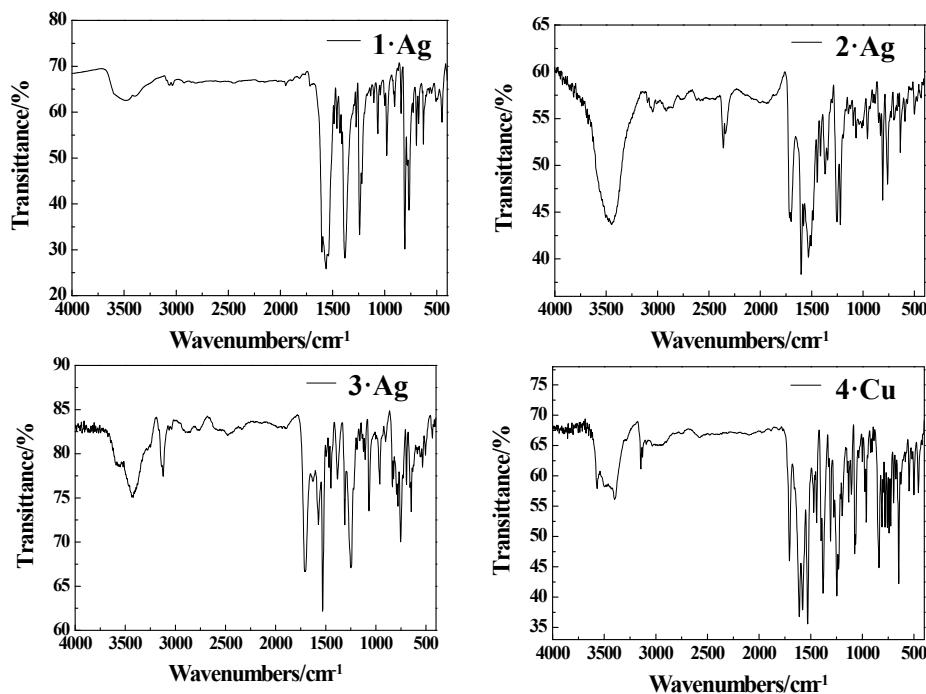


## Supporting Information

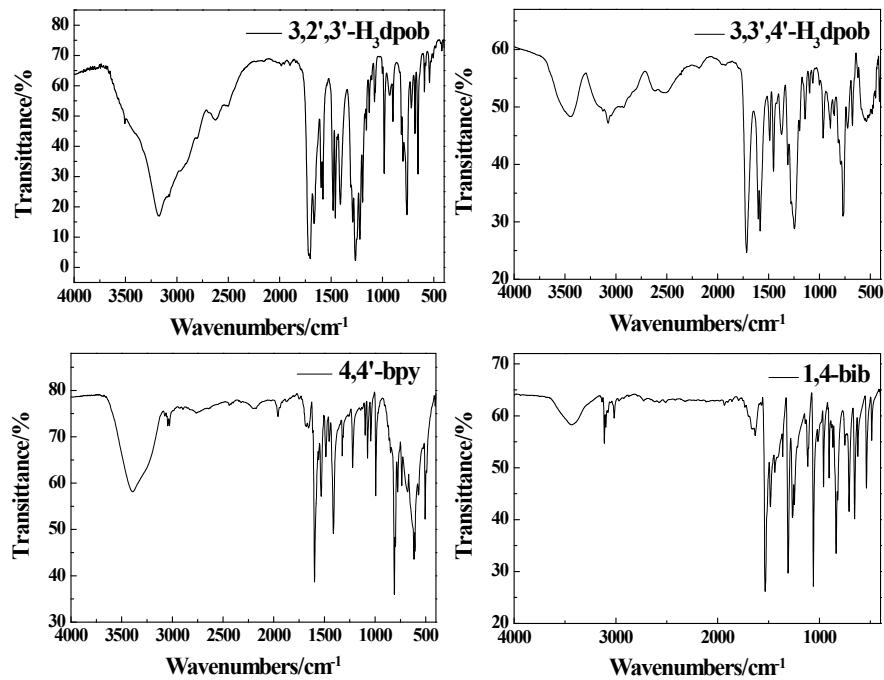
### **Effect of Noncovalent Interactions on Ag(I)/Cu(II) Supramolecular Architecture for Dual-functional Luminescent and Semiconductivity Properties**

Yang Song<sup>a</sup>, Ruiqing Fan<sup>\*a</sup>, Xi Du<sup>a</sup>, Kai Xing<sup>a</sup>, Ping Wang<sup>a</sup>, Yuwei Dong<sup>a</sup>, and Yulin Yang<sup>\*a</sup>

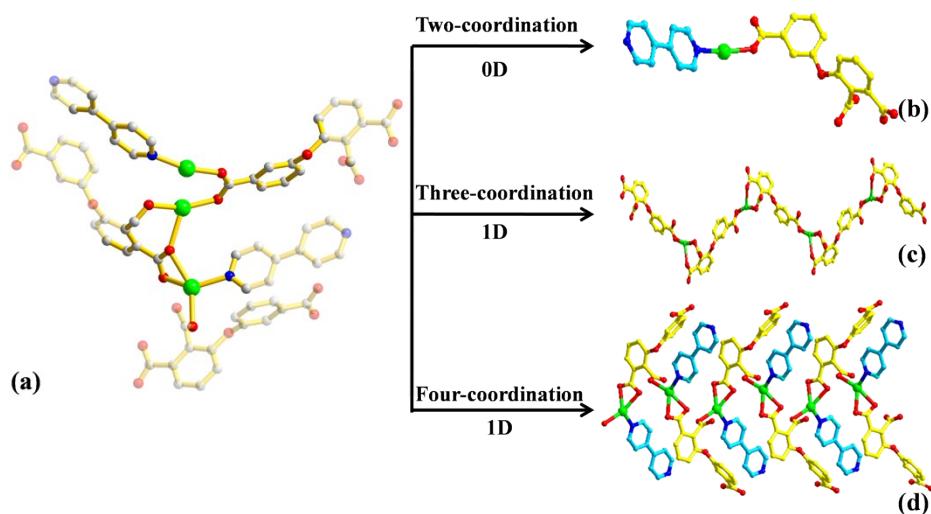
<sup>a</sup> MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, P. R. of China



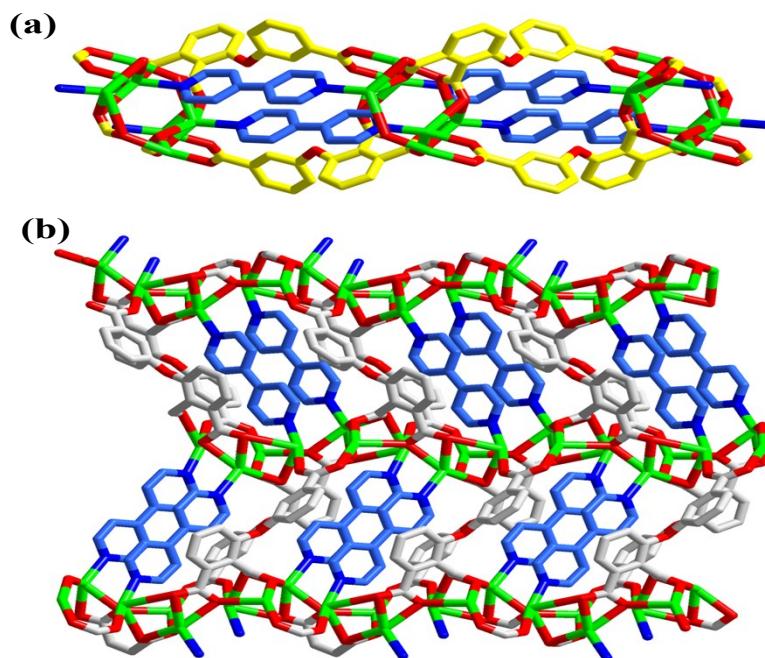
**Fig. S1** The IR spectra of  $1\cdot\text{Ag}$ ,  $2\cdot\text{Ag}$ ,  $3\cdot\text{Ag}$  and  $4\cdot\text{Cu}$ .



