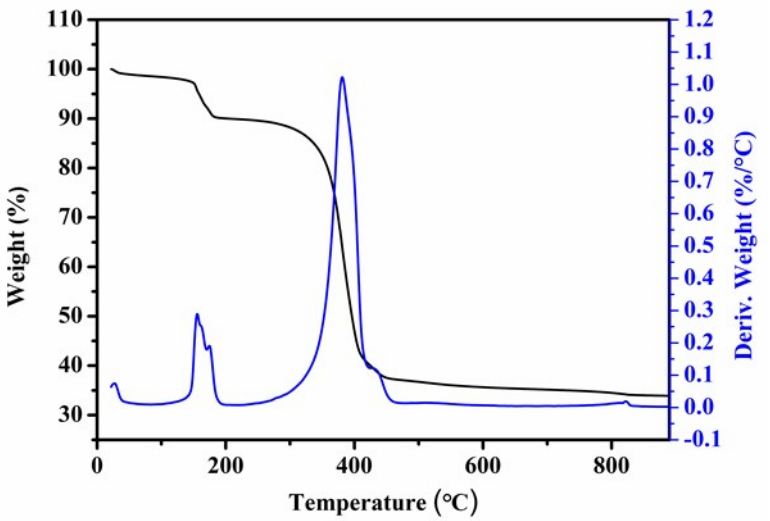


Fig. S8 TGA/DSC curve of compound **2** (in N_2).

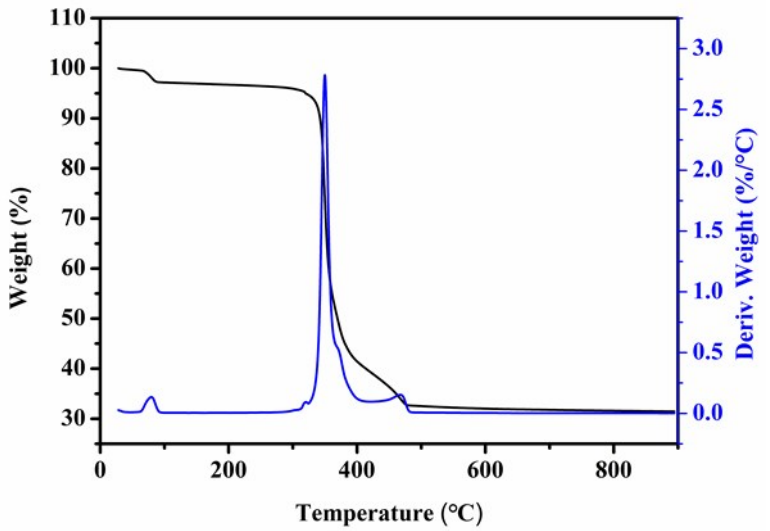


Fig. S9 TGA/DSC curve of compound **3** (in N_2).

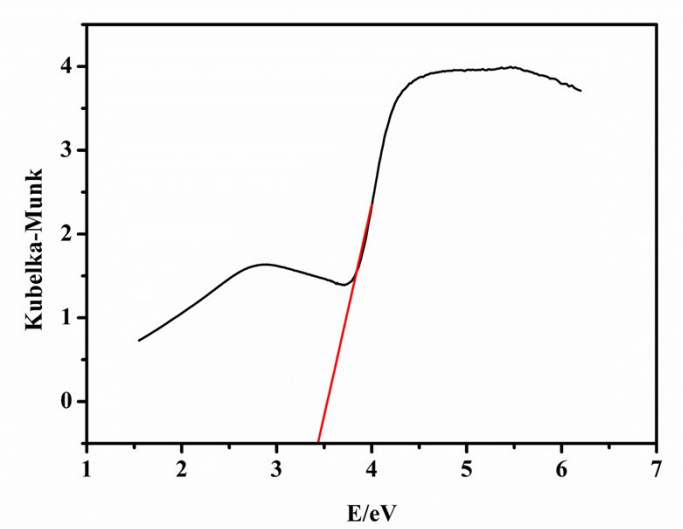


Fig. S10 Kubelka-Munk function vs energy (eV) of compound **1**.

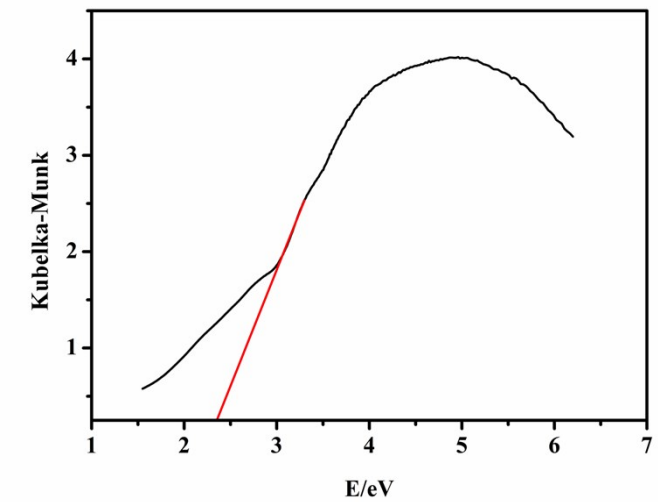


Fig. S11 Kubelka-Munk function vs energy (eV) of compound **2**.

