# Four new dual-functional electro-catalysts formed of small molybdenum clusters and Cu-pyridyl complexes

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**Electronic Supplementary Information**

**Table S1** X-ray crystallographic data for compounds **1-4**

| Compound | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{30}H_{22.50}N_6Cu_2$ $Mo_8O_{26.25}$ | $C_{30}H_{26}N_6Cu_2$ $Mo_8O_{28}$ | $C_{11}H_{11}N_5Cu$ $Mo_3O_{11}$ | $C_{11}H_9N_5Cu$ $Mo_4O_{14}$ |
| Formula weight | 1781.64 | 1813.17 | 740.61 | 882.53 |
| Crystal system | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | *P***Error!** | $P2_1/n$ | *P***Error!** | $P2_1/c$ |
| a(Å) | 12.531(5) | 12.0868(6) | 7.633(5) | 9.638(5) |
| b(Å) | 13.190(5) | 15.3515(7) | 10.979(5) | 14.761(5) |
| c(Å) | 13.589(5) | 12.4671(6) | 11.349(5) | 15.417(5) |
| α(°) | 77.378(5) | 90 | 77.076(5) | 90 |
| β(°) | 89.683(5) | 102.5040(10) | 85.348(5) | 104.889(5) |
| γ(°) | 89.474(5) | 90 | 74.767(5) | 90 |
| V(Å$^{-3}$) | 2191.7(15) | 2258.41 (19) | 894.2(8) | 2119.7(15) |
| Z | 2 | 2 | 2 | 4 |
| μ (mm$^{-1}$) | 3.257 | 3.166 | 3.303 | 3.371 |
| F(000) | 1697 | 1732 | 710 | 1676 |
| Limiting indices | -14<=*h*<=14<br>-15<=*k*<=15<br>-16<=*l*<=14 | -11<=*h*<=16<br>-20<=*k*<=19<br>-15<=*l*<=16 | -10<=*h*<=10<br>-14<=*k*<=14<br>-15<=*l*<=15 | -11<=h<=11<br>-17<=k<=17<br>-18<=l<=18 |

| | | | | |
|---|---|---|---|---|
| Reflections collected unique | 14155/7632 | 18370/5491 | 12537/4425 | 21593/ 3696 |
| R(int) | 0.0391 | 0.0959 | 0.0169 | 0.0795 |
| Data/restraints/parameters | 7632/6/659 | 5491/0/334 | 4425/2 /286 | 3696/24/316 |
| Goodness-of-fit on $F^2$ | 1.010 | 1.066 | 1.023 | 1.079 |
| Final R indices [I>2sigma(I) ] | $R_1$ = 0.0357<br>$wR_2$ = 0.0878 | $R_1$ = 0.0701<br>$wR_2$ = 0.1209 | $R_1$ = 0.0241<br>$wR_2$ = 0.0615 | $R_1$ = 0.0710<br>$wR_2$ = 0.1537 |
| R indices (all data) | $R_1$ = 0.0486<br>$wR_2$ = 0.0947 | $R_1$ = 0.1175<br>$wR_2$ = 0.1365 | $R_1$ = 0.0252<br>$wR_2$= 0.0621 | $R_1$ = 0.0914<br>$wR_2$= 0.1652 |

