

## Supporting Information

# Assembly of Silver(I)–Organic Frameworks from Flexible Supramolecular Synthons with Pendant Ethynide Arms Attached to Biphenyl and Phenoxybenzene Skeletons

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**Table S1. X-ray Crystal Data and Structure Refinement for Compounds 1–3.**

|  | <b>1</b>  | <b>2</b>   | <b>3</b>   |
|--|---|--|--|
| formula  | C <sub>19</sub> H <sub>11</sub> Ag <sub>3</sub> F <sub>6</sub> O <sub>5</sub> | C <sub>27</sub> H <sub>16</sub> Ag <sub>6</sub> F <sub>15</sub> NO <sub>12</sub> | C <sub>60</sub> H <sub>44</sub> Ag <sub>6</sub> N <sub>2</sub> O <sub>10</sub> |
| fw   | 756.89  | 1478.63  | 1600.19  |
| cryst syst   | monoclinic  | triclinic  | triclinic  |
| space group  | <i>C2/c</i>   | <i>P</i> $\bar{1}$   | <i>P</i> $\bar{1}$   |
| <i>a</i> (Å)   | 20.9095(16)   | 11.746(2)  | 7.6485(2)  |
| <i>b</i> (Å)   | 19.3423(8)  | 12.454(3)  | 11.1943(3)   |
| <i>c</i> (Å)   | 11.6313(8)  | 14.005(3)  | 30.1822(7)   |
| $\alpha$ (deg)                                       | 90  | 76.38(3)   | 94.781(2)  |
| $\beta$ (deg)  | 119.100(10)   | 74.67(3)   | 92.459(2)  |
| $\gamma$ (deg)                                       | 90  | 87.77(3)   | 90.367(2)  |
| volume (Å <sup>3</sup> )                             | 4110.3(5)   | 1919.6(7)  | 2572.70(11)  |
| <i>Z</i>   | 8   | 2  | 2  |
| <i>D</i> <sub>calc</sub> (g·cm <sup>-3</sup> )       | 2.446   | 2.558  | 2.066  |
| <i>F</i> (000)                                       | 2880  | 1396   | 1560   |
| <i>R</i> (int)                                       | 0.0287  | 0.0280   | 0.0309   |
| GOF  | 1.086   | 1.030  | 1.024  |
| <i>R</i> <sub>1</sub> [ <i>I</i> > 2σ ( <i>I</i> )]  | 0.0484  | 0.0524   | 0.0542   |
| <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ ( <i>I</i> )] | 0.1214  | 0.1180   | 0.1253   |
| <i>R</i> <sub>1</sub> (all data)                     | 0.0619  | 0.0594   | 0.0709   |
| <i>wR</i> <sub>2</sub> (all data)                    | 0.1298  | 0.1226   | 0.1351   |

**Table S2. X-ray Crystal Data and Structure Refinement for Compounds 4–6.**

|  | <b>4</b>  | <b>5</b>   | <b>6</b>   |
|--|---|--|--|
| formula  | C <sub>23</sub> H <sub>11</sub> Ag <sub>5</sub> F <sub>12</sub> O <sub>10</sub> | C <sub>36</sub> H <sub>22</sub> Ag <sub>5</sub> F <sub>9</sub> O <sub>10</sub> | C <sub>82</sub> H <sub>54</sub> Ag <sub>8</sub> F <sub>18</sub> N <sub>8</sub> O <sub>14</sub> |
| fw   | 1214.67   | 1324.89  | 2580.29  |
| cryst syst                                     | monoclinic  | monoclinic   | monoclinic   |
| space group                                    | <i>P2</i> <sub>1</sub> / <i>c</i>   | <i>C2/c</i>  | <i>P2</i> <sub>1</sub> / <i>c</i>  |
| <i>a</i> (Å)                                   | 9.0069(18)  | 32.536(6)  | 13.8833(14)  |
| <i>b</i> (Å)                                   | 23.389(5)   | 11.670(2)  | 24.923(3)  |
| <i>c</i> (Å)                                   | 16.537(5)   | 26.226(5)  | 13.0817(13)  |
| $\alpha$ (deg)                                 | 90  | 90   | 90   |
| $\beta$ (deg)                                  | 118.56(2)   | 127.60(3)  | 114.308(2)   |
| $\gamma$ (deg)                                 | 90  | 90   | 90   |
| volume (Å <sup>3</sup> )                       | 3059.8(13)  | 7890(2)  | 4125.1(7)  |
| <i>Z</i>                                       | 4   | 8  | 2  |
| <i>D</i> <sub>calc</sub> (g·cm <sup>-3</sup> ) | 2.637   | 2.231  | 2.077  |
| <i>F</i> (000)                                 | 2288  | 5072   | 2504   |
| <i>R</i> (int)                                 | 0.0537  | 0.0993   | 0.0886   |

