Amperometric sensing and photocatalytic properties under sunlight

irradiation of a series Keggin-Ag^I compounds through tuning single

and mixed ligands

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Table. S1. Selected bond distances (Å) and angles (°) for compounds 1–8.

| | Cor | npound 1 | |
|-----------------------------|----------------------|--------------------|-----------|
| Ag(1)-N(2) | 2.265(8) | Ag(1)-N(3)#1 | 2.191(8) |
| Ag(1)-O(54) | 2.483(7) | N(1)-Ag(2) | 2.320(9) |
| Ag(2)-N(5) | 2.300(9) | Ag(3)-N(4) | 2.234(8) |
| Ag(3)-N(7) | 2.512(13) | Ag(3)-N(1AA) | 2.247(8) |
| N(3)-Ag(1)#2 | 2.191(8) | Ag(4)-N(6) | 2.243(9) |
| Ag(4)-N(0AA) | 2.278(9) | N(2)-Ag(1)-O(54) | 97.6(3) |
| N(3)#1-Ag(1)-N(2) | 139.5(3) | N(3)#1-Ag(1)-O(54) | 104.7(3) |
| C(1)-N(1)-Ag(2) | 124.3(8) | C(4)-N(1)-Ag(2) | 116.6(7) |
| N(5)-Ag(2)-N(1) | 131.9(3) | C(2)-N(2)-Ag(1) | 124.5(7) |
| C(3)-N(2)-Ag(1) | 114.2(7) | N(4)-Ag(3)-N(7) | 91.1(3) |
| N(4)-Ag(3)-N(1AA) | 153.6(3) | N(1AA)-Ag(3)-N(7) | 113.3(3) |
| C(17)-N(3)-Ag(1)#2 | 122.2(7) | C(19)-N(3)-Ag(1)#2 | 118.5(7) |
| N(6)-Ag(4)-N(0AA) | 141.4(3) | C(18)-N(4)-Ag(3) | 120.0(7) |
| C(20)-N(4)-Ag(3) | 121.8(7) | C(34)-N(5)-Ag(2) | 122.8(7) |
| C(35)-N(5)-Ag(2) | 117.9(7) | C(33)-N(6)-Ag(4) | 124.4(8) |
| C(36)-N(6)-Ag(4) | 117.4(7) | C(49)-N(7)-Ag(3) | 122.7(11) |
| C(51)-N(7)-Ag(3) | 115.2(9) | C(68)-N(1AA)-Ag(3) | 118.6(7) |
| C(66)-N(1AA)-Ag(3) | 122.5(7) | C(67)-N(0AA)-Ag(4) | 114.0(8) |
| C(65)-N(0AA)-Ag(4) | 123.6(8) | | |
| Symmetry codes for 1: #1 x+ | 1,y,z+1 #2 x-1,y,z-1 | | |
| | Cor | npound 2 | |
| Ag(1)-N(1) | 2.21(2) | Ag(1)-N(4)#1 | 2.22(2) |
| Ag(2)-N(2) | 2.26(2) | Ag(2)-N(3) | 2.45(2) |
| Ag(2)-N(5) | 2.31(2) | Ag(3)-N(6) | 2.20(2) |
| Ag(3)-N(7) | 2.19(2) | N(4)-Ag(1)#2 | 2.22(2) |
| N(1)-Ag(1)-N(4)#1 | 166.2(9) | C(1)-N(1)-Ag(1) | 114.6(17) |
| C(4)-N(1)-Ag(1) | 124.9(19) | N(2)-Ag(2)-N(3) | 104.9(8) |
| N(2)-Ag(2)-N(5) | 145.8(7) | N(5)-Ag(2)-N(3) | 108.9(8) |
| C(2)-N(2)-Ag(2) | 121.1(17) | C(3)-N(2)-Ag(2) | 123.5(18) |
| N(7)-Ag(3)-N(6) | 166.5(9) | C(17)-N(3)-Ag(2) | 118.5(19) |
| C(20)-N(3)-Ag(2) | 119(2) | C(18)-N(4)-Ag(1)#2 | 118(2) |
| C(19)-N(4)-Ag(1)#2 | 126(2) | C(33)-N(5)-Ag(2) | 115.7(19) |
| C(36)-N(5)-Ag(2) | 124(2) | C(34)-N(6)-Ag(3) | 125(2) |
| C(35)-N(6)-Ag(3) | 118(2) | C(49)-N(7)-Ag(3) | 123(2) |

