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A series of A- and B-type Anderson compounds with Al, Te and Cr as centers by tunning different ligands: syntheses, electrochemical, photocatalytic and CO_2RR properties

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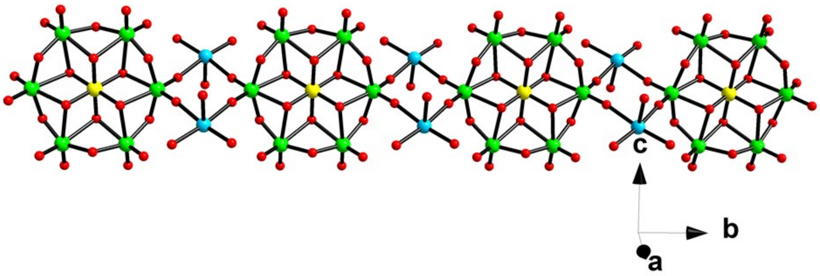


Fig. S1. The 1D inorganic chain of **1** with Anderson anions linked by two Zn atoms.

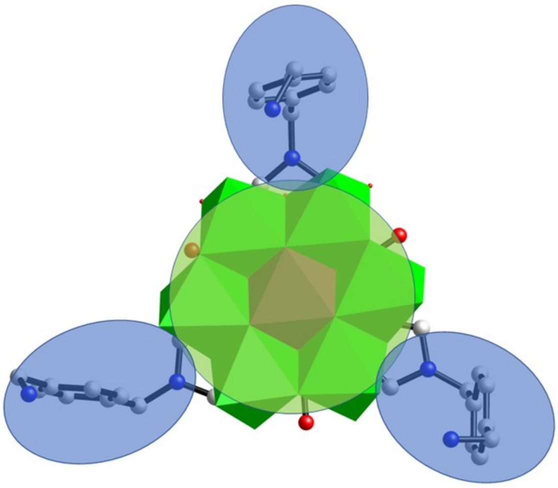


Fig. S2. This tri-nuclear $[Cu^{II}_3(tybm)_3(H_2O)_4]^{6+}$ cluster with three benzylamine groups as petals and the Te1-containing Anderson anion as the centre of the flower.

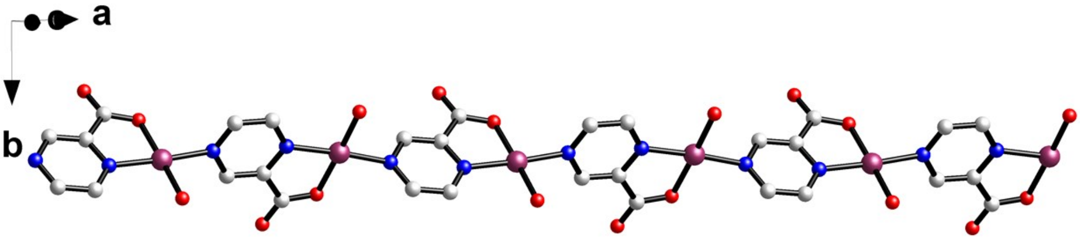


Fig. S3. The metal-organic chain $[Zn^{II}(2\text{-pyc})(H_2O)]_n^{2n+}$ in compound **5**.

Experimental

Materials and methods

All reagents and solvents for syntheses were used without further purification from commercial sources. Elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were obtained on a Varian FT-IR 640 spectrometer with KBr pellets. The EDS were got by Scanning Electron Microscope S-3000N. We used a Lambda 750 UV/VIS/NIR spectrophotometer to measure UV-Vis absorption spectra. Electrochemical measurements and data collection were completed with a CHI 440 electrochemical workstation. We used a conventional three-electrode system: a saturated calomel electrode (SCE) as reference electrode, a Pt wire as counter electrode and the title compounds modified carbon paste electrodes (CPEs) as the working electrodes.

X-Ray crystallography

We collected X-ray diffraction analyses data collection for compounds **1**–**6** on a Bruker SMART APEX II with Mo Kα ($\lambda = 0.71073$ Å) by ω and θ scan mode at 293K. All the structures were solved by direct methods and refined on F^2 by full-matrix least squares using the SHELXL package.[18] Table 1 shows The detailed crystal data and structures refinement for **1**–**6**. Table S1 exhibits the selected bond lengths and angles. Crystallographic data for these structures **1**–**6** have been deposited in the Cambridge Crystallographic Data Center with CCDC Numbers of 1985478–1985483 for **1**–**6**.

Preparation of compounds 1–6

Synthesis of $\{[Zn^{II}_5(trz)_6(H_2O)_{12}][AlMo_6(OH)_6O_{18}]_2\}\cdot(HAlMo_6(OH)_6O_{18})\cdot 23H_2O$ (1). The reactants $ZnCl_2$ (0.068 g, 0.5 mmol) and trz (0.012 g, 0.18 mmol) were dissolved in 30 mL distilled water (solution A). The reactant $(NH_4)_3[AlMo_6H_6O_{24}]\cdot 8H_2O$ (0.24 g, 0.2 mmol) was dissolved in 30 mL distilled water (solution B). Pour solution B to solution A and mix. The mixture was stirred for 5h and filtered. The pH of filtrate is about 6.5. The filtrate was placed in a 100 mL beaker with plastic wrap. Slow evaporation of the solvent at room temperature produced colourless block crystals of **1** about one week later (40% yield based on Mo). Anal. Calcd for **1** $C_{12}H_{101}Al_3Mo_{18}N_{18}O_{107}Zn_5$ (4344.8): C 3.32, H 2.32, N 5.80%. Found: C 3.36, H 2.28, N, 5.85%. IR (KBr, cm^{-1}): 3239(s), 1764(w), 1609(m), 1525(s), 1387(s), 1299(w), 1220(w), 1178(s), 1089(m), 1001(m), 889(s), 822(w), 654(s), 574(w), 440(s).