|                        |        |        |        |
|------------------------|--------|--------|--------|
| GOF                    | 1.101  | 1.082  | 1.003  |
| $R_1[I > 2\sigma(I)]$  | 0.0727 | 0.1225 | 0.0270 |
| $wR_2[I > 2\sigma(I)]$ | 0.1752 | 0.4347 | 0.0645 |
| $R_1$ (all data)       | 0.0854 | 0.1495 | 0.0345 |
| $wR_2$ (all data)      | 0.1855 | 0.4614 | 0.0671 |

**Table S3.** Selected Bond Lengths (Å) for Complexes **1–6<sup>a</sup>**

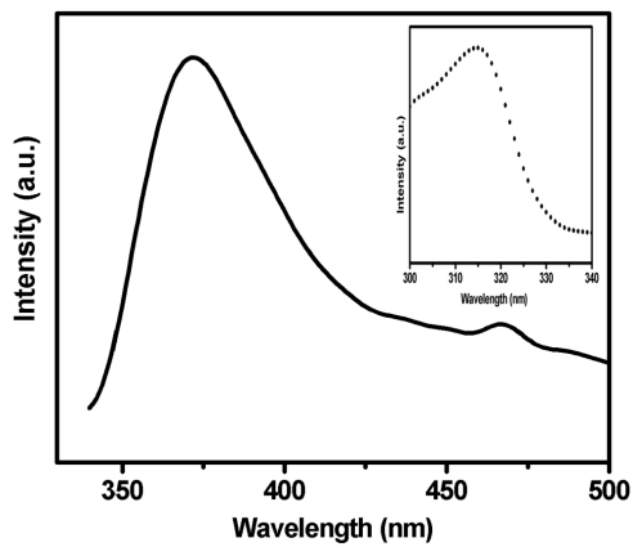
| 1             |            |               |            |               |            |
|---------------|------------|---------------|------------|---------------|------------|
| C1≡C2         | 1.202(7)   | Ag1–C1        | 2.122(6)   | Ag2–C1        | 2.293(7)   |
| Ag2–C2        | 2.654(8)   | Ag3–C1        | 2.371(7)   | Ag3–C2        | 2.843(9)   |
| Ag2–C9        | 2.989(9)   | Ag3–C5#2      | 2.499(7)   | Ag3–C6#2      | 2.690(8)   |
| Ag1–Ag1#1     | 3.134(10)  | Ag1–Ag1#2     | 3.250(11)  | Ag1–Ag2       | 2.964(9)   |
| Ag1–Ag2#2     | 3.108(9)   | Ag2–Ag3#2     | 3.268(9)   |               |            |
| 2             |            |               |            |               |            |
| C1≡C2         | 1.207(11)  | Ag1–C1        | 2.169(7)   | Ag2–C1        | 2.227(7)   |
| Ag2–C2        | 2.999(6)   | Ag3–C1        | 2.672(7)   | Ag3–C2        | 2.845(6)   |
| Ag4–C1        | 2.455(7)   | Ag4–C2        | 2.644(8)   | Ag5–C1        | 2.348(7)   |
| Ag5–C2        | 3.049(5)   | Ag6–C4        | 2.894(2)   | Ag6–C5        | 2.912(1)   |
| Ag3#1–C12     | 2.776(11)  | Ag6#1–C14     | 3.029(11)  | Ag1…Ag2       | 2.787(11)  |
| Ag1…Ag3       | 3.162(13)  | Ag1…Ag4       | 2.907(12)  | Ag1…Ag5       | 2.983(12)  |
| Ag2…Ag3       | 3.185(17)  | Ag2…Ag5       | 3.073(14)  | Ag4…Ag5       | 3.324(17)  |