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|-------------------------------------|---------------------|-----------------------|-----------|
| C(52)-N(7)-Ag(3) | 117(2) | | |
| Symmetry codes for 2: #1 x-1 | /2,-y,z #2 x+1/2,-y | /,Z | |
| | Co | mpound 3 | |
| O(1W)-Ag(1) | 2.22(3) | O(20)-Ag(1) | 2.45(2) |
| Ag(1)-N(1) | 2.29(3) | Ag(2)-N(2) | 2.18(2) |
| Ag(2)-N(2)#2 | 2.18(2) | Ag(1)-O(1W)-H(1WA) | 117.2 |
| Ag(1)-O(1W)-H(1WB) | 131.9 | W(4)-O(20)-Ag(1) | 136.5(12) |
| O(1W)-Ag(1)-O(20) | 119.2(12) | O(1W)-Ag(1)-N(1) | 136.3(14) |
| N(1)-Ag(1)-O(20) | 98.2(9) | N(2)#2-Ag(2)-N(2) | 180.0 |
| C(2)-N(1)-Ag(1) | 120(2) | C(4)-N(1)-Ag(1) | 120(2) |
| C(1)-N(2)-Ag(2) | 120(2) | C(3)-N(2)-Ag(2) | 120.8(19) |
| Symmetry codes for 3: #1 -x- | +1,-y+1,-z+1 #2 -x | ,-y+1,-z+2 | |
| | | | |
| | Co | mpound 4 | |
| N(1)-Ag(1) | 2.235(15) | Ag(1)-N(3)#2 | 2.228(16) |
| Ag(1)-O(19) | 2.279(12) | N(2)-Ag(3) | 2.152(14) |
| Ag(2)-N(4) | 2.314(16) | Ag(2)-N(4)#3 | 2.314(16) |
| Ag(2)-O(8)#3 | 2.472(13) | Ag(2)-O(8) | 2.472(13) |
| Ag(3)-N(2)#4 | 2.152(14) | N(3)-Ag(1)#5 | 2.228(16) |
| C(1)-N(1)-Ag(1) | 128.4(14) | C(8)-N(1)-Ag(1) | 113.0(13) |
| N(1)-Ag(1)-O(19) | 134.9(6) | N(3)#2-Ag(1)-N(1) | 125.2(5) |
| N(3)#2-Ag(1)-O(19) | 99.4(6) | C(6)-N(2)-Ag(3) | 125.0(13) |
| C(7)-N(2)-Ag(3) | 118.3(12) | N(4)#3-Ag(2)-N(4) | 91.4(8) |
| N(4)-Ag(2)-O(8)#3 | 154.5(5) | N(4)-Ag(2)-O(8) | 96.0(5) |
| N(4)#3-Ag(2)-O(8) | 154.5(5) | N(4)#3-Ag(2)-O(8)#3 | 96.0(5) |
| O(8)#3-Ag(2)-O(8) | 87.7(6) | N(2)#4-Ag(3)-N(2) | 180.0 |
| C(41)-N(3)-Ag(1)#5 | 123.6(12) | C(48)-N(3)-Ag(1)#5 | 117.7(13) |
| C(46)-N(4)-Ag(2) | 106.9(13) | C(47)-N(4)-Ag(2) | 130.4(13) |
| W(5)-O(8)-Ag(2) | 133.2(8) | W(2)-O(19)-Ag(1) | 146.9(8) |
| Symmetry codes for 4: #1 -x- | +3/2,-y+1/2,-z+1 #2 | 2 -x+3/2,y+1/2,-z+1/2 | |
| #3 -x+1,y,-z+1/2 #4 -x+1 | ,-y+1,-z #5 -x+3/2 | ,y-1/2,-z+1/2 | |
| | Co | mpound 5 | |
| Ag(1)-N(1) | 2.299(11) | Ag(1)-N(3) | 2.245(9) |
| Ag(1)-O(10) | 2.308(9) | Ag(2)-N(4)#3 | 2.171(10) |
| Ag(2)-N(4) | 2.171(9) | O(1)-K(1)#2 | 2.530(11) |
| N(2)-K(1) | 2.209(13) | C(2)-K(1) | 2.798(16) |
| C(3)-K(1) | 2.63(2) | W(4)-K(1)#2 | 3.828(2) |
| C(7)-K(1) | 3.292(14) | K(1)-O(1)#4 | 2.530(11) |
| K(1)-O(1)#5 | 2.530(11) | K(1)-N(2)#6 | 2.209(13) |
| K(1)-C(2)#6 | 2.798(17) | K(1)-C(3)#6 | 2.63(2) |
| K(1)-W(4)#5 | 3.828(2) | K(1)-W(4)#4 | 3.828(2) |
| K(1)-C(7)#6 | 3.292(14) | N(1)-Ag(1)-O(10) | 99.4(4) |
| N(3)-Ag(1)-N(1) | 126.1(4) | N(3)-Ag(1)-O(10) | 134.5(4) |

