Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Synthesis and photo-/electro-catalytic properties of Keggin polyoxometalate inorganic-organic hybrid layers based on d10 metal and rigid benzo-diazole/-triazole ligands

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## 1. Structural figures

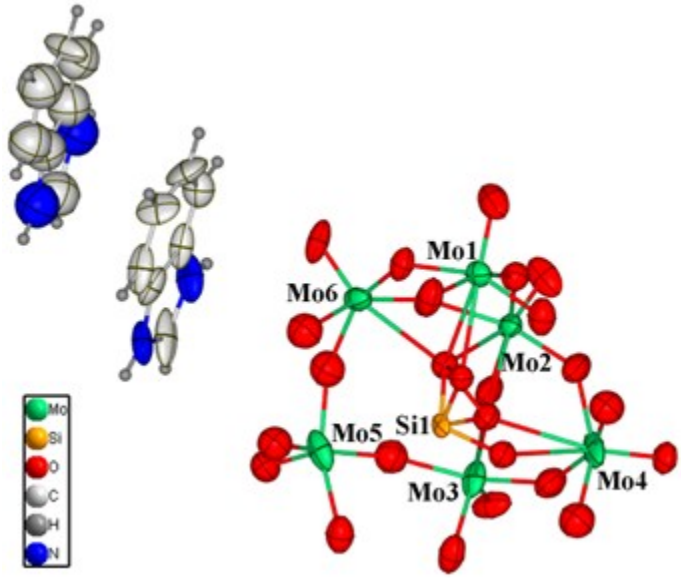


**Fig. S1** Stick-ellipsoid representation of molecule structure of compound **1**

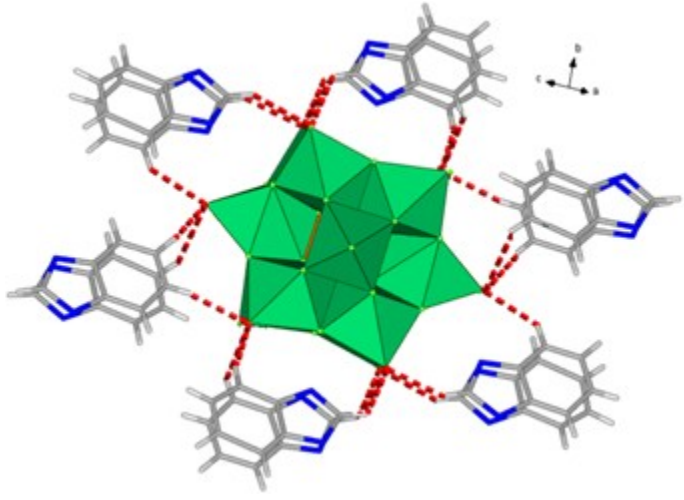

**Fig. S2** The arrangement of six pairs of biz ligands in 2D layer of compound **1**

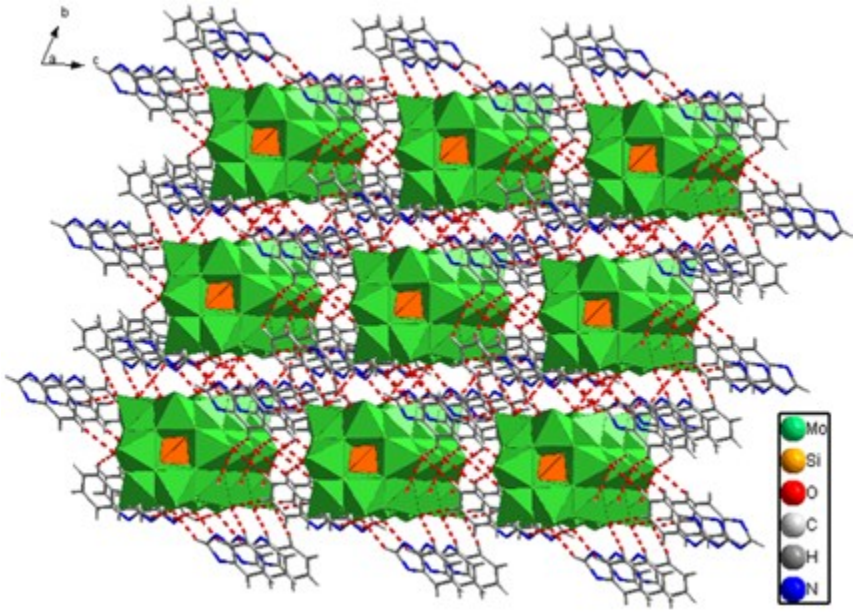


**Fig. S3** The 3-D supramolecular network on the bc plane of compound **1**.

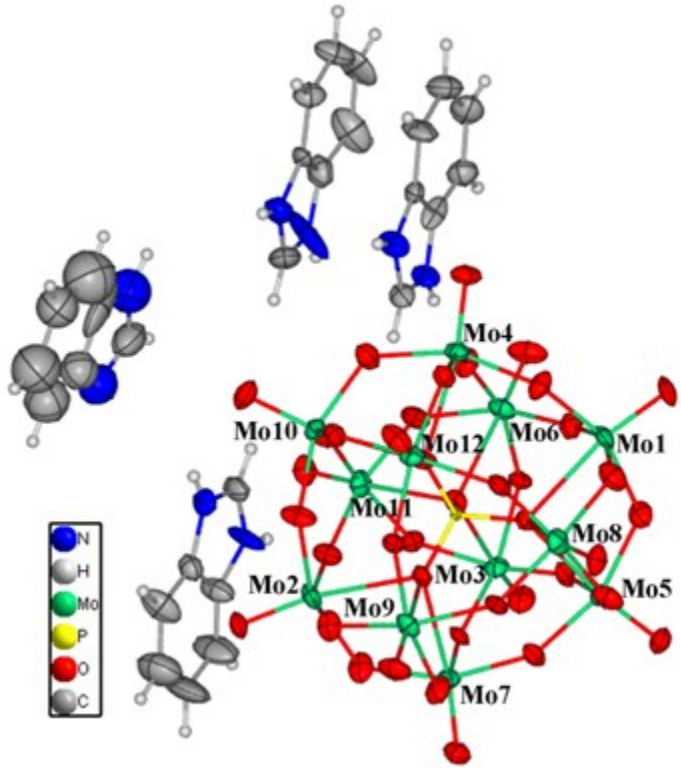


