

# Surface-exposed silver nanoclusters inside molecular metal oxide cavities

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**Supplementary Table 1.** X-ray crystallographic parameters of **Ag16**, **Ag30** and **Ag30'**.

|                                                             | <b>Ag16</b>                                                                                                       | <b>Ag30</b>                                                                                                       | <b>Ag30'</b>                                                                                                      |
|-------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|
| Formula                                                     | C <sub>128</sub> H <sub>296</sub> N <sub>8</sub> Ag <sub>16</sub> P <sub>8</sub> W <sub>48</sub> O <sub>192</sub> | C <sub>128</sub> H <sub>288</sub> N <sub>8</sub> Ag <sub>30</sub> P <sub>8</sub> W <sub>48</sub> O <sub>184</sub> | C <sub>128</sub> H <sub>288</sub> N <sub>8</sub> Ag <sub>30</sub> P <sub>8</sub> W <sub>48</sub> O <sub>184</sub> |
| Crystal system                                              | Tetragonal                                                                                                        | Tetragonal                                                                                                        | Tetragonal                                                                                                        |
| Space group                                                 | <i>I4/m</i> (#87)                                                                                                 | <i>I4/m</i> (#87)                                                                                                 | <i>I4/m</i> (#87)                                                                                                 |
| <i>a</i> (Å)                                                | 28.4631(2)                                                                                                        | 32.19662(13)                                                                                                      | 32.2989(3)                                                                                                        |
| <i>b</i> (Å)                                                | 28.4631(2)                                                                                                        | 32.19662(13)                                                                                                      | 32.2989(3)                                                                                                        |
| <i>c</i> (Å)                                                | 32.4471(5)                                                                                                        | 27.0415(2)                                                                                                        | 27.2939(4)                                                                                                        |
| $\alpha$ (deg)                                              | 90                                                                                                                | 90                                                                                                                | 90                                                                                                                |
| $\beta$ (deg)                                               | 90                                                                                                                | 90                                                                                                                | 90                                                                                                                |
| $\gamma$ (deg)                                              | 90                                                                                                                | 90                                                                                                                | 90                                                                                                                |
| <i>V</i> (Å <sup>3</sup> )                                  | 26287.0(5)                                                                                                        | 28031.8(3)                                                                                                        | 28473.5(7)                                                                                                        |
| <i>Z</i>                                                    | 2                                                                                                                 | 2                                                                                                                 | 2                                                                                                                 |
| Temp (K)                                                    | 123(2)                                                                                                            | 100(2)                                                                                                            | 123(2)                                                                                                            |
| $\rho_{\text{calc}}$ (g/cm <sup>-3</sup> )                  | 1.989                                                                                                             | 2.037                                                                                                             | 2.005                                                                                                             |
| <i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | 0.0681                                                                                                            | 0.0686                                                                                                            | 0.0694                                                                                                            |
| <i>wR</i> <sub>2</sub>                                      | 0.2377                                                                                                            | 0.2254                                                                                                            | 0.2498                                                                                                            |
| GOF                                                         | 1.020                                                                                                             | 1.055                                                                                                             | 1.005                                                                                                             |

**Supplementary Table 2.** BVS values for P and W atoms of **Ag16**.

|    |      |    |      |    |      |
|----|------|----|------|----|------|
| P1 | 4.58 | P2 | 4.50 |    |      |
| W1 | 6.16 | W2 | 6.12 | W3 | 6.13 |
| W4 | 6.13 | W5 | 6.12 | W6 | 6.27 |

**Supplementary Table 3.** Results of curve fitting analysis of Ag 3d XPS spectra of **Ag16**, **Ag30** and **Ag30'**.

|              |                 |                   | Binding energy (eV) | FWHM (eV) | Gauss (%) | Area (%) |
|--------------|-----------------|-------------------|---------------------|-----------|-----------|----------|
| <b>Ag16</b>  | Ag <sup>+</sup> | 3d <sub>5/2</sub> | 368.6               | 1.28      | 86        | 58.8     |
|              |                 | 3d <sub>3/2</sub> | 374.6               |           | 83        | 41.2     |
| <b>Ag30</b>  | Ag <sup>0</sup> | 3d <sub>5/2</sub> | 369.1               | 1.26      | 75        | 16.0     |
|              |                 | 3d <sub>3/2</sub> | 375.1               |           |           | 10.7     |
|              | Ag <sup>+</sup> | 3d <sub>5/2</sub> | 368.6               |           |           | 44.0     |
|              |                 | 3d <sub>3/2</sub> | 374.6               |           |           | 29.3     |
| <b>Ag30'</b> | Ag <sup>0</sup> | 3d <sub>5/2</sub> | 369.1               | 1.07      | 70        | 27.8     |
|              |                 | 3d <sub>3/2</sub> | 375.1               |           |           | 18.9     |
|              | Ag <sup>+</sup> | 3d <sub>5/2</sub> | 368.7               |           |           | 31.7     |
|              |                 | 3d <sub>3/2</sub> | 374.8               |           |           | 21.6     |

**Supplementary Table 4.** BVS values for P and W atoms of **Ag30**.

|    |      |    |      |    |      |
|----|------|----|------|----|------|
| P1 | 4.82 | P2 | 4.78 |    |      |
| W1 | 6.15 | W2 | 6.13 | W3 | 6.16 |
| W4 | 6.18 | W5 | 6.08 | W6 | 6.23 |

**Supplementary Table 5.** Ag...Ag separations (Å) within {Ag<sub>30</sub>} nanocluster of **Ag30**.

|     |     |      |      |     |     |     |      |     |     |     |      |
|-----|-----|------|------|-----|-----|-----|------|-----|-----|-----|------|
| Ag1 | ... | Ag1  | 3.20 | Ag1 | ... | Ag3 | 3.17 | Ag2 | ... | Ag2 | 3.02 |
| Ag2 | ... | Ag3  | 3.27 | Ag2 | ... | Ag3 | 3.36 | Ag2 | ... | Ag4 | 3.27 |
| Ag2 | ... | Ag4* | 3.27 | Ag3 | ... | Ag4 | 3.21 | Ag3 | ... | Ag5 | 3.37 |
| Ag4 | ... | Ag4* | 3.43 | Ag4 | ... | Ag5 | 2.89 | Ag5 | ... | Ag5 | 3.15 |

**Supplementary Table 6.** BVS parameters for P and W atoms of **Ag30'**.

|     |      |     |      |     |      |
|-----|------|-----|------|-----|------|
| P1A | 5.10 | P2A | 4.68 |     |      |
| P1B | 4.85 | P2B | 4.52 |     |      |
| W1A | 5.92 | W2A | 6.13 | W3A | 6.19 |
| W4A | 6.22 | W5A | 6.37 | W6A | 5.95 |
| W1B | 6.15 | W2B | 6.12 | W3B | 6.30 |
| W4B | 6.45 | W5B | 6.14 | W6B | 5.96 |

**Supplementary Table 7.** Ag...Ag separations (Å) within {Ag<sub>30</sub>} nanocluster of **Ag30'**.

|      |     |      |      |      |     |      |      |      |     |      |      |
|------|-----|------|------|------|-----|------|------|------|-----|------|------|
| Ag1  | ... | Ag1  | 3.11 | Ag2A | ... | Ag5A | 2.72 | Ag2A | ... | Ag6B | 2.80 |
| Ag1  | ... | Ag3  | 2.88 | Ag2A | ... | Ag7A | 2.77 | Ag2A | ... | Ag8B | 2.78 |
| Ag1  | ... | Ag4  | 3.06 | Ag2B | ... | Ag6A | 2.75 | Ag2B | ... | Ag5B | 2.65 |
| Ag2A | ... | Ag2A | 2.82 | Ag2B | ... | Ag8A | 2.77 | Ag2B | ... | Ag7B | 2.76 |
| Ag2A | ... | Ag3  | 2.85 | Ag3  | ... | Ag5A | 2.89 | Ag3  | ... | Ag5B | 2.90 |
| Ag2A | ... | Ag4  | 2.88 | Ag3  | ... | Ag6A | 2.83 | Ag3  | ... | Ag6B | 2.78 |
| Ag2B | ... | Ag2B | 2.82 | Ag4  | ... | Ag6A | 2.82 | Ag4  | ... | Ag6B | 2.91 |
| Ag2B | ... | Ag3  | 2.89 | Ag4  | ... | Ag7A | 2.80 | Ag4  | ... | Ag7B | 2.81 |
| Ag2B | ... | Ag4  | 2.90 | Ag5A | ... | Ag6A | 2.88 | Ag5B | ... | Ag6B | 2.91 |
| Ag3  | ... | Ag4  | 2.78 | Ag5A | ... | Ag6A | 2.93 | Ag5B | ... | Ag6B | 2.96 |
|      |     |      |      | Ag5A | ... | Ag7A | 2.82 | Ag5B | ... | Ag7B | 2.88 |
|      |     |      |      | Ag6A | ... | Ag6A | 2.88 | Ag6B | ... | Ag6B | 2.81 |
|      |     |      |      | Ag6A | ... | Ag6A | 2.80 | Ag6B | ... | Ag6B | 3.06 |
|      |     |      |      | Ag6A | ... | Ag7A | 2.83 | Ag6B | ... | Ag7B | 2.87 |
|      |     |      |      | Ag6A | ... | Ag7A | 2.80 | Ag6B | ... | Ag7B | 2.86 |
|      |     |      |      | Ag6A | ... | Ag8A | 2.82 | Ag6B | ... | Ag8B | 2.92 |
|      |     |      |      | Ag7A | ... | Ag8A | 2.81 | Ag7B | ... | Ag8B | 2.85 |

**Supplementary Table 8.** Fitting parameters in Ag K-edge EXAFS of **Ag30** and **Ag30'** ( $R = 2.05\text{--}2.90$  Å and back  $k$  range =  $3\text{--}16$  Å<sup>-1</sup>, measured at  $-263^\circ\text{C}$ ).

|                                               | Bond  | CN <sup>[a]</sup> | $R$ (Å) | $\Delta E$ (eV) | $(DW^{[b]})^2$ (Å <sup>2</sup> ) | $R$ factor (%) |
|-----------------------------------------------|-------|-------------------|---------|-----------------|----------------------------------|----------------|
| <b>Ag30</b>                                   | Ag–Ag | 1.0(2)            | 2.74(4) | −6.9(7)         | $6.8(9)\times 10^{-3}$           | 8.8            |
| <b>Ag30'</b>                                  | Ag–Ag | 3.7(2)            | 2.77(3) | −4.4(4)         | $8.7(4)\times 10^{-3}$           | 7.5            |
| <b>Ag30</b> + H <sub>2</sub> (in solid state) | Ag–Ag | 4.3(2)            | 2.80(2) | −1.6(3)         | $7.1(2)\times 10^{-3}$           | 3.3            |
| <b>Ag30</b> + H <sub>2</sub> (in DMF)         | Ag–Ag | 4.2(2)            | 2.78(3) | −1.3(4)         | $9.2(4)\times 10^{-3}$           | 4.8            |

[a] Coordination number, [b] Debye-Waller factor.