| C(1)-N(1)-Ag(1) | 126.2(9) | C(8)-N(1)-Ag(1) | 112.7(9) |
|--------------------|-----------|--------------------|------------|
| N(4)-Ag(2)-N(4)#3 | 180.0(4) | C(21)-N(3)-Ag(1) | 129.7(8) |
| C(27)-N(3)-Ag(1) | 111.1(8) | C(26)-N(4)-Ag(2) | 122.8(8) |
| C(28)-N(4)-Ag(2) | 119.6(8) | W(2)-O(10)-Ag(1) | 141.0(5) |
| W(4)-O(1)-K(1)#2 | 130.4(6) | C(2)-N(2)-K(1) | 100.4(9) |
| C(7)-N(2)-K(1) | 137.7(10) | C(1)-C(2)-K(1) | 165.4(10) |
| N(2)-C(2)-K(1) | 50.9(8) | C(3)-C(2)-K(1) | 68.4(11) |
| C(2)-C(3)-K(1) | 81.0(10) | C(4)-C(3)-K(1) | 156.6(16) |
| K(1)-C(3)-H(3) | 42.5 | O(1)-W(4)-K(1)#2 | 30.2(4) |
| O(4)-W(4)-K(1)#2 | 82.5(5) | O(5)#1-W(4)-K(1)#2 | 139.2(3) |
| O(15)-W(4)-K(1)#2 | 117.6(4) | O(17)-W(4)-K(1)#2 | 145.0(4) |
| O(18)-W(4)-K(1)#2 | 75.7(3) | O(25)-W(4)-K(1)#2 | 124.5(6) |
| N(2)-C(7)-K(1) | 26.9(7) | C(8)-C(7)-K(1) | 145.7(9) |
| C(9)-C(7)-K(1) | 93.1(7) | O(1)#4-K(1)-O(1)#5 | 86.0(4) |
| O(1)#4-K(1)-C(2) | 94.2(4) | O(1)#4-K(1)-C(2)#6 | 131.4(4) |
| O(1)#5-K(1)-C(2)#6 | 94.2(4) | O(1)#5-K(1)-C(2) | 131.4(4) |
| O(1)#4-K(1)-C(3) | 84.4(5) | O(1)#4-K(1)-C(3)#6 | 101.9(5) |
| O(1)#5-K(1)-C(3) | 101.9(5) | O(1)#5-K(1)-C(3)#6 | 84.4(5) |
| O(1)#4-K(1)-W(4)#5 | 104.3(2) | O(1)#5-K(1)-W(4)#4 | 104.3(2) |
| O(1)#4-K(1)-W(4)#4 | 19.4(2) | O(1)#5-K(1)-W(4)#5 | 19.4(2) |
| O(1)#4-K(1)-C(7) | 104.5(3) | O(1)#5-K(1)-C(7)#6 | 104.5(3) |
| O(1)#5-K(1)-C(7) | 168.1(3) | O(1)#4-K(1)-C(7)#6 | 168.1(3) |
| N(2)#6-K(1)-O(1)#5 | 98.4(4) | N(2)#6-K(1)-O(1)#4 | 159.5(4) |
| N(2)-K(1)-O(1)#4 | 98.4(4) | N(2)-K(1)-O(1)#5 | 159.5(4) |
| N(2)#6-K(1)-N(2) | 84.4(6) | N(2)#6-K(1)-C(2) | 97.6(4) |
| N(2)-K(1)-C(2) | 28.7(4) | N(2)#6-K(1)-C(2)#6 | 28.7(4) |
| N(2)-K(1)-C(2)#6 | 97.6(4) | N(2)#6-K(1)-C(3)#6 | 59.0(5) |
| N(2)#6-K(1)-C(3) | 113.9(5) | N(2)-K(1)-C(3)#6 | 113.9(5) |
| N(2)-K(1)-C(3) | 59.0(5) | N(2)#6-K(1)-W(4)#4 | 145.2(3) |
| N(2)#6-K(1)-W(4)#5 | 83.3(3) | N(2)-K(1)-W(4)#5 | 145.2(3) |
| N(2)-K(1)-W(4)#4 | 83.3(3) | N(2)#6-K(1)-C(7) | 73.7(4) |
| N(2)-K(1)-C(7) | 15.5(4) | N(2)-K(1)-C(7)#6 | 73.7(4) |
| N(2)#6-K(1)-C(7)#6 | 15.5(4) | C(2)#6-K(1)-C(2) | 119.7(6) |
| C(2)#6-K(1)-W(4)#4 | 122.4(3) | C(2)-K(1)-W(4)#4 | 86.8(3) |
| C(2)-K(1)-W(4)#5 | 122.4(3) | C(2)#6-K(1)-W(4)#5 | 86.8(3) |
| C(2)-K(1)-C(7) | 43.6(4) | C(2)#6-K(1)-C(7)#6 | 43.6(4) |
| C(2)-K(1)-C(7)#6 | 83.0(4) | C(2)#6-K(1)-C(7) | 83.0(4) |
| C(3)-K(1)-C(2)#6 | 141.9(5) | C(3)#6-K(1)-C(2) | 141.9(5) |
| C(3)#6-K(1)-C(2)#6 | 30.5(5) | C(3)-K(1)-C(2) | 30.5(5) |
| C(3)-K(1)-C(3)#6 | 171.6(8) | C(3)#6-K(1)-W(4)#5 | 86.9(4) |
| C(3)#6-K(1)-W(4)#4 | 97.1(4) | C(3)-K(1)-W(4)#5 | 97.1(4) |
| C(3)-K(1)-W(4)#4 | 86.9(4) | C(3)#6-K(1)-C(7) | 98.6(5) |
| C(3)-K(1)-C(7) | 74.2(4) | C(3)-K(1)-C(7)#6 | 98.6(5) |
| C(3)#6-K(1)-C(7)#6 | 74.2(4) | W(4)#4-K(1)-W(4)#5 | 123.10(13) |

