

**Supplementary information for**

**From Chain to Framework: Atomically Precise Silver Cluster-Assembled**

**Architectures**

Xiaolin Liu,<sup>‡a,b</sup> Taeyoung Ki,<sup>‡a,b</sup> Seungwoo Yoo,<sup>a,b</sup> Guocheng Deng,<sup>\*a,b</sup> Megalamane S. Bootharaju,<sup>\*a,b,c</sup> and Taeghwan Hyeon<sup>\*a,b</sup>

<sup>a</sup>Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 08826, Republic of Korea.

<sup>b</sup>School of Chemical and Biological Engineering, and Institute of Chemical Processes, Seoul National University, Seoul 08826, Republic of Korea.

<sup>c</sup>Centre for Nano and Soft Matter Sciences (CeNS), Shivanapura, Bengaluru 562162, India

\*Email: gcdeng@snu.ac.kr, msbootharaju@snu.ac.kr, thyeon@snu.ac.kr

<sup>‡</sup>These authors contributed equally to this work.

## EXPERIMENTAL SECTION

**Reagents.** Silver nitrate and triethylamine were purchased from Sigma-Aldrich. Silver(I) trifluoroacetate, 3,3'-bipyridyl, 4,4'-dipyridyl sulfide, 4,4'-trimethylene dipyridine, *tert*-butyl mercaptan and 4-nitrophenol were purchased from TCI. Dichloromethane, acetonitrile, acetone, ethanol and diethyl ether were purchased from Samchun. The water used in all experiments was ultrapure. All reagents were used as received without further purification.

**Synthesis of silver *tert*-butylthiolate (AgS<sup>t</sup>Bu).** AgS<sup>t</sup>Bu was synthesized following previous reports.<sup>[1,2]</sup>

### Synthesis of 1D Ag<sub>12</sub>-Py<sub>2</sub>S

Add 20 mg of AgS<sup>t</sup>Bu and 20 mg of CF<sub>3</sub>COOAg to 2 mL of acetonitrile solution in a glass vial and stir continuously at room temperature until the solution becomes clear. Dissolve 9.5 mg of Py<sub>2</sub>S linker in another glass vial containing 2 mL of ethanol. Gradually add the linker solution dropwise to the other solution. After allowing the mixture to stand for one week, rod-shaped colorless crystals were obtained with a yield of ~39% (based on Ag).

### Synthesis of 2D Ag<sub>12</sub>-bpm

Add 20 mg of AgS<sup>t</sup>Bu and 20 mg of CF<sub>3</sub>COOAg to 2 mL of acetone solution in a glass vial and stir continuously at room temperature until the solution becomes clear. Dissolve 20 μL of bpm linker in another glass vial containing 2 mL of ethanol. Gradually add the linker solution dropwise to the other solution. After allowing the mixture to stand for two weeks, plate-shaped crystals were obtained with a yield of ~41% (based on Ag).

### Synthesis of 3D Ag<sub>12</sub>-tmdp

Add 20 mg of AgS<sup>t</sup>Bu and 20 mg of CF<sub>3</sub>COOAg to 2 mL of acetonitrile solution in a glass vial and stir continuously at room temperature until the solution becomes clear. Dissolve 29 mg of tmdp linker in another glass vial containing 2 mL of ethanol. Gradually add the linker solution dropwise to the other solution, after allowing the mixture to stand for two weeks, block-shaped crystals were obtained with a yield of ~49% (based on Ag).

## Characterization

**UV-vis absorption spectroscopy.** The ultraviolet-visible (UV-vis) optical absorption spectra were recorded using Cary 5000 UV-vis-NIR spectrophotometer (Agilent).

**Photoluminescence spectroscopy.** The photoluminescence excitation profiles of silver cluster-assembled materials were recorded using an FLS 980 spectrometer (Edinburgh Instruments).

