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# Different Anderson-type polyoxometalate-based metal-organic complexes exhibiting -OH groups-directed structures and electrochemical sensing performance

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**Table S1** Bond lengths [Å] and angles [°] for complex **1**

| | | | |
|---|---|---|---|
| Co(1)-O(1) | 2.174(2) | Co(1)-O(1W) | 2.073(2) |
| Co(1)-O(2) | 2.046(2) | Co(1)-N(1) | 2.066(3) |
| Co(1)-O(3)#2 | 2.127(2) | Co(1)-N(3)#2 | 2.120(3) |
| O(2)-Co(1)-O(1) | 168.45(8) | N(1)-Co(1)-N(2)#2 | 170.54(10) |
| O(2)-Co(1)-O(3)#2 | 94.24(10) | N(2)#2-Co(1)-O(1) | 101.76(9) |
| O(2)-Co(1)-O(1W) | 97.79(10) | N(2)#2-Co(1)-O(3)#2 | 76.75(9) |
| O(2)-Co(1)-N(1) | 92.05(10) | N(1)-Co(1)-O(1W) | 100.19(10) |
| O(2)-Co(1)-N(2)#2 | 89.75(9) | N(1)-Co(1)-O(3)#2 | 93.84(10) |
| O(3)#2-Co(1)-O(1) | 89.40(9) | N(1)-Co(1)-O(1) | 76.78(9) |
| O(1W)-Co(1)-O(1) | 81.67(10) | O(1W)-Co(1)-N(2)#2 | 88.77(10) |
| O(1W)-Co(1)-O(3)#2 | 161.12(10) | | |

Symmetry code for **1**: #1 -x+1,-y+1,-z+2 #2 -x+1,-y+2,-z+1

**Table S2** Bond lengths [Å] and angles [°] for complex **2**

| | | | |
|---|---|---|---|
| Ni-O(1) | 2.143(3) | Ni-O(1W) | 2.056(3) |
| Ni-O(3)#2 | 2.106(3) | Ni-N(2)#2 | 2.050(3) |
| Ni-O(2) | 2.029(3) | Ni-N(1) | 2.019(3) |
| O(3)#2-Ni-O(1) | 90.21(12) | O(2)-Ni-O(1) | 169.05(11) |
| O(2)-Ni-O(3)#2 | 93.00(12) | O(2)-Ni-O(1W) | 95.32(13) |
| N(1)-Ni-N(2)#2 | 171.10(13) | O(2)-Ni-N(2)#2 | 91.70(12) |
| O(1W)-Ni-O(1) | 83.40(12) | O(1W)-Ni-O(3)#2 | 166.78(12) |
| N(2)#2-Ni-O(1) | 99.18(12) | N(2)#2-Ni-O(3)#2 | 78.67(12) |
| N(2)#2-Ni-O(1W) | 90.93(12) | N(1)-Ni-O(1) | 78.50(12) |
| N(1)-Ni-O(3)#2 | 92.70(12) | N(1)-Ni-O(2) | 90.91(12) |
| N(1)-Ni-O(1W) | 97.30(13) | | |

Symmetry code for **2**: #1 -x+1,-y+1,-z+2 #2 -x+1,-y+2,-z+1

**Table S3** Bond lengths [Å] and angles [°] for complex **3**

| | | | |
|---|---|---|---|
| Co(1)-O(1) | 2.106(2) | Co(1)-O(1W) | 2.053(2) |
| Co(1)-O(2) | 2.073(2) | Co(1)-O(3)#2 | 2.101(2) |
| Co(1)-N(1) | 2.101(3) | Co(1)-N(2)#2 | 2.111(3) |
| Co(2)-O(2W) | 2.037(2) | Co(2)-O(2W)#3 | 2.037(2) |
| Co(2)-O(3W)#3 | 2.049(2) | Co(2)-O(3W) | 2.049(2) |