| $\begin{array}{c} C(7)\#6\text{-}K(1)\text{-}W(4)\#5 & 86.9(2) & C(7)\text{-}K(1)\text{-}W(4)\#4 \\ C(7)\#6\text{-}K(1)\text{-}W(4)\#4 & 148.8(2) & C(7)\text{-}K(1)\text{-}W(4)\#5 \\ C(7)\#6\text{-}K(1)\text{-}C(7) & 65.6(4) \\ \\ \text{Symmetry codes for } \mathbf{5:} \#1 \text{-}x+3/2, \text{-}y+1/2, \text{-}z & \#2 x+1/2, \text{y}-1/2, z & \#3 \text{-}x+2, \text{-}y+1, \text{-}z+1 \\ \#4 \text{-}x+3/2, \text{y}+1/2, \text{-}z+1/2 & \#5 x-1/2, \text{y}+1/2, z & \#6 \text{-}x+1, \text{y}, \text{z}+1/2 \\ \hline \\ & Compound 6 \\ \\ \text{Ag}(1)\text{-}N(1) & 2.227(7) & \text{Ag}(1)\text{-}N(2)\#1 \\ \text{Ag}(1)\text{-}O(7) & 2.539(6) & \text{N}(2)\text{-}\text{Ag}(1)\#12 \\ \text{N}(1)\text{-}\text{Ag}(1)\text{-}O(7) & 2.539(6) & \text{N}(2)\text{-}\text{Ag}(1)\#12 \\ \text{N}(1)\text{-}\text{Ag}(1)\text{-}O(7) & 91.0(2) & C(1)\text{-}\text{N}(1)\text{-}\text{Ag}(1) \\ \text{C}(8)\text{-}\text{N}(1)\text{-}\text{Ag}(1) & 122.8(6) & C(2)\text{-}\text{N}(2)\text{-}\text{Ag}(1)\#12 \\ \text{C}(3)\text{-}\text{N}(2)\text{-}\text{Ag}(1)\#12 & 126.5(6) \\ \\ \text{Symmetry codes for } \mathbf{6:} \#1 \text{-}x+y+2/3, \text{-}x+4/3, \#1/3 & \#2 \text{-}x+2/3, \text{-}y+4/3, \text{-}z+4/3 \\ \#3 x-y+2/3, \text{x}+1/3, z+4/3 & \#4 \text{-}x+y, \text{-}x+1, z & \#5 y-1/3, \text{-}z+4/3 \\ \#6 \text{-}y+1, \text{x}-y+1, z & \#7 \text{-}y+1, \text{x}-y, z & \#8 \text{-}x+4/3, \text{-}y+2/3, \text{-}z+5/3 \\ \end{array}$ | 86.9(2) 148.8(2) 2.246(7) 2.246(7) 100.4(2) 115.9(6) 113.6(6) |
|--|---|
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 148.8(2) 2.246(7) 2.246(7) 100.4(2) 115.9(6) 113.6(6) |
| $\begin{array}{cccc} C(7)\#6-K(1)-C(7) & 65.6(4) \\ \\ \mbox{Symmetry codes for 5: } \#1 - x + 3/2, -y + 1/2, -z & \#2 x + 1/2, y - 1/2, z & \#3 - x + 2, -y + 1, -z + 1 \\ \mbox{$\#4 - x + 3/2, y + 1/2, -z + 1/2$} & \#5 x - 1/2, y + 1/2, z & \#6 - x + 1, y, -z + 1/2$ \\ \hline & & Compound 6 \\ \\ \mbox{Ag(1)-N(1)} & 2.227(7) & Ag(1)-N(2)\#1 \\ Ag(1)-O(7) & 2.539(6) & N(2)-Ag(1)\#12 \\ N(1)-Ag(1)-N(2)\#1 & 162.5(3) & N(1)-Ag(1)-O(7) \\ N(2)\#1-Ag(1)-O(7) & 91.0(2) & C(1)-N(1)-Ag(1) \\ C(8)-N(1)-Ag(1) & 122.8(6) & C(2)-N(2)-Ag(1)\#12 \\ C(3)-N(2)-Ag(1)\#12 & 126.5(6) \\ \\ \mbox{Symmetry codes for 6: } \#1 - x + y + 2/3, - x + 4/3, z + 1/3 & \#2 - x + 2/3, - y + 4/3, - z + 4/3 \\ \#3 x - y + 2/3, x + 1/3, - z + 4/3 & \#4 - x + y, - x + 1, z & \#5 y - 1/3, - x + y + 1/3, - z + 4/3 \\ \#6 - y + 1, x - y + 1, z & \#7 - y + 1, x - y, z & \#8 - x + 4/3, - y + 2/3, - z + 5/3 \\ \hline \end{array}$ | 2.246(7) 2.246(7) 100.4(2) 115.9(6) 113.6(6) |