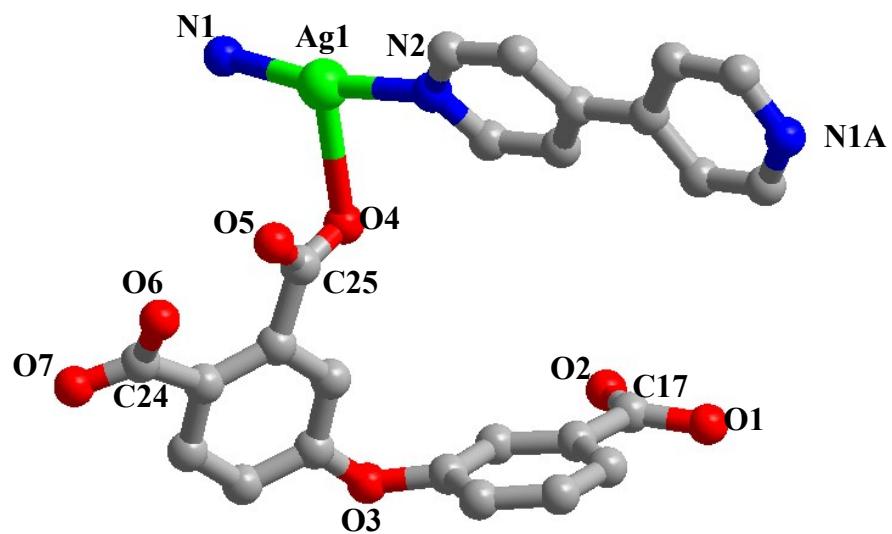
**Fig. S2** The IR spectra of  $3,2',3'\text{-H}_3\text{dpob}$ ,  $3,3',4'\text{-H}_3\text{dpob}$ ,  $4,4'\text{-bpy}$  and  $1,4\text{-bib}$  ligands.



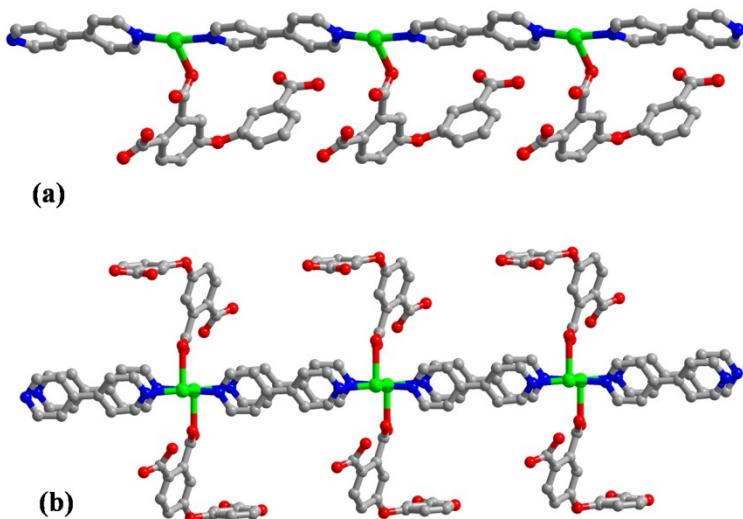
**Fig. S3** (a) Asymmetric unit and the asymmetry-operated components in 60% transparency; (b) Two-coordination 0D structure based on Ag1 ion; (c) Three-coordination 1D wave chain based on Ag2 ion; (d) Four-coordination 1D chain based on Ag3 ion.



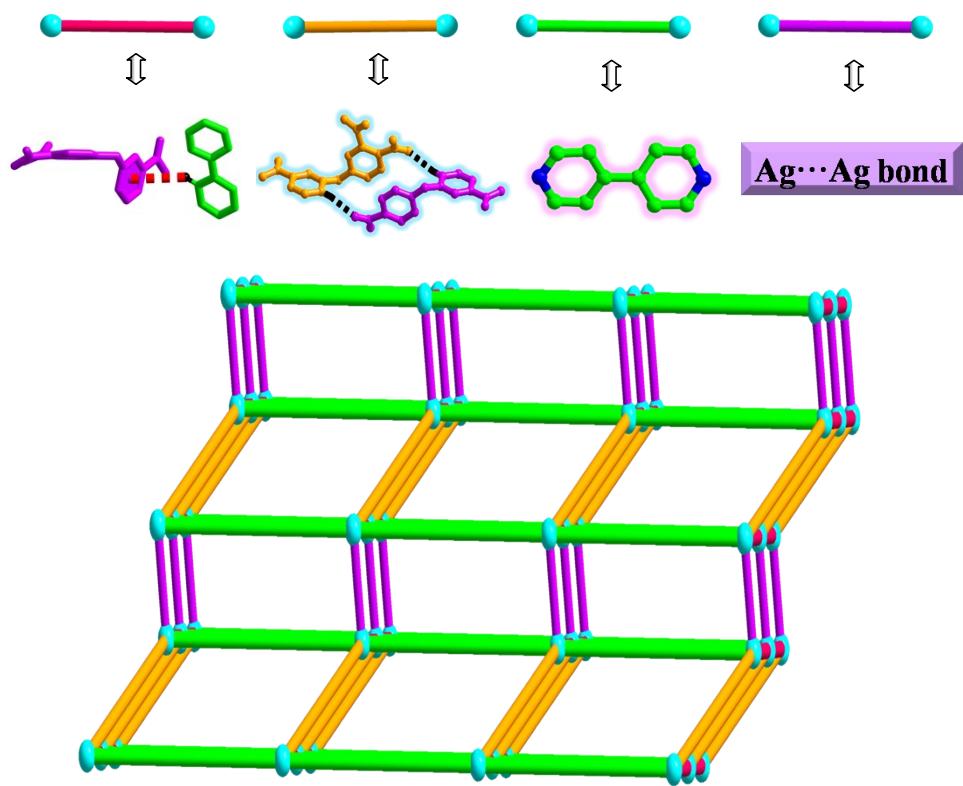
**Fig. S4** (a) The illustration of the 2D layer of **1•Ag** along *b* axis; (b) The illustration of the 2D compact layer of **1•Ag** in the *bc* plane.



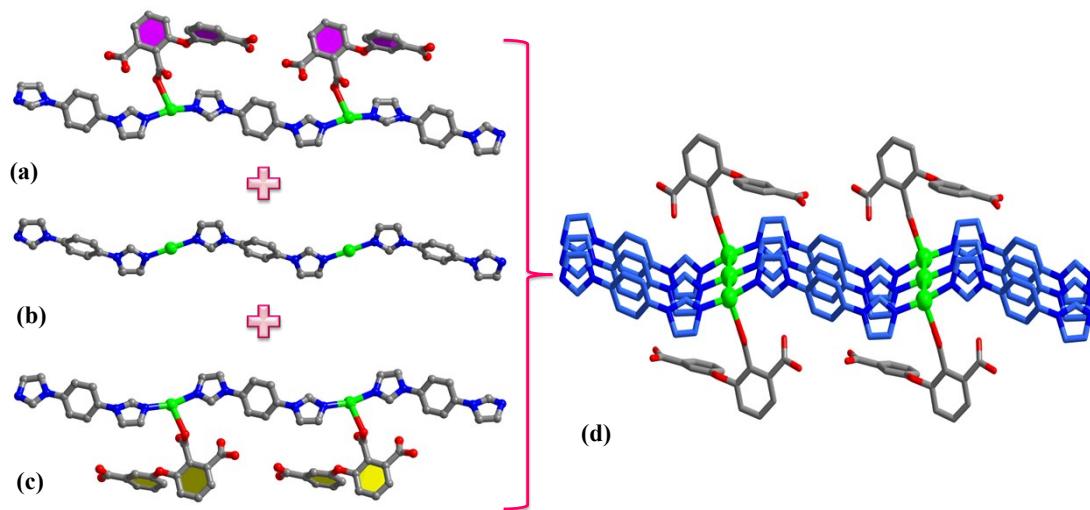
**Fig. S5** The structural unit of **2•Ag** with labeling scheme and 50% thermal ellipsoids (hydrogen atoms are omitted for clarity).