**Fig. S4** Stick-ellipsoid representation of molecule structure of compound **2**

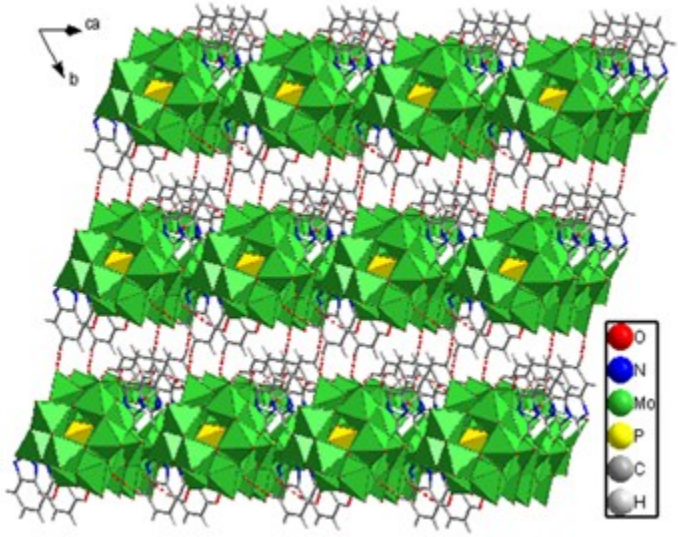


**Fig. S5** The 3-D supramolecular network on the bc plane of compound **2**.

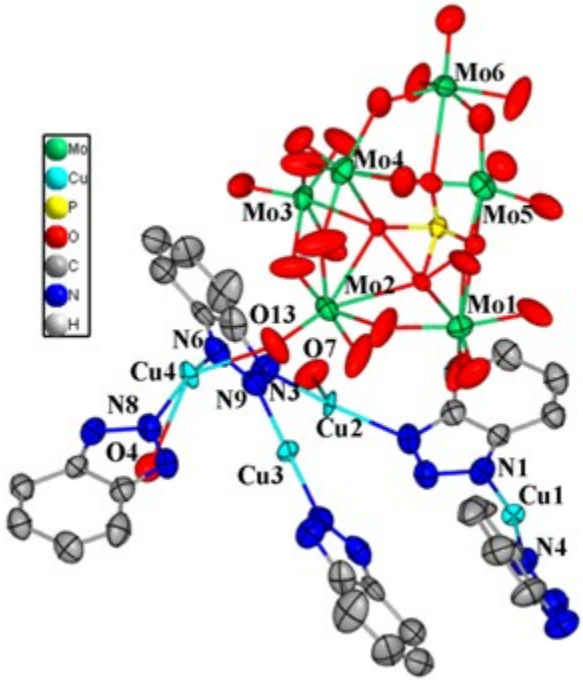


**Fig. S6** Stick-ellipsoid representation of molecule structure of compound **3**

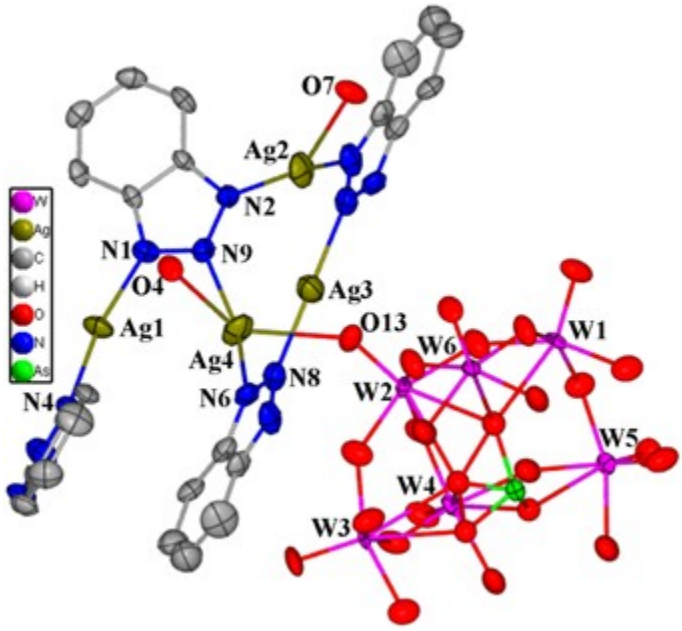


**Fig. S7** Stick-ellipsoid representation of molecule structure of compound **4**

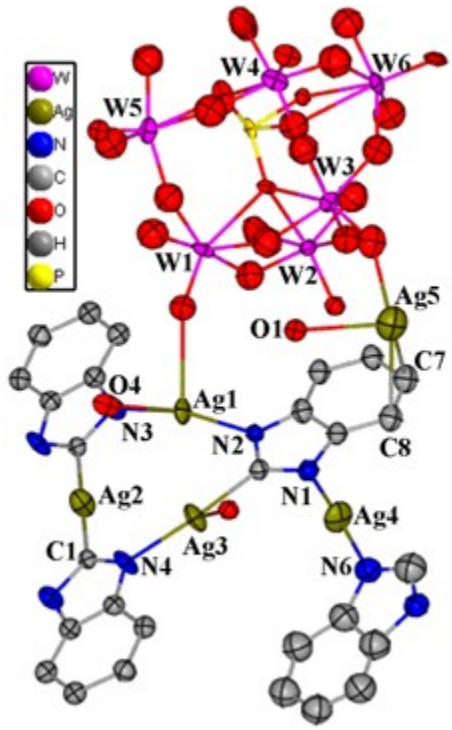


**Fig. S8** Stick-ellipsoid representation of molecule structure of compound **5**

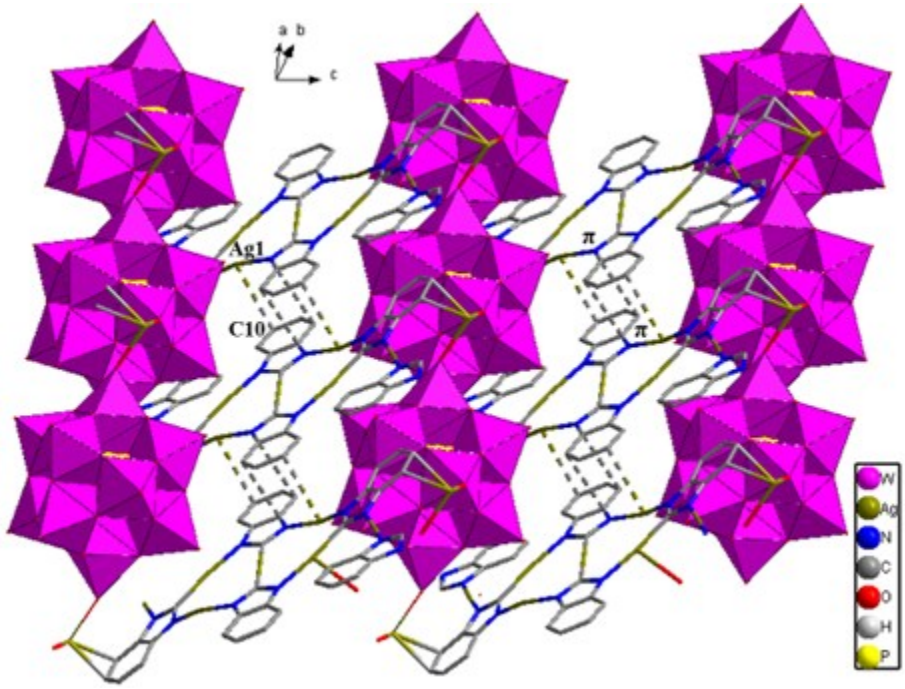


**Fig. S9** The π–π stacking and $Ag^{I}$–π interactions between adjacent {$Ag_9$} complexes of 2-D layer in compound **5.**