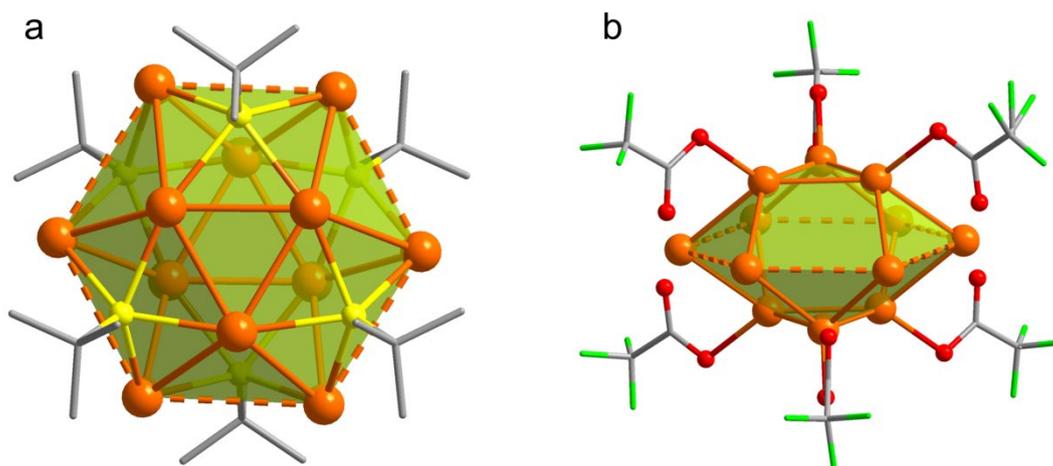
**Powder X-ray diffraction (PXRD).** PXRD data for the samples were recorded using a SmartLab diffractometer (Rigaku) equipped with a Cu Kα (1.5406 Å) X-ray source.

**Single crystal structure analysis.** The diffraction data of 1D Ag<sub>12</sub>-Py<sub>2</sub>S, 2D Ag<sub>12</sub>-bpm and 3D Ag<sub>12</sub>-tmdp were collected by X-ray single crystal diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 100 K on a Rigaku XtaLab Synergy R system. The data were processed using CrysAlis<sup>Pro</sup>.<sup>[3]</sup> The structure was solved and refined using Full-matrix least-squares based on

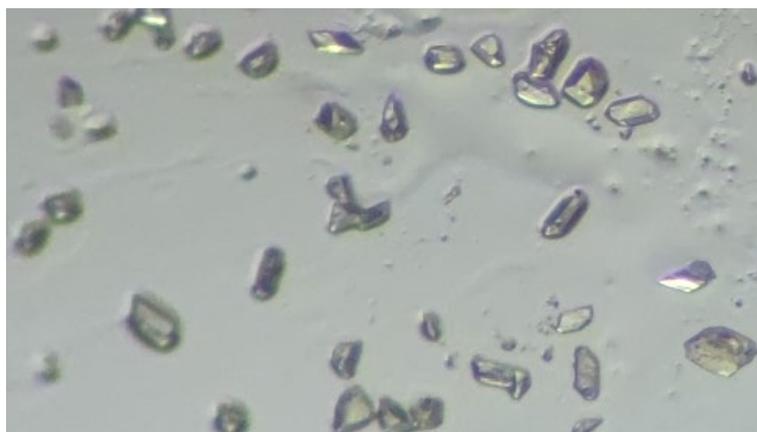
$F^2$  with program ShelXT and ShelXL within Olex2.<sup>[4-6]</sup> The electron densities corresponding to the disordered solvent molecules in the void were flattened by SQUEEZE procedure in PLATON. More refined data are provided in Tables S1-S3. CCDC 2450210, 2450211 and 2450418 contain the supplementary crystallographic data for this paper.

**Van der Waals surfaces calculation.** The total and Ag-contributed van der Waals surface areas were calculated using the Multiwfn program with an electron density isosurface value of 0.002 a.u.

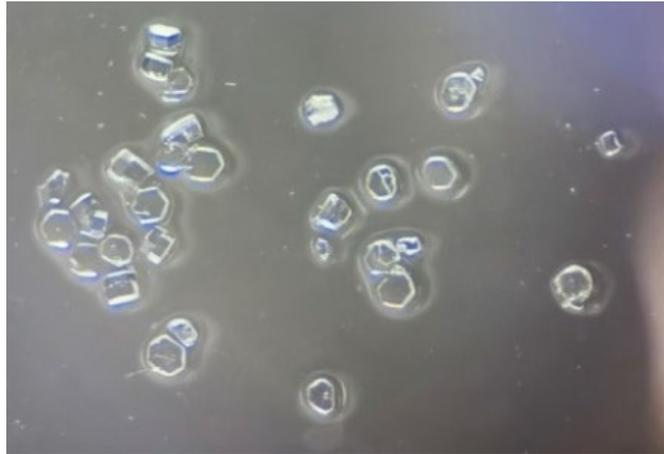
**Catalytic reduction of 4-nitrophenol (4-NP).** To 1 mL of aqueous suspension of silver cluster-assembled catalyst (1 mg), 4-NP (6.4 mg) was added at room temperature, and the mixture was stirred for 10 min. Time-dependent UV-vis absorption spectra were recorded after the addition of solid  $\text{NaBH}_4$  (51.4 mg). The reduction of 4-NP was followed by observing the decrease in absorbance at 400 nm over time.