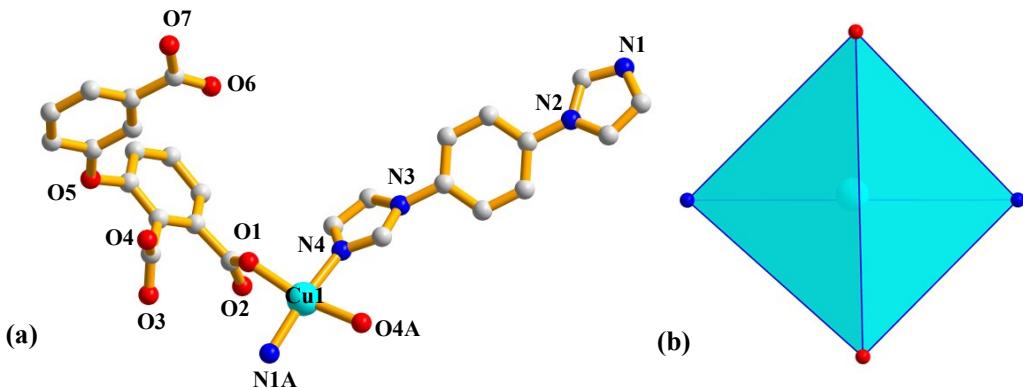
**Fig. S6** (a) The 1D chain of **2•Ag**; (b) The 1D double-chain of **2•Ag**.



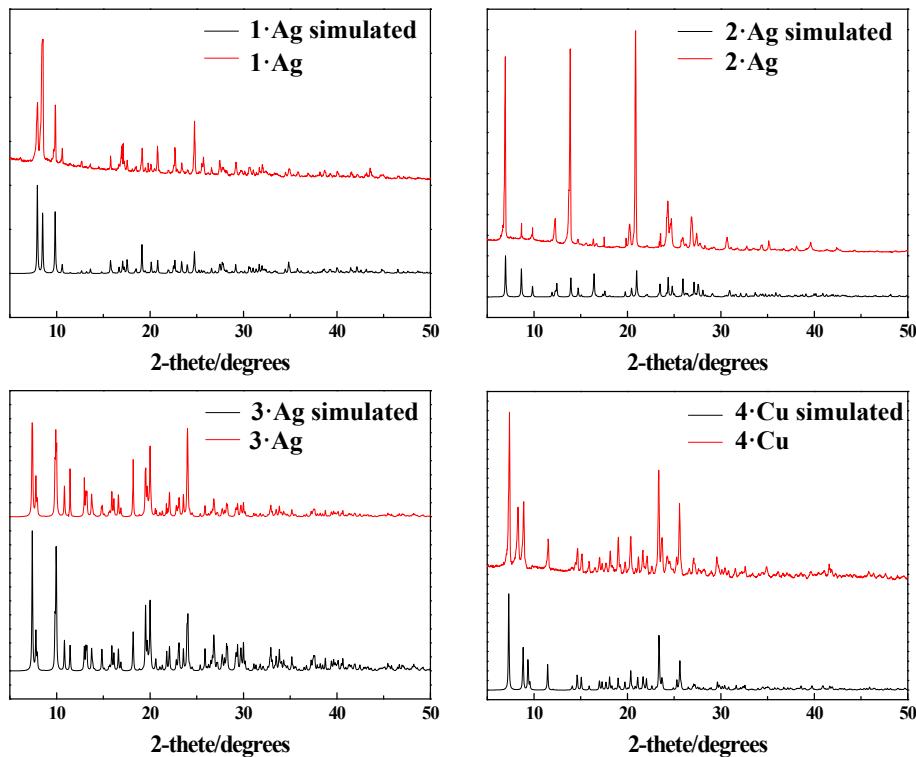
**Fig. S7** Topological view of the 3D structure of **2•Ag** with the 6-connected **pcu** net (color code: the silver ions, blue ball; the defined linkers of C-H···O and  $\pi\cdots\pi$  interactions, rose and yellow sticks; the defined linkers of bpy and Ag···Ag bond, green and purple sticks)



**Fig. S8** (a) The three-coordination 1D chain in **3•Ag**; (b) The two-coordination 1D chain in **3•Ag**; (c) The other three-coordination 1D chain in **3•Ag**; (d) The 1D triple chain structure of **3•Ag**.

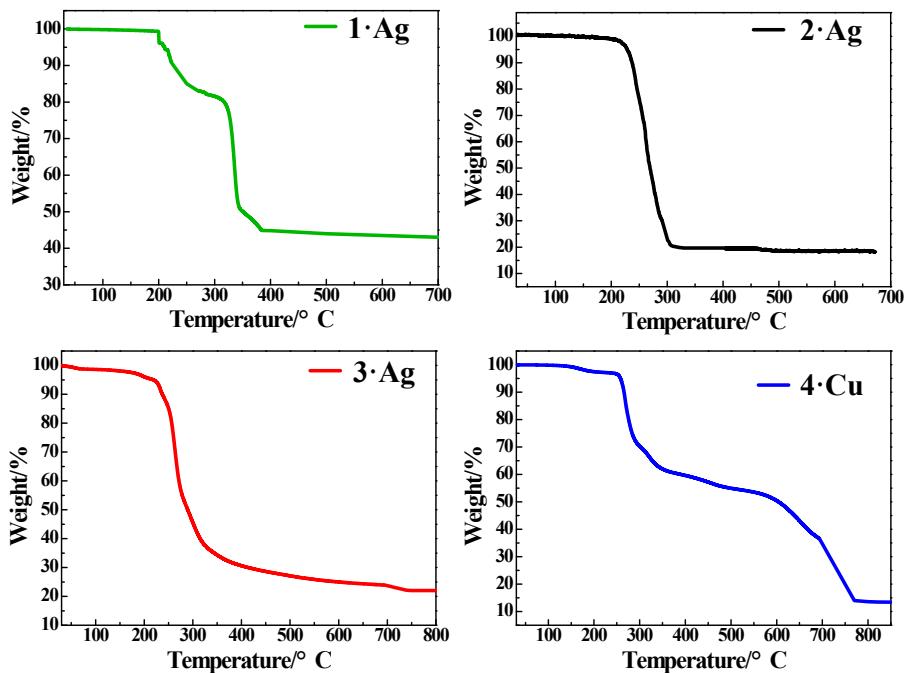


**Fig. S9** (a) The structural unit of **4·Cu** with labeling scheme and 50% thermal ellipsoids (hydrogen atoms are omitted for clarity). (b) Polyhedral representation of the coordination sphere of the  $\text{Cu}^{2+}$  centre.



