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# Assembly, structures and properties of polyoxometalate-based supramolecular complexes involving in situ transformation of single-branch N-donor cyano ligands

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**Table S1.** Selected bond lengths (Å) and angles (°) of complexes **1**-**6**.

| | | | |
|---|---|---|---|
| Complex **1** | | | |
| Cu(1)-O(2) | 1.963(6) | Cu(1)-N(1) | 1.988(7) |
| Cu(1)-O(1W) | 1.970(6) | Cu(1)- N(3) | 1.978(7) |
| Cu(1)-O(2W) | 2.263(6) | Cu(2)- N(4) | 1.865(6) |
| Cu(2)-O(1) | 2.367(5) | Cu(2)- N(5) | 1.867(6) |
| O(2)-Cu(1)-O(2W) | 90.4(2) | O(2)-Cu(1)-O(1W) | 87.7(2) |
| O(2)-Cu(1)-N(1) | 89.8(3) | O(2)-Cu(1)-N(3) | 170.4(3) |
| O(1W)-Cu(1)-O(2W) | 92.8(3) | O(1W)-Cu(1)-N(1) | 172.8(3) |
| O(1W)-Cu(1)-N(3) | 86.7(3) | N(1)-Cu(1)-O(2W) | 94.0(3) |
| N(3)-Cu(1)-O(2W) | 97.7(3) | N(3)-Cu(1)-N(1) | 94.8(3) |
| N(4)-Cu(2)-O(1) | 92.4(2) | N(4)-Cu(2)-N(5) | 172.5(3) |
| N(5)-Cu(2)-O(1) | 94.0(2) | | |
| Complex **2** | | | |
| Cu(1)-O(3) | 2.476(6) | Cu(1)-N(1) | 1.869(8) |
| Cu(1)-N(2) | 1.863(8) | Cu(2)-N(6) | 1.869(8) |
| Cu(2)-N(7) | 1.877(8) | Cu(2)-O(15) | 2.554(7) |
| Cu(3)-O(5) | 2.613(8) | Cu(3)-N(10) | 1.861(10) |
| Cu(3)-N(12) | 1.888(11) | N(6)-Cu(2)-N(7) | 176.6(4) |
| N(6)-Cu(2)-O(15) | 91.4(3) | N(7)-Cu(2)-O(15) | 90.6(3) |
| N(10)-Cu(3)-O(5) | 98.8(4) | N(10)-Cu(3)-N(12) | 166.3(5) |
| N(12)-Cu(3)-O(5) | 90.8(4) | | |

Complex **3**

| | | | |
|---|---|---|---|
| Cu(1)-O(1W) | 1.971(6) | Cu(1)-O(4) | 1.966(5) |
| Cu(1)-O(2W) | 2.261(6) | Cu(1)-N(12) | 1.990(6) |
| Cu(1)-N(14) | 1.972(7) | Cu(2)-N(2) | 1.880(6) |
| Cu(2)-O(8) | 2.375(5) | Cu(2)-N(8) | 1.875(6) |
| O(1W)-Cu(1)-O(2W) | 94.0(3) | O(1W)-Cu(1)-N(12) | 87.3(3) |
| O(1W)-Cu(1)-N(14) | 172.1(3) | O(4)-Cu(1)-O(1W) | 87.3(2) |
| O(4)-Cu(1)-O(2W) | 90.2(2) | O(4)-Cu(1)-N(12) | 170.5(3) |
| O(4)-Cu(1)-N(14) | 90.1(3) | N(12)-Cu(1)-O(2W) | 97.9(3) |
| N(14)-Cu(1)-O(2W) | 93.4(3) | N(14)-Cu(1)-N(12) | 94.2(3) |
| N(2)-Cu(2)-O(8) | 92.6(2) | N(8)-Cu(2)-N(2) | 172.5(3) |
| N(8)-Cu(2)-O(8) | 94.0(2) | | |