| Symmetry codes for 5: #1 -x+ $3/2$,-y+ $1/2$,-z#2 x+ $1/2$,y- $1/2$,z#3 -x+ 2 ,-y+ 1 ,-z+ 1 #4 -x+ $3/2$,y+ $1/2$,-z+ $1/2$ #5 x- $1/2$,y+ $1/2$,z#6 -x+ 1 ,y,-z+ $1/2$ Compound 6Ag(1)-N(1)2.227(7)Ag(1)-N(2)#1Ag(1)-O(7)2.539(6)N(2)-Ag(1)#12N(1)-Ag(1)-N(2)#1162.5(3)N(1)-Ag(1)-O(7)N(2)#1-Ag(1)-O(7)91.0(2)C(1)-N(1)-Ag(1)C(8)-N(1)-Ag(1)122.8(6)C(2)-N(2)-Ag(1)#12C(3)-N(2)-Ag(1)#12126.5(6)Symmetry codes for 6: #1 -x+y+ $2/3$,-x+ $4/3$,z+ $1/3$ #2 -x+ $2/3$,-y+ $4/3$,-z+ $4/3$ #3 x- $y+2/3$,x+ $1/3$,-z+ $4/3$ #4 -x+ y ,-x+ 1 ,z#5 y- $1/3$,-x+ $y+1/3$,-z+ $4/3$ #6 -y+1,x-y+1,z#7 -y+1,x-y,z#8 -x+ $4/3$,-y+ $2/3$,-z+ $5/3$ | 2.246(7) 2.246(7) 100.4(2) 115.9(6) 113.6(6) |
| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | 2.246(7) 2.246(7) 100.4(2) 115.9(6) 113.6(6) |
| Compound 6Ag(1)-N(1)2.227(7)Ag(1)-N(2)#1Ag(1)-O(7)2.539(6)N(2)-Ag(1)#12N(1)-Ag(1)-N(2)#1162.5(3)N(1)-Ag(1)-O(7)N(2)#1-Ag(1)-O(7)91.0(2)C(1)-N(1)-Ag(1)C(8)-N(1)-Ag(1)122.8(6)C(2)-N(2)-Ag(1)#12C(3)-N(2)-Ag(1)#12126.5(6)Symmetry codes for 6 : #1 -x+y+2/3,-x+4/3,z+1/3#2 -x+2/3,-y+4/3,-z+4/3#3 x-y+2/3,x+1/3,-z+4/3#4 -x+y,-x+1,z#5 y-1/3,-x+y+1/3,-z+4/3#6 -y+1,x-y+1,z#7 -y+1,x-y,z#8 -x+4/3,-y+2/3,-z+5/3 | 2.246(7) 2.246(7) 100.4(2) 115.9(6) 113.6(6) |
| Ag(1)-N(1)2.227(7)Ag(1)-N(2)#1Ag(1)-O(7)2.539(6)N(2)-Ag(1)#12N(1)-Ag(1)-N(2)#1162.5(3)N(1)-Ag(1)-O(7)N(2)#1-Ag(1)-O(7)91.0(2)C(1)-N(1)-Ag(1)C(8)-N(1)-Ag(1)122.8(6)C(2)-N(2)-Ag(1)#12C(3)-N(2)-Ag(1)#12126.5(6)Symmetry codes for 6: #1 -x+y+2/3,-x+4/3,z+1/3#2 -x+2/3,-y+4/3,-z+4/3#3 x-y+2/3,x+1/3,-z+4/3#4 -x+y,-x+1,z#5 y-1/3,-x+y+1/3,-z+4/3#6 -y+1,x-y+1,z#7 -y+1,x-y,z#8 -x+4/3,-y+2/3,-z+5/3 | 2.246(7) 2.246(7) 100.4(2) 115.9(6) 113.6(6) |
| Ag(1)-O(7)2.539(6)N(2)-Ag(1)#12N(1)-Ag(1)-N(2)#1162.5(3)N(1)-Ag(1)-O(7)N(2)#1-Ag(1)-O(7)91.0(2)C(1)-N(1)-Ag(1)C(8)-N(1)-Ag(1)122.8(6)C(2)-N(2)-Ag(1)#12C(3)-N(2)-Ag(1)#12126.5(6)Symmetry codes for 6 : #1 -x+y+2/3,-x+4/3,z+1/3#2 -x+2/3,-y+4/3,-z+4/3#3 x-y+2/3,x+1/3,-z+4/3#4 -x+y,-x+1,z#5 y-1/3,-x+y+1/3,-z+4/3#6 -y+1,x-y+1,z#7 -y+1,x-y,z#8 -x+4/3,-y+2/3,-z+5/3 | 2.246(7) 100.4(2) 115.9(6) 113.6(6) |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 100.4(2) 115.9(6) 113.6(6) |
| $\begin{array}{cccc} N(2)\#1-Ag(1)-O(7) & 91.0(2) & C(1)-N(1)-Ag(1) \\ C(8)-N(1)-Ag(1) & 122.8(6) & C(2)-N(2)-Ag(1)\#12 \\ C(3)-N(2)-Ag(1)\#12 & 126.5(6) \\ \\ Symmetry codes for 6: \#1 -x+y+2/3,-x+4/3,z+1/3 \#2 -x+2/3,-y+4/3,-z+4/3 \\ \#3 x-y+2/3,x+1/3,-z+4/3 \#4 -x+y,-x+1,z \#5 y-1/3,-x+y+1/3,-z+4/3 \\ \#6 -y+1,x-y+1,z \#7 -y+1,x-y,z \#8 -x+4/3,-y+2/3,-z+5/3 \\ \\ \#0$ | 115.9(6) 113.6(6) |