**Fig. S10** The PXRD patterns of **1·Ag**, **2·Ag**, **3·Ag** and **4·Cu** with the relevant simulated patterns.

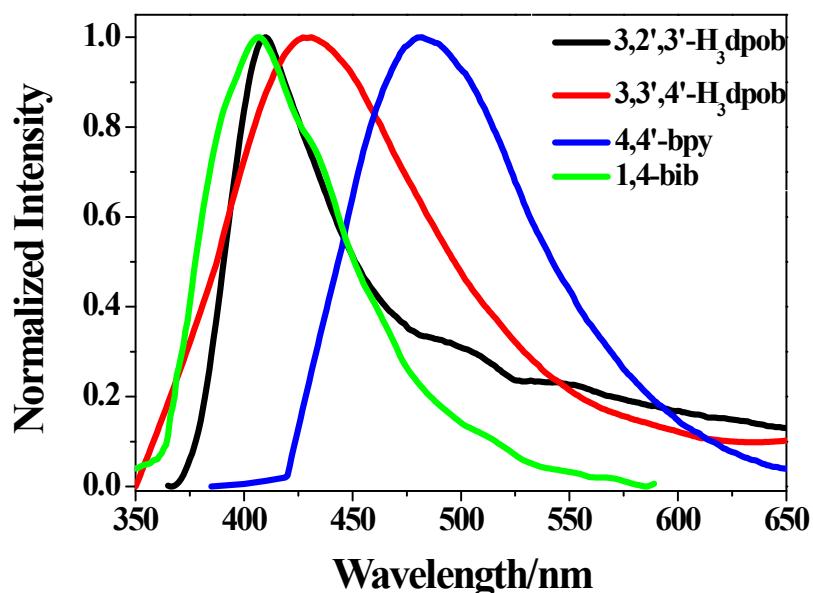
In order to check the phase purity of **1·Ag**, **2·Ag**, **3·Ag** and **4·Cu** the X-ray powder diffraction (PXRD) pattern was checked at room temperature. The simulated and experimental PXRD patterns of **1·Ag**, **2·Ag**, **3·Ag** and **4·Cu** are in good agreement with each other (Fig. S7), indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.



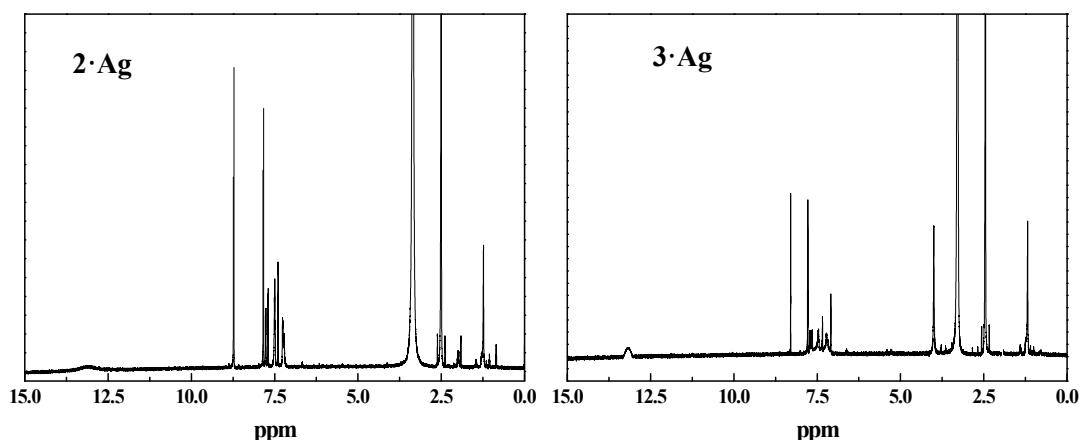
**Fig. S11** The TGA curves of compounds **1·Ag**, **2·Ag**, **3·Ag** and **4·Cu**.

To estimate the stability of the compounds, thermogravimetric analyses (TGA) in purified air were carried out and the TGA curves are shown in Fig. S8. In the TGA curve of **1·Ag**, there are two weight-loss steps. The loss 19.53% occurring at the first step is attributed to the decomposition of bpy 200.1~313.7 °C (calculated 20.02%). The second weight-loss of 37.83% from 313.8 to 393.1 °C, which corresponds to the decomposition of dpob<sup>3-</sup> (calculated 38.39%). Host framework of **2·Ag** could keep until 216.2 °C and the rapid weight loss occurs from 217.5 to 308.2 °C owing to the decomposition of organic ligands (found 81.08 %, calcd 81.89 %). After further heating, the TGA curve keeps horizontal. For **3·Ag**, the TGA curve displays one continuous weight loss step from 211.8 °C (found 77.99 %, calcd 79.64 %), which is attributed to the decomposition of the framework including the three bib ligands, two H<sub>3</sub>dpob ligands and two uncoordinated water molecules. The remaining weight of 42.64% for **1·Ag**, 19.92% for **2·Ag** and 22.01% for **3·Ag**, which is in good agreement with the calculated value (41.59% for **1·Ag**, 19.11% for **2·Ag** and 20.35% for **3·Ag**), indicating that the final product is Ag<sub>2</sub>O. In the TGA curve of **4·Cu**, the first weight loss from 252.2 to 339.6 °C is consistent with the decomposition of bib ligand (found 36.62 %, calcd 34.48 %). After further heating, the following smooth weight-loss is

7.45% during 338.2~578.8°C, which is consistent with the removal of uncoordinated 3'-position carboxyl (calculated 7.39%). The last weight loss from 580.5 to 768.7 °C, which is attributed to the decomposition 13.47%, correspond to the percentage (calcd: 13.13%) of Cu and O components, indicating that the final product is CuO.



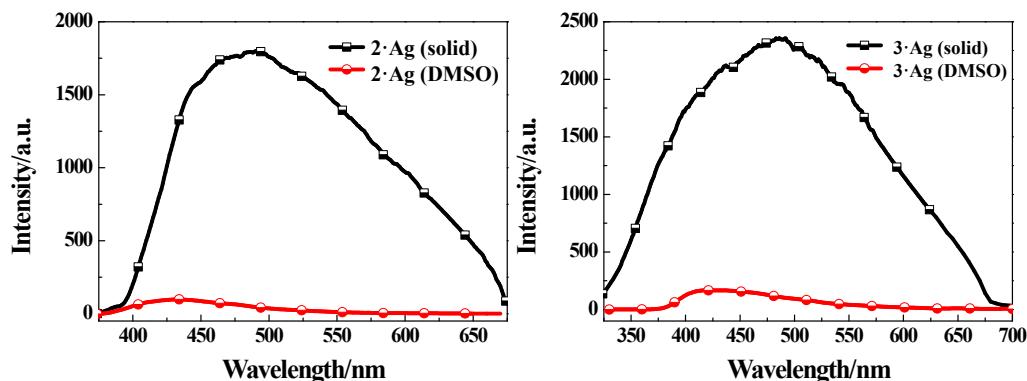
**Fig. S12** Emission spectra of ligands 3,2',3'-H<sub>3</sub>dpob, 3,3',4'-H<sub>3</sub>dpob, 4,4'-bpy and 1,4-bib in the solid state at 298 K.



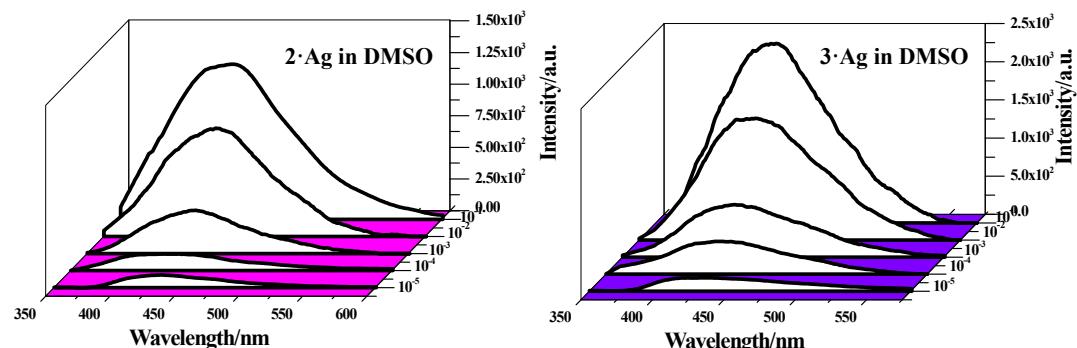
**Fig.S13** The <sup>1</sup>H NMR spectra of 2•Ag and 3•Ag.