Complex **4**

| | | | |
|---|---|---|---|
| Cu(1)-N(1) | 1.966(6) | Cu(1)-N(2) | 2.003(6) |
| Cu(1)-O(5) | 2.429(4) | Cu(1)-O(10) | 2.392(4) |
| Cu(1)-O(14) | 2.023(4) | Cu(1)-O(2W) | 2.007(5) |
| Cu(2)-O(1W) | 2.026(4) | Cu(2)-N(4) | 1.999(5) |
| Cu(2)-N(5) | 1.987(5) | Cu(2)-N(34) | 2.090(5) |
| Cu(2)-N(39) | 2.122(4) | N(1)-Cu(1)-N(2) | 82.5(3) |
| N(1)-Cu(1)-O(5) | 88.9(2) | N(1)-Cu(1)-O(10) | 107.2(2) |
| N(1)-Cu(1)-O(14) | 103.0(2) | N(1)-Cu(1)-O(2W) | 168.3(2) |
| N(2)-Cu(1)-O(5) | 96.8(2) | N(2)-Cu(1)-O(10) | 114.7(2) |
| N(2)-Cu(1)-O(14) | 171.7(2) | N(2)-Cu(1)-O(2W) | 89.2(3) |
| O(10)-Cu(1)-O(5) | 145.87(15) | O(14)-Cu(1)-O(5) | 89.56(16) |
| O(14)-Cu(1)-O(10) | 57.97(16) | O(2W)-Cu(1)-O(5) | 83.8(2) |
| O(2W)-Cu(1)-O(10) | 83.79(19) | O(2W)-Cu(1)-O(14) | 86.2(2) |
| O(1W)-Cu(2)-N(34) | 137.28(17) | O(1W)-Cu(2)-N(39) | 119.37(18) |
| N(4)-Cu(2)-O(1W) | 87.9(2) | N(4)-Cu(2)-N(34) | 100.7(2) |
| N(4)-Cu(2)-N(39) | 80.0(2) | N(5)-Cu(2)-O(1W) | 89.3(2) |
| N(5)-Cu(2)-N(4) | 176.8(2) | N(5)-Cu(2)-N(34) | 80.4(2) |
| N(5)-Cu(2)-N(39) | 102.67(19) | N(34)-Cu(2)-N(39) | 103.35(17) |

Complex **5**

| | | | |
|---|---|---|---|
| Cu(1)-N(5) | 1.90(2) | Cu(1)-N(2) | 1.99(2) |
| Cu(1)-N(4) | 2.03(3) | Cu(1)-N(3) | 2.07(3) |
| Cu(1)-N(1) | 2.20(3) | N(5)-Cu(1)-N(2) | 177.4(12) |
| N(5)-Cu(1)-N(4) | 94.3(10) | N(2)-Cu(1)-N(4) | 85.9(10) |
| N(5)-Cu(1)-N(3) | 80.4(11) | N(2)-Cu(1)-N(3) | 97.8(11) |
| N(4)-Cu(1)-N(3) | 139.1(13) | N(5)-Cu(1)-N(1) | 102.5(11) |
| N(2)-Cu(1)-N(1) | 79.8(11) | N(4)-Cu(1)-N(1) | 111.1(12) |
| N(3)-Cu(1)-N(1) | 109.7(11) | | |

Complex **6**

| | | | |
|---|---|---|---|
| Co(1)-O(13) | 2.128(15) | Co(1)-O(1W) | 2.09(2) |
| Co(1)-N(1) | 2.09(2) | Co(1)-N(4) | 2.123(19) |
| Co(1)-N(3) | 2.143(17) | Co(1)-O(2W) | 2.053(18) |
| O(13)-Co(1)-N(3) | 94.4(7) | O(1W)-Co(1)-O(13) | 85.1(8) |
| O(1W)-Co(1)-N(4) | 95.3(8) | O(1W)-Co(1)-N(3) | 171.1(7) |
| N(1)-Co(1)-O(13) | 169.7(7) | N(1)-Co(1)-O(1W) | 88.5(8) |
| N(1)-Co(1)-N(4) | 102.5(7) | N(1)-Co(1)-N(3) | 93.2(7) |
| N(4) -Co(1)-O(13) | 86.1(6) | N(4) -Co(1)-N(3) | 75.9(7) |
| O(2W)-Co(1)-O(13) | 85.0(6) | O(2W)-Co(1)-O(1W) | 89.4(9) |
| O(2W)-Co(1)-N(1) | 86.9(7) | O(2W)-Co(1)-N(4) | 169.6(7) |
| O(2W)-Co(1)-N(3) | 99.4(8) | | |

