# A series of POM/Ag-based hybrids: distinct forms and assembly of $[Ag_xL_y]$ complexes through combinational effects of POM and isomeric ligands

**Min Zhu,[†,‡] Sheng-Qun Su,[†,‡] Xue-Zhi Song,[†,‡] Zhao-Min Hao,[†,‡] Shu-Yan Song,[†] Hong-Jie Zhang[*,†]**

[†]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China

Tel: +86-431-85262127; Fax: +86-431-85698041; E-mail: hongjie@ciac.jl.cn

[‡]Graduate School of the Chinese Academy of Sciences, Beijing, 100039, China

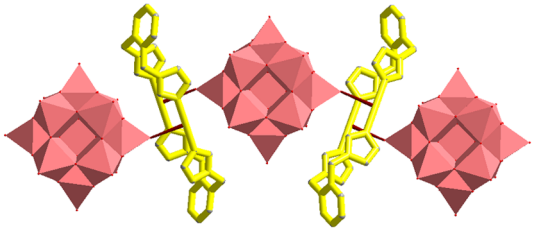

**Fig. S1** a) View of the 1D "*S*"-like chain in compound **1** (red bonds, Ag–O bonds).

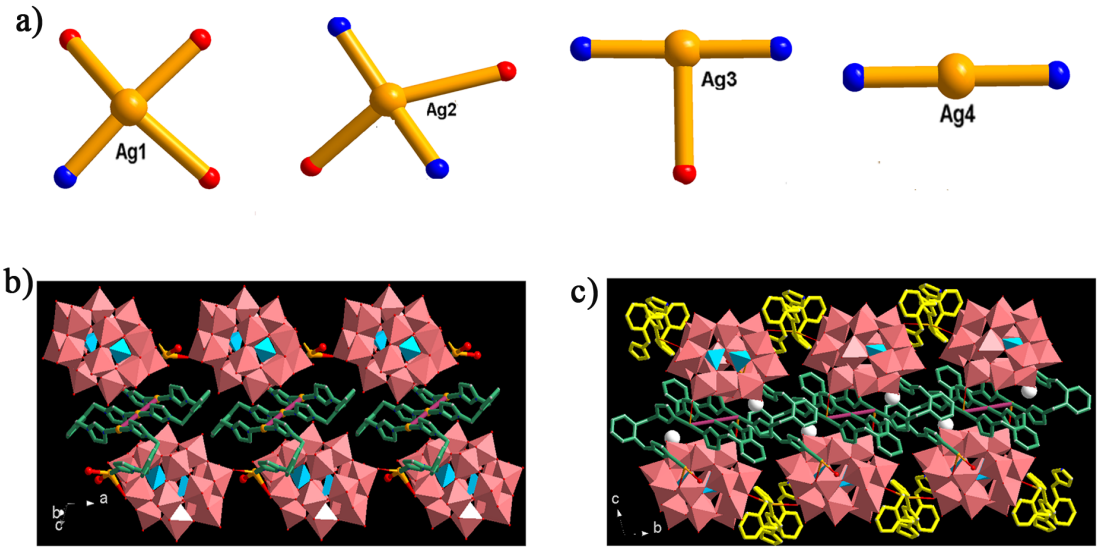

**Fig. S2** a) The coordination modes of four distinct Ag centers in compound **3**; b) View of the {Dawson-$Ag_5\mathbf{L}^{a}_4$} double-chain structure; c) View of the $Na^+$ locating in the 2D layer structure (white ball, $Na^+$).