Compound 2•Ag: <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, Fig. S13†): δ = 13.06 (s, 2H, COOH) 8.79 (d, 4 H, Py-H<sub>1,5,8,9</sub>), 7.88 (d, 4 H, Py-H<sub>2,4,7,10</sub>), 7.84 (d, 1 H, Ph-H<sub>20</sub>), 7.76 (d, 1 H, Ph-H<sub>23</sub>), 7.69 (d, 1 H, Ph-H<sub>14</sub>), 7.53 (s, 1 H, Ph-H<sub>12</sub>), 7.49 (t, 1 H, Ph-H<sub>15</sub>), 7.39 (d, 1 H, Ph-H<sub>19</sub>), 7.26 (d, 1 H, Ph-H<sub>16</sub>) ppm.

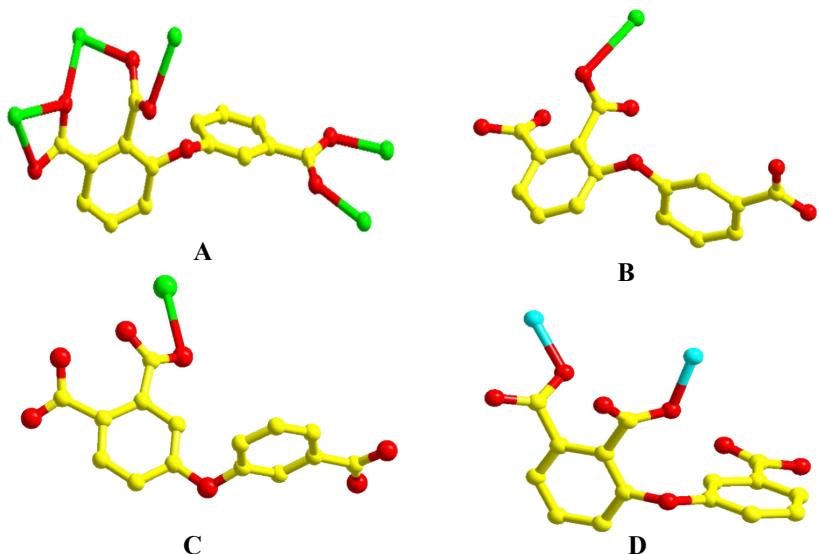
Compound **3•Ag**:  $^1\text{H}$  NMR (400 MHz, DMSO-*d*<sub>6</sub>, Fig. S13†):  $\delta$  = 13.21 (s, 3 H, –COOH), 8.29 (s, 6 H, Imi–*H*<sub>3,7,15,22,25,36</sub>), 7.79 (s, 6 H, Imi–*H*<sub>2,8,14,23,26,34</sub>), 7.78 (d, 12 H, Ph–*H*<sub>5,6,11,12,17,18,20,21,29,30,32,33</sub>), 7.72 (d, 2 H, Ph–*H*<sub>38,53</sub>), 7.65 (d, 2 H, Ph–*H*<sub>48,63</sub>), 7.45 (t, 4 H, Ph–*H*<sub>39,50,54,65</sub>), 7.33 (s, 2 H, Ph–*H*<sub>40,55</sub>), 7.23 (d, 2 H, Ph–*H*<sub>47,62</sub>), 7.18 (s, 2 H, Ph–*H*<sub>46,61</sub>), 7.08 (s, 6 H, Imi–*H*<sub>1,9,13,24,27,35</sub>) ppm.



**Fig. S14** The comparative solid state and solution (DMSO) luminescence intensities for compounds **2•Ag** and **3•Ag**.



**Fig. S15** Luminescence intensities of compounds **2•Ag** and **3•Ag** in DMSO at different concentrations.



**Scheme S1** Coordination modes and configurations of  $\text{H}_3\text{dpob}$  ligands in compounds **1•Ag**, **2•Ag**, **3•Ag** and **4•Cu**.

Firstly, when using the same reaction mixtures ( $\text{AgNO}_3$  and bpy), the coordination mode of  $3,2',3'$ - $\text{H}_3\text{dpob}$  is different from  $3,3',4'$ - $\text{H}_3\text{dpob}$  completely, owing to the effects of carboxylate positions (Scheme 2 A and B). For **1•Ag**,  $3,2',3'$ - $\text{H}_3\text{dpob}$  ligand shows a *cis*-typed configuration with  $\mu_5$ -bridging mode, and 3-, 2'-, and 3'-carboxylic groups exhibit  $\mu_2\text{-}\eta^1\text{-}\eta^1$ ,  $\mu_2\text{-}\eta^1\text{-}\eta^1$ , and  $\mu_2\text{-}\eta^2\text{-}\eta^1$  coordination mode, respectively. Due to the rich way of coordination, unique 2D compact structure has been obtained. However, in **2•Ag**,  $3,3',4'$ - $\text{H}_3\text{dpob}$  in a *trans*-typed configuration possesses  $\mu_1$ -bridging mode with 3'-carboxylic group in a monodentate coordination mode, which results in forming a 1D chain structure. Secondly, compounds **1•Ag** and **3•Ag** imply the influence of the secondary ligands on the resulting frameworks. The length of the rigid auxiliary ligand is increased from 7.06 Å (bpy) to 9.86 Å (bib), and changing the modes of the  $3,2',3'$ - $\text{H}_3\text{dpob}$  ligand from  $\mu_5$  to  $\mu_1$  (Scheme 2A and C ), *cis*- and *trans*-type configurations have been observed for each connection, which finally generate different 2D and 1D structure. Thirdly, the same reaction mixtures ( $3,2',3'$ - $\text{H}_3\text{dpob}$  and bib) were subjected to different synthetic routes by varying metal ions to form diverse architectures in **3•Ag** and **4•Cu**. Comparison of Cu(II) to Ag(I), their ionic radius and valance state are distinct different, which may lead to diversity in bond strength, bond lengths and bond angles even with the same organic ligands forming the covalent bonds.