**Fig. S1** (a) Ag<sub>12</sub> core connection to *tert*-butaneithiol ligand. (b) Ag<sub>12</sub> core connection to trifluoroacetic acid molecule.



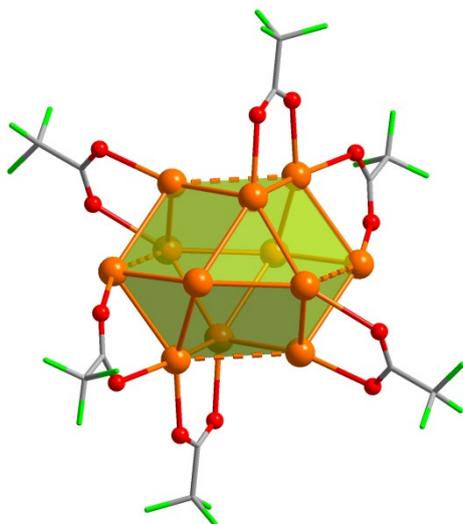
**Fig. S2** Optical microscope image of 1D Ag<sub>12</sub>-Py<sub>2</sub>S.



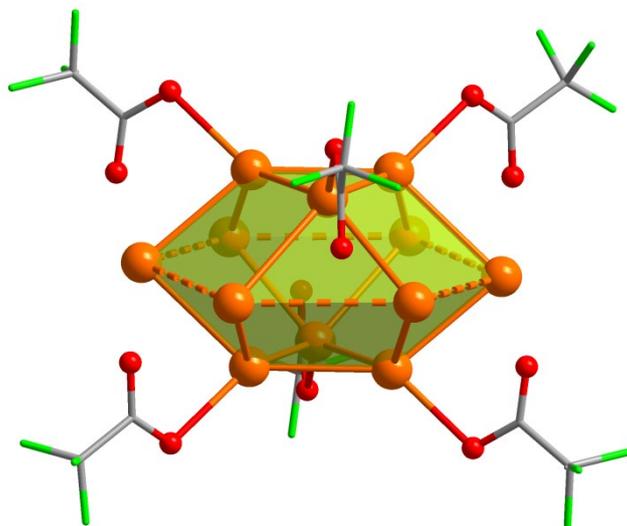
**Fig. S3** Optical microscope image of **2D Ag<sub>12</sub>-bpm**.



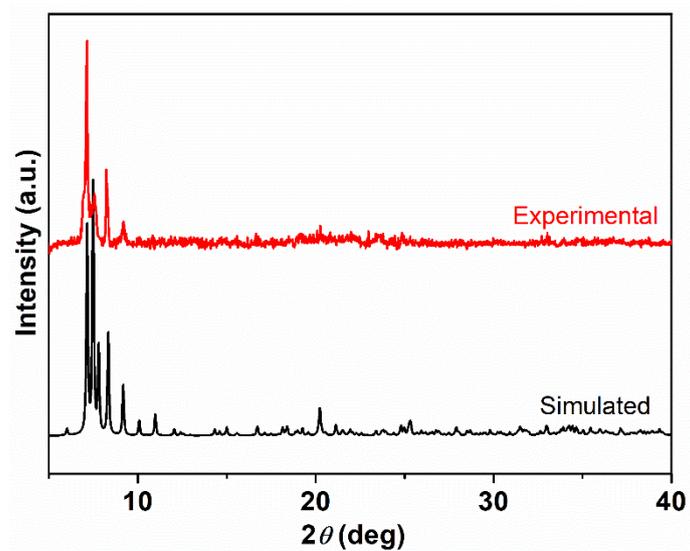
**Fig. S4** Optical microscope image of **3D Ag<sub>12</sub>-tmdp**.