## 2. Physical characterization

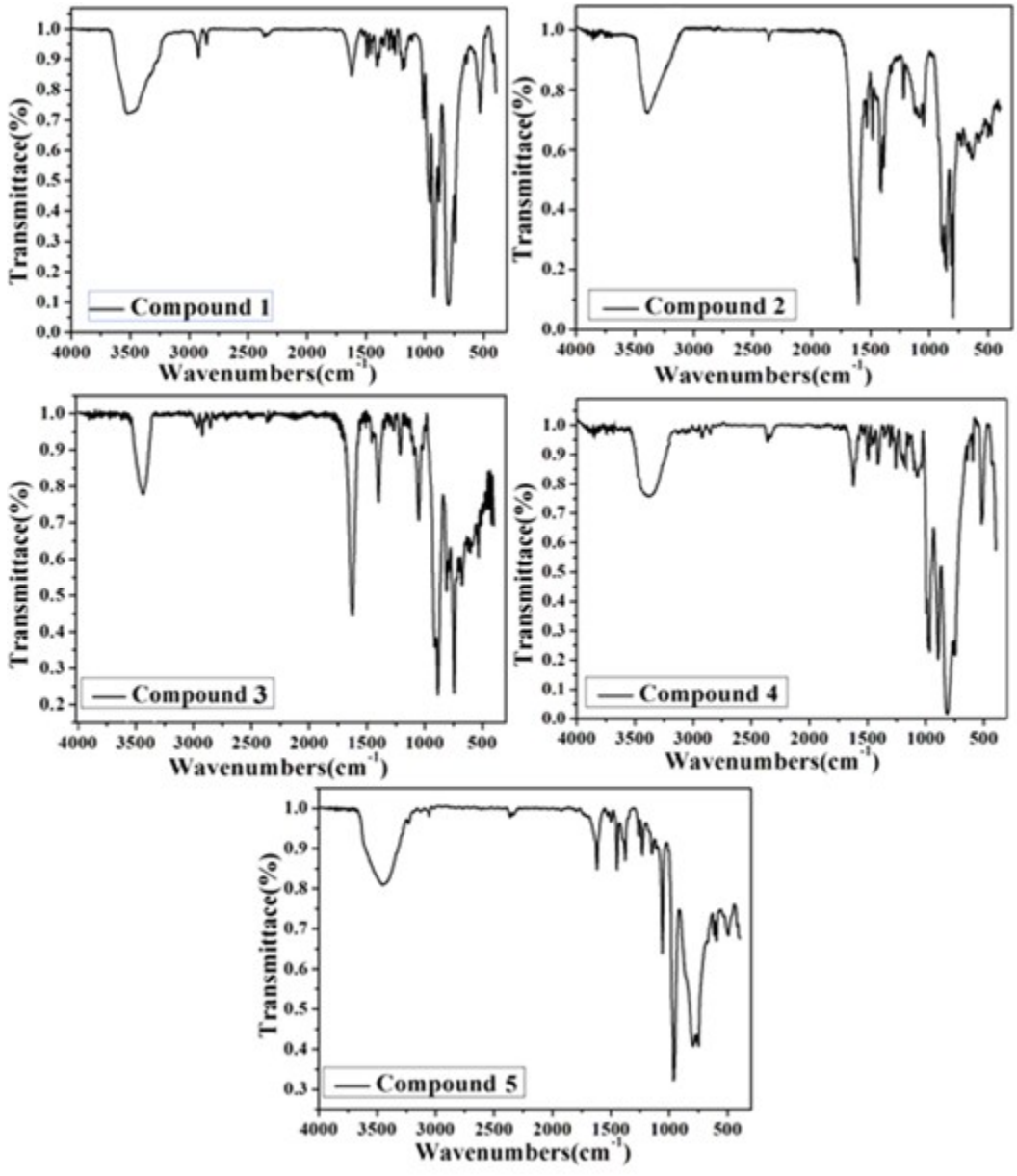


**Fig.S10** IR spectra of compounds **1-5**

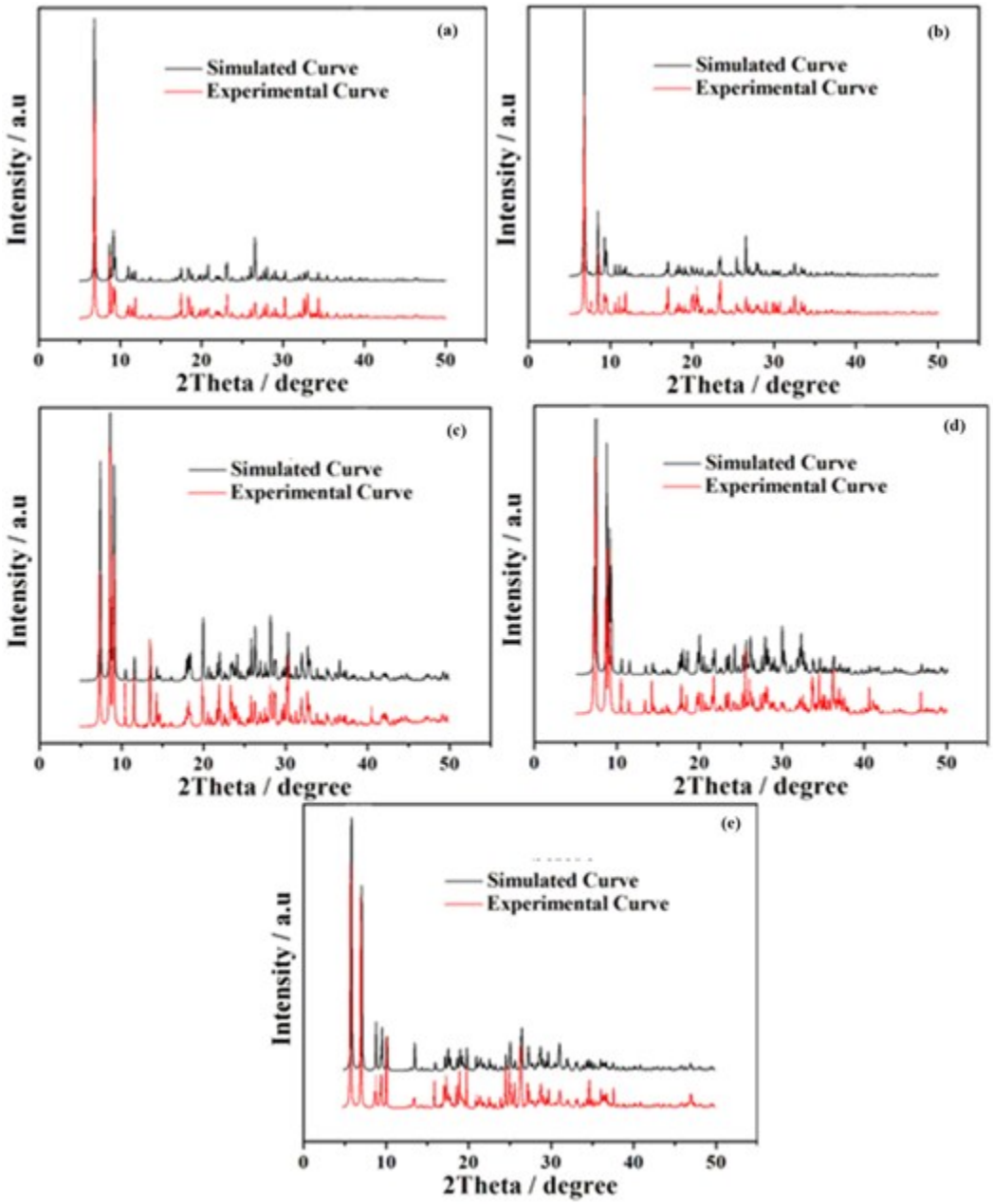


**Fig.S11** XRPD analysis of **(a)** compound **1**, **(b)** compound **2**, **(c)** compound **3**, **(d)** compound **4**, and **(e)** compound **5.**

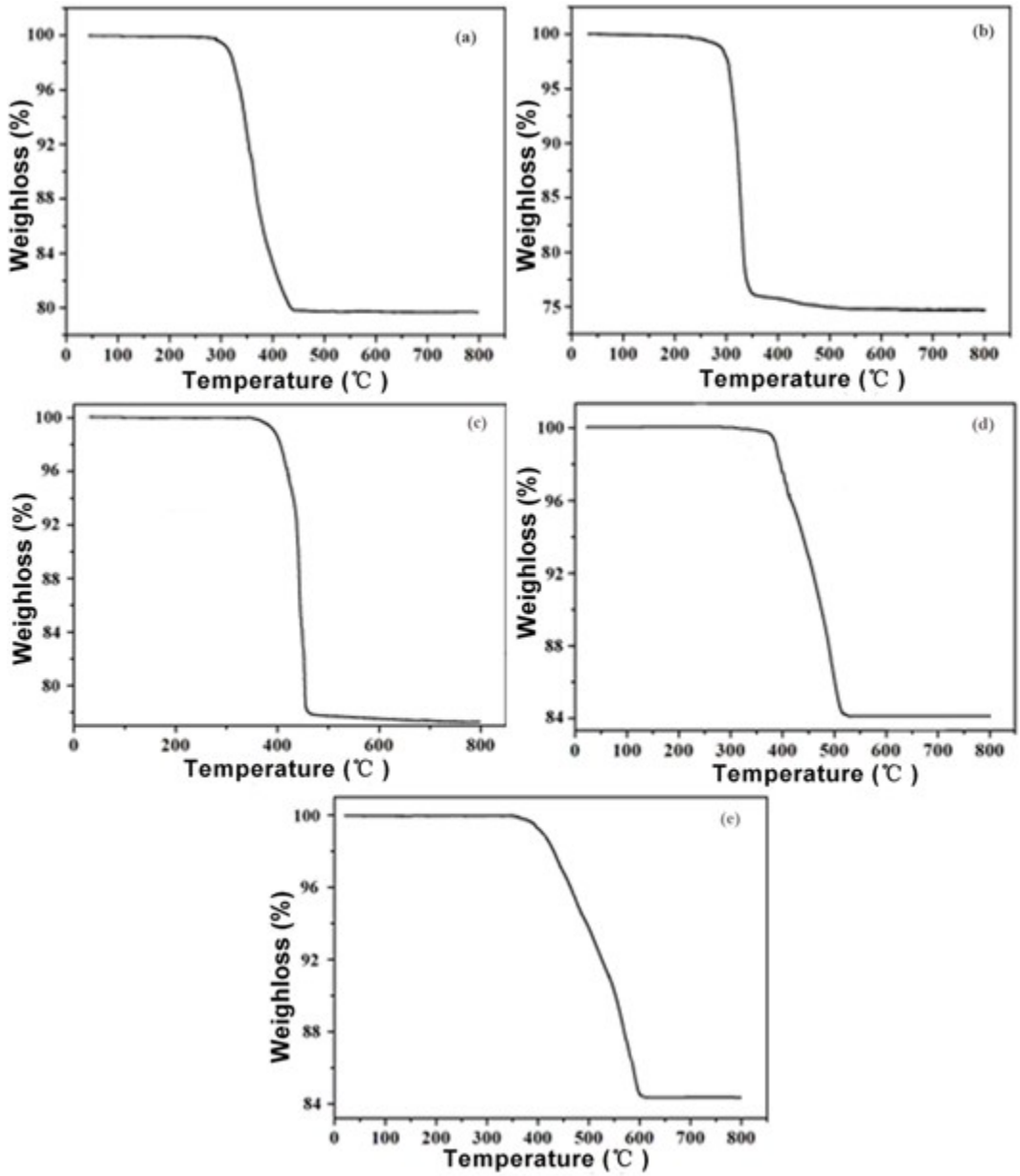


**Fig.S12** TG curves of **(a)** compound **1**, **(b)** compound **2**, **(c)** compound **3**, **(d)** compound **4**, and **(e)** compound **5.**