**Table S1** Selected bond lengths [Å] and angles [°] for **1•Ag**, **2•Ag**, **3•Ag** and **4•Cu**.

| Bond length   | (Å)       | Bond angle          | (°)        | Bond angle           | (°)         |
|---------------|-----------|---------------------|------------|----------------------|-------------|
| <b>1•Ag</b>   |           |                     |            |                      |             |
| Ag(1)-O(6)    | 2.152(3)  | O(6)-Ag(1)-O(1)     | 157.27(10) | Ag(1)-Ag(2)-Ag(3)    | 150.004(16) |
| Ag(1)-O(1)    | 2.193(3)  | O(6)-Ag(1)-O(4)#1   | 120.74(10) | N(2)-Ag(3)-O(2)      | 104.55(10)  |
| Ag(1)-O(4)#1  | 2.538(4)  | O(1)-Ag(1)-O(4)#1   | 76.91(10)  | N(2)-Ag(3)-O(4)      | 104.25(11)  |
| Ag(1)-Ag(2)   | 2.9665(6) | O(6)-Ag(1)-Ag(2)    | 84.71(8)   | O(2)-Ag(3)-O(4)      | 148.55(11)  |
| Ag(2)-O(5)    | 2.163(3)  | O(1)-Ag(1)-Ag(2)    | 72.57(7)   | N(2)-Ag(3)-O(3)      | 123.43(10)  |
| Ag(2)-N(1)    | 2.166(3)  | O(4)#1-Ag(1)-Ag(2)  | 132.49(8)  | O(2)-Ag(3)-O(3)      | 118.15(9)   |
| Ag(2)-Ag(3)   | 3.0649(6) | O(5)-Ag(2)-N(1)     | 164.57(12) | O(4)-Ag(3)-O(3)      | 52.11(9)    |
| Ag(3)-N(2)    | 2.257(3)  | O(5)-Ag(2)-Ag(1)    | 74.96(8)   | N(2)-Ag(3)-Ag(2)     | 137.48(8)   |
| Ag(3)-O(2)    | 2.351(3)  | N(1)-Ag(2)-Ag(1)    | 110.04(8)  | O(2)-Ag(3)-Ag(2)     | 59.46(7)    |
| Ag(3)-O(4)    | 2.469(3)  | O(5)-Ag(2)-Ag(3)    | 75.07(8)   | O(4)-Ag(3)-Ag(2)     | 105.07(7)   |
| Ag(3)-O(3)    | 2.500(3)  | N(1)-Ag(2)-Ag(3)    | 98.64(8)   | O(3)-Ag(3)-Ag(2)     | 58.85(6)    |
| <b>2•Ag</b>   |           |                     |            |                      |             |
| Ag(1)-N(2)#1  | 2.167(4)  | N(2)#1-Ag(1)-N(1)   | 168.88(16) | N(1)-Ag(1)-Ag(1)#2   | 86.75(12)   |
| Ag(1)-N(1)    | 2.183(4)  | N(2)#1-Ag(1)-O(4)   | 94.59(16)  | O(4)-Ag(1)-Ag(1)#2   | 102.44(11)  |
| Ag(1)-O(4)    | 2.689(4)  | N(1)-Ag(1)-O(4)     | 91.39(16)  | N(2)#1-Ag(1)-Ag(1)#2 | 101.07(12)  |
| Ag(1)-Ag(1)#2 | 3.451(9)  |                     |            |                      |             |
| <b>3•Ag</b>   |           |                     |            |                      |             |
| Ag(1)-N(3)    | 2.076(12) | N(3)-Ag(1)-N(1)     | 179.7(7)   | O(5)-Ag(2)-Ag(1)     | 103.4(3)    |
| Ag(1)-N(1)    | 2.081(14) | N(3)-Ag(1)-Ag(2)    | 100.4(4)   | N(9)-Ag(2)-Ag(1)     | 85.6(4)     |
| Ag(1)-Ag(2)   | 3.150(3)  | N(1)-Ag(1)-Ag(2)    | 79.8(4)    | N(5)-Ag(2)-Ag(1)     | 108.6(3)    |
| Ag(1)-Ag(3)#1 | 3.153(3)  | N(3)-Ag(1)-Ag(3)#1  | 79.6(4)    | N(8)#2-Ag(3)-N(12)   | 160.7(6)    |
| Ag(2)-N(9)    | 2.174(13) | N(1)-Ag(1)-Ag(3)#1  | 100.2(4)   | N(8)#2-Ag(3)-O(12)   | 90.9(4)     |
| Ag(2)-N(5)    | 2.177(13) | Ag(2)-Ag(1)-Ag(3)#1 | 179.93(9)  | N(12)-Ag(3)-O(12)    | 97.9(5)     |
| Ag(2)-O(5)    | 2.638(10) | N(9)-Ag(2)-N(5)     | 159.9(5)   | N(8)#2-Ag(3)-Ag(1)#1 | 84.8(3)     |
| Ag(3)-N(8)#2  | 2.163(14) | N(9)-Ag(2)-O(5)     | 91.3(4)    | N(12)-Ag(3)-Ag(1)#1  | 109.5(4)    |
| Ag(3)-N(12)   | 2.175(14) | N(5)-Ag(2)-O(5)     | 98.9(5)    | O(12)-Ag(3)-Ag(1)#1  | 103.3(3)    |
| Ag(3)-O(12)   | 2.652(10) |                     |            |                      |             |
| Ag(3)-Ag(1)#1 | 3.153(3)  |                     |            |                      |             |
| <b>4•Cu</b>   |           |                     |            |                      |             |
| Cu(1)-O(1)    | 1.951(3)  | O(1)-Cu(1)-O(4)#1   | 161.87(12) | O(1)-Cu(1)-N(4)      | 91.12(13)   |
| Cu(1)-O(4)#1  | 1.965(3)  | O(1)-Cu(1)-N(1)     | 93.58(13)  | O(4)#1-Cu(1)-N(4)    | 85.37(13)   |
| Cu(1)-N(1)    | 1.972(3)  | O(4)#1-Cu(1)-N(1)   | 92.49(13)  | N(1)-Cu(1)-N(4)      | 170.87(15)  |
| Cu(1)-N(4)    | 1.986(3)  |                     |            |                      |             |

Symmetry transformations used to generate equivalent atoms: #1: -x, -y+2, -z; #2: -x, -y+1, -z+1.

**Table S2** The Dihedral Angles for **1•Ag**, **2•Ag**, **3•Ag** and **4•Cu**.

| Compounds    | Dihedral angle between of the plane three atomic carboxylic group and its benzene ring (°) |                               |                               | Dihedral angle between the two benzene rings (°) |
|--------------|--|-------------------------------|-------------------------------|--|
|              | 3-carboxylic group   | 2'-carboxylic group           | 3'-carboxylic group           |  |
| <b>1•Ag</b>  | 16.32°   | 85.09°                        | 18.59°                        | 76.73°   |
| <b>2•Ag</b>  | 3-carboxylic group<br>10.28°   | 3'-carboxylic group<br>30.19° | 4'-carboxylic group<br>24.08° | 75.62°   |
| <b>3•Ag</b>  | 3-carboxylic group<br>3.18°  | 2'-carboxylic group<br>69.60° | 3'-carboxylic group<br>34.32° | 79.41°   |
| <b>4• Cu</b> | 3-carboxylic group<br>7.39°  | 2'-carboxylic group<br>54.09° | 3'-carboxylic group<br>52.73° | 88.12°   |

**Table S3** Summary of the luminescent properties of Ag(I) compounds.

| No. | Cite                                     | Complex   | Excitation and emission (compounds)  | Excitation and emission (ligands)                     | Assignment  |
|-----|--|---|--|---|---|
| 1   | <i>CrystEng Comm,</i> 2015, 17, 5538     | {[Ag(HDSPTP)]·30H <sub>2</sub> O} <sub>n</sub><br>(3){[Ag(HDSPTP)(H <sub>2</sub> O)]·3H <sub>2</sub> O} <sub>n</sub><br>(4), [Ag <sub>2</sub> (DSPTP)] <sub>n</sub> (5),<br>{[Ag <sub>4</sub> (DSPTP) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]·2H <sub>2</sub> O} <sub>n</sub> (6)<br>(H <sub>2</sub> DSPTP=4'-(2,4-disulfophenyl)-<br>4,2':6',4''-terpyridine  | $\lambda_{\text{ex}} = 357$ nm for 3<br>$\lambda_{\text{em}} = 430$ nm<br>$\lambda_{\text{ex}} = 366$ nm for 4<br>$\lambda_{\text{em}} = 488$ nm<br>$\lambda_{\text{ex}} = 336$ nm for 5<br>$\lambda_{\text{em}} = 446$ nm<br>$\lambda_{\text{ex}} = 333$ nm for 6<br>$\lambda_{\text{em}} = 460$ nm | $\lambda_{\text{em}} = 430$ nm                        | The ligand-centered nature of the emission because the d <sup>10</sup> ions are difficult to oxidize or reduce. |
| 2   | <i>Cryst. Growth Des.</i> 2014, 14, 2230 | [Ag <sub>2</sub> (bpz) <sub>4</sub> (mal)·7H <sub>2</sub> O] <sub>n</sub> (1L and 1R) , [Ag <sub>4</sub> (bpz) <sub>5</sub> (glu) <sub>2</sub> ] <sub>n</sub> (3),<br>[Ag <sub>4</sub> (bpz) <sub>5</sub> (adip) <sub>2</sub> ] <sub>n</sub> (4),<br>[Ag <sub>4</sub> (bpz) <sub>7</sub> (pim) <sub>2</sub> ·12H <sub>2</sub> O] <sub>n</sub><br>(5),[Ag <sub>2</sub> (bpz) <sub>4</sub> (sub)·7H <sub>2</sub> O] <sub>n</sub> (6),<br>[Ag <sub>2</sub> (bpz) <sub>3</sub> (aze)·3.5H <sub>2</sub> O] <sub>n</sub> (7)<br>(H <sub>2</sub> mal = malonic acid, H <sub>2</sub> suc = succinic acid, H <sub>2</sub> glu = glutaric acid, H <sub>2</sub> adip = adipic acid, H <sub>2</sub> pim = pimelic acid, H <sub>2</sub> sub = suberic acid, H <sub>2</sub> aze = azelaic acid) | 298 K<br>$\lambda_{\text{ex}} = 365$ nm<br>$\lambda_{\text{em}} = \text{ca. } 465$ nm for 1, 3, 4, 6, and 7<br>$\lambda_{\text{em}} = 454$ nm for 5<br>77 K<br>Enhanced but no obvious emission shifts   | bpz<br>$\lambda_{\text{em}} = 342$ nm                 | Ligand-centered transitions   |
| 3   | <i>Chem. Commun.,</i> 2014, 50, 9000     | [Ag <sub>2</sub> (Hpidc)(NH <sub>3</sub> ) <sub>2</sub> ] (1),<br>[Ag <sub>2</sub> (Hpidc)(NH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ·2H <sub>2</sub> O (2),<br>[Ag <sub>4</sub> (Hpidc) <sub>2</sub> (en) <sub>2</sub> ] (3)<br>[Ag <sub>4</sub> (Hpidc) <sub>2</sub> (pn) <sub>2</sub> ] (4)<br>NH <sub>3</sub> =ammonia<br>en=1,2-diaminoethane<br>pn=1,3-diaminopropane   | $\lambda_{\text{ex}} = 250$ nm<br>High energy emission is 400 nm<br>Low energy emission is 550 nm  | H <sub>3</sub> pidc<br>$\lambda_{\text{em}} = 300$ nm | HE bands probably result from intra-ligand n-π or π-π transitions in Hpidc <sup>2-</sup>                        |