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

**Table S2** Selected bond lengths (Å) and angles (°) for compound **1**

| | | | |
|---|---|---|---|
| Mo(1)-O(13) | 1.682(4) | Mo(5)-O(21) | 2.167(4) |
| Mo(1)-O(1) | 1.748(4) | Mo(6)-O(16) | 1.676(4) |
| Mo(1)-O(4)#1 | 1.857(4) | Mo(6)-O(15) | 1.702(5) |
| Mo(1)-O(11) | 2.006(4) | Mo(6)-O(23)#2 | 1.892(4) |
| Mo(1)-O(10) | 2.275(4) | Mo(6)-O(17) | 2.011(4) |
| Mo(1)-O(12) | 2.290(4) | Mo(6)-O(18) | 2.217(4) |
| Mo(2)-O(2) | 1.696(4) | Mo(6)-O(20)#2 | 2.341(4) |
| Mo(2)-O(3) | 1.751(4) | Mo(7)-O(19) | 1.676(4) |
| Mo(2)-O(11) | 1.948(4) | Mo(7)-O(20) | 1.746(4) |
| Mo(2)-O(10)#1 | 1.951(4) | Mo(7)-O(18) | 1.877(4) |
| Mo(2)-O(12) | 2.113(4) | Mo(7)-O(21) | 1.954(4) |
| Mo(2)-O(12)#1 | 2.390(4) | Mo(7)-O(17) | 2.197(4) |
| Mo(3)-O(6) | 1.685(4) | Mo(7)-O(18)#2 | 2.503(4) |
| Mo(3)-O(5) | 1.687(4) | Mo(8)-O(26) | 1.685(5) |
| Mo(3)-O(7) | 1.910(4) | Mo(8)-O(25) | 1.691(4) |
| Mo(3)-O(4) | 1.973(4) | Mo(8)-O(23) | 1.913(4) |
| Mo(3)-O(3) | 2.261(4) | Mo(8)-O(24) | 2.048(4) |
| Mo(3)-O(12)#1 | 2.478(4) | Mo(8)-O(21) | 2.117(4) |
| Mo(4)-O(9) | 1.687(5) | Cu(1)-N(1) | 1.913(5) |
| Mo(4)-O(8) | 1.691(5) | Cu(1)-O(14) | 1.922(4) |
| Mo(4)-O(7) | 1.894(4) | Cu(1)-N(3) | 2.004(5) |
| Mo(4)-O(10) | 2.021(4) | Cu(1)-N(2) | 2.017(5) |
| Mo(4)-O(11) | 2.329(4) | Cu(1)-O(15) | 2.375(5) |
| Mo(4)-O(12)#1 | 2.373(4) | Cu(2)-N(5) | 1.920(5) |
| Mo(5)-O(22) | 1.682(5) | Cu(2)-O(1) | 1.933(4) |
| Mo(5)-O(14) | 1.741(4) | Cu(2)-N(4) | 2.006(5) |

| | | | |
|---|---|---|---|
| Mo(5)-O(24) | 1.834(4) | Cu(2)-N(6) | 2.040(5) |
| Mo(5)-O(17) | 1.915(4) | C(1)-N(3) | 1.335(8) |
| N(1)-Cu(1)-O(14) | 178.2(2) | C(5)-C(6) | 1.471(8) |
| N(1)-Cu(1)-N(3) | 80.9(2) | O(2)-Mo(2)-O(3) | 103.7(2) |
| N(1)-Cu(1)-N(2) | 100.8(2) | C(3)-C(2)-C(1) | 118.3(7) |
| O(14)-Cu(1)-N(3) | 81.0(2) | N(3)-C(1)-C(2) | 122.3(7) |

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

**Table S3** Selected bond lengths (Å) and angles (°) for compound **2**

| | | | |
|---|---|---|---|
| Mo(1)-O(3) | 1.694(7) | Mo(3)-O(4)#1 | 2.334(6) |
| Mo(1)-O(12) | 1.696(6) | Mo(3)-O(2) | 2.372(6) |
| Mo(1)-O(6) | 1.933(7) | Mo(4)-O(5) | 1.695(6) |
| Mo(1)-O(4) | 1.998(6) | Mo(4)-O(10) | 1.763(6) |
| Mo(1)-O(2) | 2.318(6) | Mo(4)-O(11) | 1.942(6) |
| Mo(1)-O(11)#1 | 2.326(6) | Mo(4)-O(4) | 1.957(5) |
| Mo(2)-O(13) | 1.683(8) | Mo(4)-O(2) | 2.136(6) |
| Mo(2)-O(1) | 1.714(7) | Mo(4)-O(2)#1 | 2.343(6) |
| Mo(2)-O(9) | 1.909(6) | Cu(1)-N(2) | 1.932(8) |
| Mo(2)-O(6) | 1.948(6) | Cu(1)-O(1W) | 1.969(7) |
| Mo(2)-O(10)#1 | 2.277(6) | Cu(1)-N(3) | 2.015(8) |
| Mo(2)-O(2) | 2.421(6) | Cu(1)-N(1) | 2.021(8) |
| Mo(3)-O(7) | 1.696(7) | Cu(1)-O(1) | 2.227(6) |
| Mo(3)-O(8) | 1.701(7) | N(2)-C(2) | 1.329(13) |
| Mo(3)-O(9) | 1.895(7) | N(2)-C(4) | 1.333(14) |
| Mo(3)-O(11) | 1.990(6) | C(1)-C(13) | 1.385(14) |
| | | | |
| O(3)-Mo(1)-O(12) | 105.1(4) | N(2)-Cu(1)-N(3) | 80.2(4) |
| O(3)-Mo(1)-O(6) | 100.8(3) | O(1W)-Cu(1)-N(3) | 97.1(3) |
| O(3)-Mo(1)-O(4) | 98.3(3) | N(2)-Cu(1)-N(1) | 80.3(3) |
| O(12)-Mo(1)-O(4) | 102.2(3) | N(3)-C(3)-C(15) | 124.3(11) |
| N(2)-Cu(1)-O(1W) | 171.3(3) | N(2)-C(2)-C(12) | 119.6(11) |