| $\begin{array}{cccc} C(8)-N(1)-Ag(1) & 122.8(6) & C(2)-N(2)-Ag(1)\#12 \\ C(3)-N(2)-Ag(1)\#12 & 126.5(6) \\ \\ \text{Symmetry codes for } \mathbf{6:} \#1 - x + y + 2/3, -x + 4/3, z + 1/3 & \#2 - x + 2/3, -y + 4/3, -z + 4/3 \\ \#3 x - y + 2/3, x + 1/3, -z + 4/3 & \#4 - x + y, -x + 1, z & \#5 y - 1/3, -x + y + 1/3, -z + 4/3 \\ \#6 - y + 1, x - y + 1, z & \#7 - y + 1, x - y, z & \#8 - x + 4/3, -y + 2/3, -z + 5/3 \\ \#0 - 1/2 & 0 & 0 & 0 \\ \end{array}$ | 113.6(6) |
| C(3)-N(2)-Ag(1)#12 126.5(6) Symmetry codes for 6: #1 -x+y+2/3,-x+4/3,z+1/3 #2 -x+2/3,-y+4/3,-z+4/3 #3 x-y+2/3,x+1/3,-z+4/3 #4 -x+y,-x+1,z #5 y-1/3,-x+y+1/3,-z+4/3 #6 -y+1,x-y+1,z #7 -y+1,x-y,z #8 -x+4/3,-y+2/3,-z+5/3 | |
| Symmetry codes for 6: #1 -x+y+2/3,-x+4/3,z+1/3 #2 -x+2/3,-y+4/3,-z+4/3 #3 x-y+2/3,x+1/3,-z+4/3 #4 -x+y,-x+1,z #5 y-1/3,-x+y+1/3,-z+4/3 #6 -y+1,x-y+1,z #7 -y+1,x-y,z #8 -x+4/3,-y+2/3,-z+5/3 | |
| #3 x-y+2/3,x+1/3,-z+4/3 #4 -x+y,-x+1,z #5 y-1/3,-x+y+1/3,-z+4/3 #6 -y+1,x-y+1,z #7 -y+1,x-y,z #8 -x+4/3,-y+2/3,-z+5/3 | |
| #6-y+1,x-y+1,z #7-y+1,x-y,z #8-x+4/3,-y+2/3,-z+5/3 | |
| | |
| #9 y+1/3,-x+y+2/3,-z+5/3 #10 -x+y+1,-x+1,z #11 x-y+1/3,x-1/3,-z+5/3 | |
| #12 -y+4/3,x-y+2/3,z-1/3 | |
| Compound 7 | |
| Ag(1)-N(1) 2.254(13) Ag(1)-N(4)#1 | 2.240(12) |
| O(1)-Ag(3) 2.463(13) Ag(2)-N(2) | 2.206(12) |
| Ag(2)-N(3) 2.189(13) Ag(3)-N(5) | 2.226(13) |
| Ag(3)-N(8)#1 2.209(13) Ag(4)-N(6) | 2.200(13) |
| Ag(4)-N(7) 2.192(15) N(4)-Ag(1)#2 | 2.240(12) |
| N(8)-Ag(3)#2 2.209(13) N(4)#1-Ag(1)-N(1) | 172.7(5) |
| W(9)-O(1)-Ag(3) 169.3(9) C(1)-N(1)-Ag(1) | 110.7(11) |
| C(4)-N(1)-Ag(1) 127.9(11) N(3)-Ag(2)-N(2) | 178.1(5) |
| C(2)-N(2)-Ag(2) 115.5(10) $C(3)-N(2)-Ag(2)$ | 123.2(11) |
| N(5)-Ag(3)-O(1) 84.1(5) N(8)#1-Ag(3)-O(1) | 108.9(5) |
| N(8)#1-Ag(3)-N(5) 166.7(5) C(17)-N(3)-Ag(2) | 121.5(10) |
| C(24)-N(3)-Ag(2) 120.2(11) $N(7)-Ag(4)-N(6)$ | 171.9(7) |
| C(22)-N(4)-Ag(1)#2 121.2(10) C(23)-N(4)-Ag(1)#2 | 118.3(11) |
| C(37)-N(5)-Ag(3) 121.5(11) $C(43)-N(5)-Ag(3)$ | 117.1(12) |
| C(38)-N(6)-Ag(4) 122.4(12) $C(44)-N(6)-Ag(4)$ | 115.9(11) |
| C(57)-N(7)-Ag(4) 121.2(12) $C(63)-N(7)-Ag(4)$ | 119.7(15) |
| C(62)-N(8)-Ag(3)#2 124.4(11) C(64)-N(8)-Ag(3)#2 | 114.7(10) |
| Symmetry codes for 7: #1 x-1,y,z #2 x+1,y,z | |
| Compound 8 | |
| O(15)-Ag(2) 2.648(14) Ag(1)-N(2) | 2.167(9) |
| Ag(1)-N(3) 2.177(8) Ag(2)-N(5) | 2.218(9) |
| Ag(2)-N(4) 2.233(8) Mo(1)-O(15)-Ag(2) | 124.6(6) |
| Mo(6)-O(15)-Ag(2) 113.6(7) N(2)-Ag(1)-N(3) | 167.7(4) |
| N(5)-Ag(2)-O(15) 105.5(4) N(5)-Ag(2)-N(4) | 159.1(3) |
| N(4)-Ag(2)-O(15) 90.7(4) C(7)-N(2)-Ag(1) | 118.3(7) |