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|   |   |  |  |   |   |
|---|---|--|--|---|---|
|   |   |  |  |   | LE emissions<br>should be<br>phosphorescence  |
| 4 | <i>Cryst.</i><br><i>Growth Des.,</i><br>2014, 14,<br>4674 | $[\text{Ag}_2(\mu_4\text{-bztpy})\{\text{Ag}(\text{CN})_2\}_2]\cdot\text{EtOH}(1)$<br>$[\text{Ag}(\mu_3\text{-bztpy})\{\text{Ag}(\text{CN})_2\}] (2)$  | $\lambda_{\text{ex}} = 471 \text{ nm}(1) \text{ and } 479 \text{ nm}(2)$<br>$\lambda_{\text{em}} = 538 \text{ nm}(1) \text{ and } 547 \text{ nm}(2)$ | bztpy<br>$\lambda_{\text{ex}} = 332 \text{ nm}$ and<br>450 nm<br>$\lambda_{\text{em}} = 378 \text{ nm}$ and<br>534 nm | Intraligand transition  |
| 5 | <i>Cryst.</i><br><i>Growth Des.</i><br>2014,<br>14, 1888  | $[\text{Ag}_3\text{L}_2(\text{H}_2\text{O})_2](\text{NO}_2)_3\cdot 10\text{H}_2\text{O}$ ,<br>$[\text{Ag}_3\text{L}_2(\text{H}_2\text{O})_2](\text{NO}_3)_3\cdot 4\text{CH}_3\text{OH}\cdot 4\text{H}_2\text{O}$<br>$[\text{Ag}_3(\text{NO}_3)_2\text{L}_2](\text{NO}_3)\cdot \text{C}_2\text{H}_5\text{OH}\cdot 3\text{H}_2\text{O}$<br>N,N',N"-Tris(2-pyridinylethyl)-<br>1,3,5-benzenetricarboxamide (L)  | $\lambda_{\text{ex}} = 255 \text{ nm}$<br>$\lambda_{\text{em}} = 399, 365 \text{ and } 366 \text{ nm}$   | L<br>$\lambda_{\text{ex}} = 255 \text{ nm}$<br>$\lambda_{\text{em}} = 400 \text{ nm}$                                 | closed-shell<br>argentophilic<br>(d <sup>10</sup> -d <sup>10</sup> )<br>interactions                      |
| 6 | <i>CrystEng Comm,</i><br>2014, 16,<br>3015                | $[\text{Ag}(\text{Htzsuc})]_n$ (1, H <sub>2</sub> tzsuc = 2-(1H-1,2,4-triazol-1-yl)succinic acid)  | $\lambda_{\text{ex}} = 330 \text{ nm}$<br>$\lambda_{\text{em}} = 467 \text{ nm}$   |   | The charge transfer transition between ligands and metal centers and/or intraligand fluorescence emission |
| 7 | <i>CrystEng Comm,</i><br>2014, 16,<br>5110                | $[\text{Ag}_2(\text{hpyb})_{0.5}(\text{L}_1)_{0.5}(\text{NO}_3)]\cdot\text{H}_2\text{O}(1)$ ,<br>$[\text{Ag}_4(\text{hpyb})(\text{HL}_2)(\text{NO}_3)_2]\cdot 2\text{H}_2\text{O}(2)$ ,<br>$[\text{Ag}_3(\text{hpyb})_{0.5}(\text{L}_3)(\text{NO}_3)](3)$ ,<br>$[\text{Ag}_6(\text{hpyb})(\text{L}_4)_2(\text{NO}_3)]\cdot\text{NO}_3\cdot 2\text{H}_2\text{O}$<br>(4)<br>$[\text{Ag}_5(\text{hpyb})_{0.5}(\text{L}_5)_2(\text{NO}_3)]\cdot\text{H}_2\text{O}(5)$ ,<br>$\{\text{Ag}_4(\text{hpyb})[\text{L}_6(\text{CH}_3)_2]_2\}(6)$ ,<br>$\{\text{Ag}_6(\text{hpyb})(\text{HL}_7)_2[\text{L}_7(\text{CH}_3)]\}(7)$<br>$[\text{Ag}_3(\text{hpyb})_{0.5}(\text{HL}_8)]\cdot\text{H}_2\text{O}$ (8)<br>(H <sub>2</sub> L <sub>1</sub> =p-phthalic acid, H <sub>3</sub> L <sub>2</sub> =<br>1,2,3-benzenetricarboxylic acid,<br>H <sub>2</sub> L <sub>3</sub> =cis-2-butenedioic acid, H <sub>2</sub> L <sub>4</sub> =<br>2,3-pyridinedicarboxylic acid, | $\lambda_{\text{ex}} = 370 \text{ nm}$<br>$\lambda_{\text{em}} = 514, 590, 546, 522, 516, 572, 524 \text{ and } 588 \text{ nm}$                      | Hpyb<br>$\lambda_{\text{ex}} = 343 \text{ nm}$<br>$\lambda_{\text{em}} = 529 \text{ nm}$                              | Ligand-based luminescence.  |