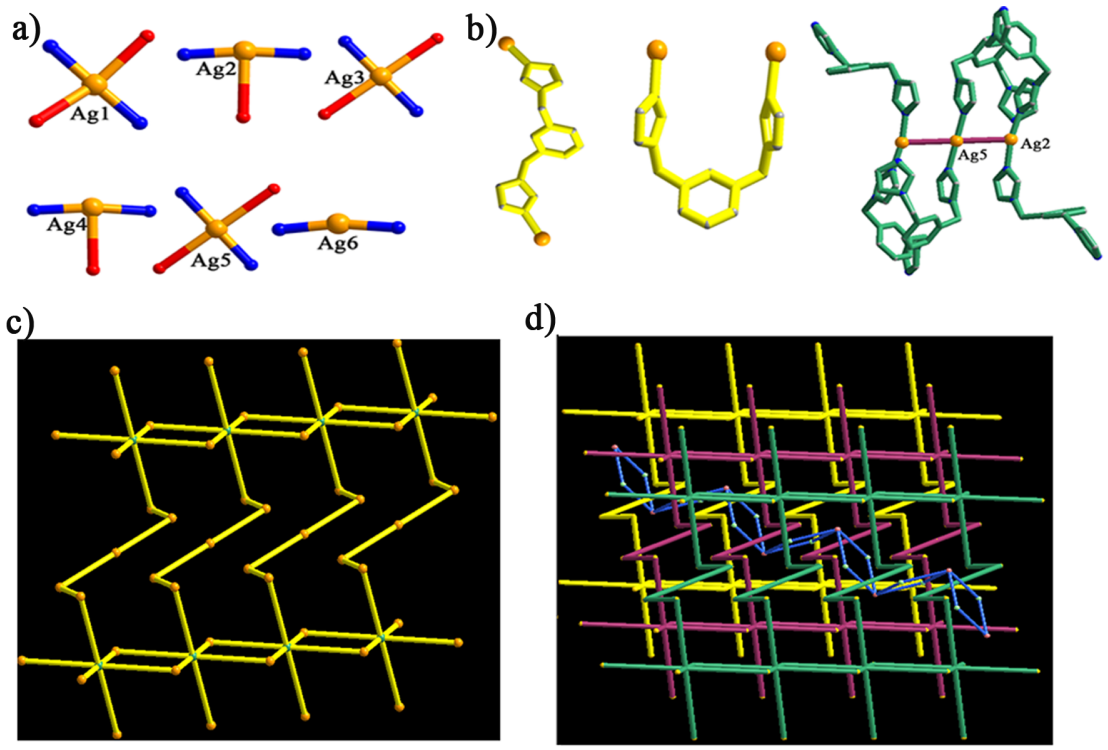


**Fig. S3** a) The coordination modes of six different Ag centers in compound **4**; b) two types of $\mathbf{L}^{b}$ ligand (yellow) and $Ag_3$ trimer (green); c) the schematic view of the layer (green balls, $Ag_3$ trimers; yellow bonds, $\mathbf{L}^{b}$ ligands; orange balls, the rest of Ag ions); d) a single {Dawson-K} chain going through interdigitated layers (blue chain, {Dawson-K} chain).