Synthesis of $\{[Cu^{II}_3(tybm)_3(H_2O)_4][TeMo_6O_{24}]\}_2\cdot(H_6TeMo_6O_{24})\cdot 16H_2O$ (2). Mix $(NH_4)_6[TeMo_6O_{24}]\cdot 7H_2O$ (0.2 g, 0.16 mmol), $CuCl_2\cdot 2H_2O$ (0.1 g, 0.6 mmol) and tybm (0.02 g, 0.09 mmol) and dissolve in 10 mL distilled water at room temperature. The suspension was stirred for 1h. The pH was adjusted to about 2.4 with 1.0 mol·L^{-1} HNO_3. The suspension was sealed in a 25 mL Teflon-lined autoclave and kept at 160 °C for 5 days. After cooling to room temperature, blue block crystals of **2** (yield 30% based on Mo). Anal. Calcd for **2** $C_{60}H_{126}Cu_6Mo_{18}N_{24}O_{96}Te_3$ (5210.7): C 13.83, H 2.42, N 6.45%. Found: C 13.46, H 2.47, N, 6.52%. IR (KBr, cm^{-1}): 3405(s), 1677(s), 1601(m), 1498(w), 1375(m), 1219(w), 1109(w), 875(s), 686(m), 621(w).

Synthesis of $\{Cu_2^I(H_2bdpm)_2[HCr(OH)_6Mo_6O_{18}]\}$ (3). Mix $(NH_4)_3[CrMo_6H_6O_{24}]\cdot 8H_2O$ (0.24 g, 0.2 mmol), $Cu(NO_3)_2\cdot 3H_2O$ (0.12 g, 0.5 mmol), H_2bdpm (0.03 g, 0.18 mmol) and dissolve in 10 mL distilled water at room temperature. The suspension was stirred for 1h. The pH was adjusted to about 2.9 with 1.0 mol·L^{-1} HCl. The suspension was sealed in a 25 mL Teflon-lined autoclave and kept at 170 °C for 7 days. After cooling to room temperature, blue block crystals of **3** (yield 30% based on Mo). Anal. Calcd for **3** $C_{22}H_{35}CrCu_2Mo_6N_8O_{24}$ (1550): C 17.05, H 2.26, N 7.23%. Found: C 16.96, H 2.32, N, 7.17%. IR (KBr, cm^{-1}): 3268(s), 1627(m), 1542(w), 1450(w), 1370(w), 1316(w), 1278(m), 1137(w), 1048(w), 947(s), 892(s), 796(w), 637(s), 415(s).

Synthesis of {[Cu^{II}_2(2-pyc)$_2$][$H_5Cr(OH)_6Mo_6O_{18}$]}·$17H_2O$ (4). The reactants $Cu(NO_3)_2\cdot 3H_2O$ (0.12 g, 0.5 mmol) and 2-pyc (0.022 g, 0.18 mmol) were dissolved in 30 mL distilled water (solution A). The reactant $(NH_4)_3[CrMo_6H_6O_{24}]\cdot 8H_2O$ (0.24 g, 0.2 mmol) was dissolved in 30 mL distilled water (solution B). Pour solution B to solution A and mix. The mixture was stirred for 5h and filtered. The filtrate was placed in a 100 mL beaker with plastic wrap. Slow evaporation of the solvent at room temperature produced blue block crystals of **4** about two week later (40% yield based on Mo). Anal. Calcd for **4** $C_{10}H_{55}CrCu_2Mo_6N_4O_{49}$ (1770): C 6.79, H 3.11, N 3.17%. Found: C 6.85, H 3.05, N, 3.25%. IR (KBr, cm^{-1}): 3255(s), 1696(w), 1626(m), 1538(m), 1446(w), 1362(w), 1308(w), 1228(w), 1128(m), 1048(w), 951(s), 901(s), 792(w), 633(s), 415(s).

Synthesis of {[Zn^{II}_2(2-pyc)$_2$(H_2O)$_2$][$HCr(OH)_6Mo_6O_{18}$]}·$18H_2O$ (5). The synthetic process of **5** is similar to **4**, except the replacement of $Cu(NO_3)_2$ by $ZnCl_2$ (0.068 g, 0.5 mmol). Slow evaporation of the solvent at room temperature produced purple block crystals of **5** about two week later (40% yield based on Mo). Calcd for **5** $C_{10}H_{53}CrMo_6N_4O_{48}Zn_2$ (1756): C 6.84, H 3.02, N 3.19%. Found: C 6.77, H 3.09, N, 3.13%. IR (KBr, cm^{-1}): 3490(w), 3192(s), 1759(w), 1626(w), 1533(m), 1387(s), 1303(w), 1220(w), 1174(w), 1094(m), 1044(w), 1006(m), 947(s), 892(s), 822(w), 654(s), 574(w), 415(s).

Synthesis of {[Co^{II}(2-pyc)(H_2O)$_2$]$_2$[$HCr(OH)_6Mo_6O_{18}$]}·$15H_2O$ (6). The synthetic process of **6** is similar to **4**, except the replacement of $Cu(NO_3)_2$ by $Co(NO_3)_2$ (0.08 g, 0.4 mmol). Slow evaporation of the solvent at room temperature produced purple block crystals of **6** about one month later (40% yield based on Mo). Calcd for **6** $C_{10}H_{45}CrCo_2Mo_6N_4O_{47}$ (1719): C 6.99, H 2.62, N 3.26%. Found: C 6.91, H 2.69, N, 3.21%. IR (KBr, cm^{-1}): 3360(s), 1685(s), 1602(w), 1423(s), 1287(w), 1217(m), 1175(w), 921(s), 893(s), 791(w), 694(s), 602(w), 503(w), 455(s).