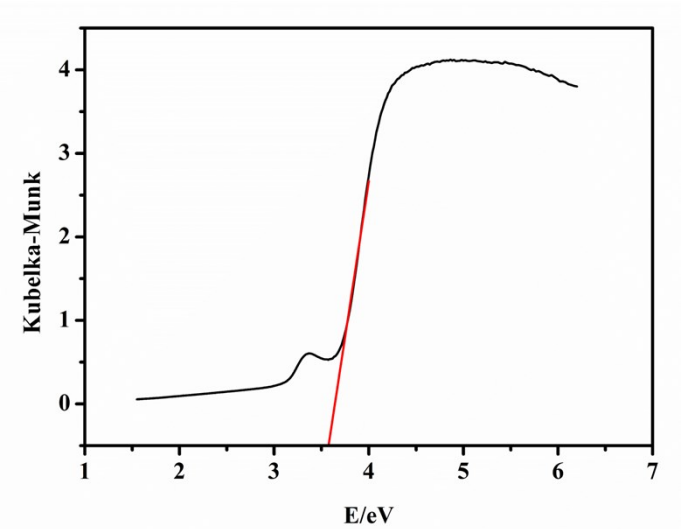


Fig. S12 Kubelka-Munk function vs energy (eV) of compound **3**.

Photocurrent measurement

The photocurrent test was carried out on a CHI660E electrochemistry workstation[1] and in a typical three-electrode system. The crystals (10 mg) of compounds **1-3** were dispersed in 1 mL ethanol, the mixture was sonicated for about 30 min and then 50 μL of a dilute solution of naphthol was added to the above mixed solution. Then a 50 μL solution was transferred by Pipetting gun dropped on the cleaned FTO glass, which apply twice in the same way after evaporation under ambient atmosphere. Then a conductive layer of 0.8 × 1 cm^2 compounds made of AB glue were transferred into a drying oven and kept at 65 °C for 10 h. The coated film was obtained. The prepared FTO glass film was used as working electrode, platinum wire as the assisting electrode, Ag/AgCl as the reference electrode and keeping the bias voltage at 0.6 V, and a 0.2 M Na_2SO_4 aqueous solution was used as the electrolyte.

Electrochemical measurement

The electrochemical test was carried out on a CHI660E electrochemistry workstation and in a typical three-electrode system. The compound carbon-paper electrodes were used as the working electrode.[2] Hg/HgO electrode was used as a reference electrode and carbon rod as a counter electrode, and a 0.1 M KOH aqueous solution was used as the electrolyte. Additionally, Ag/AgCl electrode was used as a reference electrode and carbon rod as a counter electrode, and 0.01 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte.The crystals (2 mg) of compounds **1-3** were dispersed in 200 μL ethanol. The mixture was sonicated for about 30 min. Then a 200 μL solution was transferred by Pipetting gun dropped on the carbon-paper. Carbon paper (0.5 × 2 cm^2) loaded with compounds were transferred into a drying oven and kept at 80 °C for 10 h.

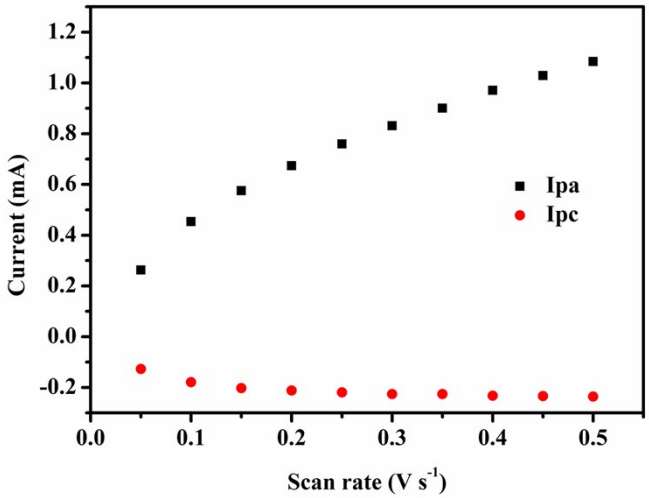


Fig. S13 The plotting of peak current of CPE-**1** anode and cathode versus scanning rate.