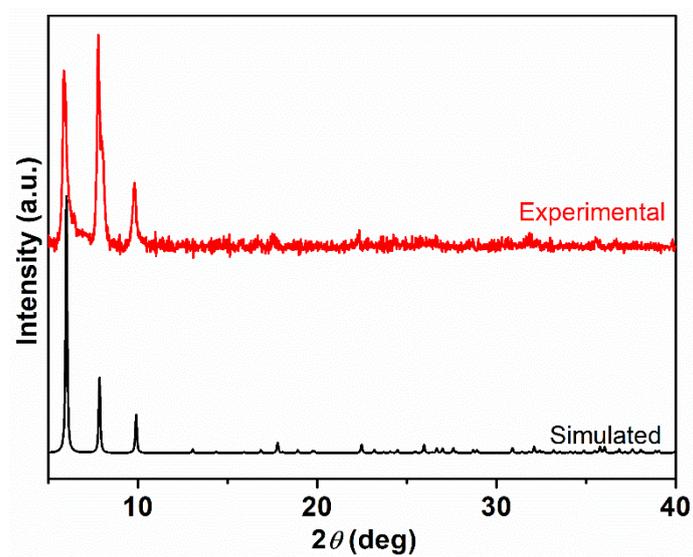
**Fig. S5**  $\text{Ag}_{12}$  core connection to  $\text{CF}_3\text{COO}^-$  ligands of **1D  $\text{Ag}_{12}$ - $\text{Py}_2\text{S}$** . Color legend: orange, Ag; red, O; green, F; gray, C. All hydrogen atoms are omitted for clarity.



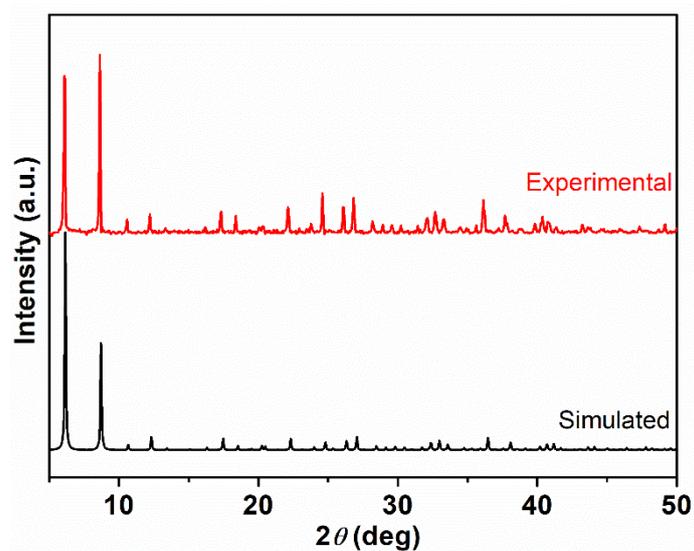
**Fig. S6**  $\text{Ag}_{12}$  core connection to  $\text{CF}_3\text{COO}^-$  ligands of **2D  $\text{Ag}_{12}$ - $\text{bpm}$** . Color legend: orange, Ag; red, O; green, F; gray, C. All hydrogen atoms are omitted for clarity.



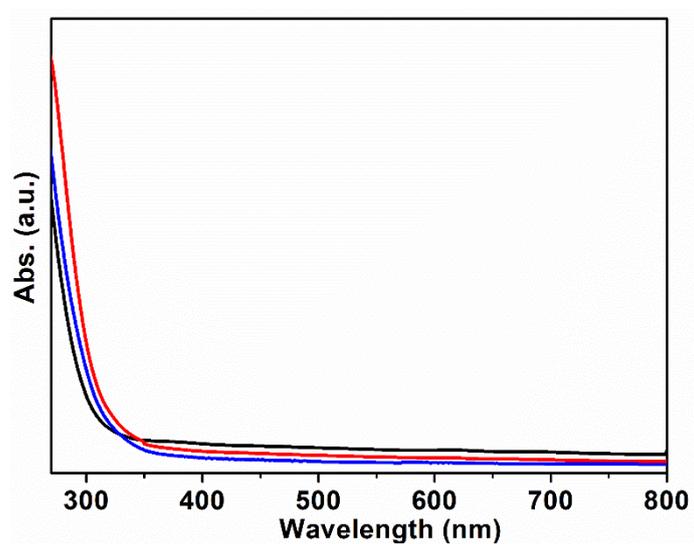
**Fig. S7** Experimental and simulated PXR D of **1D Ag<sub>12</sub>-Py<sub>2</sub>S**.