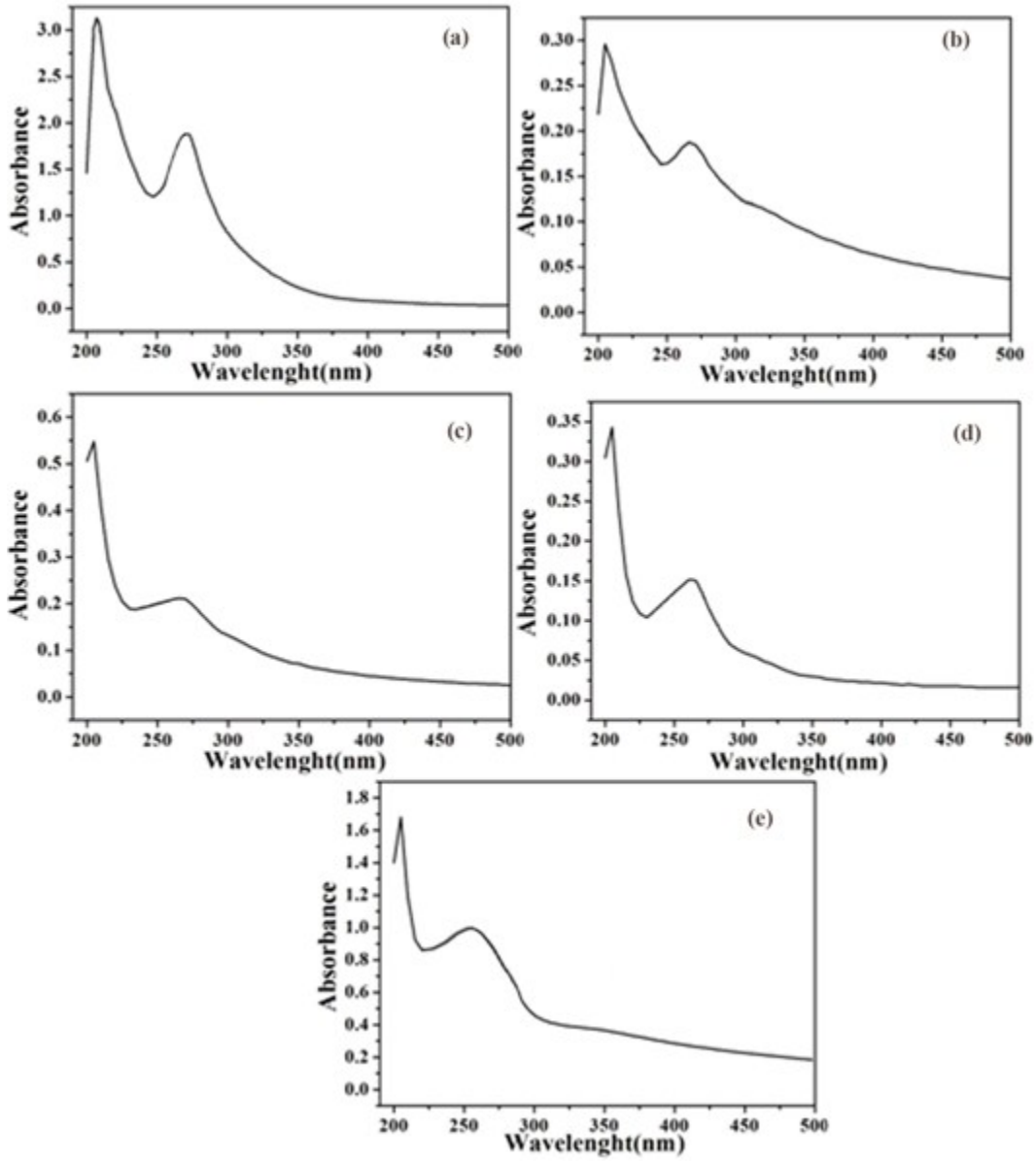


**Fig. S13** Solid state UV-vis spectra of **(a)** compound **1**, **(b)** compound **2**, **(c)** compound **3**, **(d)** compound **4**, and **(e)** compound **5.**

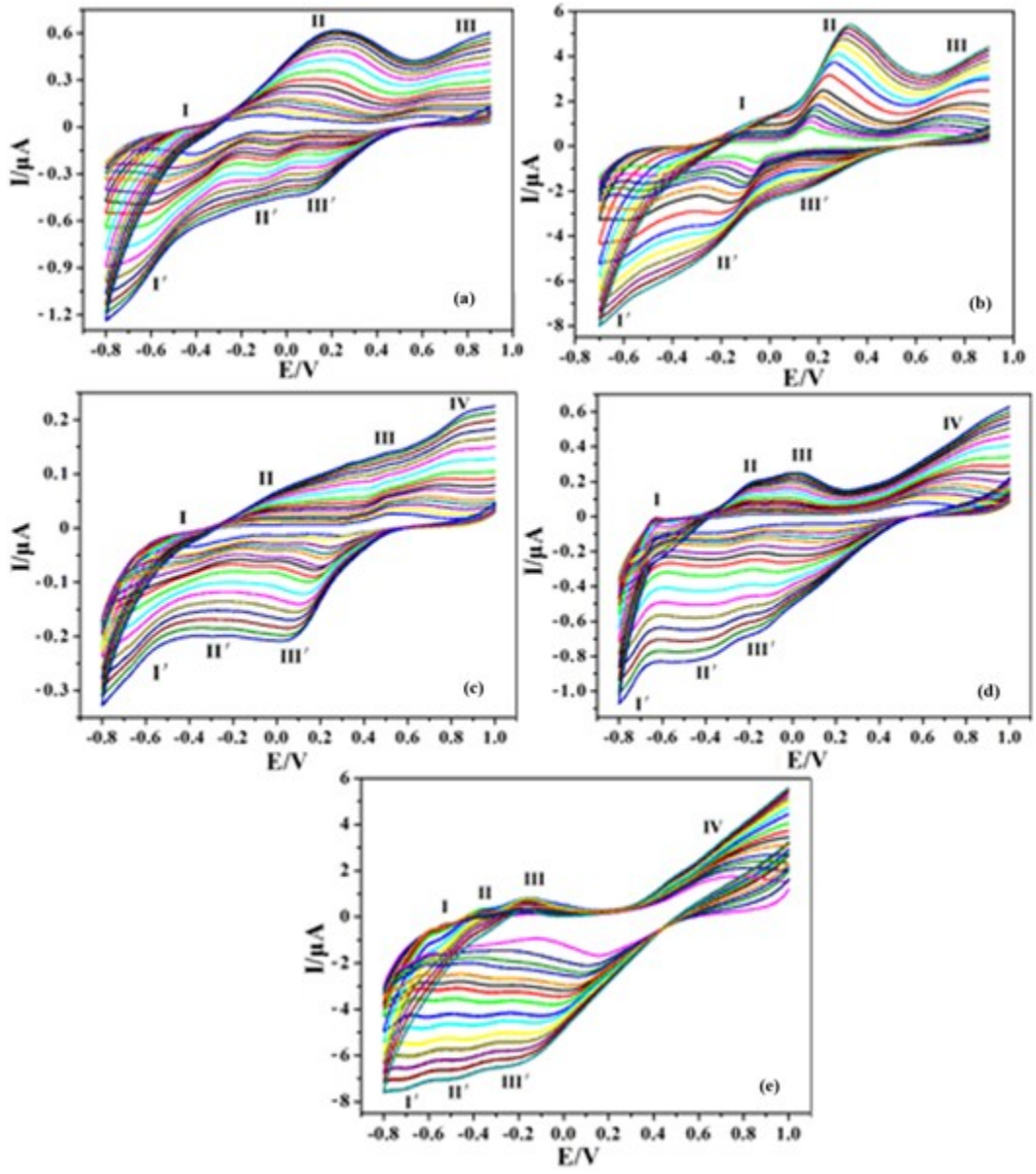


**Fig.S14** Cyclic voltammograms of (a) **1-CPE**, (b) **2-CPE**, (c) **3-CPE**, (d) **4-CPE**, and (e) **5-CPE** in the 1.0 M $H_2SO_4$ solution at scan rate of 20 mV $s^{-1}$;scan rates (from inner to outer: 20, 30, 40, 60, 80, 100, 120, 150, 200, 250, 300, 350, 400, 450, 500 mV $s^{-1}$).

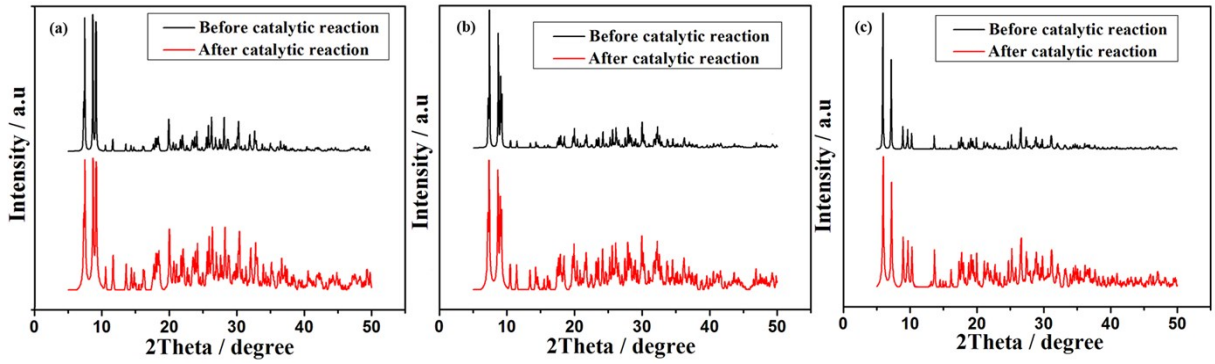


**Fig.S15** XRPD contrast curves of **(a)** compound **3**, **(b)** compound **4**, and **(c)** compound **5** before and after photocatalytic reaction.