| Supplementary Material (ESI) for CrystEngComm | l |
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| C(6)-N(2)-Ag(1) | 123.3(7) | C(41)-N(5)-Ag(2) | 126.1(8) |
|---|----------|------------------|----------|
| C(47)-N(5)-Ag(2) | 113.5(7) | C(28)-N(4)-Ag(2) | 120.8(7) |
| C(22)-N(4)-Ag(2) | 120.9(7) | C(41)-N(5)-Ag(2) | 126.1(8) |
| C(47)-N(5)-Ag(2) | 113.5(7) | C(28)-N(4)-Ag(2) | 120.8(7) |
| C(22)-N(4)-Ag(2) | 120.9(7) | C(21)-N(3)-Ag(1) | 121.9(7) |
| C(27)-N(3)-Ag(1) | 119.7(6) | | |
| Symmetry codes for 8: $\#1 - x + 1 - y + 1 - z + 1$ | | | |



Fig. S1. Ball/stick view of the asymmetric unit of 1. The hydrogen atoms are omitted for clarity.



Fig. S2. Ball/stick view of the asymmetric unit of 2. The hydrogen atoms are omitted for clarity.



Fig. S3. Ball/stick view of the asymmetric unit of 3. The hydrogen atoms are omitted for clarity.



Fig. S4. Ball/stick view of the symmetric unit of 4. The hydrogen atoms are omitted for clarity.



Fig. S5. Ball/stick view of the symmetric unit of 5. The hydrogen atoms are omitted for clarity.



Fig. S6. The XPS spectra of compound 5.



Fig. S7. Ball/stick view of the symmetric unit of 6. The hydrogen atoms are omitted for clarity.



Fig. S8. Ball/stick view of the symmetric unit of 7. The hydrogen atoms are omitted for clarity.



Fig. S9. Two kinds of metal-organic chains: chain I (a) with L^a and L^b arranging alternately and chain II (b) only containing L^b .