| Ag3…Ag6       | 2.938(16)  |               |            |               |            |
| 3             |            |               |            |               |            |
| C1≡C2         | 1.211(9)   | C16≡C17       | 1.216(7)   | C31≡C32       | 1.198(9)   |
| C46≡C47       | 1.204(9)   | Ag1–C1        | 2.089(6)   | Ag1–C46       | 2.093(6)   |
| Ag2–C1        | 2.306(7)   | Ag2–C2        | 2.676(7)   | Ag2–C16#4     | 2.273(7)   |
| Ag3–C46       | 2.216(7)   | Ag3–C16#2     | 2.277(7)   | Ag3–C17#2     | 2.547(6)   |
| Ag3–C47       | 2.685(7)   | Ag4–C46       | 2.275(7)   | Ag4–C31       | 2.291(7)   |
| Ag5–C31       | 2.100(7)   | Ag5–C16       | 2.105(6)   | Ag6–C1#2      | 2.256(7)   |
| Ag6–C32       | 2.571(7)   | Ag6–C2#2      | 2.673(6)   | Ag6–C31       | 2.262(7)   |
| Ag1…Ag6#2     | 2.985(9)   | Ag1…Ag4       | 3.061(9)   | Ag1…Ag5#3     | 3.231(7)   |
| Ag1…Ag2       | 3.296(8)   | Ag1…Ag3       | 2.981(8)   | Ag2…Ag5#4     | 3.099 (10) |
| Ag3…Ag5#2     | 3.053(9)   | Ag4…Ag5       | 3.229(10)  | Ag5…Ag6       | 2.991(8)   |
| 4             |            |               |            |               |            |
| C1≡C2         | 1.205(14)  | Ag1–C1        | 2.214(10)  | Ag2–C1        | 2.308(10)  |
| Ag2#3–C1      | 2.601(10)  | Ag2#3–C2      | 2.591(11)  | Ag3#2–C1      | 2.309(10)  |
| Ag3#2–C2      | 2.507(11)  | Ag4#1–C1      | 2.429(10)  | Ag4#1–C2      | 2.971(9)   |
| Ag4#1–C5      | 2.683(12)  | Ag4#1–C6      | 2.684(12)  | Ag5#4–C13     | 2.518(3)   |
| Ag5#4–C14     | 2.523(2)   | Ag1…Ag2       | 2.7941(14) | Ag(1)…Ag(4)#1 | 2.9492(16) |
| Ag(1)…Ag(3)#2 | 2.9937(14) | Ag(2)…Ag(2)#3 | 2.822(2)   | Ag(2)…Ag(4)#1 | 3.2142(19) |
| Ag2#3…Ag3#2   | 2.226(2)   |               |            |               |            |
| 5             |            |               |            |               |            |