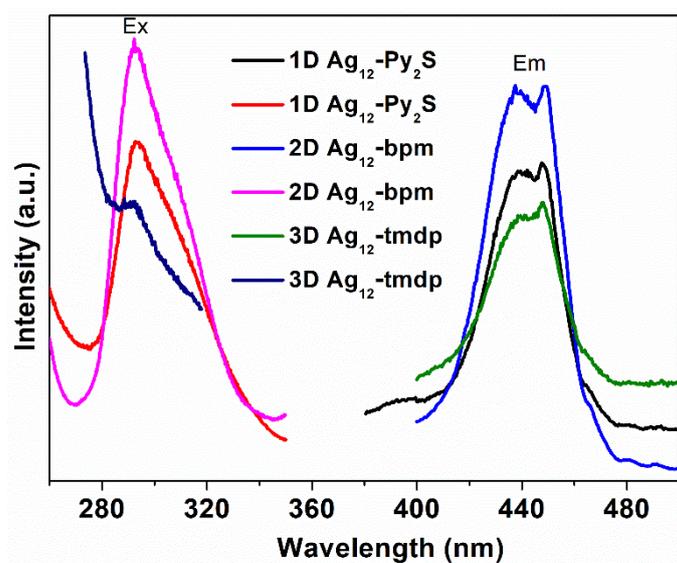
**Fig. S8** Experimental and simulated PXR D of **2D Ag<sub>12</sub>-bpm**.



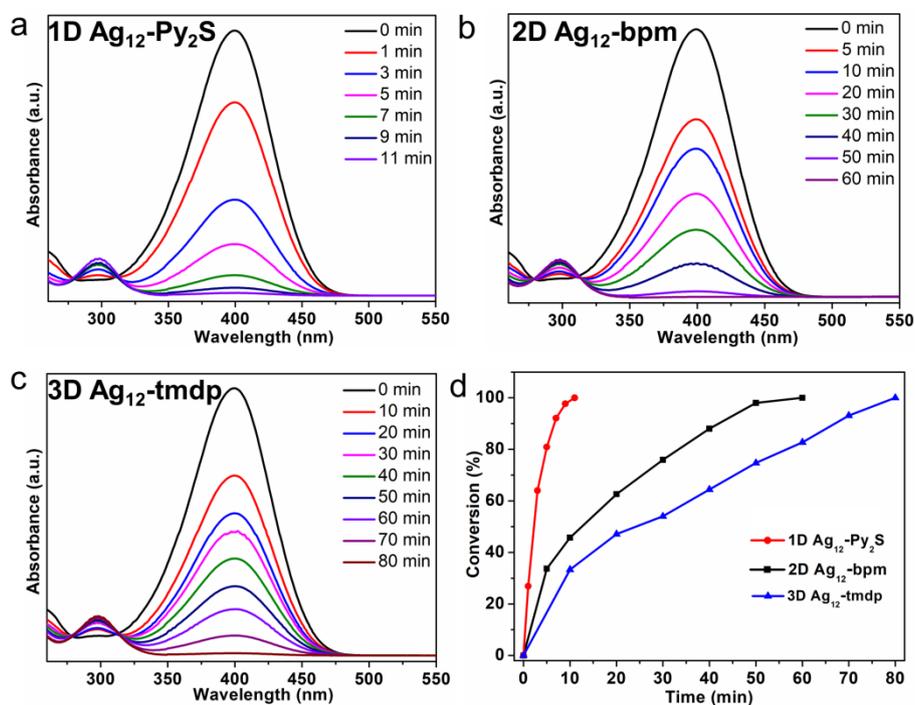
**Fig. S9** Experimental and simulated PXRD of **3D Ag<sub>12</sub>-tmdp**.