**Supplementary Table 9.** Comparison of the present **Ag30** and **Ag30'**-catalysed nitroarene reductions with the previously reported systems using Ag-catalysts and H<sub>2</sub> as the reductant.

| Catalyst                                                                      | Pressure of H <sub>2</sub><br>(atm) | Temperature<br>(°C) | Substrate            | Yield (%) | Ref               |
|-------------------------------------------------------------------------------|-------------------------------------|---------------------|----------------------|-----------|-------------------|
| <b>Ag30 (0.5 mol%)</b>                                                        | <b>4</b>                            | <b>60</b>           | <b>Nitrobenzene</b>  | <b>97</b> | <b>This study</b> |
| <b>Ag30' (0.5 mol%)</b>                                                       | <b>4</b>                            | <b>60</b>           | <b>Nitrobenzene</b>  | <b>98</b> | <b>This study</b> |
| Ag/PVP (10 mol%)                                                              | 4                                   | 60                  | Nitrobenzene         | <1        | This study        |
| Ag/SiO <sub>2</sub> (~1.2 mol%)                                               | 5                                   | 140                 | 2-Chloronitrobenzene | 20        | S1                |
| Ag/SiO <sub>2</sub> (~1.2 mol%)                                               | 20                                  | 100                 | 2-Chloronitrobenzene | 29        | S1                |
| Ag/SiO <sub>2</sub> (~1.2 mol%)                                               | 20                                  | 140                 | 2-Chloronitrobenzene | 100       | S1                |
| Ag/SiO <sub>2</sub> (~0.9 mol%)                                               | 20                                  | 140                 | Nitrobenzene         | 94        | S1                |
| Ag@C/ZrPP-500<br>(~0.22 mol%)                                                 | 40                                  | 130                 | Nitrobenzene         | 48        | S2                |
| Ag@C/ZrPP-500<br>(~0.22 mol%)                                                 | 40                                  | 140                 | Nitrobenzene         | 69        | S2                |
| Ag@C/ZrPP-500<br>(~0.22 mol%)                                                 | 40                                  | 160                 | Nitrobenzene         | 100       | S2                |
| Ag/Al <sub>2</sub> O <sub>3</sub> (2 mol%)                                    | 30                                  | 160                 | 4-Nitrostyrene       | 96        | S3                |
| Ag nanoparticles@CeO <sub>2</sub><br>(~18 mol%)                               | 6                                   | 110                 | 4-Nitrostyrene       | 98        | S4                |
| Ag@rice husk ash<br>(1.4 mol%)                                                | 5                                   | 100                 | Nitrobenzene         | 11        | S5                |
| Ag@rice husk ash<br>(1.4 mol%)                                                | 10                                  | 100                 | Nitrobenzene         | 97        | S5                |
| Ag/Al <sub>2</sub> O <sub>3</sub> (~0.73 mol%)                                | 17                                  | 100                 | 4-Chloronitrobenzene | 15        | S6                |
| Ag/Al <sub>2</sub> O <sub>3</sub> (~0.73 mol%)<br>+ silver acetate (100 mol%) | 17                                  | 100                 | 4-Chloronitrobenzene | 99        | S6                |

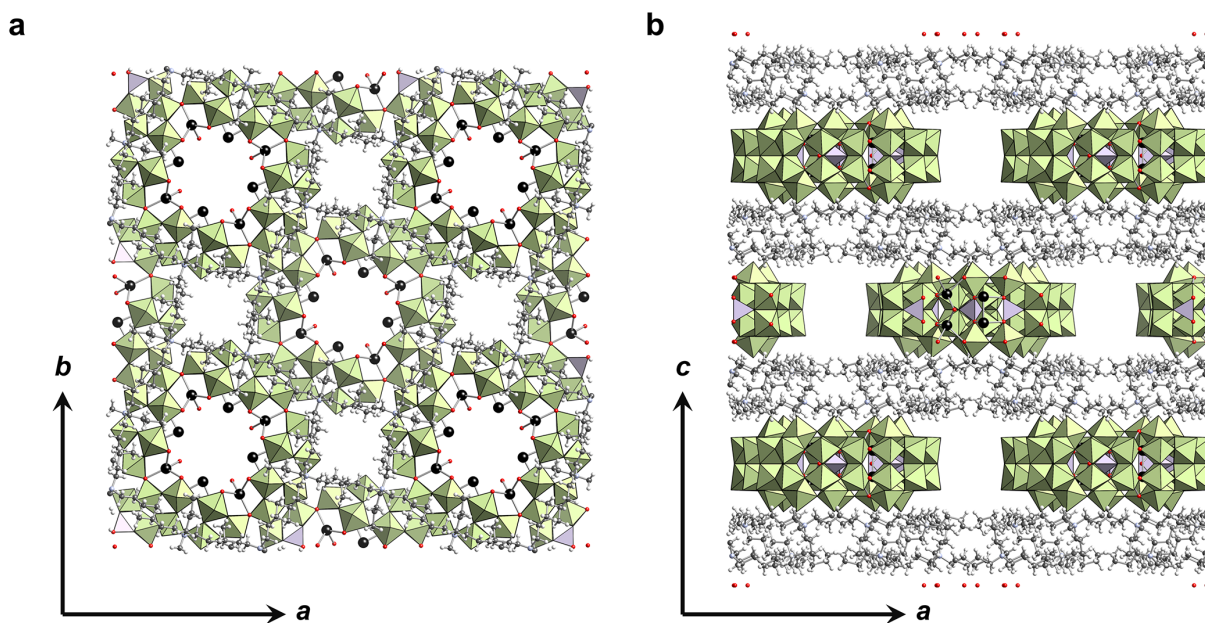
PVP = polyvinylpyrrolidone, ZrPP = zirconium pyrophosphate.

**Supplementary Table 10.** Fitting parameters for Ag–Ag interactions in operand Ag K-edge EXAFS of **Ag30'** (DMA solution) after the reaction with H<sub>2</sub> (4 atm, 60°C), and after the catalytic reaction (*R* range = 2.15–2.80 Å and back *k* range = 3 – 14 Å<sup>−1</sup>, measured at ~25°C).

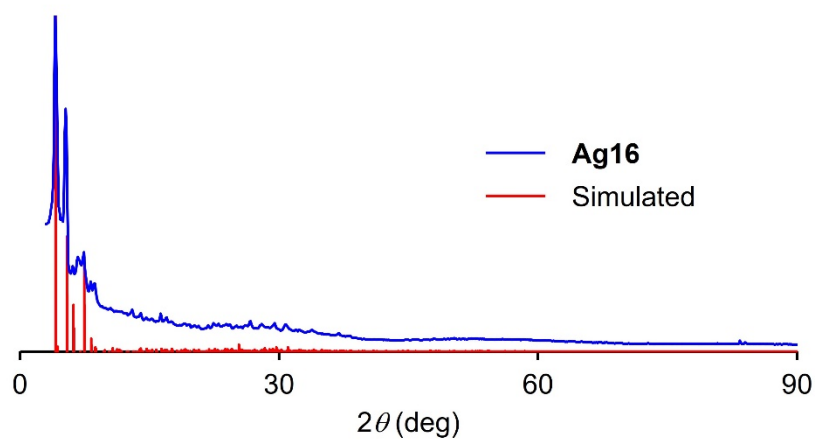
|                                                                       | CN <sup>[a]</sup> | <i>R</i> (Å) | $\Delta E$ (eV) | (DW <sup>[b]</sup> ) <sup>2</sup> (Å <sup>2</sup> ) | <i>R</i> factor (%) |
|-----------------------------------------------------------------------|-------------------|--------------|-----------------|-----------------------------------------------------|---------------------|
| <b>Ag30'</b>                                                          | 2.9(3)            | 2.71(4)      | −7.2(6)         | $1.17(8) \times 10^{-2}$                            | 4.0                 |
| <b>Ag30'</b><br>after the reaction with H <sub>2</sub> <sup>[c]</sup> | 3.1(3)            | 2.72(4)      | −4.2(5)         | $1.12(8) \times 10^{-2}$                            | 3.4                 |
| <b>Ag30'</b><br>after the catalytic reaction <sup>[d]</sup>           | 3.4(3)            | 2.75(4)      | −3.1(5)         | $1.10(7) \times 10^{-2}$                            | 2.4                 |
| Ag foil                                                               | 9.3(3)            | 2.85(2)      | 1.5(3)          | $9.2(2) \times 10^{-3}$                             | 2.4                 |

[a] Coordination number, [b] Debye-Waller factor, [c] **Ag30'** (1 mM), under H<sub>2</sub> (4 atm), 60°C, 1 h (measured at 60°C),

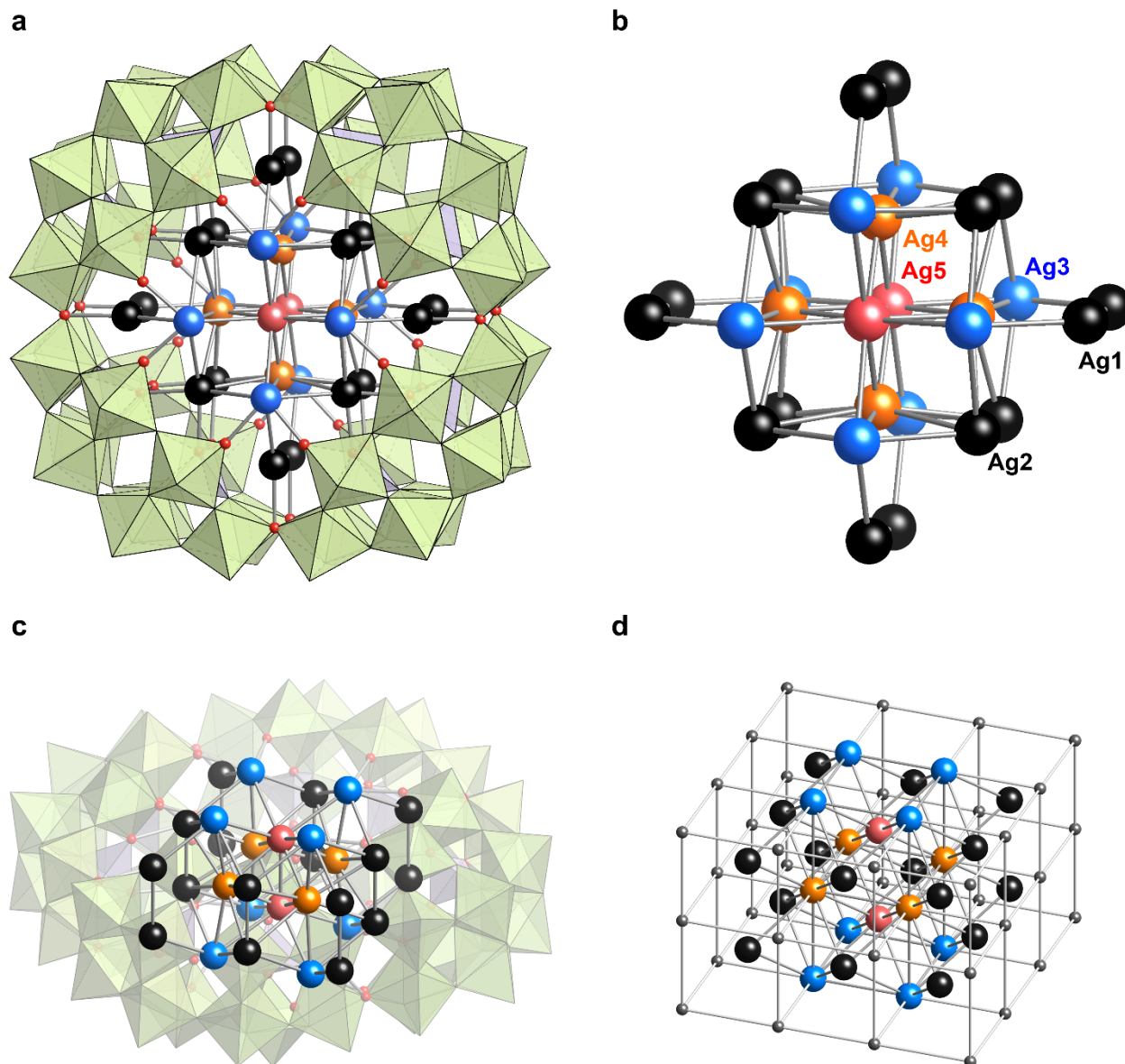
[d] **Ag30'** (0.5 mM; 0.5 mol% for nitrobenzene), nitrobenzene (0.10 M), under H<sub>2</sub> (4 atm), 60°C, 20 h.



