**Electric Supplemental Information**

pH-Dependent assembly of two polyoxometalate-based coordination polymers: Structures and electrocatalytic properties

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Table S1. Selected bond lengths (Å) and angles (º) for **1** and **2**.

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| --- |
| Compound **1** |
| Mo(1)-O(1) | 1.881(17) | Mo(1)-O(2)#1 | 2.465(12) |
| Mo(1)-O(2) | 2.398(12) | Mo(1)-O(7)#2 | 1.848(16) |
| Mo(2)-O(3) | 1.946(4) | Mo(2)-O(5) | 1.976(8) |
| O(7)-P(1) | 1.711(16) | P(1)-O(7)#2 | 1.548(16) |
| Cu(1)-N(1) | 1.872(14) | Cu(1)-O(6) | 2.694(12) |
| O(1)-Mo(1)-O(2)#1 | 65.82(6) | O(2)#1-Mo(1)-O(6)#2 | 96.30(6) |
| O(4)-Mo(2)-O(2) | 66.26(5) | O(3)-Mo(2)-O(2) | 40.31(6) |
| O(4)-Mo(2)-O(5) | 65.09(6) | O(4)-Mo(2)-O(6) | 63.43(6) |
| O(2)-Mo(2)-O(6) | 41.48(5) | Mo(2)-O(2)-Mo(1) | 137.55(5) |
| N(1)-Cu(1)-O(6) | 89.30(5) | P(1)-O(7)-Mo(1)#2 | 121.19(6) |
| N(1)-Cu(1)-N(2) | 172.48(5) | P(1)-O(7)-Mo(2) | 127.15(5) |
| Compound **2** |
| Mo(1)-O(2) | 1.872(10) | Mo(1)-O(3) | 1.857(3) |
| Mo(1)-O(1) | 1.936(7) | Mo(1)-O(6)#1 | 1.904(10) |
| P(1)-O(4)#1 | 1.499(14) | P(1)-O(4) | 1.558(14) |
| Mo(2)-O(8) | 2.442(14) | Mo(2)-O(5) | 2.433(9) |
| Cu(1)-O(6) | 2.8658(10) | Cu(1)-N(3) | 1.869(11) |
| O(2)-Mo(1)-O(3) | 63.92(6) | O(2)-Mo(1)-O(5) | 63.16(5) |
| O(2)-Mo(1)-O(6)#1 | 63.27(5) | O(3)-Mo(1)-O(6)#1 | 64.12(5) |
| O(2)-Mo(1)-O(4) | 95.01(5) | O(1)-Mo(1)-O(4) | 44.91(6) |
| O(4)#1-P(1)-O(4) | 71.13(5) | O(4)-P(1)-O(4)#2 | 71.13(5) |
| O(8)-Mo(2)-O(6) | 64.65(5) | O(8)-Mo(2)-O(4)#1 | 94.93(6) |
| N(3)-Cu(1)-O(6) | 90.41(5) | O(6)-Cu(1)-O(6)#3 | 180.0(5) |
| N(1)#10-Cu(3)-N(1) | 180.0(6) | N(3)-Cu(1)-O(6)#2 | 89.59(5) |

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

Table S2. The IR stretching frequencies of **1** and **2**.

|  |  |  |
| --- | --- | --- |
| Compounds | Stretching frequencies of POM (cm-1) | Stretching frequencies of bimb ligand (cm-1) |
| **1** | 1089 948 908 786 | 1637 1523 1402 1259 |
| **2** | 1049 939 865 782 | 1629 1527 1307 1251 |

Figure S1. The images of **1** (a) and **2** (b)under an optical microscope**.**

Figure S2. The IR spectra of **1** and **2**.

Figure S3. The simulative (black) and experimental (red) powder X-ray diffraction patterns for **1** and **2**.

Figure S4. Theplots of the anodic and the cathodic peak currents for wave II of **1**-CPE against scan rates.

Figure S5. The plots of the anodic and the cathodic peak currents for wave II of **2**-CPE against scan rates.

Figure S6. The 100 consecutive CV cycles of **1**-CPE at scan rate of 0.1 V·s-1.

Figure S7. The 100 consecutive CV cycles of **2**-CPE at scan rate of 0.1 V·s-1.