| | | | |
|---|---|---|---|
| Co(2)-O(4)#3 | 2.358(2) | Co(2)-O(4) | 2.358(2) |
| O(1)-Co(1)-N(2)#2 | 90.95(11) | O(1W)-Co(1)-O(1) | 170.42(10) |
| O(1W)-Co(1)-O(2) | 83.64(9) | O(1W)-Co(1)-O(3)#2 | 89.52(10) |
| O(1W)-Co(1)-N(1) | 101.53(10) | O(1W)-Co(1)-N(2)#2 | 91.11(11) |
| O(2)-Co(1)-O(1) | 86.81(9) | O(2)-Co(1)-O(3)#2 | 171.71(9) |
| O(2)-Co(1)-N(1) | 91.35(10) | O(2)-Co(1)-N(2)#2 | 97.97(10) |
| O(3)#2-Co(1)-O(1) | 100.06(10) | O(3)#2-Co(1)-N(2)#2 | 77.43(10) |
| N(1)-Co(1)-O(1) | 77.91(10) | N(1)-Co(1)-O(3)#2 | 94.61(10) |
| N(1)-Co(1)-N(2)#2 | 165.09(11) | O(2W)-Co(2)-O(2W)#3 | 180.0 |
| O(2W)#3-Co(2)-O(3W)#3 | 88.01(11) | O(2W)#3-Co(2)-O(3W) | 91.99(11) |
| O(2W)-Co(2)-O(3W)#3 | 91.99(11) | O(2W)-Co(2)-O(3W) | 88.01(11) |
| O(2W)-Co(2)-O(4)#3 | 88.39(8) | O(2W)#3-Co(2)-O(4) | 88.39(8) |
| O(2W)#3-Co(2)-O(4)#3 | 91.61(8) | O(2W)-Co(2)-O(4) | 91.61(8) |
| O(3W)#3-Co(2)-O(3W) | 180.0 | O(3W)-Co(2)-O(4) | 86.01(8) |
| O(3W)-Co(2)-O(4)#3 | 93.99(8) | O(3W)#3-Co(2)-O(4)#3 | 86.00(8) |
| O(3W)#3-Co(2)-O(4) | 94.00(8) | O(8)#3-Co(2)-O(4) | 180.0 |

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

**Table S4** Bond lengths [Å] and angles [°] for complex **4**

| | | | |
|---|---|---|---|
| Ni(1)-O(2) | 2.038(3) | Ni(2)-O(4) | 2.327(3) |
| Ni(1)-O(1) | 2.085(3) | Ni(2)-O(4)#3 | 2.327(3) |
| Ni(1)-O(3)#2 | 2.061(3) | Ni(2)-O(3W) | 2.015(3) |
| Ni(1)-O(1W) | 2.023(3) | Ni(2)-O(3W)#3 | 2.015(3) |
| Ni(1)-N(1) | 2.058(3) | Ni(2)-O(2W)#3 | 2.032(3) |
| Ni(1)-N(2)#2 | 2.070(3) | Ni(2)-O(2W) | 2.032(3) |
| O(2)-Ni(1)-O(1) | 87.55(11) | N(1)-Ni(1)-N(2)#2 | 166.98(14) |
| O(2)-Ni(1)-O(3)#2 | 173.13(11) | N(2)#2-Ni(1)-O(1) | 90.78(12) |
| O(2)-Ni(1)-N(1) | 90.84(12) | O(4)#3-Ni(2)-O(4) | 180.00(5) |
| O(2)-Ni(1)-N(2)#2 | 97.45(12) | O(3W)#3-Ni(2)-O(4) | 91.62(10) |
| O(3)#2-Ni(1)-O(1) | 98.30(12) | O(3W)-Ni(2)-O(4)#3 | 91.62(10) |
| O(3)#2-Ni(1)-N(2)#2 | 78.96(12) | O(3W)#3-Ni(2)-O(4)#3 | 88.38(10) |
| O(1W)-Ni(1)-O(2) | 84.05(11) | O(3W)-Ni(2)-O(4) | 88.38(10) |
| O(1W)-Ni(1)-O(1) | 171.60(11) | O(3W)-Ni(2)-O(3W)#3 | 180 |
| O(1W)-Ni(1)-O(3)#2 | 90.07(12) | O(3W)-Ni(2)-O(2W) | 92.90(12) |
| O(1W)-Ni(1)-N(1) | 100.70(13) | O(3W)#3-Ni(2)-O(2W)#3 | 92.90(12) |
| O(1W)-Ni(1)-N(2)#2 | 90.18(13) | O(3W)-Ni(2)-O(2W)#3 | 87.10(12) |
| N(1)-Ni(1)-O(1) | 79.52(12) | O(3W)#3-Ni(2)-O(2W) | 87.10(12) |
| N(1)-Ni(1)-O(3)#2 | 93.76(11) | O(2W)#3-Ni(2)-O(4) | 93.78(10) |
| O(2W)-Ni(2)-O(4)#3 | 93.78(10) | O(2W)#3-Ni(2)-O(4)#3 | 86.22(10) |
| O(2W)#3-Ni(2)-O(2W) | 180 | O(2W)-Ni(2)-O(4) | 86.22(10) |