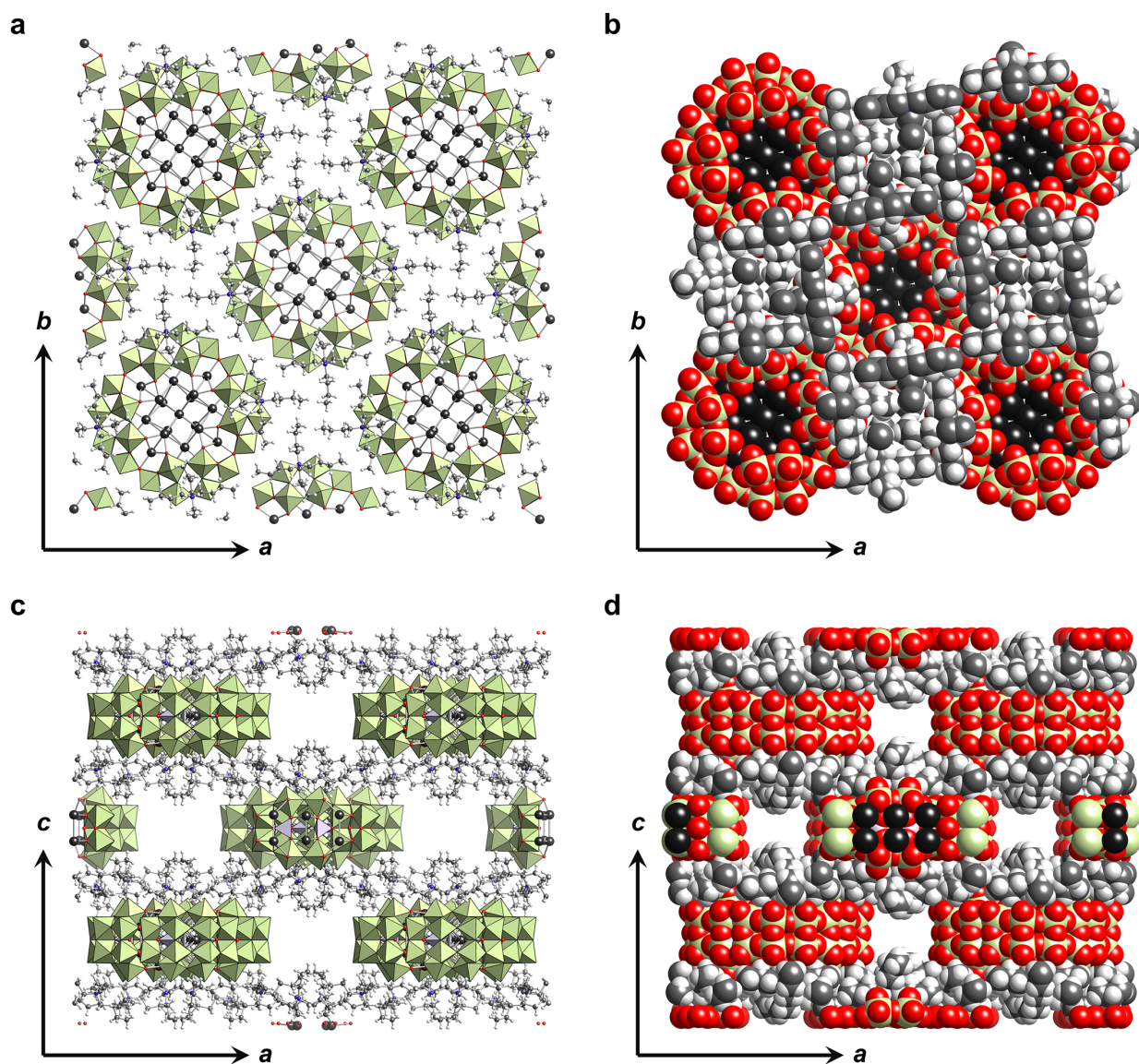
**Supplementary Fig. 1** | Packing of **Ag16** based on X-ray crystallography. **a**, A view (001) from the c-axis and **b**, a view from the b-axis direction.



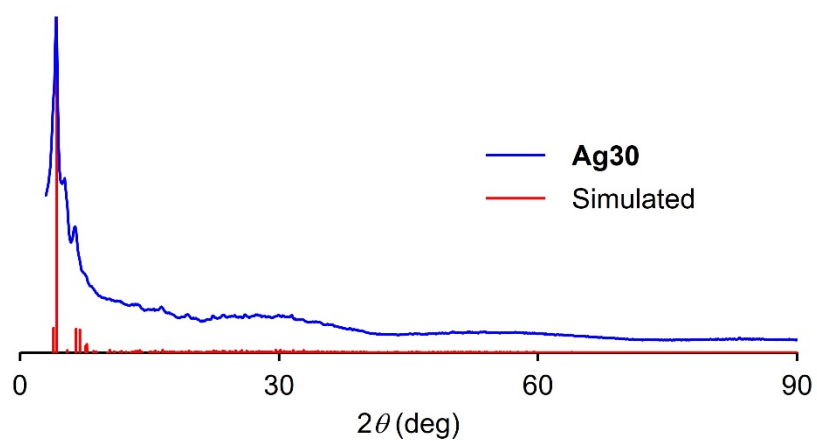
**Supplementary Fig. 2** | Powder X-ray diffraction pattern of **Ag16**. Observed diffraction pattern of **Ag16** (blue line) and simulated pattern (red line).



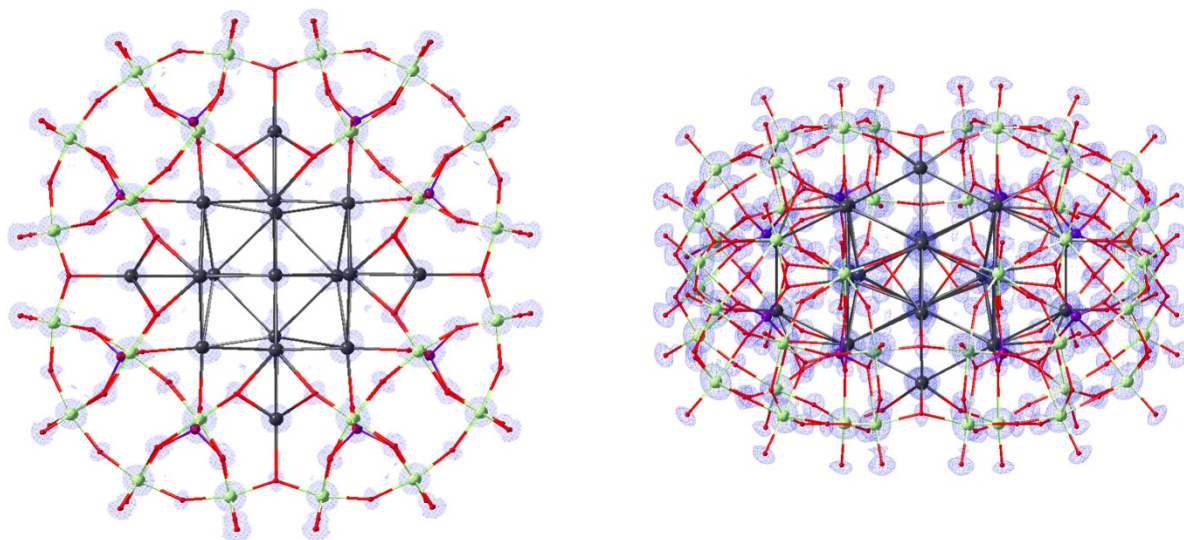
**Supplementary Fig. 3** | Crystal structure of **Ag<sub>30</sub>**. **a, b**, Total anionic structure (**a**) and {Ag<sub>30</sub>}<sup>16+</sup> core structure (**b**) of **Ag<sub>30</sub>** in polyhedral and ball-and-stick model. **c, d**, Structural comparison of {Ag<sub>30</sub>}<sup>22+</sup> core structure of **Ag<sub>30</sub>** (**c**) with **d** body-centered-cubic (bcc) arrangement of Ag atoms (**d**).



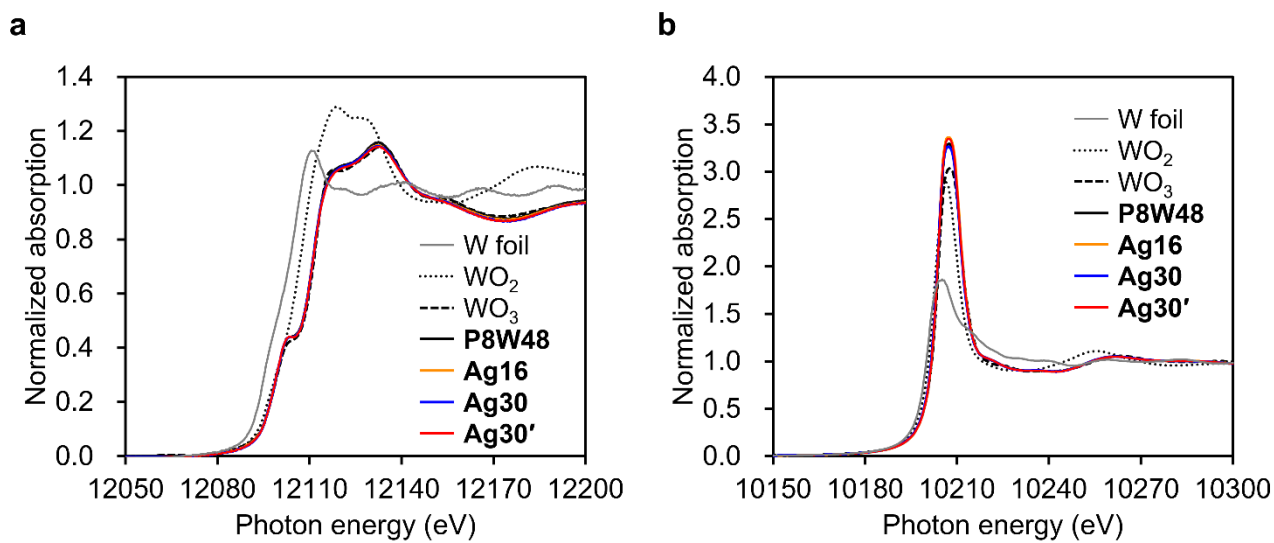
**Supplementary Fig. 4** | Packing of Ag<sub>30</sub> based on X-ray crystallography. **a,b**, Views from the c-axis in polyhedral model (**a**) and spacefill model (**b**). **c,d**, Views from the b-axis in polyhedral model (**c**) and spacefill model (**d**).



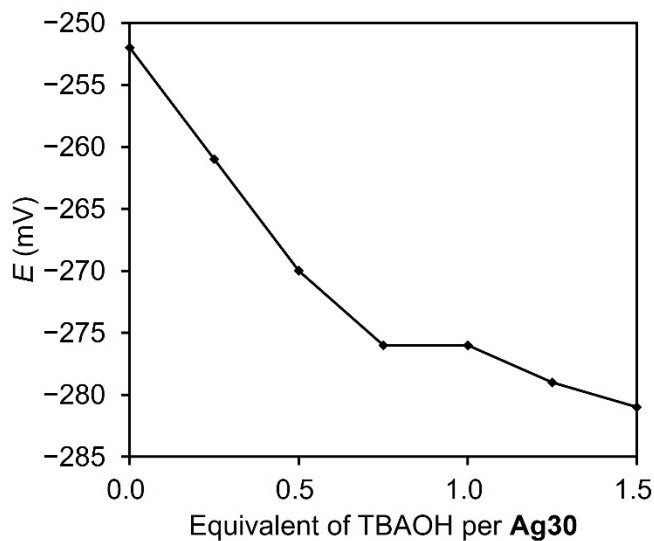
**Supplementary Fig. 5** | Powder X-ray diffraction pattern of **Ag30**. Observed diffraction pattern of **Ag30** (blue line) and simulated pattern (red line).