## 3. Structural data

**Table S1** Selected bond lengths (Å) and bond angles (º) of compounds **1-5**

| Compound **1** | | | | | |
|---|---|---|---|---|---|
| Mo(1)-O(5) | 1.67(2) | Mo(1)-O(9) | 1.822(19) | Mo(1)-O(1) | 1.867(16) |
| Mo(1)-O(13) | 1.914(19) | Mo(1)-O(4) | 1.931(17) | Mo(1)-O(14) | 2.31(3) |
| Mo(2)-O(7) | 1.652(18) | Mo(2)-O(18) | 1.821(19) | Mo(2)-O(22) | 1.899(16) |
| Mo(2)-O(15) | 1.91(2) | Mo(2)-O(1) | 1.958(17) | Mo(2)-O(19) | 2.38(3) |
| Mo(3)-O(3) | 1.667(18) | Mo(3)-O(6) | 1.86(2) | Mo(3)-O(11) | 1.88(2) |
| Mo(3)-O(13)#1 | 1.90(2) | Mo(3)-O(15) | 1.98(2) | Mo(3)-O(14)#1 | 2.47(3) |
| Mo(3)-O(19) | 2.51(3) | Mo(4)-O(10) | 1.651(17) | Mo(4)-O(21) | 1.84(2) |
| Mo(4)-O(8) | 1.90(2) | Mo(4)-O(18) | 2.00(2) | Mo(4)-O(19) | 2.47(3) |
| Mo(4)-O(6) | 1.93(2) | Mo(5)-O(16) | 1.80(2) | Mo(5)-O(11) | 1.86(2) |
| Mo(5)-O(8)#1 | 1.94(2) | Mo(5)-O(9)#1 | 1.99(2) | Mo(5)-O(2) | 1.67(2) |
| Mo(6)-O(12) | 1.641(19) | Mo(6)-O(4) | 1.847(19) | Mo(6)-O(22) | 1.852(16) |
| Mo(6)-O(21)#1 | 1.92(2) | Mo(6)-O(16) | 1.97(2) | Mo(6)-O(20)#1 | 2.33(3) |
| Si(1)-O(17) | 1.40(3) | Si(1)-O(17)#1 | 1.40(3) | Si(1)-O(19)#1 | 1.56(3) |
| Si(1)-O(19) | 1.56(3) | Si(1)-O(14) | 1.58(3) | Si(1)-O(14)#1 | 1.58(3) |
| Si(1)-O(20) | 1.58(3) | Si(1)-O(20)#1 | 1.58(3) | | |
| O(5)-Mo(1)-O(9) | 103.6(11) | O(5)-Mo(1)-O(1) | 100.5(9) | O(5)-Mo(1)-O(13) | 99.0(11) |
| O(5)-Mo(1)-O(4) | 101.0(10) | O(5)-Mo(1)-O(14) | 160.8(11) | O(7)-Mo(2)-O(18) | 99.5(12) |
| O(7)-Mo(2)-O(22) | 103.7(10) | O(7)-Mo(2)-O(15) | 101.5(11) | O(7)-Mo(2)-O(1) | 98.1(8) |
| O(7)-Mo(2)-O(19) | 160.7(10) | O(3)-Mo(3)-O(6) | 99.6(11) | O(3)-Mo(3)-O(11) | 106.6(11) |
| O(3)-Mo(3)-O(13)#1 | 99.2(10) | O(3)-Mo(3)-O(15) | 99.3(10) | O(3)-Mo(3)-O(14)#1 | 158.0(10) |
| O(3)-Mo(3)-O(19) | 156.8(10) | O(10)-Mo(4)-O(21) | 105.4(10) | O(10)-Mo(4)-O(8) | 100.7(10) |
| O(10)-Mo(4)-O(6) | 100.2(10) | O(10)-Mo(4)-O(18) | 98.7(9) | O(10)-Mo(4)-O(19) | 154.2(9) |
| O(10)-Mo(4)-O(20) | 160.5(9) | O(2)-Mo(5)-O(16) | 103.8(10) | O(2)-Mo(5)-O(11) | 103.2(10) |
| O(2)-Mo(5)-O(9)#1 | 100.7(9) | O(2)-Mo(5)-O(8)#1 | 102.2(10) | O(12)-Mo(6)-O(20)#1 | 159.1(11) |
| O(12)-Mo(6)-O(4) | 103.2(10) | O(12)-Mo(6)-O(22) | 103.8(8) | O(12)-Mo(6)-O(21)#1 | 102.1(10) |
| O(12)-Mo(6)-O(16) | 102.8(10) | | | | |
| O(17)-Si(1)-O(17)#1 | 179.998(4) | O(17)-Si(1)-O(19)#1 | 113.7(16) | O(17)#1-Si(1)-O(19)#1 | 66.3(16) |
| O(17)-Si(1)-O(19) | 66.3(16) | O(17)#1-Si(1)-O(19) | 113.7(16) | O(17)-Si(1)-O(14) | 66.5(15) |
| O(17)#1-Si(1)-O(14) | 113.5(15) | O(17)-Si(1)-O(14)#1 | 113.5(15) | O(17)#1-Si(1)-O(14)#1 | 66.5(15) |
| O(17)-Si(1)-O(20) | 115.7(16) | O(17)#1-Si(1)-O(20) | 64.3(16) | O(17)-Si(1)-O(20)#1 | 64.3(16) |
| O(17)#1-Si(1)-O(20)#1 | 115.7(16) | | | | |
| Symmetry transformations used to generate equivalent atoms:#1 -x,-y+1,-z | | | | | |
| Compound **2** | | | | | |
| Mo(1)-O(1) | 1.658(12) | Mo(1)-O(28) | 1.840(12) | Mo(1)-O(39) | 1.880(15) |
| Mo(1)-O(31) | 1.955(13) | Mo(1)-O(27) | 1.974(13) | Mo(1)-O(2) | 2.438(11) |
| Mo(2)-O(35) | 1.675(11) | Mo(2)-O(40) | 1.829(13) | Mo(2)-O(14) | 1.918(13) |
| Mo(2)-O(10) | 1.926(12) | Mo(2)-O(15) | 1.978(12) | Mo(2)-O(5) | 2.452(11) |
| Mo(3)-O(37) | 1.683(13) | Mo(3)-O(20) | 1.842(11) | Mo(3)-O(22) | 1.890(11) |
| Mo(3)-O(8) | 1.949(12) | Mo(3)-O(13) | 1.958(12) | Mo(3)-O(4) | 2.403(11) |
| Mo(4)-O(34) | 1.652(12) | Mo(4)-O(12) | 1.870(12) | Mo(4)-O(28) | 1.910(12) |
| Mo(4)-O(11) | 1.918(13) | Mo(4)-O(29) | 1.939(12) | Mo(4)-O(3) | 2.425(11) |
| Mo(5)-O(25) | 1.670(12) | Mo(5)-O(19) | 1.875(13) | Mo(5)-O(21) | 1.898(11) |
| Mo(5)-O(27) | 1.914(13) | Mo(5)-O(20) | 1.948(12) | Mo(5)-O(2) | 2.396(11) |
| Mo(6)-O(30) | 1.682(13) | Mo(6)-O(31) | 1.852(13) | Mo(6)-O(12) | 1.911(12) |
| Mo(6)-O(13) | 1.919(12) | Mo(6)-O(6) | 1.966(14) | Mo(6)-O(4) | 2.420(11) |
| Mo(7)-O(24) | 1.657(13) | Mo(7)-O(14) | 1.896(13) | Mo(7)-O(21) | 1.910(12) |
| Mo(7)-O(22) | 1.913(11) | Mo(7)-O(36) | 1.928(14) | Mo(7)-O(5) | 2.441(11) |
| Mo(8)-O(33) | 1.667(12) | Mo(8)-O(18) | 1.796(13) | Mo(8)-O(23) | 1.869(11) |
| Mo(8)-O(39) | 1.953(14) | Mo(8)-O(19) | 2.034(14) | Mo(8)-O(2) | 2.426(11) |
| Mo(9)-O(38) | 1.667(13) | Mo(9)-O(32) | 1.879(12) | Mo(9)-O(15) | 1.880(12) |
| Mo(9)-O(36) | 1.942(12) | Mo(9)-O(23) | 1.948(12) | Mo(9)-O(5) | 2.422(11) |