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

**Table S5** The average peak potentials of the redox peaks

| | I-I' | II-II' | III-III' |
|---|---|---|---|
| **1**-CPE | +258 | +72 | -156 |
| **2**-CPE | +204 | +75 | -160 |
| **3**-CPE | +165 | +36 | -186 |
| $E_{1/2} = (E_{pa} + E_{pc})/2$ (scan rate: 40 mV $s^{-1}$)（mV *vs* SCE） | | | |

**IR spectra and Powder X-ray diffraction (PXRD)**

The IR spectra of complexes **1**-**4** are depicted in Fig. S1. The characteristic bands of ν(Mo-$O_t$) ν(Mo-$O_a$), ν(Mo-$O_b$),ν(Mo-$O_c$) and ν(Mo-$O_d$) vibrations are observed in the range of 673-874 $cm^{-1}$ for **1**, 664-901 $cm^{-1}$ for **2**, 673-884 $cm^{-1}$ for **3**, and 664-903 $cm^{-1}$ for **4**, which can be assigned to the Anderson-type polyoxoanions[1]. The peaks in the range of 1120-1625 $cm^{-1}$ for **1**, 1112-1643 $cm^{-1}$ for **2**, 1119-1615 $cm^{-1}$ for **3**, and 1112-1624 $cm^{-1}$ for **4** can be assigned to the characteristic peaks of the organic ligands[2]. In addition, the broad peak around 3000 $cm^{-1}$ for the complexes can be ascribed to the water molecules.

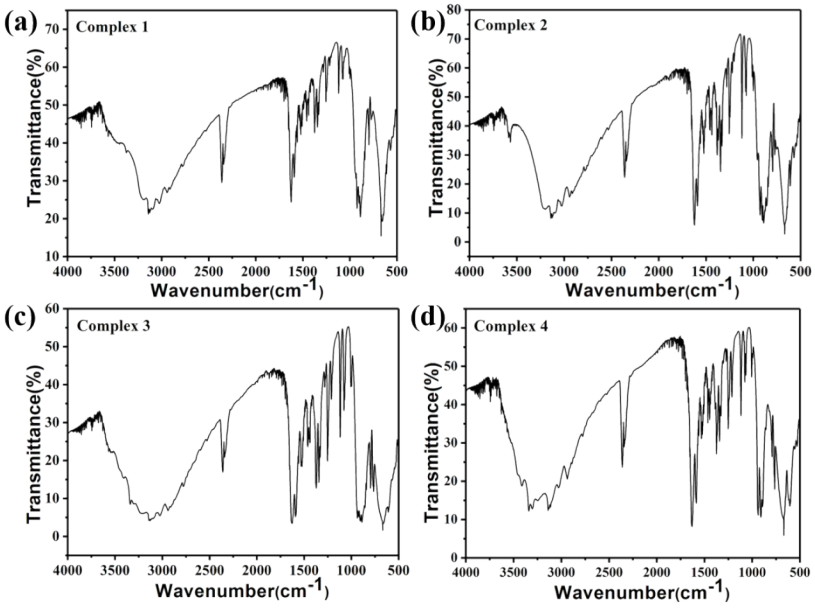


**Fig. S1**. The IR spectra of complexes **1**-**4**

The powder X-ray diffraction (PXRD) patterns for the title complexes were presented in the Fig. S2. The diffraction peaks of experimental patterns match well with those of simulated patterns, indicating the phase purities of the title complexes are good[3].