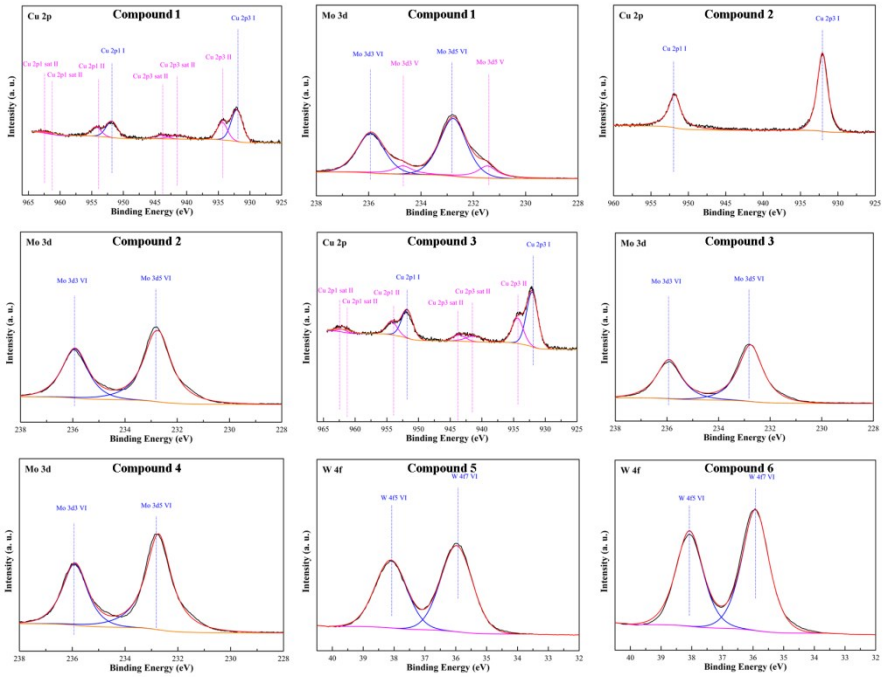


**Figure S1** The XPS patterns of complexes **1-6**.

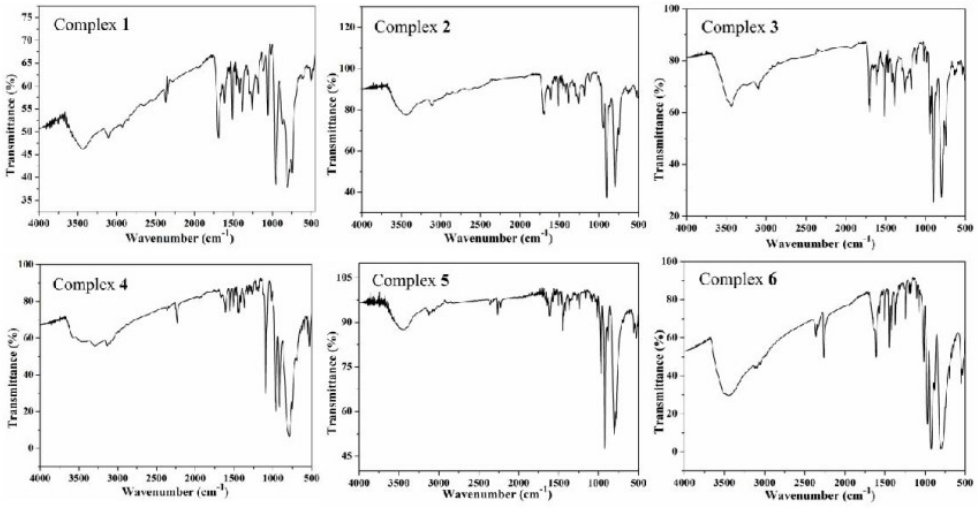


**Figure S2** IR spectra of complexes **1-6**.

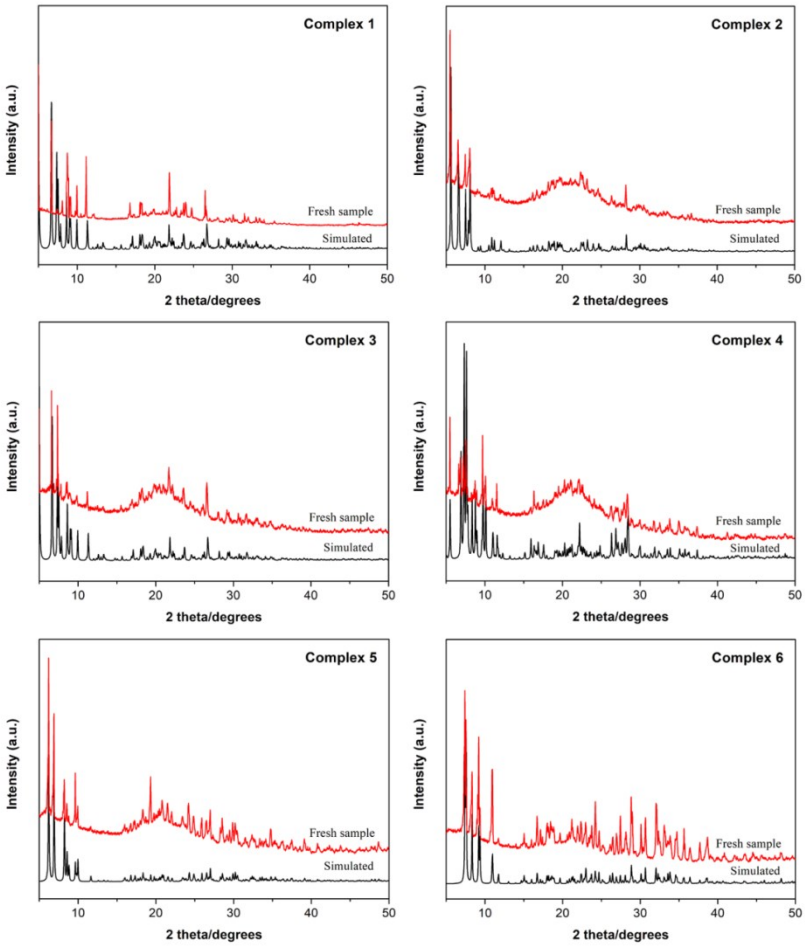


**Figure S3** The PXRD patterns for complexes **1**-**6**.

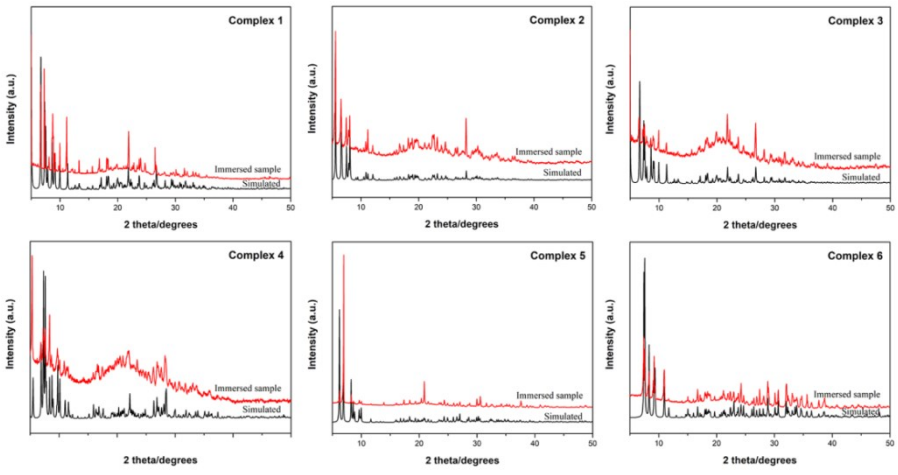