|          |           |           |           |           |           |
|----------|-----------|-----------|-----------|-----------|-----------|
| C1≡C2    | 1.206(10) | Ag1–C16   | 2.120(2)  | Ag2–C16   | 2.400(2)  |
| Ag2–C17  | 2.796(3)  | Ag2–C1    | 2.220(2)  | Ag2–C2    | 2.603(19) |
| Ag3–C16  | 2.200(2)  | Ag3–C17   | 2.650(2)  | Ag3#2–C8  | 2.744(4)  |
| Ag3#2–C9 | 2.868 (3) | Ag4–C1    | 2.160(2)  | Ag2–C24   | 2.954(2)  |
| Ag4–C20  | 2.815(2)  | Ag5#1–C16 | 2.884(2)  | Ag1…Ag2   | 3.101(3)  |
| Ag1…Ag3  | 2.989(3)  | Ag1…Ag5   | 3.236(3)  | Ag1…Ag5#1 | 3.142(3)  |
| Ag2…Ag4  | 3.240(3)  | Ag2…Ag5   | 3.322(3)  | Ag3…Ag4   | 3.118(3)  |
| <b>6</b> |           |           |           |           |           |
| C1≡C2    | 1.195(4)  | Ag1–C1    | 2.381(3)  | Ag1–N1    | 2.343(2)  |
| Ag1–N2   | 2.384(2)  | Ag2–C1    | 2.205(3)  | Ag3–C1    | 2.417(3)  |
| Ag3–C2   | 2.646(3)  | Ag4–C1    | 2.184(3)  | Ag4–C2    | 2.974(4)  |
| Ag4–N3   | 2.185(3)  | Ag4–N4    | 2.371(3)  |           |           |
| Ag1…Ag2  | 2.927(4)  | Ag1…Ag3   | 2.941(4)  | Ag1…Ag4   | 2.859(5)  |
| Ag2…Ag3  | 3.015(4)  | Ag2…Ag4   | 2.828 (6) | Ag2…Ag3#1 | 3.091 (4) |

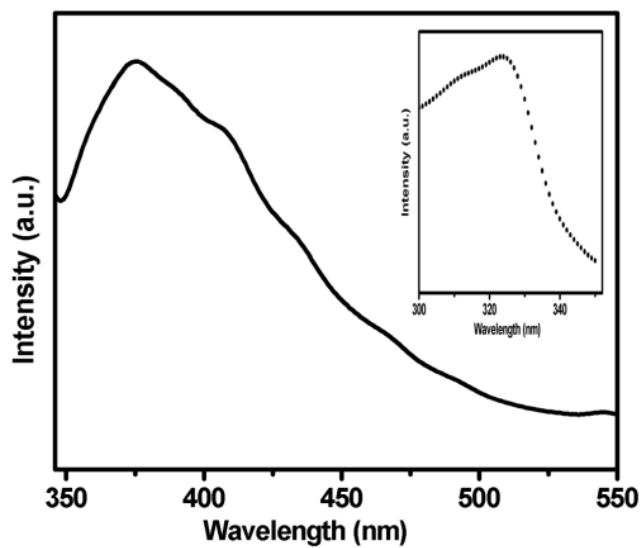
“Symmetry transformations used to generate equivalent atoms: #1  $-x, -y, 2-z$ ; #2  $-x, y, 1.5-z$  for **1**, #1  $2-x, 2-y, -z$  for **2**; #2  $-x, -y+2, -z$ ; #3  $-x+1, -y+2, -z$ ; #4  $x, y-1, z$  for **3**; #1  $1+x, y, z$ ; #2  $-x, 2-y, 1-z$ ; #3  $1-x, 2-y, 1-z$  for **4**; #1  $1/2-x, -1/2+y, 1/2-z$ ; #2  $1/2-x, 1/2+y, 1/2-z$  for **5**; #1  $-x, -y+1, -z+1$ ; #2  $x, y, z-1$  for **6**.