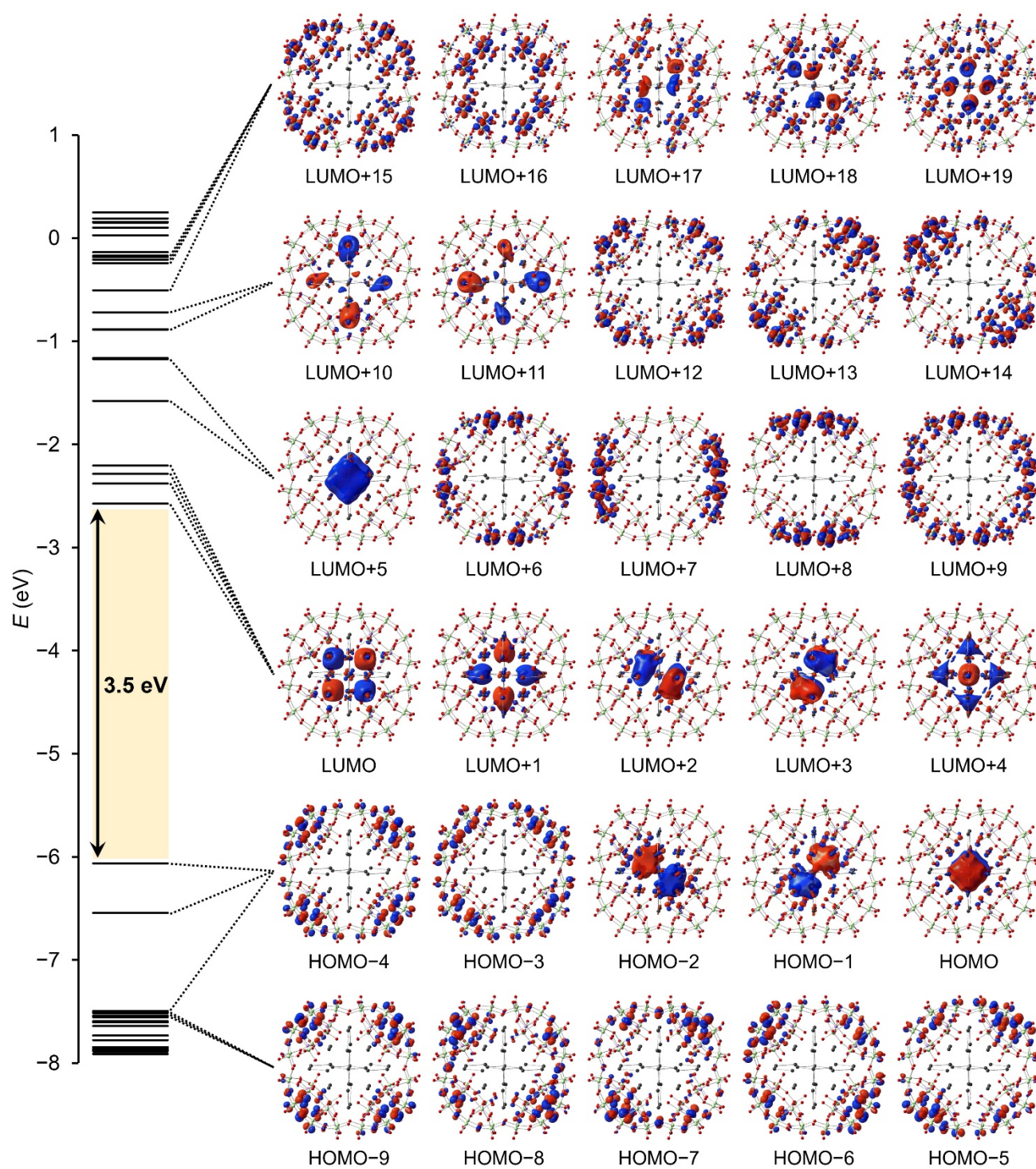
**Supplementary Fig. 6** | Overlay of electron density map ( $F_o$ , contoured at the  $1.0\sigma$  level) and crystal structure of **Ag30**.



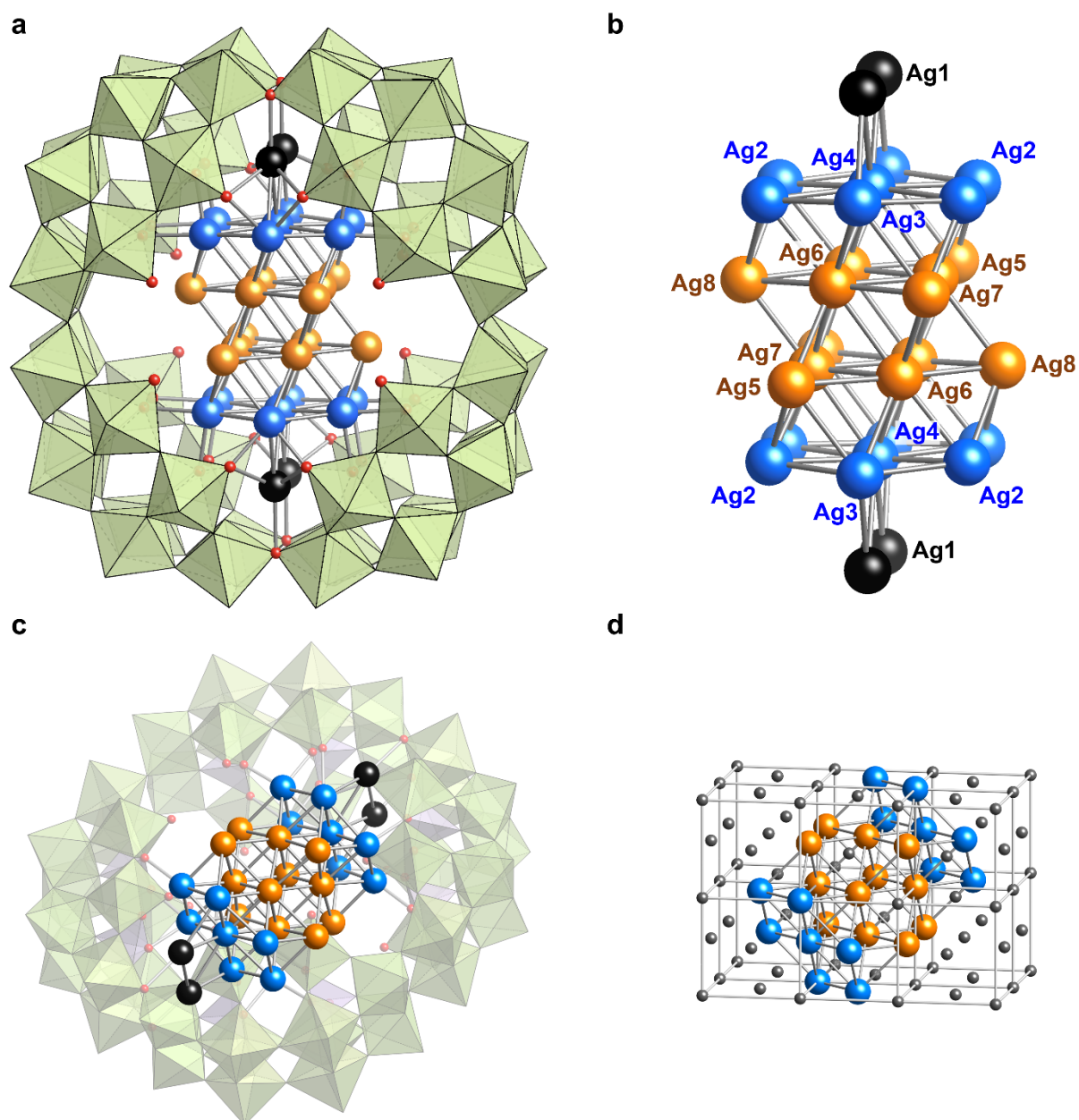
**Supplementary Fig. 7** | W L<sub>1</sub>-edge (a) and W L<sub>3</sub>-edge XANES spectra (b) of **P8W48** (black line), **Ag16** (yellow line), **Ag30** (blue line), and **Ag30'** (red line).



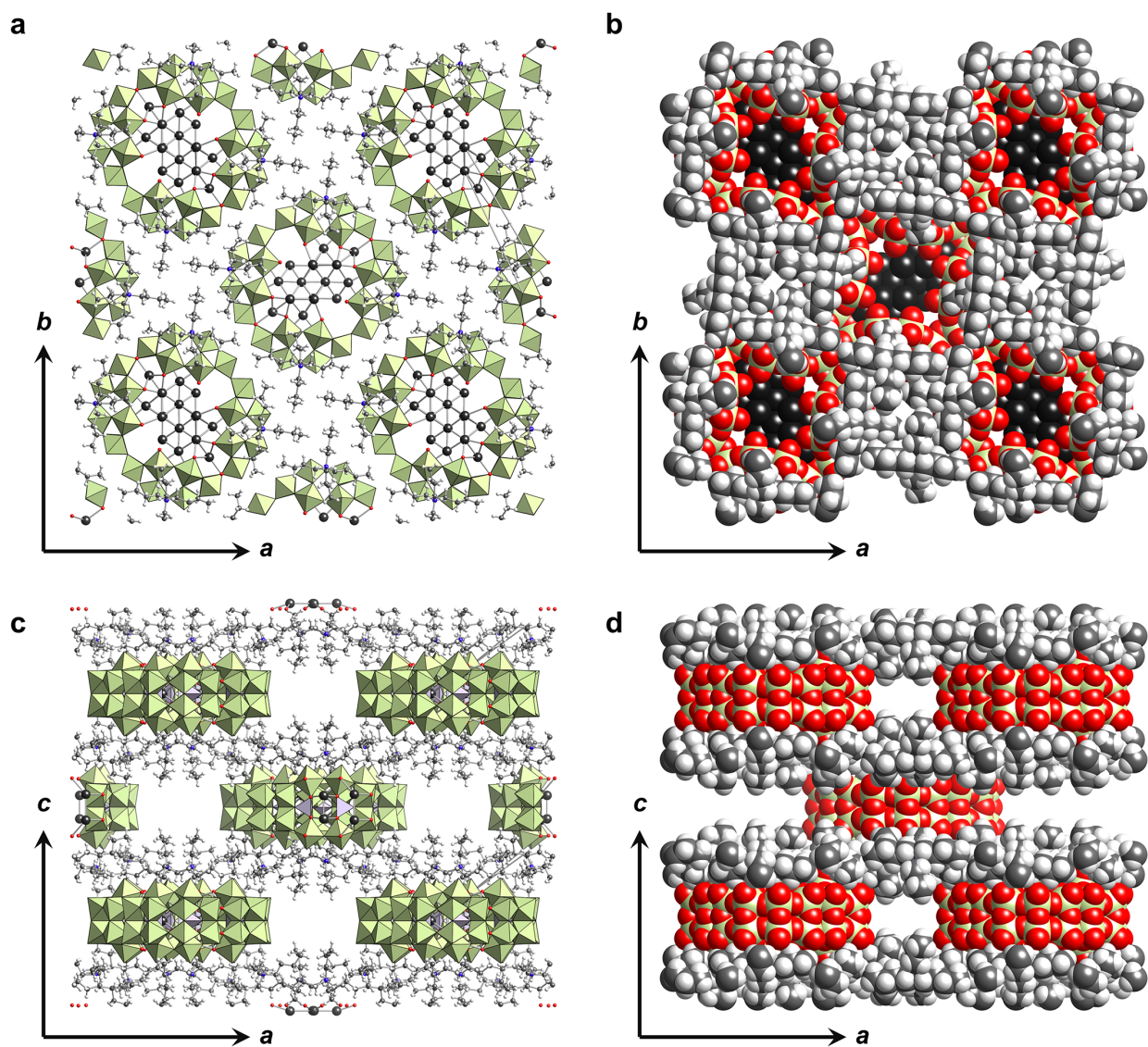
**Supplementary Fig. 8** | Proton titration curve for **Ag30** using TBAOH as titrant in acetonitrile.