**Figure S4** The PXRD patterns of **1-6** after immersion in 0.1 M $H_2SO_4$ + 0.5 M $Na_2SO_4$ aqueous solution.

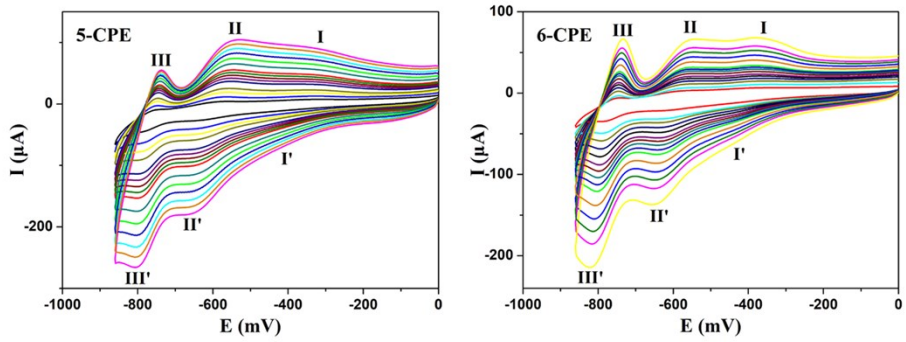


**Figure S5** Cyclic voltammograms of **5**– and **6**–CPEs in 0.1 M $H_2SO_4$ + 0.5 M $Na_2SO_4$ aqueous solution at different scan rates.