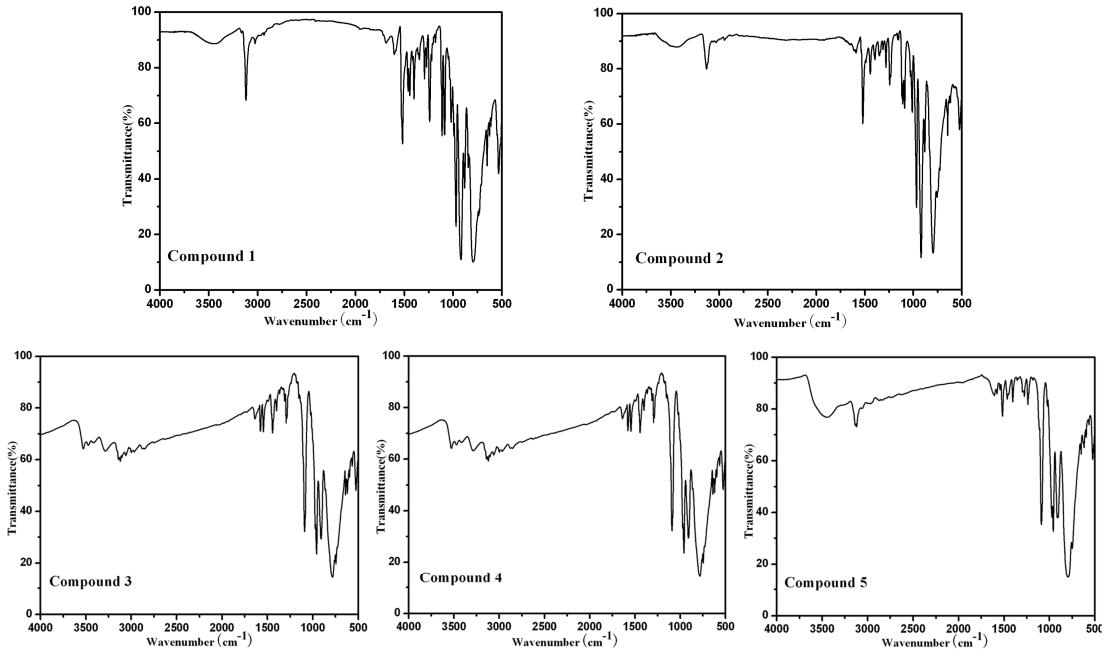


**Fig. S4** The IR spectra of compounds **1**–**5**.

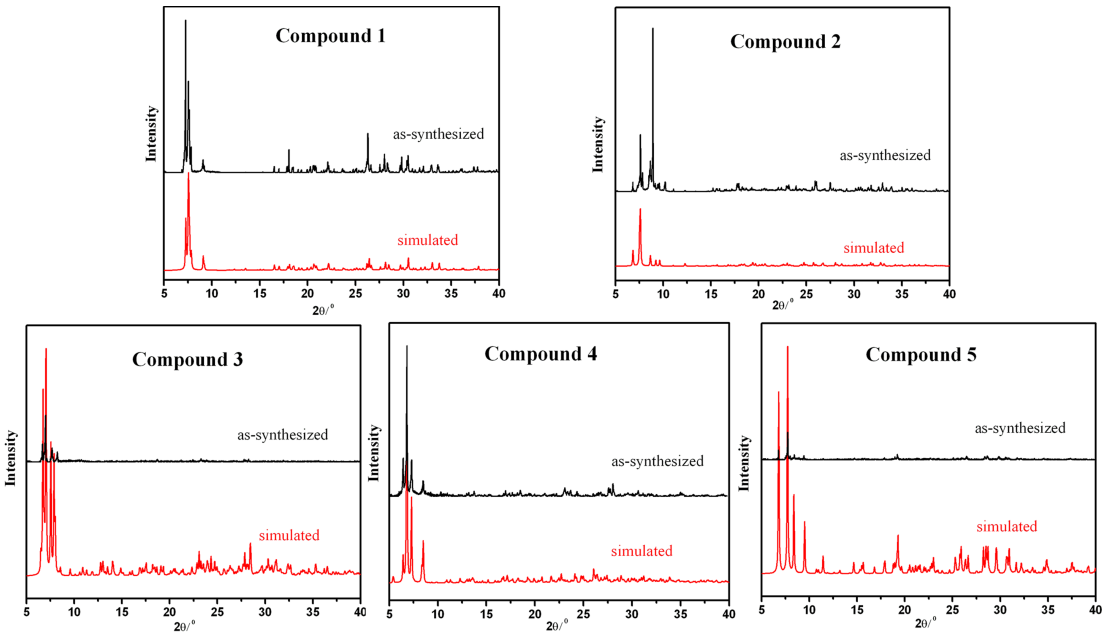


**Fig. S5** XRPD patterns of compounds **1**–**5**.

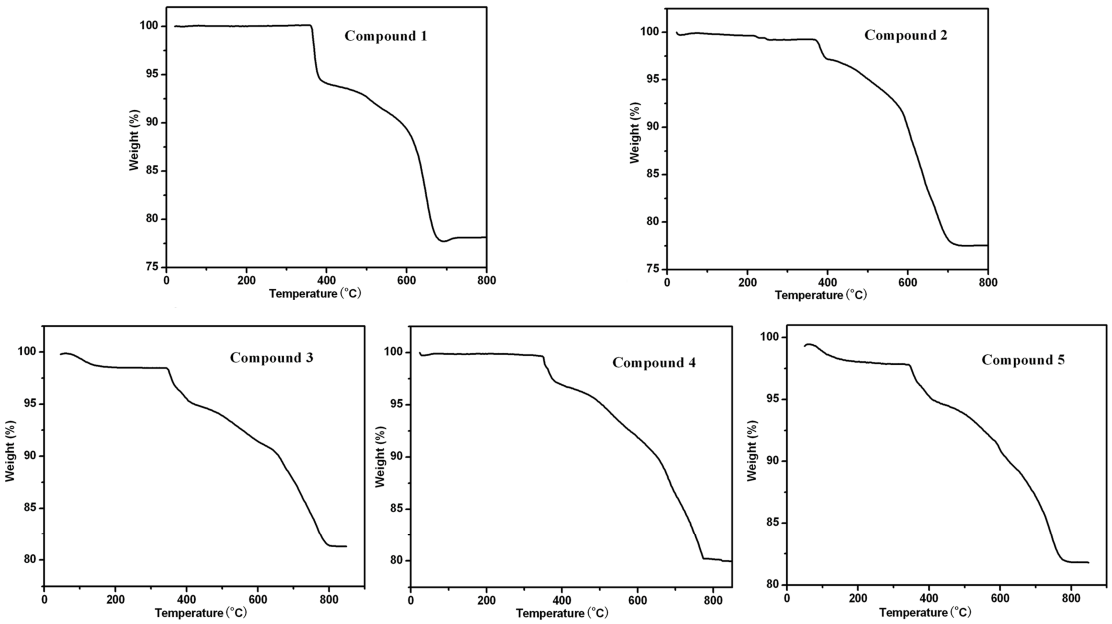


**Fig. S6** The TG analyses of compounds **1**–**5**.

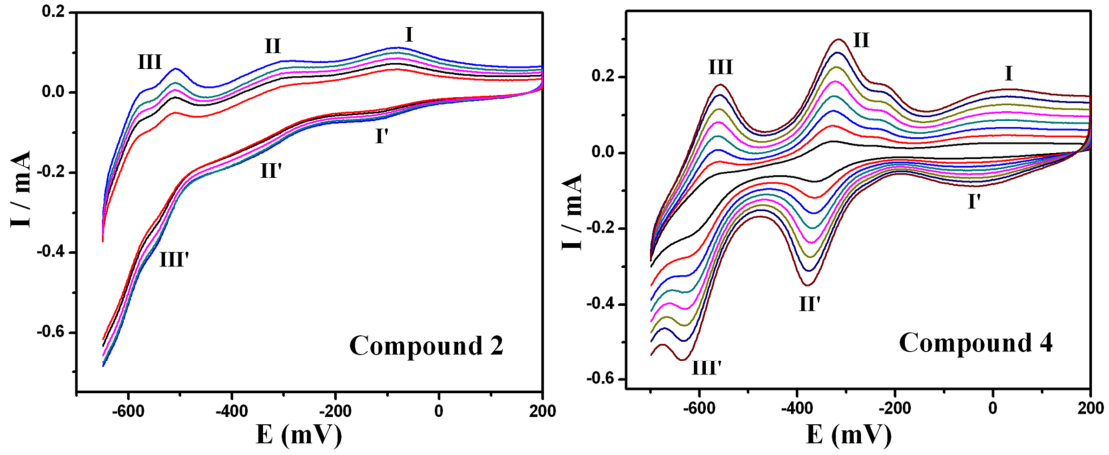


**Fig. S7** The cyclic voltammograms of **2**–CPE and **4**–CPE in 1 M $H_2SO_4$ at different scan rates (from inner to outer: 10, 50, 100, 150, 200 $mV \cdot s^{-1}$ for compound **2**; 50, 100, 150, 200, 250, 300, 350, 400 $mV \cdot s^{-1}$ for compound **4**).