| | | | | | |
|---|---|---|---|---|---|
| Mo(10)-O(26) | 1.655(13) | Mo(10)-O(7) | 1.819(13) | Mo(10)-O(10) | 1.883(12) |
| Mo(10)-O(11) | 1.913(13) | Mo(10)-O(17) | 1.982(13) | Mo(10)-O(3) | 2.435(11) |
| Mo(11)-O(9) | 1.670(12) | Mo(11)-O(6) | 1.859(13) | Mo(11)-O(8) | 1.893(12) |
| Mo(11)-O(40) | 1.953(12) | Mo(11)-O(7) | 1.978(13) | Mo(11)-O(4) | 2.461(11) |
| Mo(12)-O(16) | 1.675(12) | Mo(12)-O(17) | 1.870(12) | Mo(12)-O(32) | 1.899(12) |
| Mo(12)-O(29) | 1.924(12) | Mo(12)-O(18) | 1.971(13) | Mo(12)-O(3) | 2.456(12) |
| P(1)-O(5) | 1.513(11) | P(1)-O(3) | 1.538(11) | P(1)-O(4) | 1.547(11) |
| P(1)-O(2) | 1.550(11) | | | | |
| O(1)-Mo(1)-O(28) | 105.0(7) | O(1)-Mo(1)-O(39) | 102.4(7) | O(1)-Mo(1)-O(31) | 101.0(7) |
| O(1)-Mo(1)-O(27) | 99.4(6) | O(1)-Mo(1)-O(2) | 169.5(6) | O(35)-Mo(2)-O(40) | 105.3(6) |
| O(35)-Mo(2)-O(14) | 100.9(6) | O(35)-Mo(2)-O(10) | 103.7(6) | O(35)-Mo(2)-O(15) | 99.3(6) |
| O(35)-Mo(2)-O(5) | 167.3(5) | O(37)-Mo(3)-O(20) | 104.0(6) | O(37)-Mo(3)-O(22) | 103.6(6) |
| O(37)-Mo(3)-O(8) | 99.6(6) | O(37)-Mo(3)-O(13) | 97.4(6) | O(37)-Mo(3)-O(4) | 166.8(6) |
| O(34)-Mo(4)-O(12) | 103.9(6) | O(34)-Mo(4)-O(28) | 104.8(6) | O(34)-Mo(4)-O(11) | 100.5(6) |
| O(34)-Mo(4)-O(29) | 99.4(6) | O(34)-Mo(4)-O(3) | 167.5(6) | O(25)-Mo(5)-O(19) | 100.4(7) |
| O(25)-Mo(5)-O(21) | 100.9(6) | O(25)-Mo(5)-O(27) | 99.8(6) | O(25)-Mo(5)-O(20) | 100.8(6) |
| O(25)-Mo(5)-O(2) | 171.0(5) | O(30)-Mo(6)-O(31) | 103.9(7) | O(30)-Mo(6)-O(12) | 103.6(6) |
| O(30)-Mo(6)-O(13) | 98.1(6) | O(30)-Mo(6)-O(6) | 99.4(7) | O(30)-Mo(6)-O(4) | 166.7(6) |
| O(24)-Mo(7)-O(14) | 101.7(6) | O(24)-Mo(7)-O(21) | 101.6(6) | O(24)-Mo(7)-O(22) | 101.6(6) |
| O(24)-Mo(7)-O(36) | 99.2(6) | O(24)-Mo(7)-O(5) | 169.5(6) | O(33)-Mo(8)-O(18) | 105.1(7) |
| O(33)-Mo(8)-O(23) | 101.6(6) | O(33)-Mo(8)-O(39) | 100.1(6) | O(33)-Mo(8)-O(19) | 97.0(6) |
| O(33)-Mo(8)-O(2) | 166.0(5) | O(38)-Mo(9)-O(32) | 102.7(6) | O(38)-Mo(9)-O(15) | 102.4(7) |
| O(38)-Mo(9)-O(36) | 99.5(7) | O(38)-Mo(9)-O(23) | 100.7(7) | O(38)-Mo(9)-O(5) | 170.8(6) |
| O(26)-Mo(10)-O(7) | 105.0(7) | O(26)-Mo(10)-O(10) | 105.2(7) | O(26)-Mo(10)-O(11) | 99.4(7) |
| O(26)-Mo(10)-O(17) | 97.8(6) | O(26)-Mo(10)-O(3) | 164.7(6) | O(9)-Mo(11)-O(6) | 101.0(7) |
| O(9)-Mo(11)-O(8) | 100.6(6) | O(9)-Mo(11)-O(40) | 103.8(6) | O(9)-Mo(11)-O(7) | 101.9(6) |
| O(9)-Mo(11)-O(4) | 169.6(5) | O(16)-Mo(12)-O(17) | 100.3(6) | O(16)-Mo(12)-O(32) | 104.5(6) |
| O(16)-Mo(12)-O(29) | 100.1(6) | O(16)-Mo(12)-O(18) | 103.7(6) | O(16)-Mo(12)-O(3) | 168.3(6) |
| O(5)-P(1)-O(3) | 110.1(6) | O(5)-P(1)-O(4) | 109.3(6) | O(5)-P(1)-O(2) | 110.0(6) |
| Compound **3** | | | | | |
| Mo(1)-O(7) | 1.642(17) | Mo(1)-O(22) | 1.837(18) | Mo(1)-O(16) | 1.855(18) |
| Mo(1)-O(12) | 1.937(18) | Mo(1)-O(11) | 1.972(16) | Mo(1)-O(2) | 2.43(3) |
| Mo(1)-O(18) | 2.45(3) | Mo(2)-O(13) | 1.670(16) | Mo(2)-O(9) | 1.828(17) |
| Mo(2)-O(6) | 1.864(18) | Mo(2)-O(16) | 1.948(16) | Mo(2)-O(8) | 1.965(18) |
| Mo(2)-O(19) | 2.47(2) | Mo(2)-O(18) | 2.47(2) | Mo(3)-O(15) | 1.618(17) |
| Mo(3)-O(3) | 1.820(16) | Mo(3)-O(12)#1 | 1.868(18) | Mo(3)-O(6) | 1.932(17) |
| Mo(3)-O(14) | 1.954(18) | Mo(3)-O(2)#1 | 2.41(3) | Mo(3)-O(19) | 2.41(2) |
| Mo(4)-O(20) | 1.636(16) | Mo(4)-O(21) | 1.779(18) | Mo(4)-O(8) | 1.83(2) |
| Mo(4)-O(3) | 1.980(17) | Mo(4)-O(17) | 2.014(17) | Mo(4)-O(1) | 2.46(3) |
| Mo(4)-O(19) | 2.52(2) | Mo(5)-O(5) | 1.652(17) | Mo(5)-O(14)#1 | 1.808(18) |
| Mo(5)-O(10) | 1.837(17) | Mo(5)-O(10) | 1.837(17) | Mo(5)-O(22) | 1.934(17) |
| Mo(5)-O(21) | 1.938(17) | Mo(5)-O(1) | 2.44(2) | Mo(5)-O(2) | 2.50(3) |
| Mo(6)-O(4) | 1.662(17) | Mo(6)-O(17) | 1.813(17) | Mo(6)-O(11)#1 | 1.834(18) |
| Mo(6)-O(10) | 1.942(17) | Mo(6)-O(9)#1 | 1.964(19) | Mo(6)-O(1) | 2.39(3) |
| Mo(6)-O(18)#1 | 2.52(2) | | | | |
| P(1)-O(18) | 1.49(2) | P(1)-O(18)#1 | 1.49(2) | P(1)-O(19) | 1.51(2) |
| P(1)-O(19)#1 | 1.51(2) | P(1)-O(2)#1 | 1.54(3) | P(1)-O(2) | 1.54(3) |
| P(1)-O(1)#1 | 1.58(3) | P(1)-O(1) | 1.58(3) | | |
| Cu(1)-N(4) | 2.102(19) | Cu(1)-N(1) | 2.106(18) | Cu(2)-N(3) | 2.100(19) |
| Cu(2)-N(2) | 2.133(18) | Cu(3)-N(9)#2 | 2.10(2) | Cu(4)-N(8)#2 | 2.140(17) |
| N(6)-Cu(4) | 2.099(18) | N(8)-Cu(4)#2 | 2.141(17) | | |
| O(7)-Mo(1)-O(22) | 101.9(10) | O(7)-Mo(1)-O(16) | 101.8(10) | O(7)-Mo(1)-O(12) | 98.6(11) |
| O(7)-Mo(1)-O(11) | 101.5(10) | O(7)-Mo(1)-O(2) | 156.8(10) | O(7)-Mo(1)-O(18) | 161.3(10) |
| O(13)-Mo(2)-O(9) | 103.1(12) | O(13)-Mo(2)-O(6) | 102.2(10) | O(13)-Mo(2)-O(16) | 99.2(10) |
| O(13)-Mo(2)-O(8) | 99.5(11) | O(13)-Mo(2)-O(19) | 158.8(10) | O(13)-Mo(2)-O(18) | 160.3(10) |
| O(15)-Mo(3)-O(3) | 101.2(11) | O(15)-Mo(3)-O(12)#1 | 100.9(11) | O(15)-Mo(3)-O(6) | 100.2(10) |
| O(15)-Mo(3)-O(14) | 102.4(11) | O(15)-Mo(3)-O(2)#1 | 158.7(11) | O(15)-Mo(3)-O(19) | 159.5(11) |