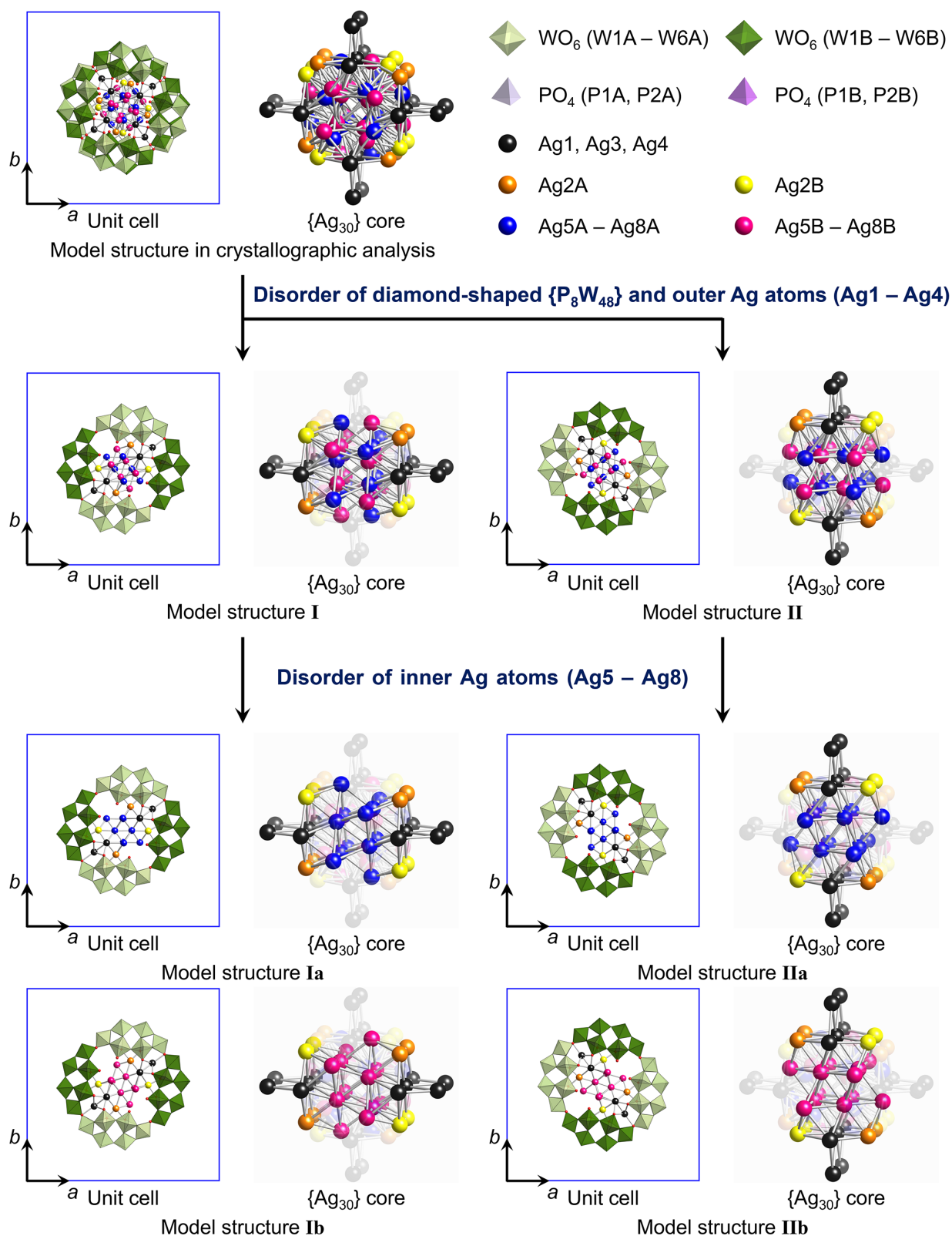
**Supplementary Fig. 9** | Energy diagram and molecular orbitals of Ag<sub>30</sub>.



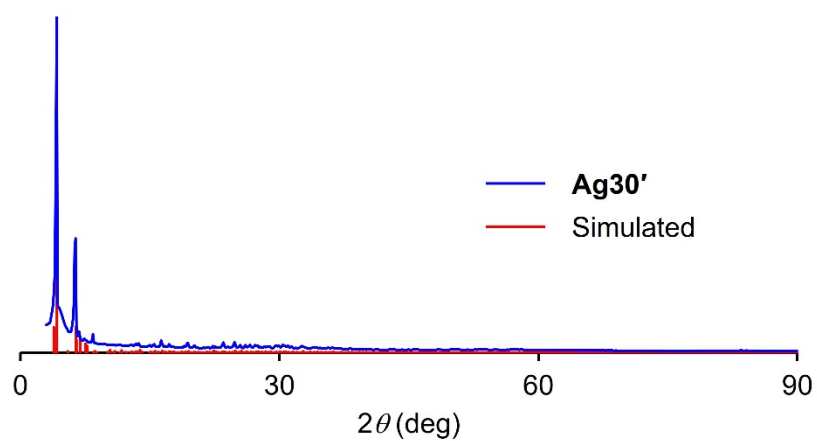
**Supplementary Fig. 10** | Crystal structure of **Ag<sub>30</sub>'**. **a,b**, Total anionic structure (**a**) and {Ag<sub>30</sub>}<sup>16+</sup> core structure (**b**) of **Ag<sub>30</sub>'** in polyhedral and ball-and-stick model. **c,d**, Structural comparison of {Ag<sub>30</sub>}<sup>22+</sup> core structure of **Ag<sub>30</sub>'** (**c**) with face-centered-cubic (fcc) arrangement of Ag atoms (**d**).



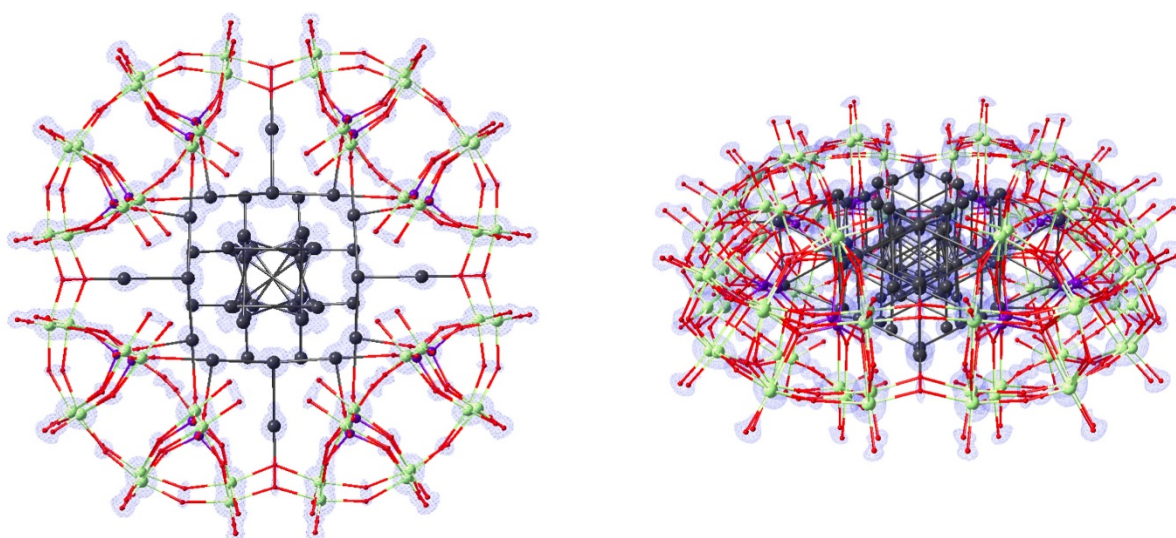
**Supplementary Fig. 11** | Packing of based on the X-ray crystallography. **a,b**, Views from the c-axis in polyhedral model (**a**) and spacefill model (**b**). **c,d**, Views from the b-axis in polyhedral model (**c**) and spacefill model (**d**).



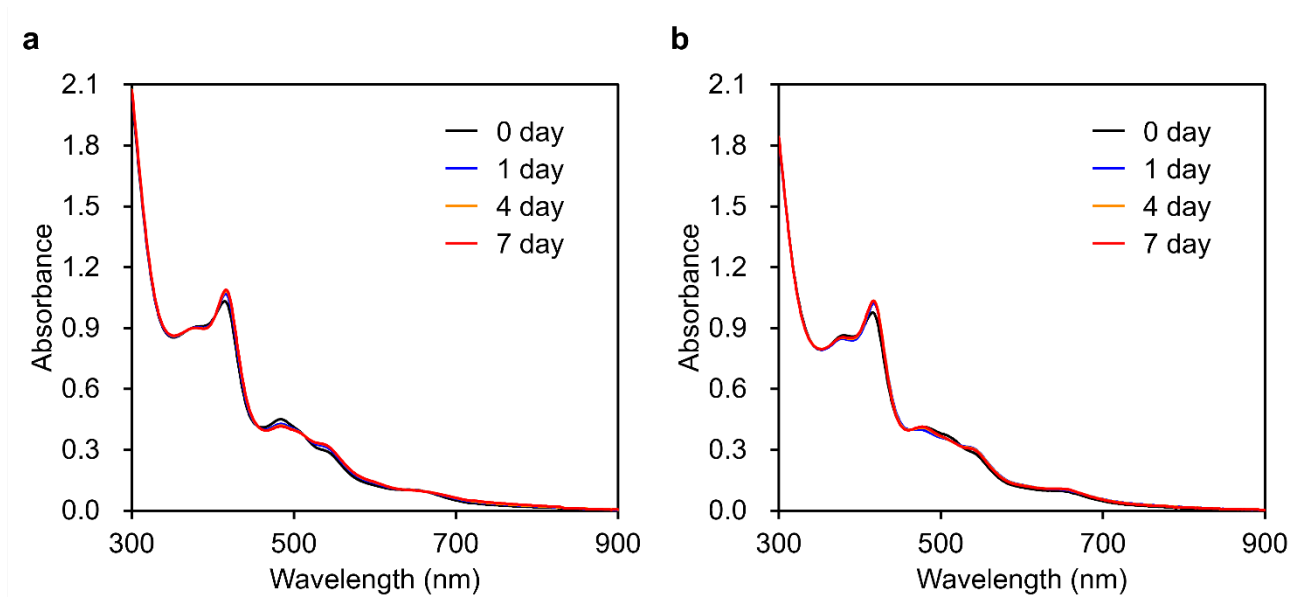
**Supplementary Fig. 12** | The detail of the structural model for disordering  $Ag_{30}'$  in the X-ray crystallographic analysis.



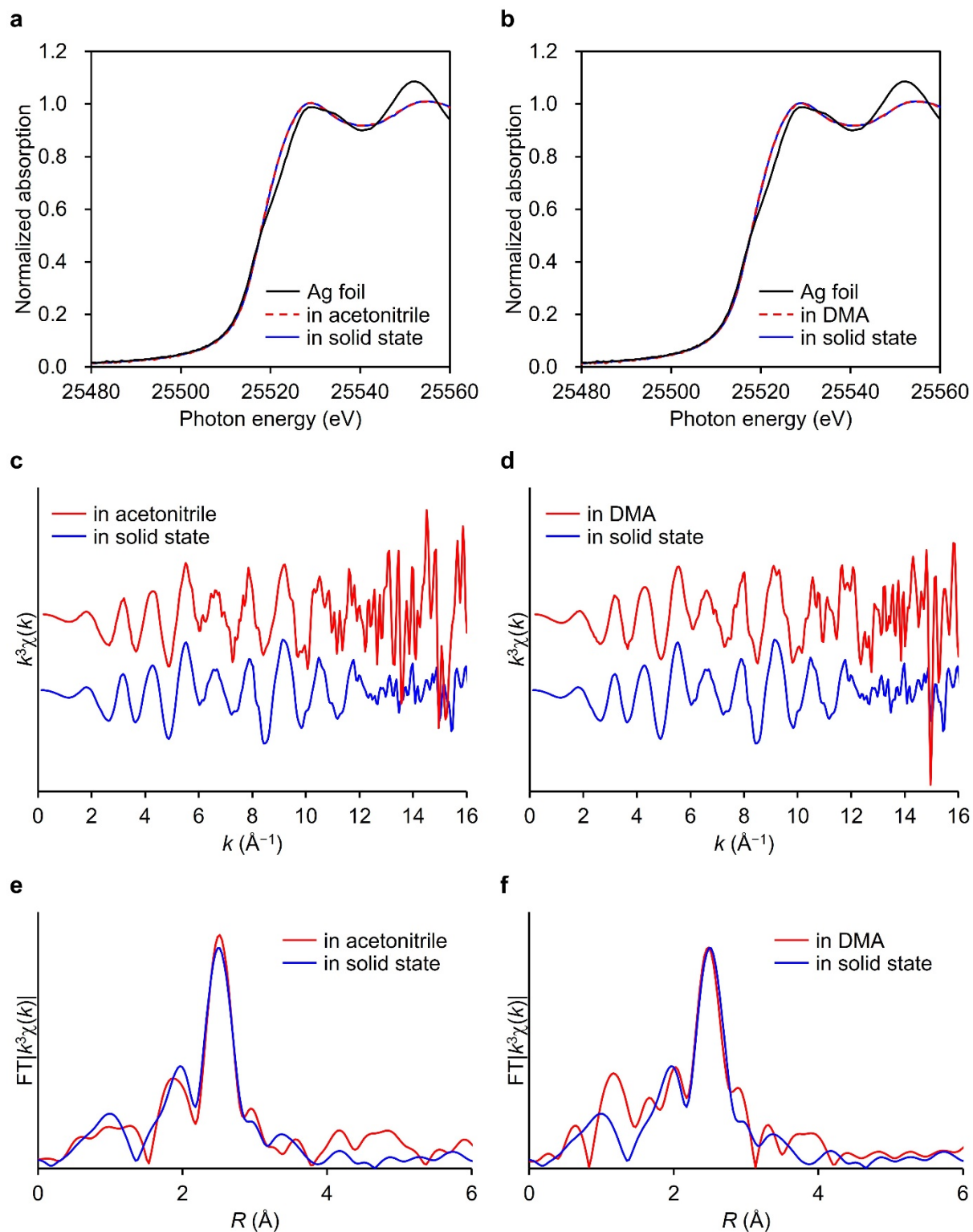
**Supplementary Fig. 13** | Powder X-ray diffraction pattern of **Ag30'**. Observed diffraction pattern of **Ag30'** (blue line) and simulated pattern (red line).