Preparation of 3–CPE. Compound **3** modified CPE (**3**−CPE) was made as follows: the graphite powder and **3** were mixed at a ratio of 10: 1, which was grounded in an agate mortar with a pestle to form a uniform mixture. 0.1 mL of Nujol was added with stirring. The homogenized mixture was packed into a glass tube with a 1.5 mm inner diameter. The tube surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode.

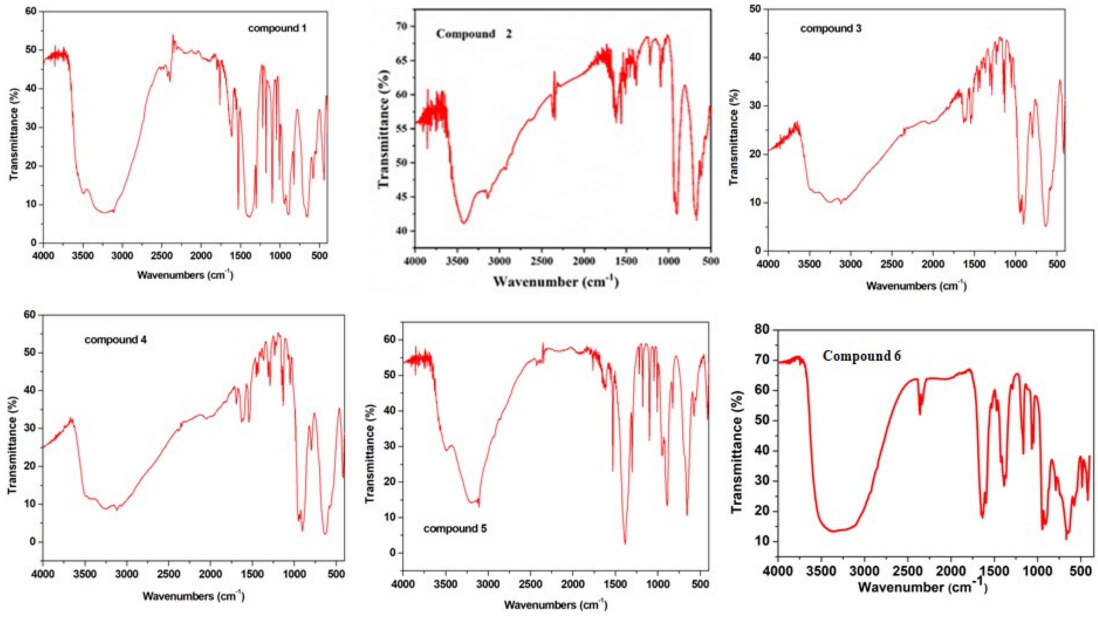
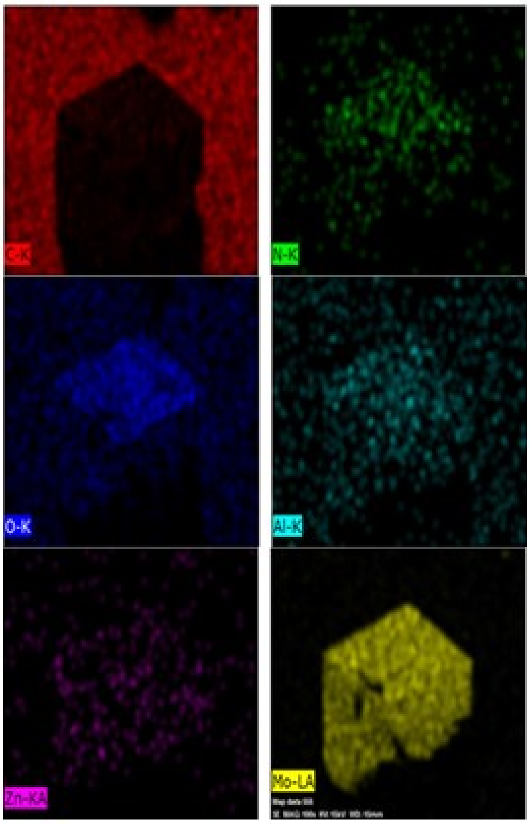
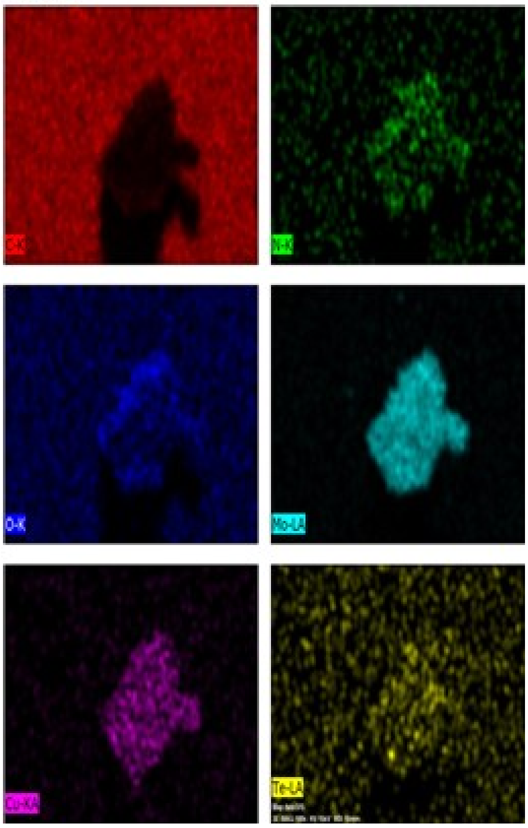


Fig. S4. The IR spectra of compounds **1**–**6**.