**Table S4.** Emission Maximums and Excitation Wavelengths (nm)

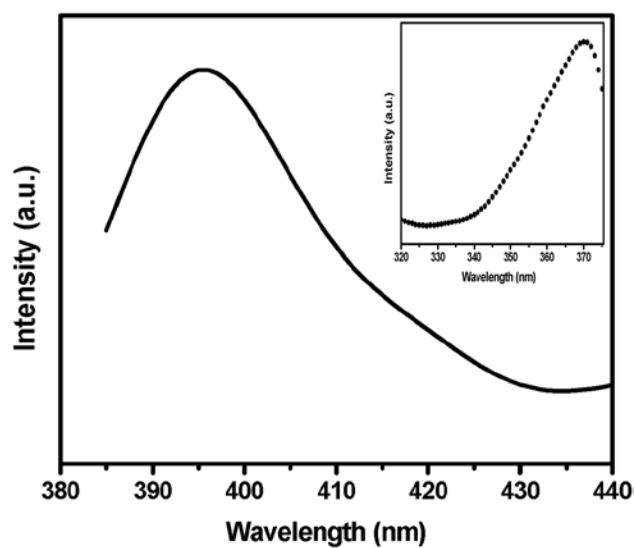
|           | $\lambda_{\text{ex}}$ (nm) | $\lambda_{\text{em}}$ (nm) |
|-----------|----------------------------|----------------------------|
| Ligand    |                            |                            |
| HL1       | 314                        | 372                        |
| HL2       | 325                        | 375                        |
| Compounds |                            |                            |
| <b>1</b>  | 369                        | 396                        |
| <b>2</b>  | 349                        | 373                        |
| <b>3</b>  | 325                        | 367                        |
| <b>4</b>  | 328                        | 396,415                    |
| <b>5</b>  | 321, 357                   | 438                        |
| <b>6</b>  | 301                        | 373                        |



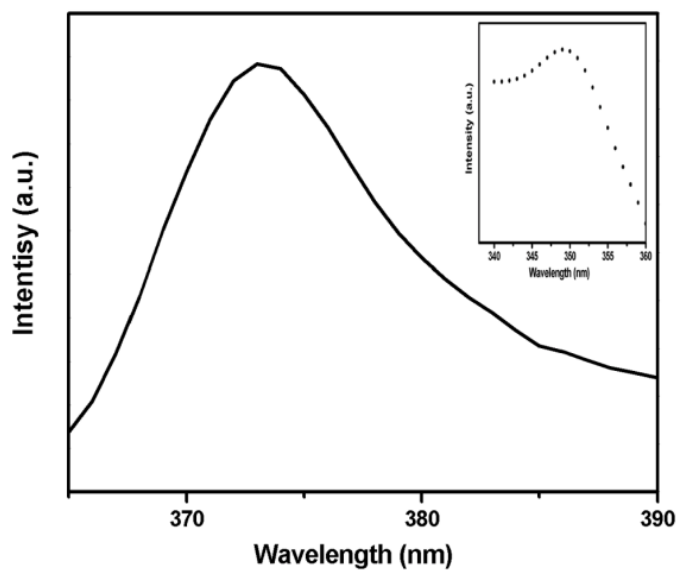
**Fig. S1.** Solid state excitation and emission spectra of ligand HL1 at room temperature.



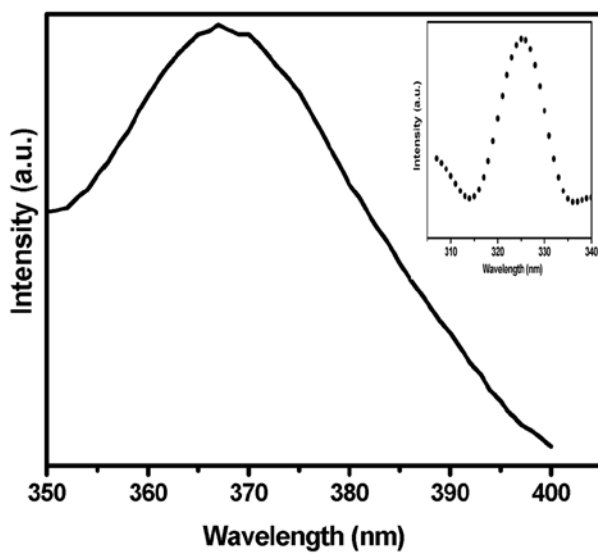
**Fig. S2.** Solid state excitation and emission spectra of ligand HL2 at room temperature.