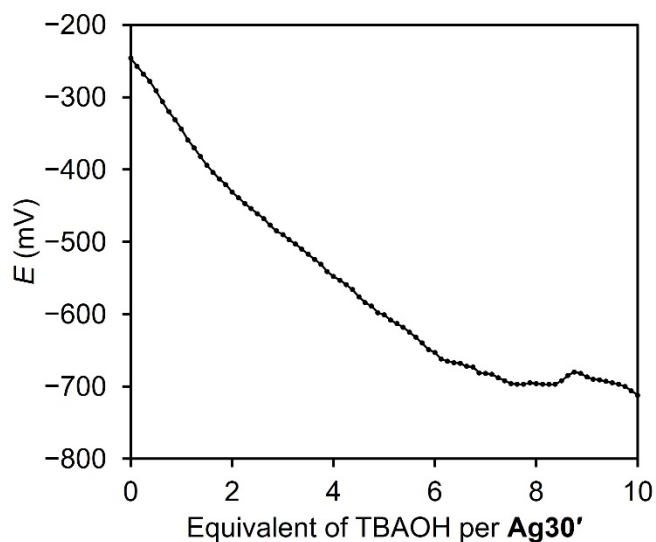
**Supplementary Fig. 14** | Overlay of electron density map ( $F_o$ , contoured at the  $1.0\sigma$  level) and crystal structure of **Ag30'**.



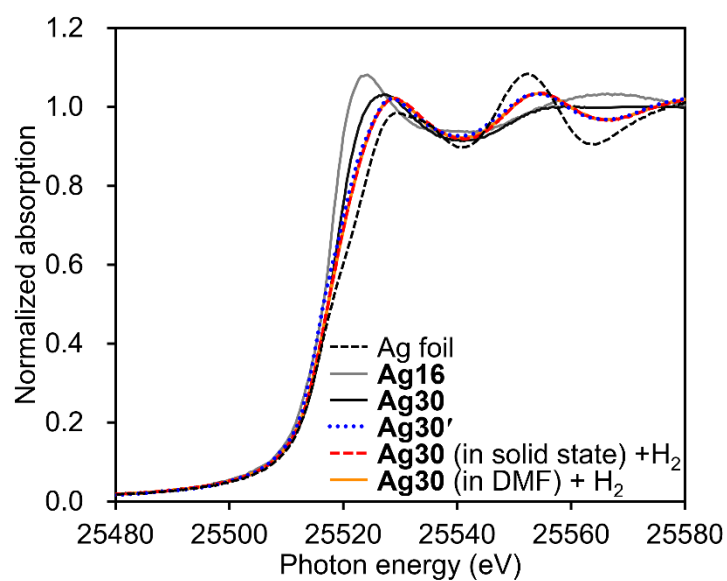
**Supplementary Fig. 15** | UV-vis spectra of Ag30' (10  $\mu$ M, 1 cm cell) in DMF (a) and in acetonitrile (b).



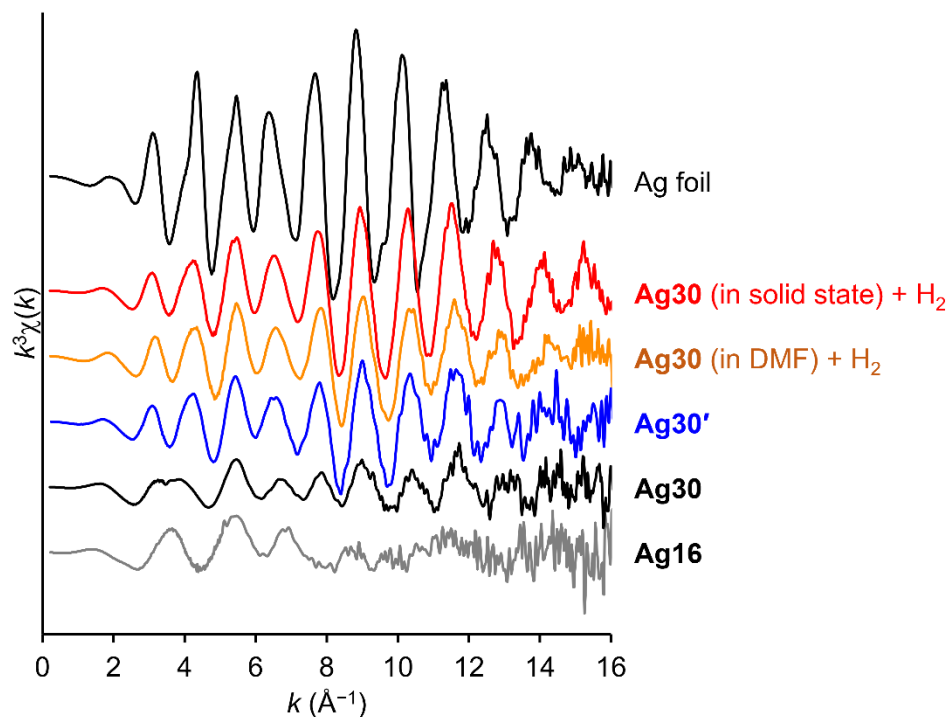
**Supplementary Fig. 16** | Ag K-edge XAFS study of the single crystals of **Ag30'** in solid state (blue lines) and **Ag30'** in organic solvents (1 mM; red lines) at room temperature ( $\sim 25^\circ\text{C}$ ). **a,b**, Ag K-edge XANES spectra of **Ag30'** in acetonitrile (**a**) and DMA (**b**). **c,d**,  $k^3$ -weighted  $k$ -space EXAFS spectra in acetonitrile (**c**) and DMA (**d**). **e,f**, Fourier-transformed  $R$ -space EXAFS spectra in acetonitrile (**e**) and DMA (**f**). Fourier-transformations were conducted in the  $k$  range of  $3\text{--}14 \text{ \AA}^{-1}$ .



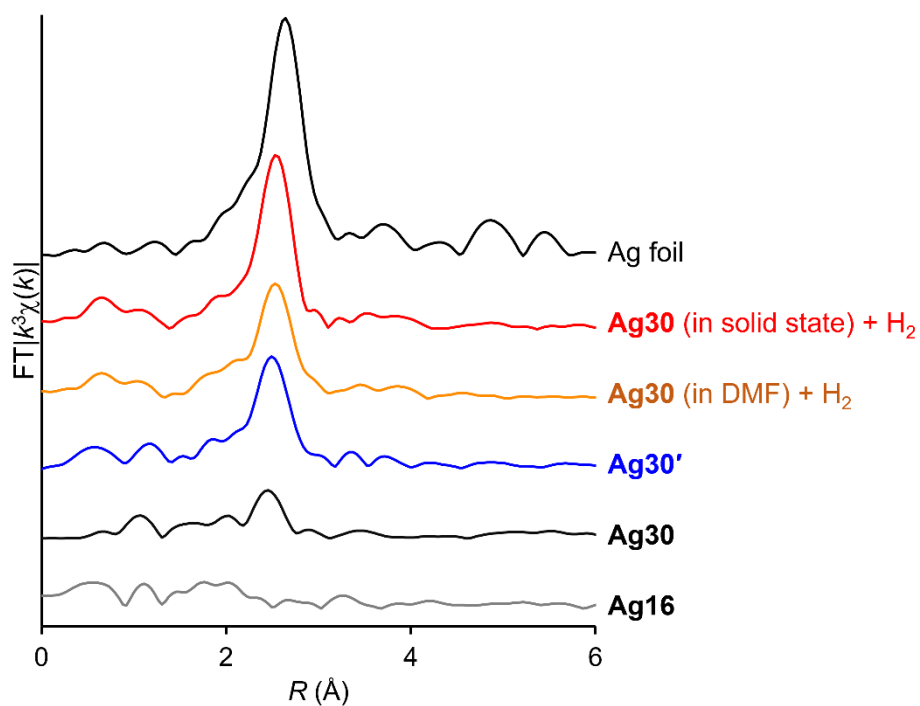
**Supplementary Fig. 17** | Proton titration curve for **Ag30'** using TBAOH as titrant in acetonitrile.



**Supplementary Fig. 18** | Ag K-edge XANES study on structural transformation of **Ag30** into **Ag30'** by the reaction with  $H_2$ . **Ag16** (gray line), **Ag30** (black line), **Ag30'** (blue dotted line), **Ag30** after the reaction with  $H_2$  in the solid state (red broken line), **Ag30** after the reaction with  $H_2$  in DMF (yellow line) and Ag foil (black broken line).