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

**Table S4** Selected bond lengths (Å) and angles (°) for compound **3**

| | | | |
|---|---|---|---|
| Mo(1)-O(5) | 1.701(3) | Mo(3)-O(9) | 1.704(3) |
| Mo(1)-O(4)#1 | 1.766(3) | Mo(3)-O(10) | 1.726(3) |
| Mo(1)-O(7)#2 | 1.880(3) | Mo(3)-O(1) | 1.926(3) |
| Mo(1)-O(3) | 2.027(3) | Mo(3)-O(6) | 1.962(3) |
| Mo(1)-O(6) | 2.078(2) | Mo(3)-O(3) | 2.202(3) |
| Mo(1)-O(6)#2 | 2.282(3) | Mo(3)-O(7) | 2.280(3) |
| Mo(2)-O(2) | 1.705(3) | Cu(1)-O(1) | 1.893(3) |
| Mo(2)-O(8) | 1.728(3) | Cu(1)-N(3) | 1.948(3) |
| Mo(2)-O(3)#1 | 1.912(3) | Cu(1)-N(2) | 1.987(3) |
| Mo(2)-O(7) | 2.033(3) | Cu(1)-N(1) | 2.013(3) |
| Mo(2)-O(1) | 2.196(3) | Cu(1)-O(2) | 2.347(3) |
| Mo(2)-O(1)#1 | 2.220(3) | C(1)-N(3) | 1.331(5) |

| | | | |
|---|---|---|---|
| O(3)-Mo(1)-O(6)#2 | 85.36(9) | O(1)-Cu(1)-N(2) | 97.20(13) |
| O(6)-Mo(1)-O(6)#2 | 74.03(10) | N(3)-Cu(1)-N(2) | 79.06(14) |
| O(2)-Mo(2)-O(8) | 103.94(14) | O(1)-Cu(1)-N(1) | 101.99(13) |
| O(2)-Mo(2)-O(3)#1 | 100.94(12) | C(3)-C(5)-C(6) | 117.2(4) |
| O(4)-Cu(1)-N(3) | 166.20(12) | N(3)-C(6)-C(5) | 121.5(4) |

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

**Table S5** Selected bond lengths (Å) and angles (°) for compound **4**

| | | | |
|---|---|---|---|
| Mo(1)-O(5) | 1.682(15) | Mo(3)-O(12)# | 1.929(13) |
| Mo(1)-O(2) | 1.769(14) | Mo(3)-O(2) | 2.267(15) |
| Mo(1)-O(10) | 1.927(14) | Mo(3)-O(7)#1 | 2.479(15) |
| Mo(1)-O(6) | 1.962(14) | Mo(4)-O(11) | 1.711(16) |
| Mo(1)-O(7) | 2.128(15) | Mo(4)-O(3) | 1.713(15) |
| Mo(1)-O(7)#1 | 2.354(14) | Mo(4)-O(12) | 1.879(13) |
| Mo(1)-Mo(2) | 3.201(3) | Mo(4)-O(10) | 2.011(12) |
| Mo(2)-O(4) | 1.695(16) | Mo(4)-O(6)#1 | 2.283(14) |
| Mo(2)-O(8) | 1.712(16) | Mo(4)-O(7) | 2.379(14) |
| Mo(2)-O(13) | 1.900(14) | Cu(1)-O(1W) | 1.949(15) |
| Mo(2)-O(6) | 1.989(14) | Cu(1)-N(1) | 1.951(16) |
| Mo(2)-O(7) | 2.277(14) | Cu(1)-N(3) | 1.99(2) |
| Mo(2)-O(10)# | 2.327(14) | Cu(1)-N(2) | 2.019(19) |
| Mo(3)-O(1) | 1.718(15) | Cu(1)-O(1) | 2.341(16) |
| Mo(3)-O(9) | 1.719(16) | C(1)-C(5) | 1.37(3) |
| Mo(3)-O(13)# | 1.914(14) | C(1)-N(2) | 1.38(2) |
| | | | |
| O(1W)-Cu(1)-N(1) | 169.0(7) | O(2)-Mo(1)-O(10) | 96.0(6) |
| O(1W)-Cu(1)-N(3) | 104.8(7) | O(5)-Mo(1)-O(6) | 99.5(7) |
| N(1)-Cu(1)-N(3) | 78.9(8) | C(5)-C(1)-C(2) | 131.4(19) |
| O(1W)-Cu(1)-N(2) | 97.2(7) | N(2)-C(1)-C(2) | 117.9(17) |
| N(1)-Cu(1)-N(2) | 79.3(7) | C(2)-C(8)-C(9) | 117(3) |