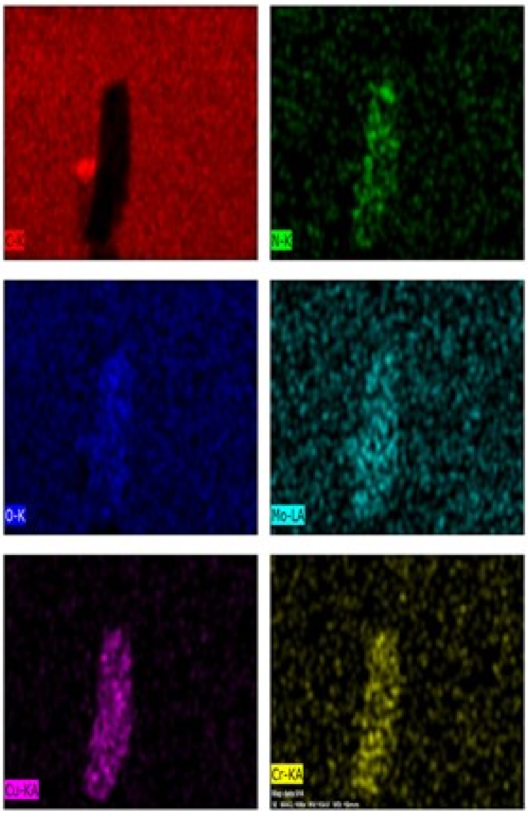
(a)


C-K
N-K
O-K
Al-K
Zn-KA
Mo-LA

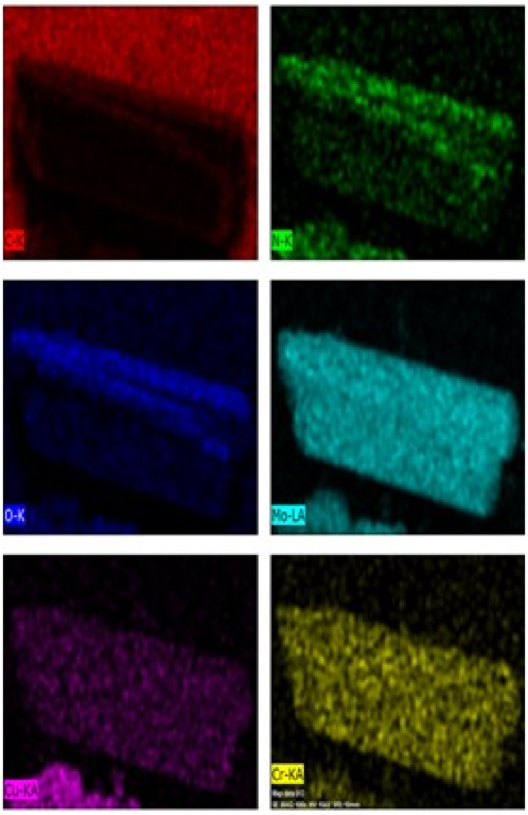
(b)


C-K
N-K
O-K
Mo-LA
Cu-KA
Te-LA

(c)


C-K
N-K
O-K
Mo-LA
Cu-KA
Cr-KA

(d)


C-K
N-K
O-K
Mo-LA
Cu-KA
Cr-KA

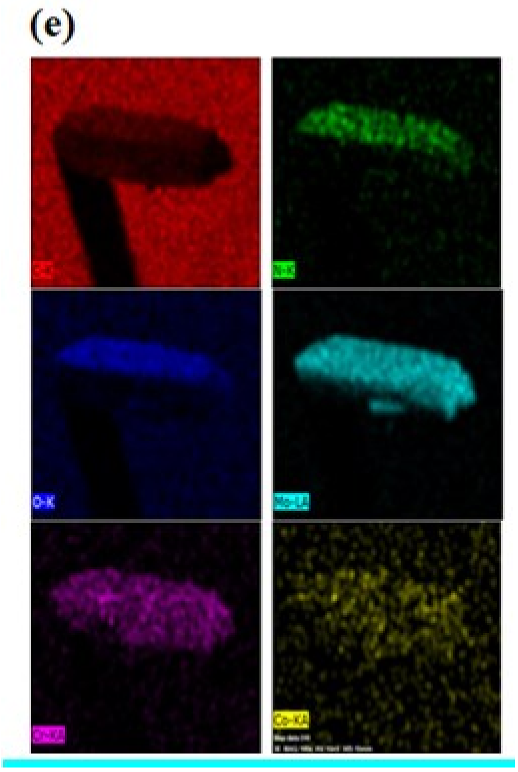


Fig. S5. The elemental mapping images of compounds **1**(a), **2**(b), **3**(c), **4**(d) and **5**(e).

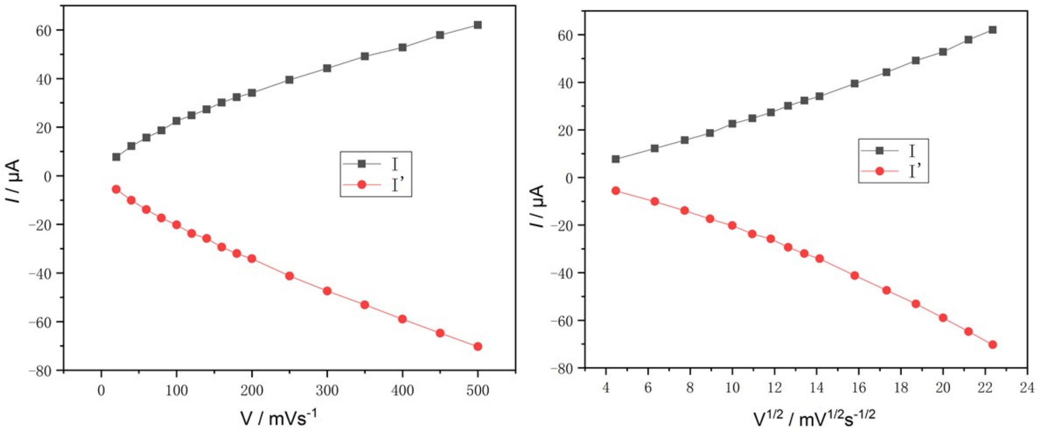


Fig. S6. Plots of the anodic and the cathodic peak II–II′ current against υ and υ$^{1/2}$.