| | | | | | |
|---|---|---|---|---|---|
| O(20)-Mo(4)-O(21) | 105.6(10) | O(20)-Mo(4)-O(8) | 103.9(10) | O(20)-Mo(4)-O(3) | 100.8(9) |
| O(20)-Mo(4)-O(17) | 97.5(9) | O(20)-Mo(4)-O(1) | 155.2(9) | O(20)-Mo(4)-O(19) | 159.5(9) |
| O(5)-Mo(5)-O(14)#1 | 104.3(10) | O(5)-Mo(5)-O(10) | 101.0(9) | O(5)-Mo(5)-O(22) | 102.6(9) |
| O(5)-Mo(5)-O(21) | 104.1(9) | O(5)-Mo(5)-O(1) | 157.2(9) | O(5)-Mo(5)-O(2) | 158.8(9) |
| O(4)-Mo(6)-O(17) | 100.5(9) | O(4)-Mo(6)-O(11)#1 | 101.5(9) | O(4)-Mo(6)-O(10) | 100.3(9) |
| O(4)-Mo(6)-O(9)#1 | 100.3(10) | O(4)-Mo(6)-O(1) | 158.7(9) | O(4)-Mo(6)-O(18)#1 | 158.2(8) |
| O(18)-P(1)-O(18)#1 | 179.998(8) | O(18)-P(1)-O(19) | 69.1(12) | O(18)#1-P(1)-O(19) | 110.9(12) |
| O(18)-P(1)-O(19)#1 | 110.9(12) | O(18)#1-P(1)-O(19)#1 | 69.1(12) | O(18)-P(1)-O(2)#1 | 110.9(13) |
| O(18)#1-P(1)-O(2)#1 | 69.1(13) | O(18)-P(1)-O(2) | 69.1(13) | O(18)#1-P(1)-O(2) | 110.9(13) |
| O(18)-P(1)-O(1)#1 | 71.2(13) | O(18)#1-P(1)-O(1)#1 | 108.8(13) | O(18)-P(1)-O(1) | 108.8(13) |
| O(18)#1-P(1)-O(1) | 71.2(13) | | | | |
| N(4)-Cu(1)-N(1) | 166.4(7) | N(3)-Cu(2)-N(2) | 158.1(7) | N(9)#2-Cu(3)-N(9) | 179.999(2) |
| N(6)-Cu(4)-N(8)#2 | 155.0(7) | | | | |
| Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1；#2 -x+2,-y+1,-z | | | | | |
| Compound **4** | | | | | |
| W(1)-O(7) | 1.667(19) | W(1)-O(22) | 1.864(19) | W(1)-O(16) | 1.87(2) |
| W(1)-O(12)#1 | 1.91(2) | W(1)-O(11) | 1.924(19) | W(1)-O(2)#1 | 2.44(3) |
| W(1)-O(18) | 2.46(3) | W(2)-O(13) | 1.682(19) | W(2)-O(9) | 1.88(2) |
| W(2)-O(6) | 1.87(2) | W(2)-O(8) | 1.908(19) | W(2)-O(16) | 1.92(2) |
| W(2)-O(18) | 2.42(3) | W(2)-O(19) | 2.47(3) | W(3)-O(15) | 1.658(18) |
| W(3)-O(12) | 1.893(19) | W(3)-O(14)#1 | 1.90(2) | W(3)-O(6) | 1.91(2) |
| W(3)-O(2) | 2.43(3) | W(3)-O(19) | 2.46(3) | W(3)-O(3) | 1.878(19) |
| W(4)-O(20) | 1.655(18) | W(4)-O(21) | 1.88(2) | W(4)-O(8) | 1.89(2) |
| W(4)-O(3) | 1.916(19) | W(4)-O(17)#1 | 1.93(2) | W(4)-O(1) | 2.44(3) |
| W(5)-O(5) | 1.666(17) | W(5)-O(14) | 1.88(2) | W(5)-O(10)#1 | 1.89(2) |
| W(5)-O(21) | 1.89(2) | W(5)-O(22) | 1.905(19) | W(5)-O(1) | 2.43(3) |
| W(6)-O(4) | 1.681(17) | W(6)-O(11) | 1.876(19) | W(6)-O(17) | 1.88(2) |
| W(6)-O(10) | 1.89(2) | W(6)-O(9) | 1.92(2) | W(6)-O(1)#1 | 2.44(3) |
| W(6)-O(18) | 2.50(3) | | | | |
| As(1)-O(19) | 1.51(3) | As(1)-O(19)#1 | 1.51(3) | As(1)-O(2)#1 | 1.55(3) |
| As(1)-O(2) | 1.55(3) | As(1)-O(18) | 1.55(3) | As(1)-O(18)#1 | 1.55(3) |
| As(1)-O(1)#1 | 1.60(3) | As(1)-O(1) | 1.60(3) | | |
| Ag(1)-N(4) | 2.10(2) | Ag(1)-N(1) | 2.11(2) | Ag(1)-Ag(4) | 3.156(3) |
| Ag(2)-N(3) | 2.12(2) | Ag(2)-N(2) | 2.14(2) | Ag(3)-N(8)#2 | 2.10(3) |
| Ag(3)-N(8) | 2.10(3) | Ag(3)-Ag(4)#2 | 3.331(3) | Ag(3)-Ag(4) | 3.330(3) |
| Ag(4)-N(6)#2 | 2.12(2) | Ag(4)-N(9) | 2.15(2) | | |
| O(7)-W(1)-O(22) | 102.6(10) | O(7)-W(1)-O(16) | 102.4(10) | O(7)-W(1)-O(12)#1 | 101.0(10) |
| O(7)-W(1)-O(11) | 102.6(10) | O(7)-W(1)-O(2)#1 | 158.3(11) | O(7)-W(1)-O(18) | 159.3(11) |
| O(13)-W(2)-O(9) | 100.8(11) | O(13)-W(2)-O(6) | 101.5(10) | O(13)-W(2)-O(8) | 102.5(11) |
| O(13)-W(2)-O(16) | 102.7(10) | O(13)-W(2)-O(18) | 159.1(12) | O(13)-W(2)-O(19) | 160.2(12) |
| O(15)-W(3)-O(3) | 101.4(11) | O(15)-W(3)-O(12) | 101.1(11) | O(15)-W(3)-O(14)#1 | 103.3(12) |
| O(15)-W(3)-O(6) | 102.2(11) | O(15)-W(3)-O(2) | 159.4(12) | O(15)-W(3)-O(19) | 159.0(12) |
| O(20)-W(4)-O(21) | 104.0(11) | O(20)-W(4)-O(8) | 102.2(10) | O(20)-W(4)-O(3) | 102.2(10) |
| O(20)-W(4)-O(17)#1 | 101.5(11) | O(20)-W(4)-O(1) | 157.7(11) | O(5)-W(5)-O(14) | 102.9(10) |
| O(5)-W(5)-O(10)#1 | 101.7(11) | O(5)-W(5)-O(21) | 103.2(11) | O(5)-W(5)-O(22) | 104.8(10) |
| O(5)-W(5)-O(1) | 157.2(11) | O(4)-W(6)-O(11) | 101.0(9) | O(4)-W(6)-O(17) | 102.1(11) |
| O(4)-W(6)-O(10) | 102.8(10) | O(4)-W(6)-O(9) | 101.0(10) | O(4)-W(6)-O(1)#1 | 158.2(10) |
| O(4)-W(6)-O(18) | 156.7(10) | | | | |
| O(19)-As(1)-O(19)#1 | 179.998(8) | O(19)-As(1)-O(2)#1 | 111.0(17) | O(19)#1-As(1)-O(2)#1 | 69.0(17) |
| O(19)-As(1)-O(2) | 69.0(17) | O(19)#1-As(1)-O(2) | 111.0(17) | O(19)-As(1)-O(18) | 67.3(18) |
| O(19)#1-As(1)-O(18) | 112.7(18) | O(19)-As(1)-O(18)#1 | 112.7(18) | O(19)#1-As(1)-O(18)#1 | 67.3(18) |
| O(19)-As(1)-O(1)#1 | 107.8(17) | O(19)#1-As(1)-O(1)#1 | 72.2(17) | O(19)-As(1)-O(1) | 72.2(17) |
| O(19)#1-As(1)-O(1) | 107.8(17) | | | | |
| N(4)-Ag(1)-N(1) | 168.2(8) | N(4)-Ag(1)-Ag(4) | 102.5(6) | N(1)-Ag(1)-Ag(4) | 65.7(6) |
| N(3)-Ag(2)-N(2) | 157.8(9) | N(8)#2-Ag(3)-N(8) | 179.999(2) | N(8)#2-Ag(3)-Ag(4) | 61.2(6) |
| N(8)-Ag(3)-Ag(4) | 118.8(6) | N(8)#2-Ag(3)-Ag(4)#2 | 118.8(6) | N(8)-Ag(3)-Ag(4)#2 | 61.2(6) |