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

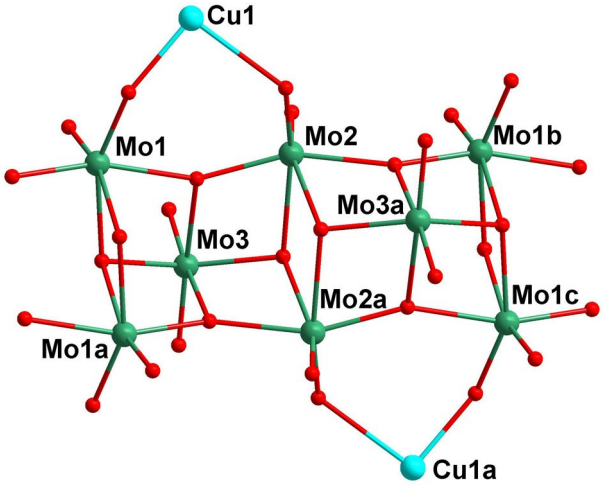


**Fig. S1** The environments of three molybdenum atoms in compound **3**.

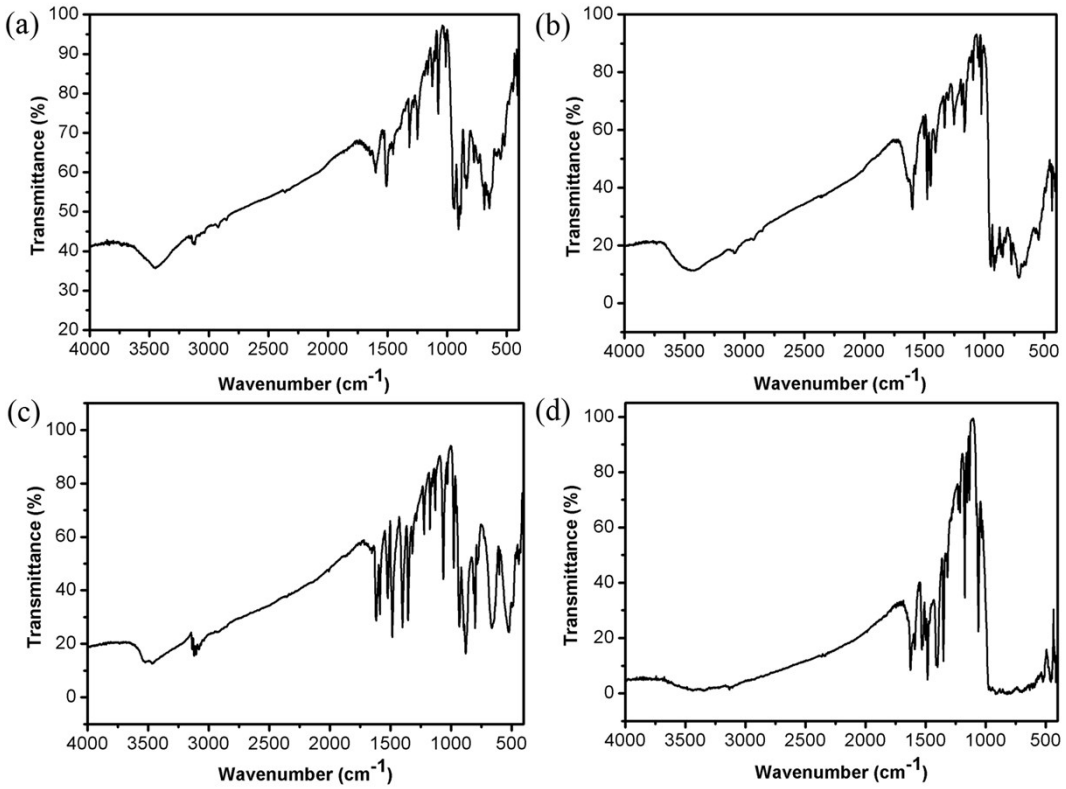


**Fig. S2** IR spectra obtained from compounds **1**-**4**.

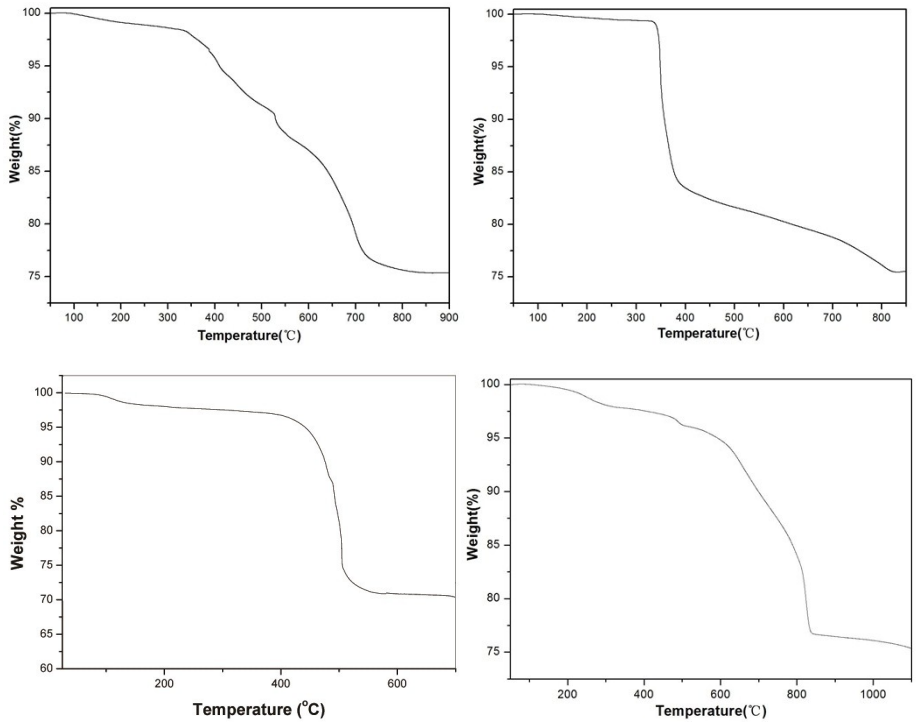


**Fig. S3** TG curve obtained from compounds **1**-**4**.

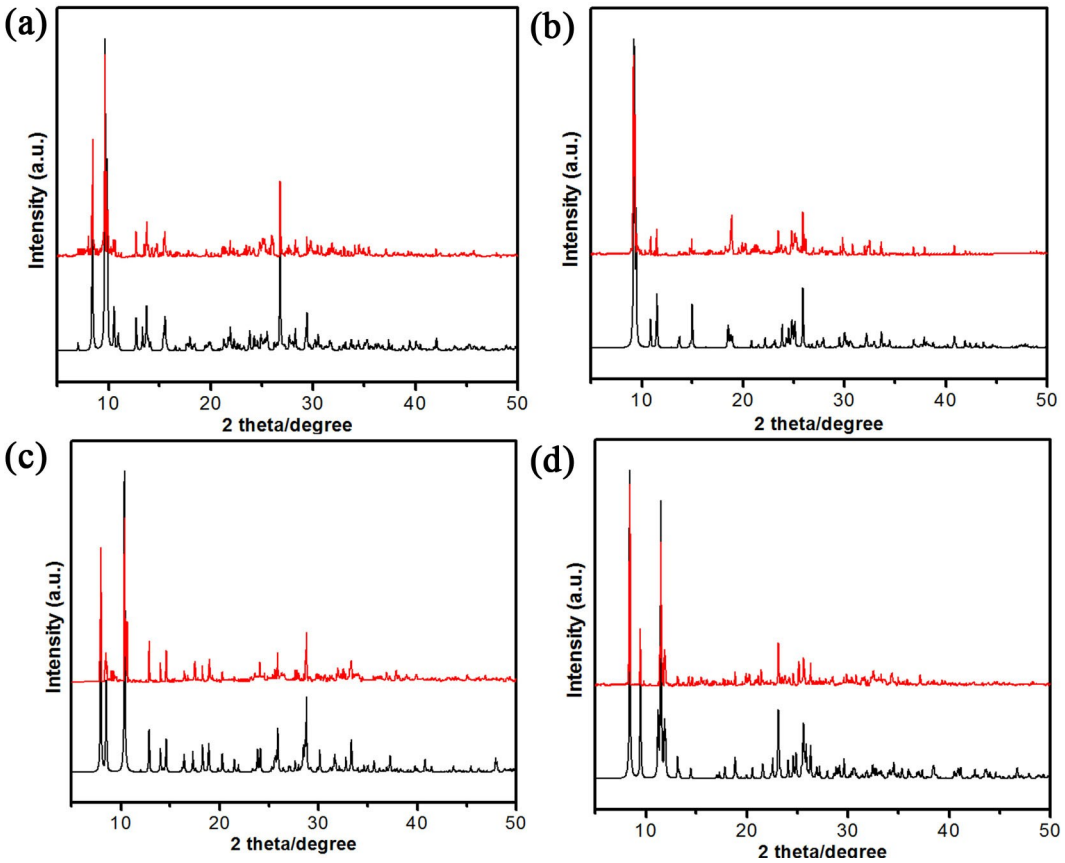