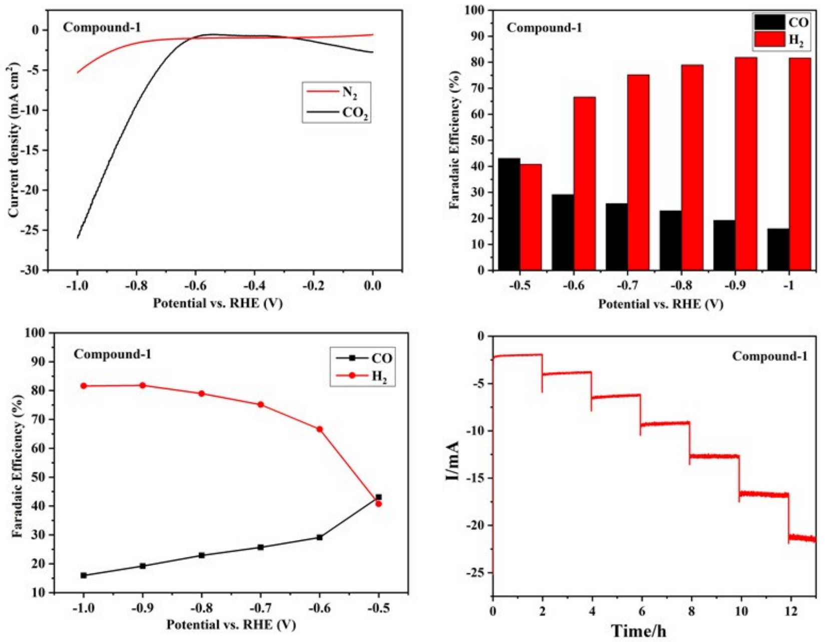


Fig. S7. (a) LSV curves of compound **1** in CO_2-saturated and N_2-saturated 0.5 M $KHCO_3$ electrolyte on carbon paper at a scan rate of 5 mV s^{-1}. (b) The Faradaic efficiency of compound **1** for CO (red bars) and H_2 (black bars). (c) The FE of CO and H_2 products on compound **1** at selected potentials. (d) The i-t curve of compound **1** during the electrolysis.

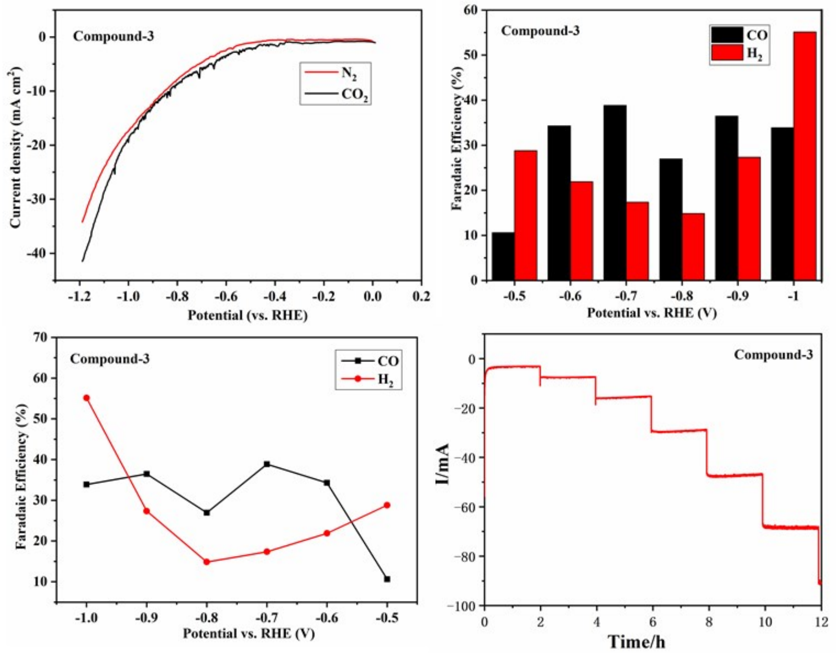


Fig. S8. (a) LSV curves of compound **3** in CO_2-saturated and N_2-saturated 0.5 M $KHCO_3$ electrolyte on carbon paper at a scan rate of 5 mV s^{-1}. (b) The Faradaic efficiency of compound **3** for CO (red bars) and H_2 (black bars). (c) The FE of CO and H_2 products on compound **3** at selected potentials. (d) The i-t curve of compound **3** during the electrolysis.