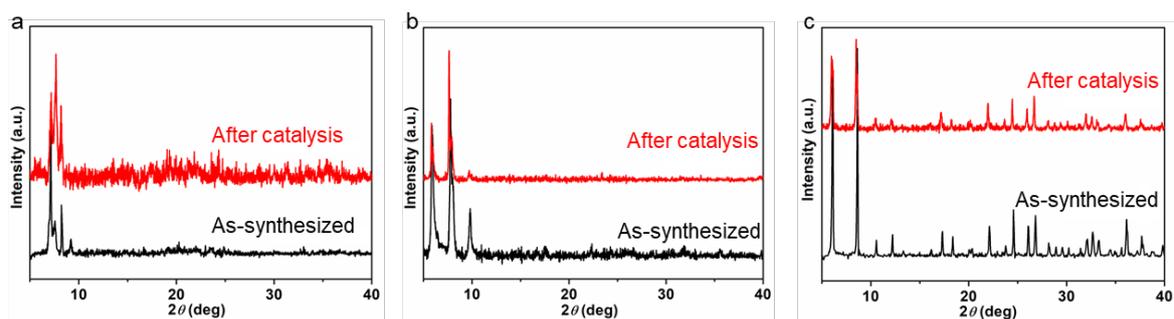
**Fig. S10** Solid-state UV-vis absorption spectra of **1D Ag<sub>12</sub>-Py<sub>2</sub>S** (black line), **2D Ag<sub>12</sub>-bpm** (red line) and **3D Ag<sub>12</sub>-tmdp** (blue line).



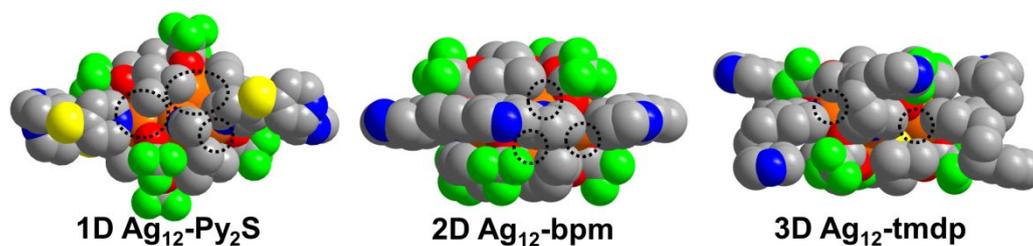
**Fig. S11** Excitation and emission spectra of **1D Ag<sub>12</sub>-Py<sub>2</sub>S**, **2D Ag<sub>12</sub>-bpm** and **3D Ag<sub>12</sub>-tmdp** in solid state.



**Fig. S12** Time-dependent UV-vis absorption spectra showing gradual reduction of 4-NP catalyzed by different catalysts: (a) **1D Ag<sub>12</sub>-Py<sub>2</sub>S**, (b) **2D Ag<sub>12</sub>-bpm** and (c) **3D Ag<sub>12</sub>-tmdp**. (d) The conversion 4-NP to 4-AP versus time in the presence of 1D-3D SCAMs.



**Fig. S13** PXR D of (a) **1D Ag<sub>12</sub>-Py<sub>2</sub>S**, (b) **2D Ag<sub>12</sub>-bpm**, and (c) **3D Ag<sub>12</sub>-tmdp** measured from the as-synthesized single crystals and the solid samples recovered after catalysis. After completion of the reaction, the catalysts were recovered from the reaction mixture by centrifugation, thoroughly washed with water and ethanol, and then dried under vacuum at room temperature prior to PXR D measurements.



**Fig. S14** Exposed silver atoms (black dashed circles) on 1D-3D SCAMs.

**Table S1.** Crystal data and structure refinement for **1D Ag<sub>12</sub>-Py<sub>2</sub>S**.

Identification code	<b>1D Ag<sub>12</sub>-Py<sub>2</sub>S</b>
Empirical formula	C <sub>64</sub> H <sub>82</sub> Ag <sub>12</sub> F <sub>18</sub> N <sub>8</sub> O <sub>12</sub> S <sub>8</sub>
Formula weight	3048.29
Temperature/K	100.01(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.7360(2)
b/Å	19.2691(2)
c/Å	21.2711(2)
α/°	90
β/°	94.3260(10)
γ/°	90
Volume/Å <sup>3</sup>	9292.37(15)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	2.179
μ/mm <sup>-1</sup>	22.296
F(000)	5888.0
Crystal size/mm <sup>3</sup>	0.27 × 0.23 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	9.178 to 130.414
Index ranges	-22 ≤ h ≤ 26, -22 ≤ k ≤ 22, -24 ≤ l ≤ 24
Reflections collected	18692
Independent reflections	7784 [R <sub>in</sub> = 0.1121, R <sub>sigma</sub> = 0.0958]
Data/restraints/parameters	7784/6/561
Goodness-of-fit on F <sup>2</sup>	1.119
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.1019, wR <sub>2</sub> = 0.2631
Final R indexes [all data]	R <sub>1</sub> = 0.1052, wR <sub>2</sub> = 0.2678
Empirical formula	C <sub>64</sub> H <sub>82</sub> Ag <sub>12</sub> F <sub>18</sub> N <sub>8</sub> O <sub>12</sub> S <sub>8</sub>
Largest diff. peak/hole / e Å <sup>-3</sup>	3.95/-2.62