**Fig. S4** The experimental (red line) and simulated (black line) PXRD patterns obtained from compounds **1-4**.

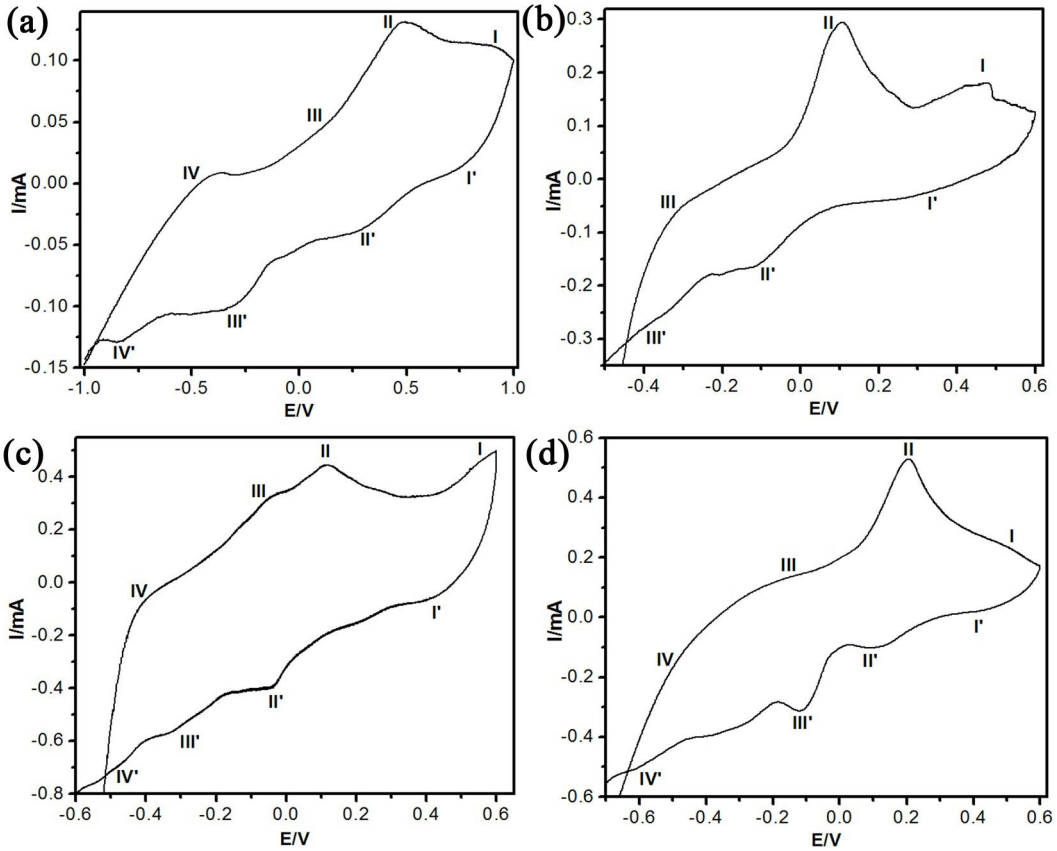

**Fig. S5** The cyclic voltammograms of *n*-CPEs (*n* = **1-4**) in $H_2SO_4$ + $Na_2SO_4$ solutions at a scan rate of 0.1 V $s^{-1}$.

It is known that oxidation of ascorbic acid undergoes a two-proton dehydrogenation process:

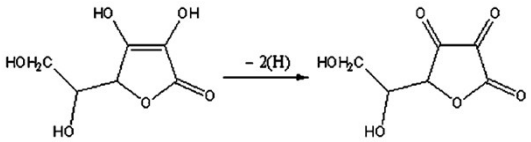


**Table S6** CAT% data of **1-4-CPEs** toward reduction of nitrite