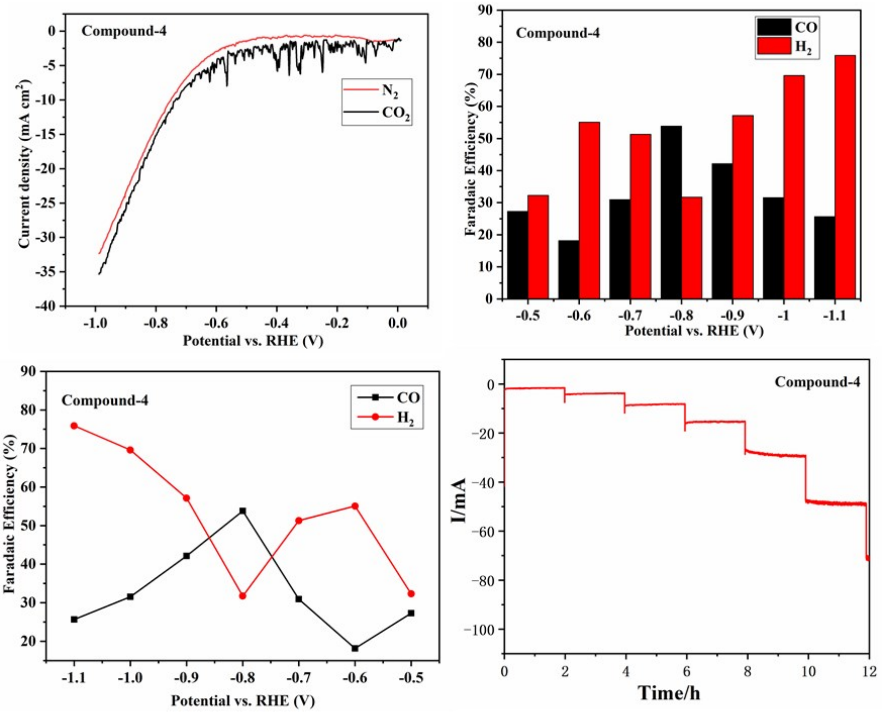


Fig. S9. (a) LSV curves of compound **4** in CO_2-saturated and N_2-saturated 0.5 M $KHCO_3$ electrolyte on carbon paper at a scan rate of 5 mV s^{-1}. (b) The Faradaic efficiency of compound **4** for CO (red bars) and H_2 (black bars). (c) The FE of CO and H_2 products on compound **4** at selected potentials. (d) The i-t curve of compound **4** during the electrolysis.

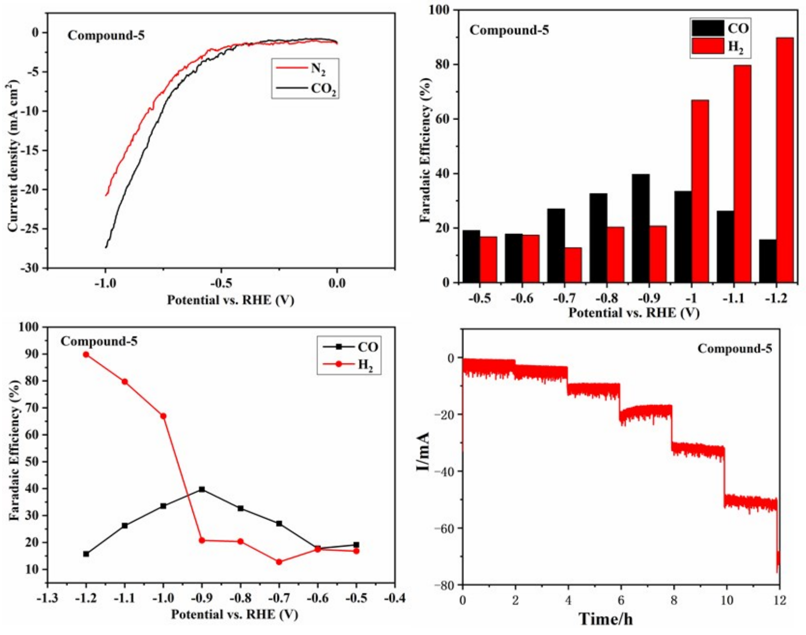


Fig. S10. (a) LSV curves of compound **5** in CO_2-saturated and N_2-saturated 0.5 M $KHCO_3$ electrolyte on carbon paper at a scan rate of 5 mV s^{-1}. (b) The Faradaic efficiency of compound **5** for CO (red bars) and H_2 (black bars). (c) The FE of CO and H_2 products on compound **5** at selected potentials. (d) The i-t curve of compound **5** during the electrolysis.

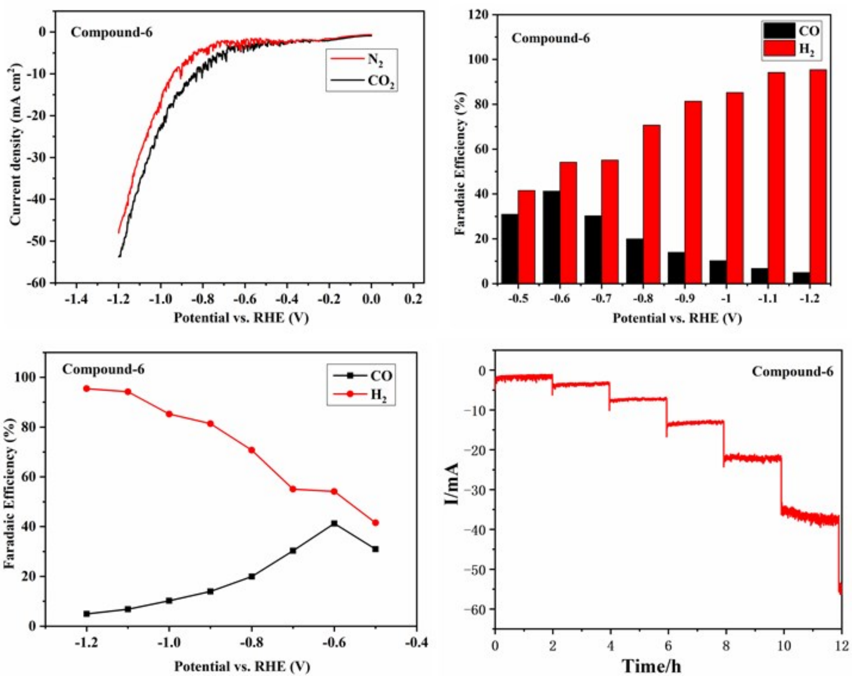


Fig. S11. (a) LSV curves of compound **6** in CO_2-saturated and N_2-saturated 0.5 M $KHCO_3$ electrolyte on carbon paper at a scan rate of 5 mV s^{-1}. (b) The Faradaic efficiency of compound **6** for CO (red bars) and H_2 (black bars). (c) The FE of CO and H_2 products on compound **6** at selected potentials. (d) The i-t curve of compound **6** during the electrolysis.