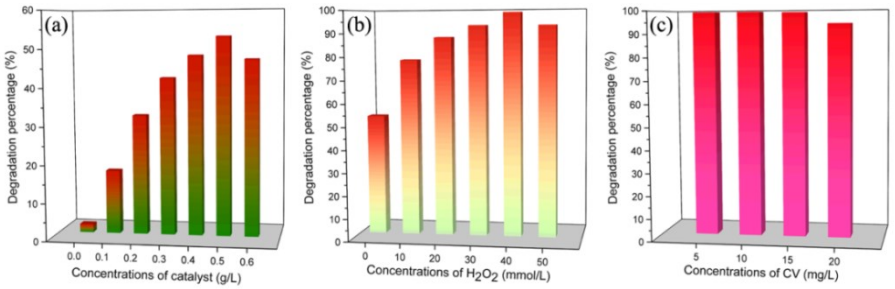


**Figure S6** The influences on the degradation efficiencies of the concentrations of catalyst (a), $H_2O_2$ (b) and dye (c).

**Table S2.** The optimized concentrations of catalyst, $H_2O_2$ and dyes.

| Complex | CV (10 mg/L) | | MB (10 mg/L) | |
|---|---|---|---|---|
| | Catalyst (g/L) | $H_2O_2$ (mmol/L) | Catalyst (g/L) | $H_2O_2$ (mmol/L) |
| 1 | 0.5 | 40 | 0.5 | 40 |
| 2 | 0.7 | 50 | 0.7 | 50 |
| 3 | 0.5 | 40 | 0.5 | 40 |
| 4 | 0.5 | 40 | 0.5 | 40 |
| 5 | 0.5 | 40 | 0.5 | 50 |
| 6 | 0.7 | 60 | 0.7 | 60 |

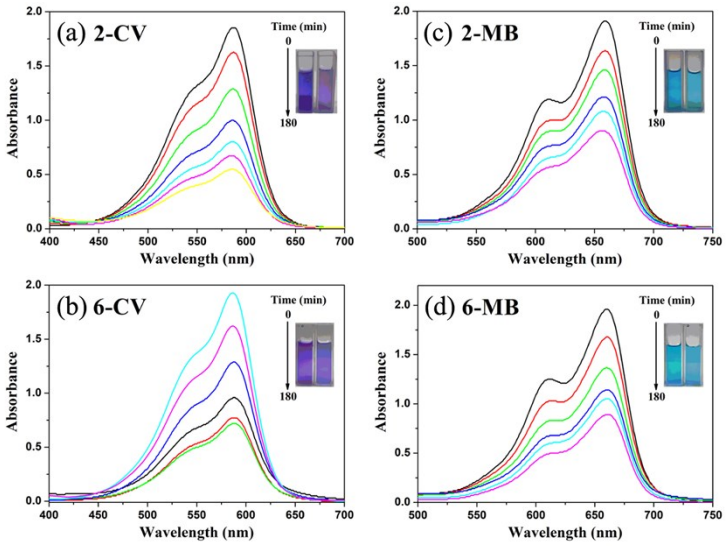


**Figure S7** Absorption spectra of the CV (a-b) and MB (c-d) solutions under UV irradiation in the presence of complexes **2** and **6**.

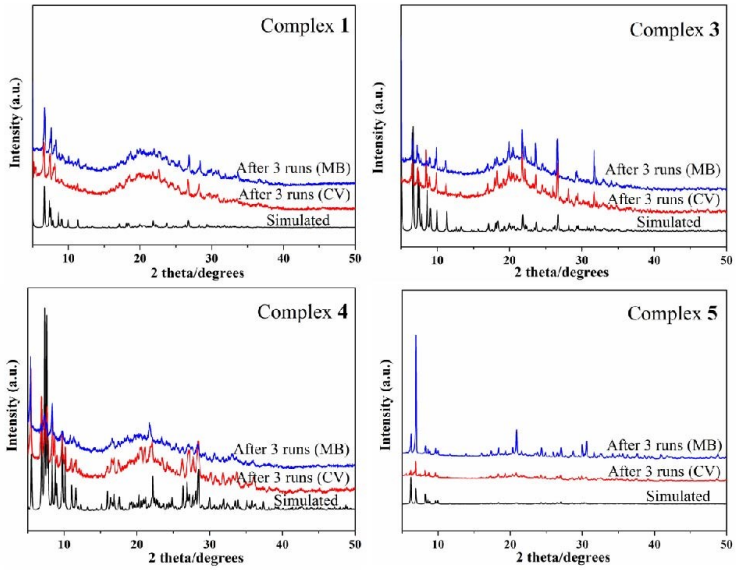


**Figure S8** The PXRD patterns of simulated and recycled after acting as catalysts of **1**, **3**, **4** and **5**.