| substrate \ CAT% | | **1-CPE** | **2-CPE** | **3-CPE** | **4-CPE** |
|---|---|---|---|---|---|
| Nitrite | 2 × $10^{-3}$M | 79 | 359 | 392 | 232 |
| | 4 × $10^{-3}$ M | 99 | 400 | 547 | 920 |
| | 6 × $10^{-3}$ M | 161 | 616 | 1012 | 1229 |
| | 8 × $10^{-3}$ M | 244 | 1721 | 1093 | 1467 |

**Table S7** CAT% data of **1-4-CPEs** toward oxidation of AA

| substrate \ CAT% | | **1-CPE** | **2-CPE** | **3-CPE**-$Cu^{II}$ | **3-CPE**-$Mo^{VI}$ | **4-CPE** |
|---|---|---|---|---|---|---|
| AA | 2 × $10^{-3}$M | 31 | 28 | 26 | 29 | 10 |
| | 4 × $10^{-3}$ M | 48 | 44 | 61 | 58 | 23 |
| | 6 × $10^{-3}$ M | 51 | 61 | 87 | 90 | 40 |
| | 8 × $10^{-3}$ M | 58 | 83 | 96 | 123 | 60 |

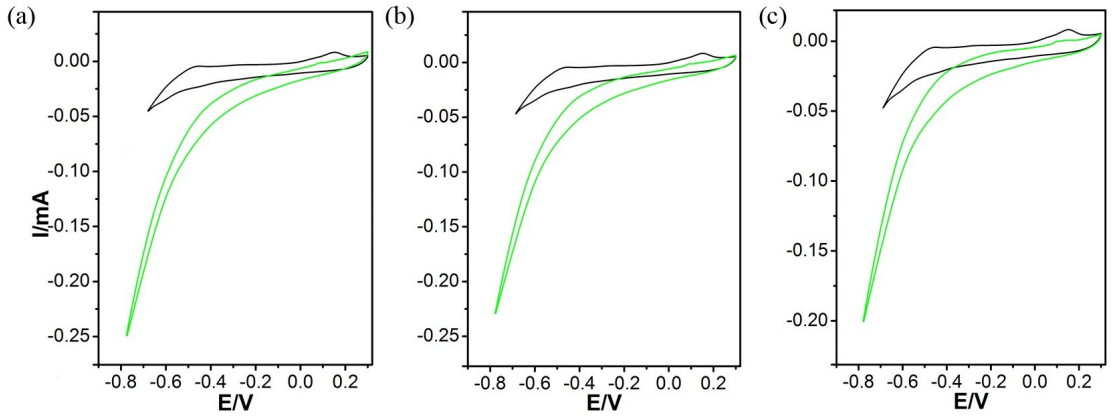


**Fig. S6** Cyclic voltammograms showing the electrocatalytic reduction of $NO_2^-$ (2 ×$10^{-3}$ mol $L^{-1}$) by **2**-CPE in 1M $H_2SO_4$ +$Na_2SO_4$ solutions (pH = 1). Scan rate: 0.1 V·$s^{-1}$.