| | | | | | |
|---|---|---|---|---|---|
| Ag(4)-Ag(3)-Ag(4)#2 | 180.0 | N(6)#2-Ag(4)-N(9) | 156.1(8) | N(6)#2-Ag(4)-Ag(1) | 104.2(6) |
| N(9)-Ag(4)-Ag(1) | 63.6(6) | N(6)#2-Ag(4)-Ag(3) | 62.1(7) | Ag(1)-Ag(4)-Ag(3) | 128.68(9) |
| Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+2 #2 -x,-y,-z+1 | | | | | |
| Compound **5** | | | | | |
| W(1)-O(6) | 1.65(3) | W(1)-O(16) | 1.89(4) | W(1)-O(7) | 1.93(3) |
| W(1)-O(11) | 1.97(4) | W(1)-O(15) | 1.97(4) | W(1)-O(20) | 2.39(5) |
| W(1)-O(22)#1 | 2.39(4) | W(2)-O(3) | 1.70(2) | W(2)-O(10) | 1.88(4) |
| W(2)-O(7) | 1.91(4) | W(2)-O(12) | 1.92(3) | W(2)-O(13) | 1.99(4) |
| W(2)-O(19)#1 | 2.36(6) | W(2)-O(20) | 2.43(4) | W(3)-O(15) | 1.89(4) |
| W(3)-O(18) | 1.89(4) | W(3)-O(2) | 1.873(10) | W(3)-O(9) | 1.91(4) |
| W(3)-O(12) | 1.95(3) | W(3)-O(21) | 2.36(7) | W(3)-O(20) | 2.37(4) |
| W(4)-O(4) | 1.70(2) | W(4)-O(13)#1 | 1.79(4) | W(4)-O(14) | 1.82(4) |
| W(4)-O(8) | 1.82(5) | W(4)-O(9) | 1.90(4) | W(4)-O(21) | 2.36(7) |
| W(4)-O(19) | 2.40(5) | W(5)-O(1) | 1.69(3) | W(5)-O(11) | 1.78(4) |
| W(5)-O(10)#1 | 1.88(4) | W(5)-O(17) | 1.90(4) | W(5)-O(14) | 1.96(4) |
| W(5)-O(22)#1 | 2.35(4) | W(5)-O(19) | 2.38(6) | W(6)-O(5) | 1.67(3) |
| W(6)-O(17)#1 | 1.87(4) | W(6)-O(18) | 1.87(4) | W(6)-O(16)#1 | 1.89(4) |
| W(6)-O(8) | 1.95(4) | W(6)-O(21) | 2.40(8) | W(6)-O(22) | 2.39(4) |
| P(1)-O(20)#1 | 1.64(4) | P(1)-O(19)#1 | 1.66(5) | P(1)-O(22)#1 | 1.67(5) |
| P(1)-O(22) | 1.67(5) | P(1)-O(21)#1 | 1.67(7) | | |
| Ag(1)-N(3) | 2.16(3) | Ag(1)-N(2) | 2.16(3) | Ag(2)-C(1)#2 | 2.07(3) |
| Ag(2)-C(1) | 2.07(3) | Ag(3)-N(4)#2 | 2.11(3) | Ag(3)-C(12) | 2.12(4) |
| Ag(4)-N(6) | 2.14(4) | O(2)-Ag(5) | 2.32(2) | Ag(5)-O(1)#3 | 2.46(3) |
| O(6)-W(1)-O(16) | 101.2(17) | O(6)-W(1)-O(7) | 97.0(15) | O(6)-W(1)-O(20) | 155.7(15) |
| O(6)-W(1)-O(11) | 105.7(16) | O(6)-W(1)-O(15) | 99.7(15) | O(6)-W(1)-O(22)#1 | 157.7(15) |
| O(3)-W(2)-O(10) | 103.6(15) | O(3)-W(2)-O(7) | 97.8(14) | O(3)-W(2)-O(12) | 98.5(13) |
| O(3)-W(2)-O(13) | 101.6(17) | O(3)-W(2)-O(19)#1 | 156.9(14) | O(3)-W(2)-O(20) | 155.1(13) |
| O(15)-W(3)-O(18) | 160.6(15) | O(15)-W(3)-O(2) | 97.4(16) | O(15)-W(3)-O(9) | 91.9(17) |
| O(15)-W(3)-O(12) | 90.2(16) | O(15)-W(3)-O(21) | 100(2) | O(15)-W(3)-O(20) | 66.5(16) |
| O(4)-W(4)-O(13)#1 | 99.6(19) | O(4)-W(4)-O(14) | 101.7(16) | O(4)-W(4)-O(8) | 100.1(17) |
| O(4)-W(4)-O(9) | 99.9(14) | O(4)-W(4)-O(21) | 156(2) | O(4)-W(4)-O(19) | 156.4(17) |
| O(1)-W(5)-O(11) | 101.2(15) | O(1)-W(5)-O(10)#1 | 102.3(15) | O(1)-W(5)-O(17) | 101.7(15) |
| O(1)-W(5)-O(14) | 103.9(15) | O(1)-W(5)-O(22)#1 | 156.5(14) | O(1)-W(5)-O(19) | 156.9(16) |
| O(5)-W(6)-O(17)#1 | 103.5(17) | O(5)-W(6)-O(18) | 102.9(15) | O(5)-W(6)-O(16)#1 | 99.6(16) |
| O(5)-W(6)-O(8) | 100.3(17) | O(5)-W(6)-O(21) | 155(2) | O(5)-W(6)-O(22) | 155.2(16) |
| O(20)-P(1)-O(20)#1 | 179.998(10) | O(20)-P(1)-O(19)#1 | 73(3) | O(20)#1-P(1)-O(19)#1 | 107(3) |
| O(20)-P(1)-O(19) | 107(3) | O(20)#1-P(1)-O(19) | 73(3) | O(20)-P(1)-O(19) | 107(3) |
| O(20)-P(1)-O(22)#1 | 70(2) | O(20)#1-P(1)-O(22)#1 | 110(2) | O(20)-P(1)-O(22) | 110(2) |
| O(20)#1-P(1)-O(22) | 70(2) | O(20)-P(1)-O(21) | 68(3) | O(20)#1-P(1)-O(21) | 112(3) |
| N(3)-Ag(1)-N(2) | 164.9(10) | C(1)#2-Ag(2)-C(1) | 180.0(7) | N(4)#2-Ag(3)-C(12) | 170.8(11) |
| N(6)-Ag(4)-N(1 | 174.2(13) | O(2)-Ag(5)-C(7) | 103.8(8) | O(2)-Ag(5)-O(1)#3 | 84.5(9) |
| C(7)-Ag(5)-O(1)#3 | 102.8(9) | C(7)-Ag(5)-C(8) | 30.3(5) | | |
| Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z+1 #2 -x+1,-y+2,-z+2 #3 -x+1,-y+2,-z+1 | | | | | |

**Table S2** Selected Hydrogen Bond Lengths ( Å) and Bond Angles (°) of compounds **1-5**

| | | | | | |
|---|---|---|---|---|---|
| | | | Compound 1 | | |
| D-H...A | d(D-H) | d(H...A) | <D-H...A | d(D...A) | Symmetry |
| N4-H12...O8 | 0.86 | 2.17 | 166.4 | 3.02(3) | x, y+1, z |
| N4-H12...O9 | 0.86 | 2.53 | 125.8 | 3.112(19) | x, y+1, z |
| N2-H1...O1 | 0.86 | 2.24 | 170.1 | 3.09(2) | x, y+1, z |
| | | | Compound 2 | | |
| N6-H17...O13 | 0.86 | 2.01 | 167.9 | 2.85(2) | x-1, y, z |
| N5-H12...O20 | 0.86 | 2.62 | 112.6 | 3.050(19) | x-1, y, z |
| N5-H12...O31 | 0.86 | 2.48 | 130.4 | 3.11(2) | x-1, y, z |

| | | | | | |
|---|---|---|---|---|---|
| N5-H12...O27 | 0.86 | 2.07 | 160.2 | 2.90(2) | x-1, y, z |
| N2-H3...O22 | 0.86 | 2.34 | 164.7 | 3.181(19) | x-1, y, z |
| N1-H1...O33 | 0.86 | 2.19 | 161.2 | 3.02(4) | x, y+1, z-1 |
| N7-H23...O11 | 0.86 | 2.38 | 122.6 | 2.94(3) | |
| N4-H10...O29 | 0.86 | 1.99 | 161.7 | 2.815(18) | |
| N3-H4...O17 | 0.86 | 2.66 | 110.0 | 3.058(19) | |
| N3-H4...O15 | 0.86 | 2.53 | 130.7 | 3.15(2) | |
| N3-H4...O10 | 0.86 | 2.24 | 161.8 | 3.07(2) | |
| | | | Compound 3 | | |
| N5-H1...O11 | 0.86 | 2.55 | 119.1 | 3.064(16) | -x+1, -y, -z |
| N5-H1...O12 | 0.86 | 2.46 | 120.5 | 2.992(15) | -x+1, -y, -z |
| N5-H1...O17 | 0.86 | 2.41 | 138.1 | 3.100(16) | x-1, y-1, z-1 |
| N5-H1...O3 | 0.86 | 2.33 | 142.0 | 3.057(16) | x-1, y-1, z-1 |
| | | | Compound 4 | | |
| N5-H1...O11 | 0.86 | 2.65 | 120.2 | 3.176(13) | x, y+1, z |
| N5-H1...O12 | 0.86 | 2.57 | 119.1 | 3.085(13) | -x+2, -y+1, -z+2 |
| N5-H1...O17 | 0.86 | 2.44 | 142.2 | 3.160(13) | x, y+1, z |
| N5-H1...O3 | 0.86 | 2.37 | 143.0 | 3.105(13) | -x+2, -y+1, -z+2 |