Table S1. Selected bond distances (Å) and angles (°) for compounds **1–6**.

Compound **1**

Zn(1)-N(2)	2.046(9)	Zn(3)-N(8)#3	2.189(13)
O(8W)-Zn(1)	2.02(2)	O(5W)-Zn(2)	2.234(15)
O(7W)-Zn(1)	2.079(15)	O(3W)-Zn(2)	2.123(12)
O(6W)-Zn(1)	2.15(2)	O(4W)-Zn(2)	2.224(15)
Zn(2)-N(6)#3	2.141(13)	Zn(3)-N(8)	2.189(13)
Zn(2)-N(7)	2.116(12)	Zn(3)-N(4)	2.212(13)

Zn(2)-N(3)	2.062(10)	Zn(3)-N(1)	2.122(9)
O(27)-Zn(1)	2.227(10)	O(25)-Zn(1)#2	2.231(10)
O(27)-Zn(1)-O25#4	81.5(3)	N(3)-Zn(2)-N(6)#3	95.1(4)
N(8)-Zn(3)-N(4)#3	90.3(4)	N(3)-Zn(2)-N(7)	91.0(4)
N(2)-Zn(1)-O(27)	85.9(4)	N(8)-Zn(3)-N(8)#3	90.7(7)
N(8)-Zn(3)-N(4)	176.1(5)	N(4)#3-Zn(3)-N(4)	88.9(7)
N(8)#3-Zn(3)-N(4)	90.3(4)	N(1)-Zn(3)-N(8)	89.0(4)
N(1)-Zn(3)-N(8)#3	92.0(4)	N(1)#3-Zn(3)-N(4)	91.7(4)
N(1)#3-Zn(3)-N8#3	89.0(4)	N(1)#3-Zn(3)-N4#3	87.2(5)
N(1)#3-Zn(3)-N(8)	92.0(4)	N(1)-Zn(3)-N(4)#3	91.7(4)
N(1)-Zn(3)-N(4)	87.2(5)	N(1)-Zn(3)-N(1)#3	178.5(8)

Symmetry codes for **1:** #1 -x,y,-z+2 #2 x,y-1,z #3 -x,y,-z+1 #4 x,y+1,z

Compound **2**

Cu(1)-O(4)	2.324(4)	Cu(2)-O(4W)	1.987(4)
Cu(1)-O(4W)	1.968(4)	Cu(2)-O(2W)	1.996(5)
Cu(1)-N(7)	1.979(6)	Cu(2)-N(8)	1.946(6)
Cu(1)-O(1W)	1.986(5)	Cu(2)-N(3)	1.935(6)
Cu(1)-N(5)	1.964(6)	Cu(3)-O(4W)	1.987(5)
Cu(3)-N(2)	1.957(6)	Cu(3)-O(24)	2.366(4)
Cu(3)-N(4)	1.955(5)	Cu(3)-O(3W)	1.985(5)
O4W-Cu(1)-O1W	164.96(19)	N(7)-Cu(1)-O(4)	97.97(19)
O(1W)-Cu(1)-O(4)	94.93(18)	N(5)-Cu(1)-O(4W)	88.1(2)
N(5)-Cu(1)-N(7)	170.8(2)	O4W-Cu(2)-O2W	163.8(2)
N(8)-Cu(2)-O(4W)	89.1(2)	N(3)-Cu(2)-O(2W)	91.5(2)
N(3)-Cu(2)-N(8)	179.1(2)	O(4W)-Cu(3)-O(24)	97.05(16)
N(2)-Cu(3)-O(4W)	88.1(2)	O3W-Cu(3)-O4W	159.8(2)
N(2)-Cu(3)-O(24)	93.67(18)	N(4)-Cu(3)-N(2)	172.4(2)

Compound **3**

Cu(1)-N(1)	1.873(5)	Cu(1)-N(3)#2	1.886(5)
Cu(1)-O(1)	2.367(4)	N(1)-Cu(1)-O(1)	98.0(2)
N(1)-Cu(1)-N(3)#2	168.4(2)	N(3)#2-Cu(1)-O(1)	93.4(2)

Symmetry codes for **3**: #2 -x+2, y+1/2, -z+1/2

Compound **4**

Cr(1)-O(5)#1	1.9834(16)	Mo(3)-O(9)#1	1.9572(18)
Cr(1)-O(5)	1.9834(16)	Mo(3)-O(11)	1.9261(19)
Cr(1)-O(8)#1	1.9713(16)	Mo(3)-O(12)	2.2966(17)
Cr(1)-O(8)	1.9713(16)	O1W-Cu(1)	2.279(2)
Cr(1)-O(12)	1.9703(17)	O2W-Cu1	1.9744(18)
Cr(1)-O(12)#1	1.9703(17)	O(8)-Mo(3)#1	2.2956(17)

Mo(1)-O(1)	1.696(2)	O(9)-Mo(3)#1	1.9572(18)
Mo(1)-O(4)	1.714(2)	O(13)-C(5)	1.222(3)
Mo(1)-O(5)	2.3123(18)	O(14)-Cu(1)	1.9535(19)
Mo(1)-O(10)	1.9477(17)	O(14)-C(5)	1.278(3)
Mo(1)-O(11)	1.9301(18)	Cu(1)-N(1)#2	2.017(2)
Mo(1)-O(12)	2.2842(17)	Cu(1)-N(2)	2.020(2)
Cr(1)-O(5)#1	1.9834(16)	Mo(3)-O(9)#1	1.9572(18)