**Table S2.** Crystal data and structure refinement for **2D Ag<sub>12</sub>-bpm**.

Identification code	<b>2D Ag<sub>12</sub>-bpm</b>
Empirical formula	C <sub>66</sub> H <sub>78</sub> Ag <sub>12</sub> F <sub>18</sub> N <sub>6</sub> O <sub>12</sub> S <sub>6</sub>
CCDC number	2450211
Formula weight	2976.14
Temperature/K	100.01(2)
Crystal system	Trigonal
Space group	<b>P<math>\bar{3}</math></b>
a/Å	16.9722(2)
b/Å	16.9722(2)
c/Å	11.2473(2)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	120
Volume/Å <sup>3</sup>	2805.79(8)
Z	1
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	1.761
$\mu$ /mm <sup>-1</sup>	18.100
F(000)	1434.0
Crystal size/mm <sup>3</sup>	0.05×0.04×0.1
Radiation	Cu K $\alpha$ ( $\lambda$ = 1.54184)
2 $\theta$ range for data collection/°	7.86 to 145.198
Index ranges	-20 ≤ h ≤ 17, -21 ≤ k ≤ 20, -13 ≤ l ≤ 10
Reflections collected	12663
Independent reflections	3629 [R <sub>int</sub> = 0.0593, R <sub>sigma</sub> = 0.0552]
Data/restraints/parameters	3629/319/253
Goodness-of-fit on F <sup>2</sup>	1.045
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0472, wR <sub>2</sub> = 0.1247
Final R indexes [all data]	R <sub>1</sub> = 0.0478, wR <sub>2</sub> = 0.1256
Largest diff. peak/hole / e Å <sup>-3</sup>	2.22/-0.94

**Table S3.** Crystal data and structure refinement for **3D Ag<sub>12</sub>-tmdp**.

Identification code	<b>3D Ag<sub>12</sub>-tmdp</b>
Empirical formula	C <sub>75</sub> H <sub>96</sub> Ag <sub>12</sub> F <sub>18</sub> N <sub>6</sub> O <sub>12</sub> S <sub>6</sub>
CCDC number	2450418
Formula weight	3102.37
Temperature/K	100.01(2)
Crystal system	Trigonal
Space group	<b>R<math>\bar{3}c</math></b>
a/Å	28.7264(3)
b/Å	28.7264(3)
c/Å	22.2243(3)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	120
Volume/Å <sup>3</sup>	15882.6(4)
Z	6
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	1.946
$\mu$ /mm <sup>-1</sup>	19.216
F(000)	9.36.0
Crystal size/mm <sup>3</sup>	0.1×0.1×0.05
Radiation	Cu K $\alpha$ ( $\lambda$ = 1.54184)
2 $\theta$ range for data collection/°	8.146 to 141.508
Index ranges	-35 ≤ h ≤ 33, -34 ≤ k ≤ 34, -27 ≤ l ≤ 26
Reflections collected	55884
Independent reflections	3402 [R <sub>int</sub> = 0.1479, R <sub>sigma</sub> = 0.0403]
Data/restraints/parameters	3402/182/209
Goodness-of-fit on F <sup>2</sup>	1.121
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0753, wR <sub>2</sub> = 0.2046
Final R indexes [all data]	R <sub>1</sub> = 0.0757, wR <sub>2</sub> = 0.2050
Largest diff. peak/hole / e Å <sup>-3</sup>	4.35/-1.42

**Table S4.** Calculated van der Waals surface area and percentage of Ag exposure of 1D-3D SCAMs.

$\text{\AA}^2$	1D Ag <sub>12</sub> -Py <sub>2</sub> S	2D Ag <sub>12</sub> -bpm	3D Ag <sub>12</sub> -tmbp
SCAM	1127.64	1232.17	1339.76
Ag	2.93	0.55	0.44
Ag/SCAM	0.26%	0.045%	0.033%

## References

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