Fig. S10. Ball/stick view of the symmetric unit of 8. The hydrogen atoms are omitted for clarity.



Fig. S11. The IR spectra of compounds 1–8.



Fig. S12. The TG curves of compounds 1–8.



Fig. S13. The dependence of anodic peak (II) and cathodic peak (II') currents of 1–, 2–, 6– and 8–CPEs on scan rates.



Fig. S14. Cyclic voltammograms of 1–, 2–, 6–, 8–CPEs in 0.1 M H₂SO₄ + 0.5 M Na₂SO₄ containing 0(a);

2.0(b); 4.0(c); 6.0(d); 8.0(e) mM potassium nitrite. Scan rate: 60 mV \cdot s⁻¹.



Fig. S15. Cyclic voltammograms of 1–, 2–, 6–, 8–CPEs in 0.1 M H₂SO₄ + 0.5 M Na₂SO₄ containing 0(a); 2.0(b); 4.0(c); 6.0(d); 8.0(e) mM potassium bromate. Scan rate: 60 mV·s⁻¹.



Fig. S16. Cyclic voltammograms of 1–, 2–, 6–, 8–CPEs in 0.1 M H₂SO₄ + 0.5 M Na₂SO₄ containing 0(a); 2.0(b); 4.0(c); 6.0(d); 8.0(e) mM hydrogen peroxide. Scan rate: 60 mV·s⁻¹.



Fig. S17. Amperometric response for the **6**–CPE (a) and **8**–CPE (b) on successive addition of 0.4mM hydrogen peroxide ((a) and (b)) and potassium nitrite ((c) and (d)) and **6**–CPE for 0.004mM potassium bromate (e) to 0.1M H₂SO₄+0.5M Na₂SO₄ aqueous solution. The inset: the steady-state calibration curve for current versus concentration. (applied potential: +200 mV for **6**–CPE and +250 mV for **8**–CPE).

The 6-CPE electrode response time was 4.2s. The inset of Fig. S13a shows the calibration graph for hydrogen peroxide reduction at the 6-CPE. The electrode response was linear for hydrogen peroxide within the concentration range $2 \times 10^{-4} - 4 \times 10^{-3}$ M, and the sensitivity was 12.97 μ A mM⁻¹ (correlation coefficient of 0.99545). The detection limit was 4.95×10^{-6} M when the signal-to-noise ratio was 3. The 8–CPE electrode response time was 4.5s. The inset of Fig. S13b shows the calibration graph for hydrogen peroxide reduction at the 8-CPE. The electrode response was linear for hydrogen peroxide within the concentration range 1×10^{-3} -6×10⁻³ M, and the sensitivity was 11.25 μ A mM⁻¹ (correlation coefficient of 0.99471). The detection limit was 5.45×10^{-6} M when the signal-to-noise ratio was 3. The **6**-CPE electrode response time was 4.2s. The inset of Fig. S13c shows the calibration graph for potassium nitrite reduction at the 6-CPE. The electrode response was linear for potassium nitrite within the concentration range $6 \times 10^{-4} - 7.2 \times 10^{-3}$ M, and the sensitivity was 87.75 μ A mM⁻¹ (correlation coefficient of 0.99881). The detection limit was 7.55×10⁻⁶ M when the signal-to-noise ratio was 3. The 8-CPE electrode response time was 4.5s. The inset of Fig. S13d shows the calibration graph for potassium nitrite reduction at the 8-CPE. The electrode response was linear for potassium nitrite within the concentration range 3.2×10^{-3} – 8×10^{-3} M, and the sensitivity was 162.46 μ A mM⁻¹ (correlation coefficient of 0.99763). The detection limit was 8.74×10^{-6} M when the signal-to-noise ratio was 3. The **6**-CPE electrode response time was 4.2s. The inset of Fig. S13e shows the calibration graph for potassium bromate reduction at the 6-CPE. The electrode response was linear for potassium bromate within the concentration range $4 \times 10^{-3} - 8 \times 10^{-3}$ M, and the sensitivity was 10.91 μ A mM⁻¹ (correlation coefficient of 0.99481). The detection limit was 2.28×10^{-6} M when the signal-to-noise ratio was 3.



Fig. S18. Diffuse reflection spectra of Kubelka-Munk (K-M) function versus energy (eV) of compounds 1–8.



Fig. S19. Absorption spectra of the MB solution during the decomposition reaction under sunlight irradiation in the presence of the title compounds.



Fig. S20. Absorption spectra of the RhB solution during the decomposition reaction under sunlight irradiation in the presence of the title compounds.



Fig. S21. The simulative (black line), experimental (red line) and recycled after photocatalysis for MB (blue line) and RhB (purple line) powder X-ray diffraction patterns for compounds 1–8.



Fig. S22. Fluorescence spectra of L^a, L^b and compounds 1–8.