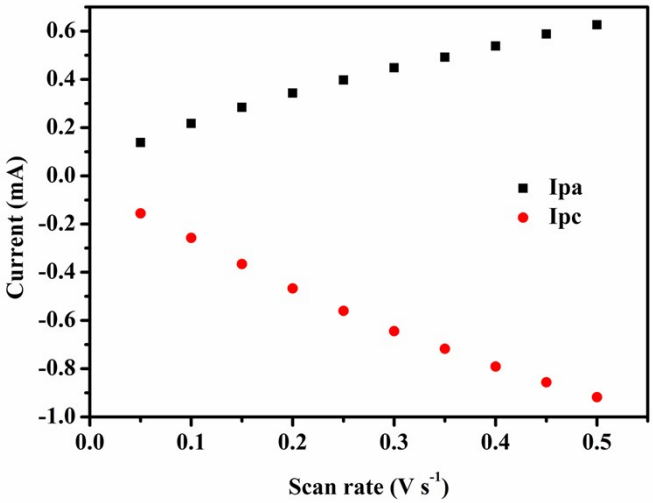
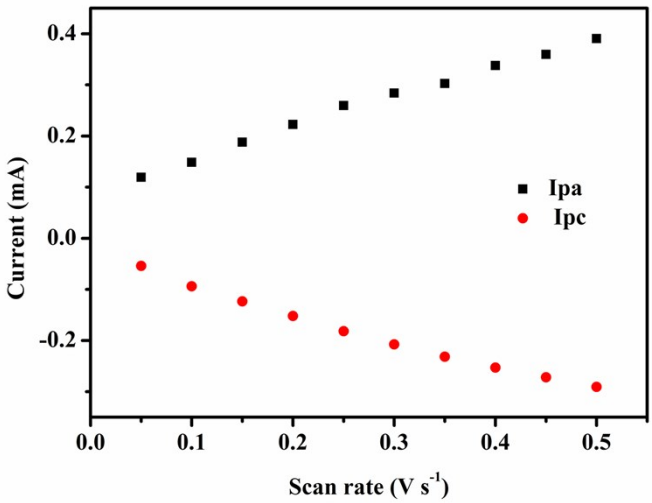


Fig. S14 The plotting of peak current of CPE-**2** anode and cathode versus scanning rate.



5

Fig. S15 The plotting of peak current of CPE-**3** anode and cathode versus scanning rate.

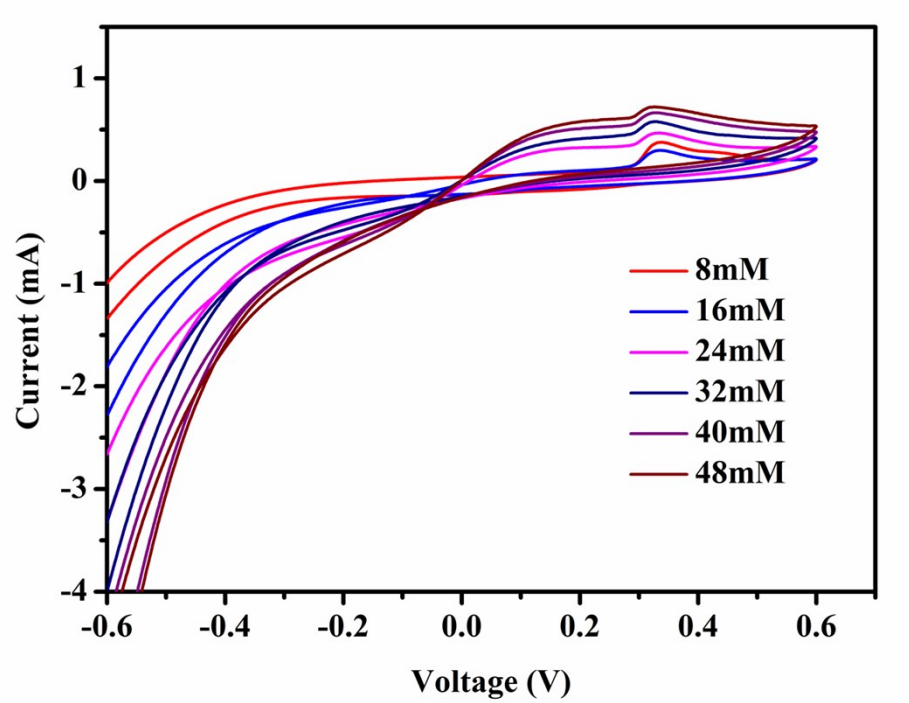


Fig. S16 Cyclic voltammograms of CPE-**1** in 0.01 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution containing different concentrations H_2O_2 under the scan rate 0.2 $V \cdot s^{-1}$.