**Table S1**. Selected bond lengths (Å) and angles (°) for compounds **1**–**5**.

| Compound **1** | | | |
|---|---|---|---|
| Ag(1)-N(3) | 2.084(7) | Ag(1)-N(2) | 2.086(7) |
| Ag(2)-N(5) | 2.101(8) | Ag(2)-N(6) | 2.135(7) |
| N(5)-Ag(2)-N(6) | 176.9(3) | N(2)-Ag(1)-N(3) | 179.5(3) |

| Compound **2** | | | |
|---|---|---|---|
| Ag(3)-N(8) | 2.053(7) | Ag(3)-Ag(2) | 3.0558(14) |
| Ag(2)-N(6) | 2.108(8) | Ag(2)-N(2) | 2.114(8) |
| Ag(2)-Ag(1)#3 | 3.2100(7) | Ag(1)-N(3) | 2.052(7) |
| N(8)#6-Ag(3)-N(8) | 180.000(3) | N(6)-Ag(2)-N(2) | 170.2(3) |
| N(3)-Ag(1)-N(3)#2 | 180.0 (5) | Ag(3)-Ag(2)-Ag(1)#5 | 172.12(3) |
| Ag(2)#3-Ag(1)-Ag(2)#4 | 180.0 | | |
| Compound **3** | | | |
| Ag(4)-N(5) | 2.106(17) | Ag(4)-Ag(3) | 3.346(2) |
| Ag(3)-N(2) | 2.09(2) | Ag(3)-N(3) | 2.147(18) |
| Ag(1)-N(4) | 2.17(2) | Ag(1)-OW1 | 2.26(2) |
| Ag(1)-O(54) | 2.496(16) | Ag(2)-N(10) | 2.19(2) |
| Ag(2)-N(20) | 2.28(3) | N(5)-Ag(4)-N(5)#1 | 180.0(10) |
| Ag(3)-Ag(4)-Ag(3)#1 | 180.00(5) | N(2)-Ag(3)-N(3) | 173.6(7) |
| N(4)-Ag(1)-OW1 | 173.2(8) | N(4)-Ag(1)-O(54) | 90.8(7) |
| OW1-Ag(1)-O(54) | 84.0(6) | N(10)-Ag(2)-N(20) | 168.5(10) |
| Compound **4** | | | |
| Ag(1)-N(16) | 2.100(12) | Ag(1)-N(18) | 2.130(12) |
| Ag(1)-O(30) | 2.579(9) | Ag(2)-N(12) | 2.086(11) |
| Ag(2)-N(15) | 2.090(10) | Ag(2)-Ag(5) | 3.3338(11) |
| Ag(3)-N(6) | 2.096(11) | Ag(4)-N(9) | 2.120(11) |
| Ag(4)-N(1)#2 | 2.127(10) | Ag(5)-N(8) | 2.121(11) |
| Ag(6)-N(3) | 2.087(14) | Ag(6)-N(4) | 2.107(13) |
| O(57)-K(2) | 2.471(9) | O(39)-K(1) | 2.509(10) |
| N(9)-Ag(4)-N(1)#2 | 170.1(4) | N(16)-Ag(1)-N(18) | 175.3(5) |
| N(16)-Ag(1)-O(30) | 85.8(4) | N(12)-Ag(2)-N(15) | 169.1(4) |
| N(3)-Ag(6)-N(4) | 169.0(6) | N(8)-Ag(5)-N(8)#3 | 180.000(2) |
| Compound **5** | | | |
| Ag(1)-N(1) | 2.116(7) | Ag(1)-N(2) | 2.126(8) |

| | | | |
|---|---|---|---|
| Ag(1)-Ag(1)#2 | 3.2379(16) | N(1)-Ag(1)-N(2) | 174.9(3) |

Symmetry transformations used to generate equivalent atoms: #1 -x, y, -z+3/2; #2 -x, -y, -z+1; #3 x, y-1, z; #4 x, y+1, z for **1**; #1 -x+1, -y, -z+1; #2 -x, -y, -z+2; #3 x-1, y-1, z; #4 -x+1, -y+2, -z+2; #5 x+1, y+1, z; #6 -x, -y+1, -z+2 for **2**; #1 -x, -y, -z; #2 -x, -y-1, -z for **3**; #1 -x+3, -y+2, -z-1; #2 -x+3, -y, -z-2; #3 -x+1, -y+1, -z-1; #4 -x+2, -y, -z-1; #5 x+1, y, z; #6 x-1, y, z; #7 -x+2, -y+1, -z-1 for **4**; #1 -x+1, -y, -z+1; #2 -x+3, -y, -z for **5**.