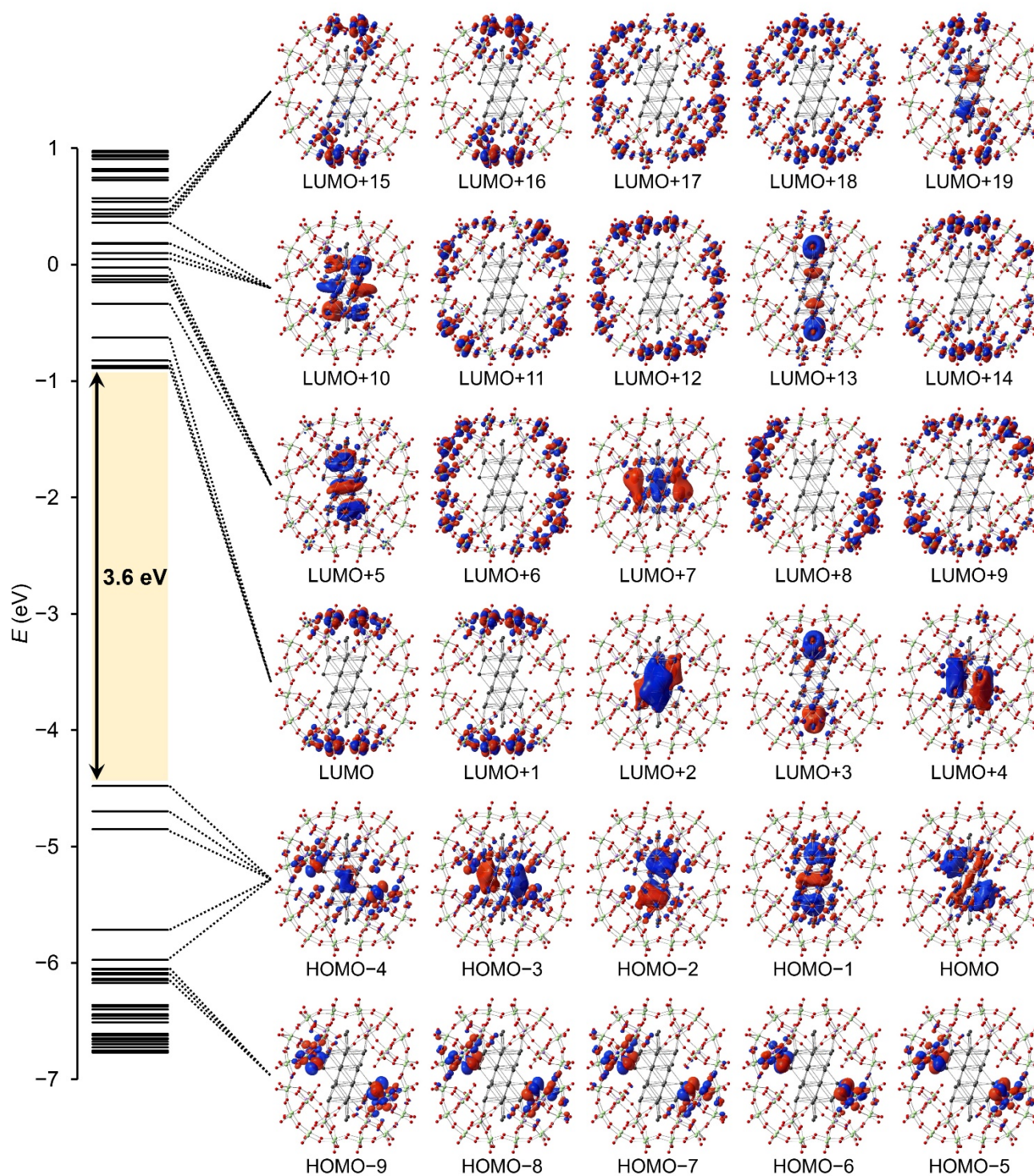


**Supplementary Fig. 19** | Ag K-edge  $k$ -space EXAFS study on structural transformation of **Ag30** into **Ag30'** by the reaction with H<sub>2</sub>. **Ag16** (gray line), **Ag30** (black line), **Ag30'** (blue line), **Ag30** after the reaction with H<sub>2</sub> in DMF (yellow line), **Ag30** after the reaction with H<sub>2</sub> in the solid state (red line) and Ag foil (black line).

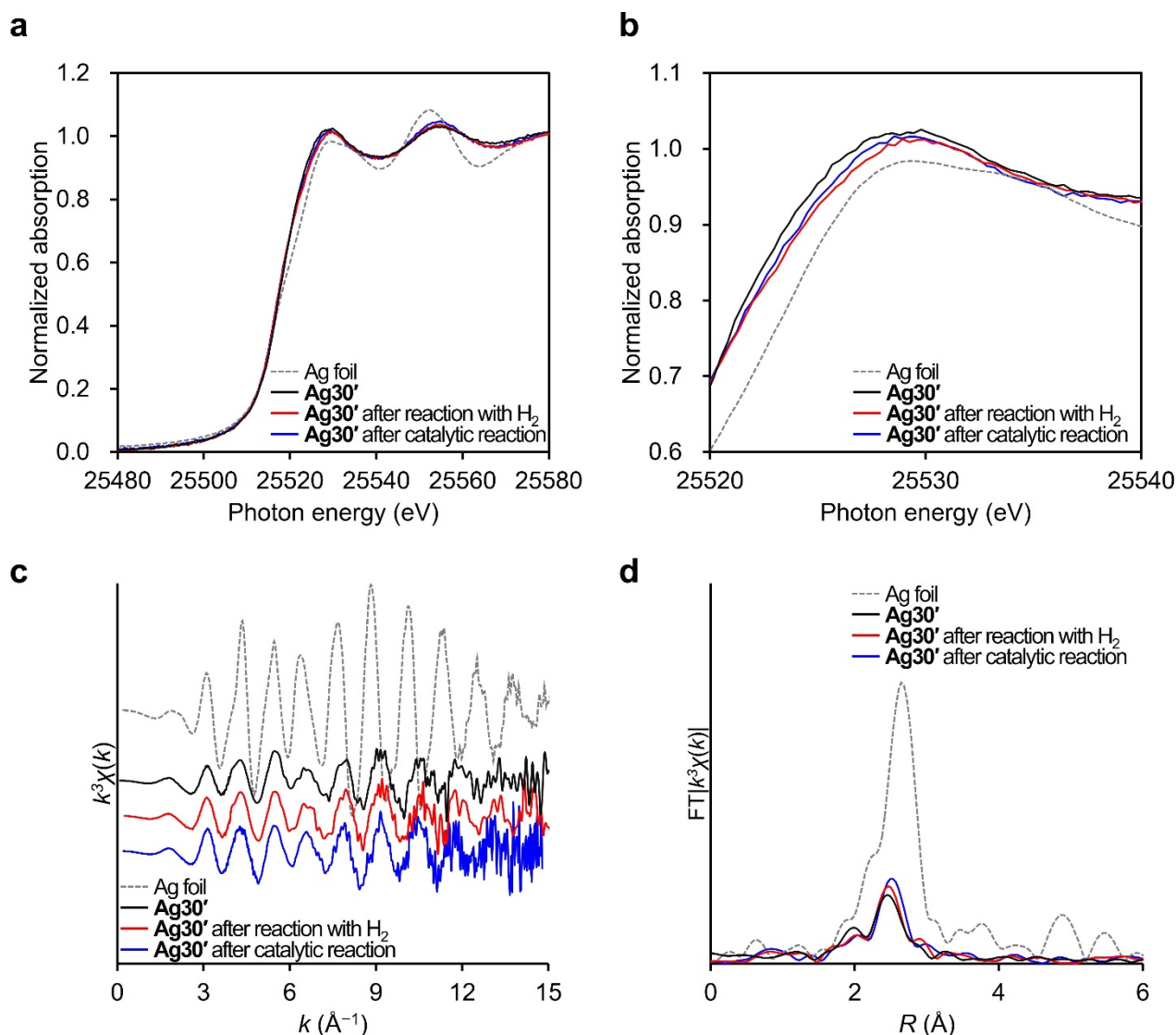


**Supplementary Fig. 20** | Ag K-edge  $R$ -space EXAFS study on structural transformation of **Ag30** into **Ag30'** by the reaction with H<sub>2</sub>. **Ag16** (gray line), **Ag30** (black line), **Ag30'** (blue line), **Ag30** after the reaction with H<sub>2</sub> in DMF

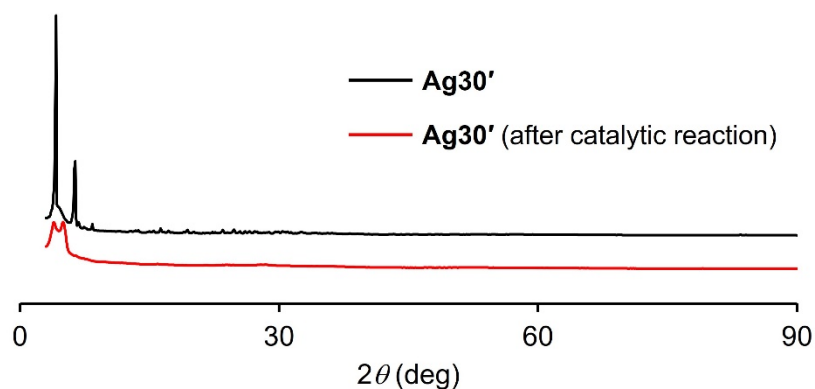
(yellow line), **Ag30** after the reaction with H<sub>2</sub> in the solid state (red line) and Ag foil (black line). The Fourier-transformation were conducted in the range of  $k = 3\text{--}16 \text{ \AA}^{-1}$ .



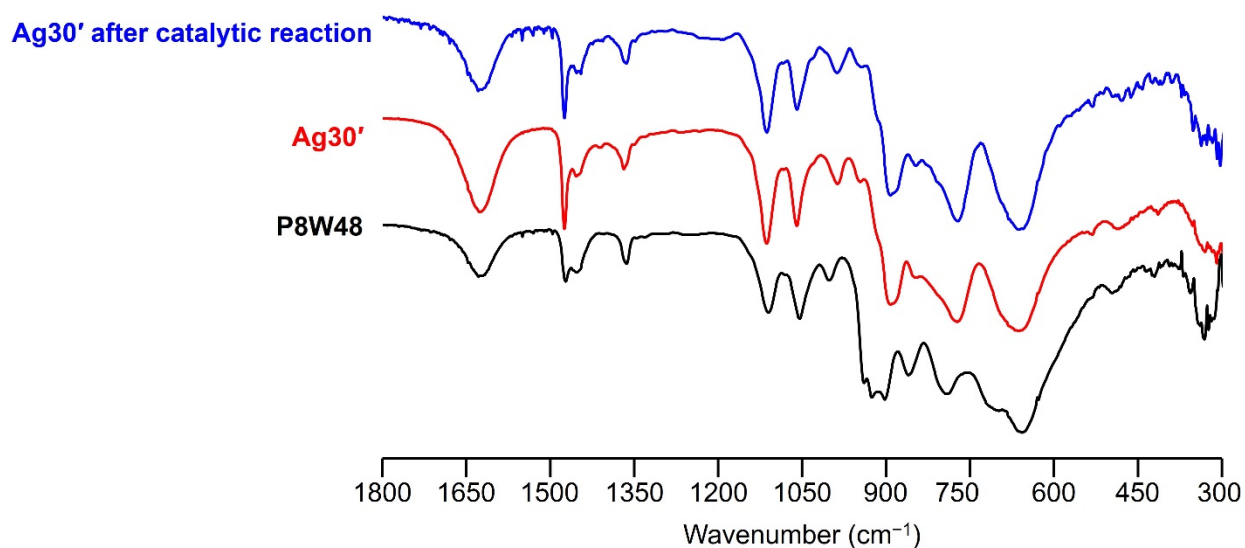
**Supplementary Fig. 21** | Energy diagram and molecular orbitals of **Ag30'**.



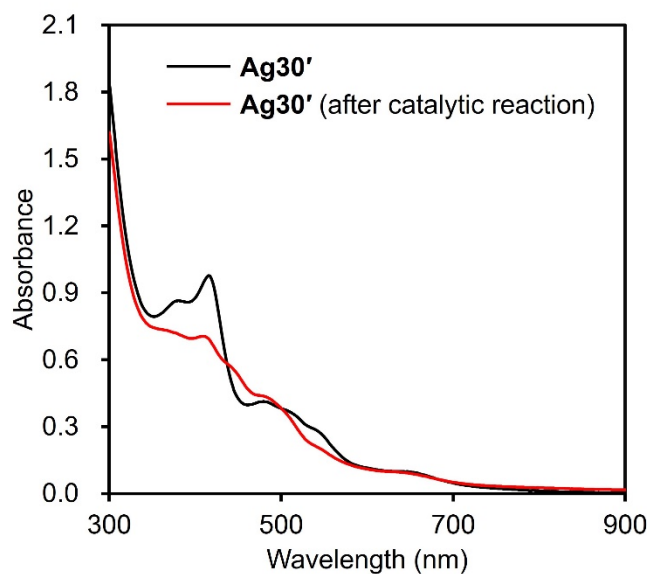
**Supplementary Fig. 22** | Ag K-edge XAFS study on **Ag30'** after reaction with H<sub>2</sub> and after catalytic reaction. **Ag30'** in DMA (**Ag30'** 1 mM; black lines), the solution of **Ag30'** after the reaction with H<sub>2</sub> in DMA (**Ag30'** 1 mM, H<sub>2</sub> 4 atm, 60°C, 1 h; red lines), and the solution of **Ag30'** after the catalytic reaction in DMA (**Ag30'** 0.5 mM, nitrobenzene 0.10 M, H<sub>2</sub> 4 atm, 60°C, 20 h; blue lines). **a,b**, XANES spectra in a wide view (**a**) and an enlarged view around white lines (**b**). **c,d**,  $k^3$ -weighted  $k$ -space (**c**) and Fourier-transformed  $R$ -space EXAFS spectra (**d**). Fourier transformation was conducted in the  $k$  range of 3–14 Å<sup>-1</sup>.