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|    |                                    |   |  |  |  |
|----|------------------------------------|---|--|--|--|
|    |                                    | H <sub>2</sub> L <sub>5</sub> = m-phthalic acid, H <sub>4</sub> L <sub>6</sub> = 1,2,4,5-benzenetetracarboxylic acid, H <sub>3</sub> L <sub>7</sub> = 1,2,4-benzenetricarboxylic acid and H <sub>4</sub> L <sub>8</sub> = 4,4'-oxydiphthalic acid)  |  |  |  |
| 8  | Dalton Trans., 2014, 43, 8774      | [Ag <sub>2</sub> (dpb) <sub>2</sub> (bdc)·9H <sub>2</sub> O] <sub>n</sub> (1)   | $\lambda_{\text{ex}} = 365 \text{ nm}$<br>$\lambda_{\text{em}} = 419 \text{ nm}$   | dpb<br>$\lambda_{\text{ex}} = 300 \text{ nm}$<br>$\lambda_{\text{em}} = 367 \text{ nm}$  | The intraligand $\pi^* \rightarrow \pi$ transition   |
| 9  | Inorg. Chim. Acta, 2014, 415, 61   | [Ag <sub>2</sub> (mpyz)(ipa)] <sub>n</sub> (1)<br>[Ag <sub>3</sub> (mpyz)(btc)] <sub>n</sub> (2)<br>[Ag <sub>4</sub> (apyz) <sub>2</sub> (ipa)·0.5DMF] <sub>n</sub> (3)<br>[Ag <sub>3</sub> (apyz) <sub>2</sub> (btc)] <sub>n</sub> (4)<br>methylpyrazine (mpyz), aminopyrazine (apyz), isophthalic acid (H <sub>2</sub> ipa), 1,3,5-benzenetricarboxylic acid (H <sub>3</sub> btc) | $\lambda_{\text{ex}} = 300 \text{ nm}$ .<br>$\lambda_{\text{em}} = 415 \text{ and } 517 \text{ nm}$ for 1<br>$\lambda_{\text{em}} = 512 \text{ nm}$ for 2<br>$\lambda_{\text{em}} = 411 \text{ nm}$ for 3<br>$\lambda_{\text{em}} = 411 \text{ and } 498 \text{ nm}$ for 4   | apyz<br>$\lambda_{\text{em}} = 422 \text{ nm}$<br>H <sub>2</sub> ipa<br>$\lambda_{\text{em}} = 350 \text{ nm}$<br>H <sub>3</sub> btc<br>$\lambda_{\text{em}} = 358 \text{ and } 496 \text{ nm}$  | Intraligand $\pi^* \pi$ transition.<br>intraligand fluorescent emission $\pi^* \pi$ transitions. |
| 10 | RSC Adv., 2012, 2, 8421            | {[Ag(L <sub>1</sub> )(CH <sub>3</sub> CN)][Ag(L <sub>1</sub> )(OTf)](OTf)} <sub>n</sub> (1)<br>{[Ag(L <sub>2</sub> )](OTf)(H <sub>2</sub> O)} <sub>n</sub> (2)<br>bis(pyridine-3-ylmethyl)terephthalate (L <sub>1</sub> )   | $\lambda_{\text{ex}} = 284 \text{ nm}$ for 1<br>$\lambda_{\text{em}} = 398 \text{ nm}$ for 1<br>Another excitation wavelength $\lambda_{\text{ex}} = 350 \text{ nm}$ for 1<br>$\lambda_{\text{em}} = 482 \text{ nm}$ for 1<br>$\lambda_{\text{ex}} = 284 \text{ nm}$ for 2<br>$\lambda_{\text{em}} = 361 \text{ nm}$ for 2 | $\lambda_{\text{ex}} = 284 \text{ nm}$ for L <sub>1</sub><br>$\lambda_{\text{em}} = 326 \text{ nm}$ for L <sub>1</sub><br>$\lambda_{\text{ex}} = 284 \text{ nm}$ for L <sub>2</sub><br>$\lambda_{\text{em}} = 326 \text{ nm}$ for L <sub>2</sub> | Argentophilic cluster centred emission $\pi^* - \pi$ and/or $\pi^* - \pi$ transmissions          |
| 11 | CrystEng Comm, 2012, 14, 480       | {[Ag(bga)(pzc)]·0.5H <sub>2</sub> O} <sub>n</sub> (1)<br>[Ag <sub>2</sub> (bga) <sub>2</sub> (pzdc)(H <sub>2</sub> O)] <sub>n</sub> (2)<br>bga=benzoguanamine, Hpzc =pyrazine-2-carboxylic acid, H <sub>2</sub> pzdc = pyrazine-2,3-dicarboxylic acid   | $\lambda_{\text{ex}} = 280 \text{ nm}$<br>$\lambda_{\text{em}} = 400 \text{ to } 470 \text{ nm}$ for 1<br>$\lambda_{\text{em}} = 422 \text{ nm}$ for 2   | bga<br>$\lambda_{\text{ex}} = 280 \text{ nm}$<br>$\lambda_{\text{em}} = 376 \text{ and } 435 \text{ nm}$   | Ag(I)- perturbed intraligand (IL) $\pi \rightarrow \pi^*$ transition                             |
| 12 | Inorg. Chem. Commun., 2012, 24, 73 | [Ag(Hcpob)(bpy)] <sub>n</sub> (1) 4-(3'-carboxylphenoxy)benzoic acid (H <sub>2</sub> cpob), 4,4'-bipyridine (bpy)   | $\lambda_{\text{ex}} = 330 \text{ nm}$<br>$\lambda_{\text{em}} = 412 \text{ nm}$ and 465 nm  | H <sub>3</sub> dpob<br>$\lambda_{\text{ex}} = 330 \text{ nm}$<br>$\lambda_{\text{em}} = 465 \text{ nm}$  | $\pi \rightarrow \pi^*$ intraligand transitions or the LMCT                                      |
| 13 | CrystEng                           | {Ag <sub>8</sub> (MDIP) <sub>2</sub> (m-bix)} <sub>n</sub> (2) (m-  | $\lambda_{\text{ex}} = 356 \text{ and } 397 \text{ nm}$  | H <sub>4</sub> MDIP  | Intraligand $\pi -$  |

|    |   |   |  |   |  |
|----|---|---|--|---|--|
|    | <i>Comm,</i><br>2011, 13,<br>1314                     | bix=1,3-bis(imidazol-1-ylmethyl)-<br>benzene)   | $\lambda_{\text{em}} = 469 \text{ nm}$   | $\lambda_{\text{ex}} = 350 \text{ nm}$<br>$\lambda_{\text{em}} = 495 \text{ nm}$  | $\pi^*$ transitions                                      |
| 14 | <i>CrystEng</i><br><i>Comm,</i><br>2008, 10, 1<br>866 | [Ag <sub>2</sub> (L <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ] <sub>n</sub> (2)<br>1,3-bis(triazol-1-ylmethyl)benzene<br>(L <sub>2</sub> )   | $\lambda_{\text{ex}} = 278 \text{ nm}$<br>$\lambda_{\text{em}} = 383 \text{ nm}$   | L <sub>2</sub><br>$\lambda_{\text{ex}} = 276 \text{ nm}$<br>$\lambda_{\text{em}} = 378 \text{ nm}$  | Intra-ligand<br>(n- $\pi^*$ or $\pi-\pi^*$ )<br>emission |
| 15 | <i>Inorg.Che</i><br><i>m.,</i> 2005,<br>44, 1031      | [Ag <sub>2</sub> (bmsb)(ClO <sub>4</sub> ) <sub>2</sub> ] (1),<br>[Ag <sub>2</sub> (bmsb)(H <sub>2</sub> O) <sub>4</sub> ](BF <sub>4</sub> ) <sub>2</sub> (2),<br>[Ag <sub>2</sub> (bdb)(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ] (3)<br>(bmsb=1,4-<br>bis(methylstyryl)benzene,<br>bdb=4,4'-bis(2,5-<br>dimethylstyryl)biphenyl) | $\lambda_{\text{ex}} = 446 \text{ nm}$ for 1<br>$\lambda_{\text{em}} = 485 \text{ nm}$ for 1<br>$\lambda_{\text{ex}} = 444 \text{ nm}$ for 2<br>$\lambda_{\text{em}} = 488 \text{ nm}$ for 2<br>$\lambda_{\text{ex}} = 448 \text{ nm}$ for 3<br>$\lambda_{\text{em}} = 477 \text{ nm}$ for 3 | bmsb<br>$\lambda_{\text{ex}} = 418 \text{ nm}$<br>$\lambda_{\text{em}} = 453,472 \text{ nm}$<br>bdb<br>$\lambda_{\text{ex}} = 419 \text{ nm}$<br>$\lambda_{\text{em}} = 422,462 \text{ nm}$ | $\pi-\pi^*$  |