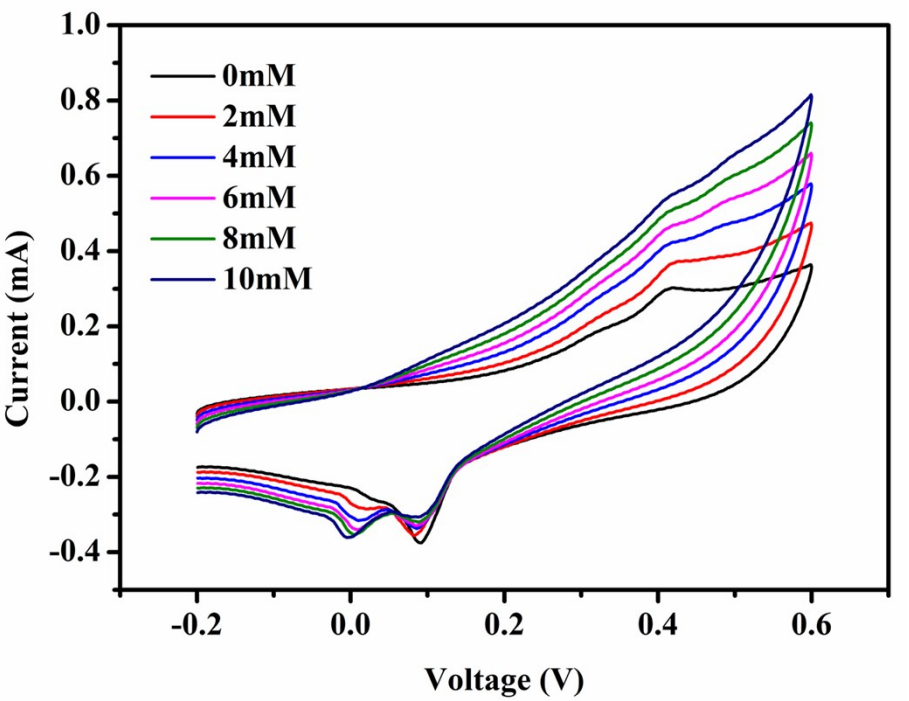


Fig. S17 Cyclic voltammograms of CPE-**2** in 0.1 M KOH aqueous solution containing different concentrations H_2O_2 under the scan rate 0.2 $V \cdot s^{-1}$.

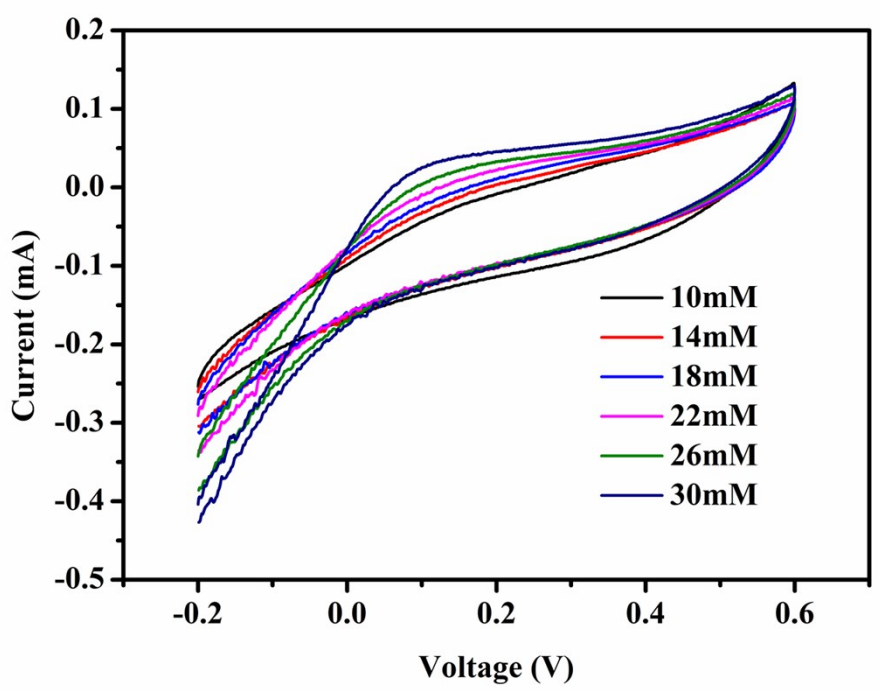


Fig. S18 Cyclic voltammograms of CPE-**3** in 0.01 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution containing different concentrations H_2O_2 under the scan rate 0.2 $V \cdot s^{-1}$.

5

10 **Reference:**

1. Z. Wang, H.-F. Su, Y.-W. Gong, Q.-P. Qu, Y.-F. Bi , C.-H. Tung, D. Sun and L.-S. Zheng, *Nat. Commun.*, 2020, **11**, 308.

2. P.-P. Zhang, J. Peng, H.-J. Pang, J.-Q. Sha, M. Zhu, D.-D. Wang and M.-G. Liu, *CrystEngComm*, 2011, **13**, 3832-3841.