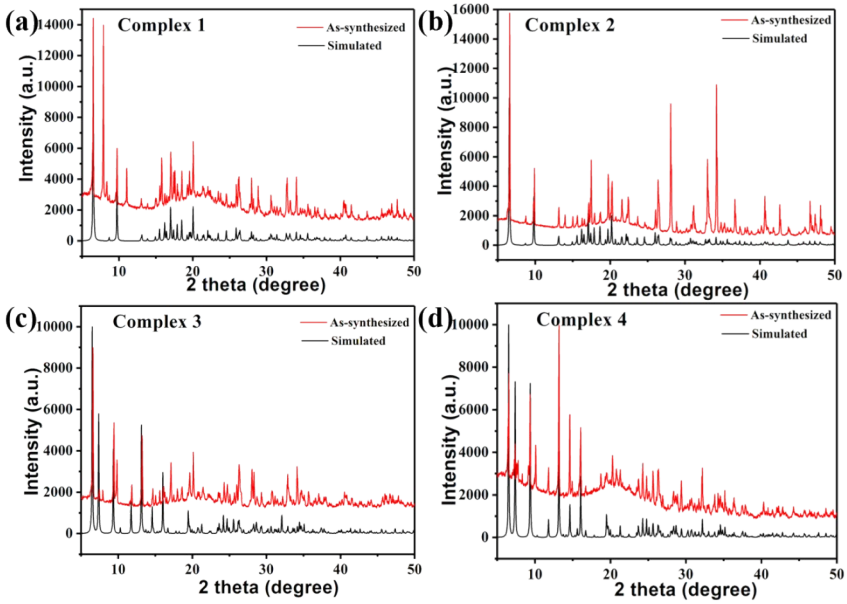


**Fig. S2** PXRD patterns of complexes **1-4**

**Preparations of 1-4 CPEs**

A mixture containing 10 mg of complex sample and 100 mg graphite powder was grounded with an agate mortar for 1 h. After adding 0.1 mL of Nujol, the obtained homogeneous mixture was packed into a glass tube with a moderate size by using a copper rod as electrical contact.

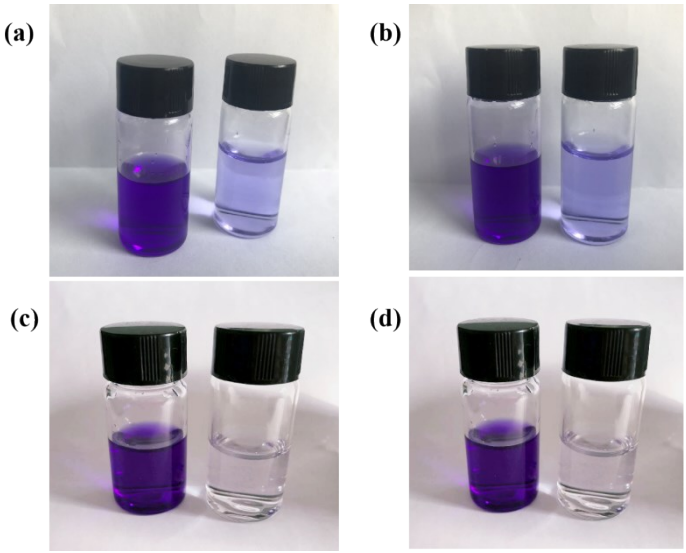


**Fig. S3** The corresponding images of CV solution before and after the adsorption experiments with **1-4**.

**Notes and references**

1.M. Yu, B. Gao, D. D. Liang, *J. Cluster Sci*., 2014, **25**, 377.
2.X. L. Wang, J. Luan, H. Y. Lin, Q. L. Lu, C. Xu, G. C. Liu, *Dalton Trans*., 2013, **42**, 8375.
3. A. X. Tian, J. Ying, J. Peng, J. Q. Sha, H. J. Pang, P. P. Zhang, Y. Chen, M. Zhu and Z. M. Su, *Cryst. Growth. Des*., 2008, **8**, 3717.