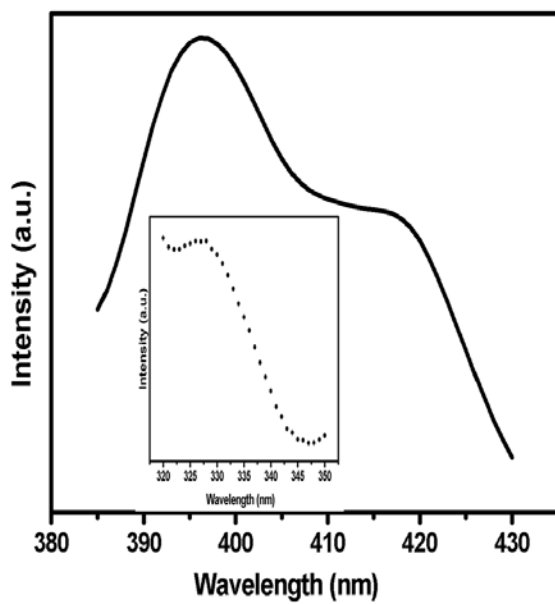
**Fig. S3.** Solid state excitation and emission spectra of complex **1** at room temperature.



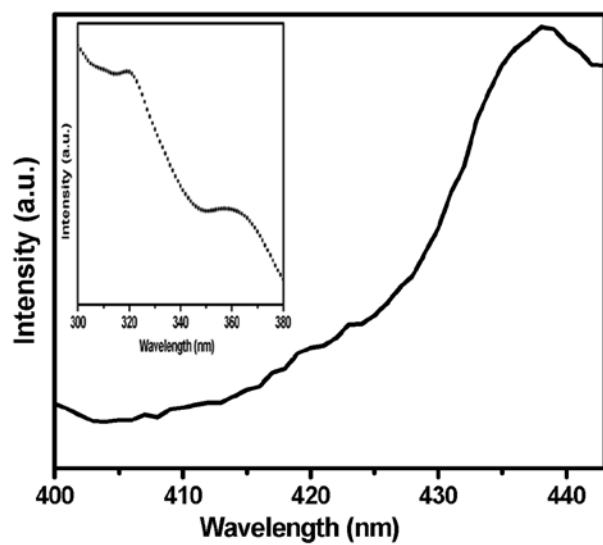
**Fig. S4.** Solid state excitation and emission spectra of complex **2** at room temperature.



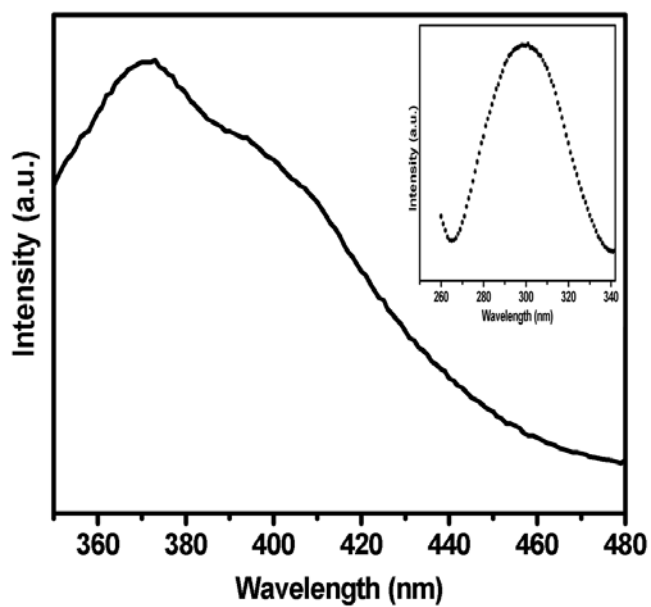
**Fig. S5.** Solid state excitation and emission spectra of complex **3** at room temperature.



**Fig. S6.** Solid state excitation and emission spectra of complex **4** at room temperature.



**Fig. S7.** Solid state excitation and emission spectra of complex **5** at room temperature.



**Fig. S8.** Solid state excitation and emission spectra of complex **6** at room temperature.