Symmetry codes for **4**: #1 -x+1,-y-2,-z #2 x-1,y,z #3 x+1,y,z

Compound **5**

Zn(1)-N(2)	2.001(3)	Zn(1)-O(14)	1.952(3)
Zn(1)-O(7)	2.382(3)	Zn(1)-O1W	1.968(3)
Zn(1)-N(1)#3	2.091(4)	Zn(1)-O(4)#2	2.404(3)
O(7)-Zn(1)-Mo(1)	140.93(18)	O(4)-Zn(1)-Mo(2)#2	137.53(18)
O1W-Zn(1)-O(4)#3	85.87(14)	O1W-Zn(1)-O7	90.86(14)
O(7)-Zn(1)-O(4)#3	171.74(11)	O(14)-Zn(1)-O1W	175.26(14)
O(14)-Zn(1)-O(4)#3	91.18(13)	O(14)-Zn(1)-O(7)	91.57(13)
O(14)-Zn(1)-N(1)	92.33(14)	O(14)-Zn(1)-N(2)	82.73(13)
N(1)#4-Zn(1)-O4#3	92.92(13)	N(1)#4-Zn(1)-O(7)	94.75(13)
N(2)-Zn(1)-O4#3	88.27(12)	N(2)-Zn(1)-O7	84.35(13)

Symmetry codes for **5**: #11-x,-y,2-z #2 1/2+x,-1/2-y,-1/2+z #3-1/2+x,-1/2-y,1/2+z #4 -1/2+x,-1/2-y,-1/2+z

Compound **6**

Co(1)-O(12)	2.109(4)	Co(1)-O(13)	2.051(4)
Co(1)-O(5W)	2.070(4)	Co(1)-O(4W)	2.102(4)
Co(1)-N(1)	2.130(4)	Co(1)-N(2)#2	2.143(4)
O(13)-Co(1)-O(5W)	171.26(15)	O(13)-Co(1)-O(4W)	91.65(16)
O(13)-Co(1)-O(12)	90.73(15)	O(13)-Co(1)-N(1)	79.07(16)
O(13)-Co(1)-N(2)#2	98.59(16)	O(5W)-Co(1)-O(12)	86.22(15)
O5W-Co(1)-O4W	91.39(17)	O(5W)-Co(1)-N(1)	92.60(16)
O5W-Co(1)-N(2)#2	89.70(16)	O(12)-Co(1)-N(1)	87.62(15)
O(12)-Co(1)-N(2)#2	91.83(16)	O(4W)-Co(1)-O(12)	177.61(16)
O(4W)-Co(1)-N(1)	92.63(16)	O4W-Co(1)-N(2)#2	88.02(16)
N(1)-Co(1)-N(2)#2	177.59(18)		

Symmetry codes for **6**: #2 x, -y+1/2, z+1/2

Table S2. Comparison of the catalytic performance with other electrodes for MB.

Catalyst(mg)	time	conversion	Ref.
1 (100mg)	120 min	55.9%	This work
2 (100mg)	120 min	54.1%	This work
3 (100mg)	120 min	60.0%	This work
4 (100mg)	120 min	54.5%	This work

5 (100mg)	120 min	48.6%	This work
6 (100mg)	120 min	59.6%	This work
1	120 min	57.3%	**S1**
2	120 min	58%	**S1**
6 (150mg)	150 min	58.6%	**S2**
7 (150mg)	150 min	74.5%	**S2**

Table S3. Comparison of the catalytic performance with other electrodes for RhB.

Catalyst(mg)	time	conversion	Ref.
1 (100mg)	120 min	62.2%	This work
2 (100mg)	120 min	54.3%	This work
3 (100mg)	120 min	53.2%	This work
4 (100mg)	120 min	50.0%	This work
5 (100mg)	120 min	45.9%	This work
6 (100mg)	120 min	34.1%	This work
4	120 min	42.4%	**S1**
5	120 min	50.8%	**S1**
1	180 min	14.3%	**S3**
2	180 min	15.7%	**S3**

Table S4. Comparison of the catalytic performance with other electrodes for GV.

Catalyst(mg)	time	conversion	Ref.
1 (100mg)	120 min	60.8%	This work
2 (100mg)	120 min	72.9%	This work
3 (100mg)	120 min	76.8%	This work
4 (100mg)	120 min	54.9%	This work
5 (100mg)	120 min	58.6%	This work
6 (100mg)	120 min	44.7%	This work
1	180 min	94.3%	**S3**
3	180 min	31.1%	**S3**
1 (50mg)	2 min	99.05%	**S4**
2 (50mg)	40 min	71.43%	**S4**

Table S5. Comparison of the CO_2RR catalytic performance with other electrodes for CO production.

Catalyst	Potential (V vs. RHE)	Electrolyte	Products	FE (%)	Ref.
1	-0.2	0.5 M $KHCO_3$	CO	43.2	This work
2	-0.8	0.5 M $KHCO_3$	CO	93.4	This work

3	-0.7	0.5 M $KHCO_3$	CO	39.0	This work
4	-0.8	0.5 M $KHCO_3$	CO	53.8	This work
5	-0.9	0.5 M $KHCO_3$	CO	39.6	This work
6	-0.6	0.5 M $KHCO_3$	CO	41.2	This work
Cu-ACs/NPC	-0.5	0.5 M $KHCO_3$	CO	93.21	**S5**
Cu-N4/GN	-0.5	0.1 M $KHCO_3$	CO	62	**S6**
Cu-N-C	-0.66	0.5 M $KHCO_3$	CO	21	**S7**

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