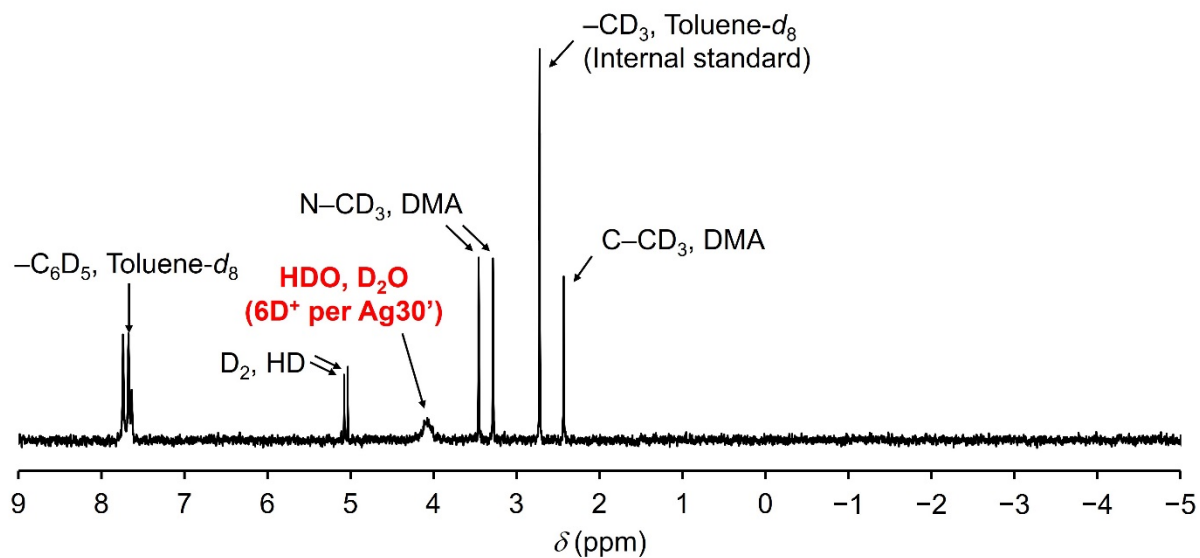
**Supplementary Fig. 23** | Powder XRD pattern of **Ag30'** after the catalytic reaction. **Ag30'** (black line) and **Ag30'** after the catalytic reaction (red line; nitrobenzene,  $H_2$  4 atm,  $60^\circ\text{C}$ , 20 h, in DMA).



**Supplementary Fig. 24** | IR spectrum of **Ag30'** after the catalytic reaction. **P8W48** (black line), **Ag30'** (red line) and **Ag30'** after the catalytic reaction (nitrobenzene,  $H_2$  4 atm,  $60^\circ\text{C}$ , 20 h, in DMA; blue line).



**Supplementary Fig. 25** | UV-vis spectra of **Ag30'** after the catalytic reaction. **Ag30'** in DMA (black line) and **Ag30'** after the catalytic reaction (nitrobenzene, H<sub>2</sub> 4 atm, 60°C, 20 h, in DMA; red line) in acetonitrile (10 μM, 1 cm cell).



**Supplementary Fig. 26** | <sup>2</sup>H NMR spectrum of the reaction solution of **Ag30'** (1 mM) and H<sub>2</sub> (4 atm, 60°C) in DMA.

### Supplementary note 1 | Bond valence sum (BVS) calculation

The BVS values were calculated by the expression for the variation of the length  $r_{ij}$  of a bond between two atoms  $i$  and  $j$  in observed crystal with valence  $V_i$ .

$$V_i = \sum \exp\left(\frac{r'_0 - r_{ij}}{B}\right)$$

where  $B$  is constant equal to 0.37 Å,  $r'_0$  is bond valence parameter for a given atom pair<sup>S7</sup>.

### Supplementary note 2 | Detail of the refinement of X-ray crystallographic model structure of Ag16.

In the model refinement of **Ag16**, the several unavoidable alert B are pointed out by CheckCIF, likely because of weak interactions between ionic Ag<sup>+</sup> and O atoms of POM structures or general difficulty in determination of TBA structure in high symmetry of space group ( $I4/m$ ). We embedded following comments in CIF files.

PLAT232\_ALERT\_2\_B Hirshfeld Test Diff (M-X) Ag2 --O2 . 12.0 s.u.

Author Response: This alert is derived from different displacement parameters along chemical bonds, which always appeared in repeated experiments using different crystals. This alert is unavoidable because Ag ions are trapped within P8W48O184 structure only by weak Ag-O and/or Ag-Ag interactions in comparison with O atoms in rigid P8W48O184 structure.

PLAT241\_ALERT\_2\_B High 'MainMol' Ueq as Compared to Neighbors of Ag2 Check

Author Response: This alert is derived from different Ueq parameters, which always appeared in repeated experiments using different crystals. This alert is unavoidable because Ag ions are trapped within P8W48O184 structure only by weak Ag-O and/or Ag-Ag interactions in comparison with O atoms in rigid P8W48O184 structure.

PLAT242\_ALERT\_2\_B Low 'MainMol' Ueq as Compared to Neighbors of O2 Check

Author Response: This alert is derived from different Ueq parameters, which always appeared in repeated experiments using different crystals. This alert is unavoidable because Ag ions are trapped within P8W48O184 structure only by weak Ag-O and/or Ag-Ag interactions in comparison with O atoms in rigid P8W48O184 structure.

PLAT342\_ALERT\_3\_B Low Bond Precision on C-C Bonds ..... 0.03917 Ang.

Author Response: This alert is derived from wide distribution of C-C bond lengths of TBA cations, which always appeared in repeated experiments using different crystals. This alert is unavoidable because of high symmetry of space group and/or quality of crystals of such a large structure.

PLAT410\_ALERT\_2\_B Short Intra H...H Contact H11B ..H14C . 1.81 Ang.  
x,y,z = 1\_555 Check

Author Response: This alert is derived from wide distribution of C-C bond lengths of TBA cations, which always appeared in repeated experiments using different crystals. This alert is unavoidable because of high symmetry of space group and/or quality of crystals of such a large structure.

**Supplementary note 3** | Detail of the refinement of X-ray crystallographic model structure of **Ag30**.

In the model refinement of **Ag30**, the several unavoidable alert B are pointed out by CheckCIF, likely because of weak Ag–O atoms and/or long Ag···Ag interactions or general difficulty in determination of TBA structure in high symmetry of space group (*I4/m*). We embedded following comments in CIF files.

PLAT241\_ALERT\_2\_B High 'MainMol' Ueq as Compared to Neighbors of Ag3 Check

Author Response: This alert is derived from different Ueq parameters, which always appeared in repeated experiments using different crystals. This alert is unavoidable because Ag ions are trapped within P8W48O184 structure only by weak Ag-O and/or Ag-Ag interactions in comparison with O atoms in rigid P8W48O184 structure.

PLAT342\_ALERT\_3\_B Low Bond Precision on C-C Bonds ..... 0.03 Ang.

Author Response: This alert is derived from wide distribution of C-C bond lengths of TBA cations, which always appeared in repeated experiments using different crystals. This alert is unavoidable because of high symmetry of space group and/or quality of crystals of such a large structure.

#### Supplementary note 4 | Detail of the refinement of X-ray crystallographic model structure of **Ag30'**.

In the X-ray crystallographic analysis, the anionic structure of **Ag30'** arranged in four molecular orientations, which caused a severe disorder of the anionic part of **Ag30'** due to mismatch of symmetry elements of **Ag30'** (ideally belonging to point group  $C_{2h}$ ) and those of the space group ( $I4/m$ , #87). The disorder was not cleared by controlling the synthetic conditions and/or recrystallization. Therefore, we built the model structure of **Ag30'** by combining the diamond-shaped  $[P_8W_{48}O_{184}]$  structure disordering in two positions and the  $\{Ag_{30}\}$  structure disordering four positions (Supplementary Fig. S11). In the crystallographic asymmetric unit of **Ag30'**, two P atoms, six W atoms, and twenty-seven O atoms could be assigned. These atoms were split into two positions (*e.g.* P1A and P1B) because the  $[P_8W_{48}O_{184}]$  structure distorted into a diamond-shaped structure with two orientations. This distortion of  $[P_8W_{48}O_{184}]$  changes the four Ag1 coordination sites of **Ag30** into two wide and two narrow coordination sites of **Ag30'**. Considering the bond length of Ag1–O9, we concluded that four Ag1 atoms remained in narrower coordination sites while the other four Ag1 did not remain the wider coordination sites. Because of the distortion of  $\{P_8W_{48}\}$  framework, Ag2 atoms of **Ag30** were also split in two positions (*i.e.* Ag2A and Ag2B of **Ag30'**). The arrangement of the other Ag atoms (Ag3, Ag4, Ag5A–Ag8A and Ag5B–Ag8B) were determined by eliminating the unusually short Ag...Ag interaction below 2.6 Å. Each model structure was properly built and divided by using PART, FREE, and BIND commands of SHELXL programs. Because the chemical occupancies for all P, Ag, W, and O atoms, which was composed of the anionic structure of **Ag30'**, cannot be refined due to mismatch of symmetry elements of **Ag30'** and those of the space group ( $I4/m$ , #87), they were fixed at 50% (for P, W, O, and Ag1, Ag2A, Ag2B, Ag3 and Ag4) or 25% (for Ag5A–Ag8A and Ag5B–Ag8B).

In the resultant model refinement of **Ag30'**, the several unavoidable alert A are pointed out by CheckCIF, which derived from the partitioning of Ag nanocluster using PART commands in SHELXL program to consider severely disordering structure of **Ag30'**. The alerted atoms are properly bonded to surrounding atoms by using BOND commands. In addition, several unavoidable alert B are also remained, likely because of general difficulty in determination of TBA structure in high symmetry of space group ( $I4/m$ ). We embedded following comments in CIF files.

PLAT308\_ALERT\_2\_A Single Bonded Metal Atom in Structure (Unusual) Ag5A Check

PLAT308\_ALERT\_2\_A Single Bonded Metal Atom in Structure (Unusual) Ag6A Check

PLAT308\_ALERT\_2\_A Single Bonded Metal Atom in Structure (Unusual) Ag5B Check

PLAT308\_ALERT\_2\_A Single Bonded Metal Atom in Structure (Unusual) Ag6B Check

Author Response: This alert is a problem originating from the partitioning of the disordered silver nanocluster parts using the PART command. These alerted atoms have been properly bonded to other Ag atoms and O atoms by using BIND command.

PLAT342\_ALERT\_3\_B Low Bond Precision on C-C Bonds ..... 0.03333 Ang.

Author Response: This alert is derived from wide distribution of C-C bond lengths of TBA cations, which always appeared in repeated experiments using different crystals. This alert is unavoidable because of high symmetry of space group and/or quality of crystals of such a large structure.

**Supplementary note 5** | Structural transformation of crystalline **Ag30** into **Ag30'** by the reaction with H<sub>2</sub>.

The crystalline **Ag30** was suspended in a mixture of DMF and ethyl acetate (1/4, v/v), and the H<sub>2</sub> gas was introduced into the mixture by bubbling for 3 min. After 40 h at room temperature, the single crystal X-ray diffraction experiment of the resulting crystal was performed. X-ray crystallographic parameters of starting **Ag30**: Tetragonal, *I4/m* (#87),  $a = b = 32.2361(2)$  Å,  $c = 27.0785(3)$  Å,  $R_1 = 0.0586$ ,  $wR_2 = 0.1874$ , GOF = 1.019. X-ray crystallographic parameters of resulting crystal (**Ag30'**): Tetragonal, *I4/m* (#87),  $a = b = 32.2206(4)$  Å,  $c = 26.9427(6)$  Å,  $R_1 = 0.0908$ ,  $wR_2 = 0.3247$ , GOF = 1.033.

## References

- S1 Chen, Y., Wang, C. Liu, H., Qiu, J. & Bao, X. Ag/SiO<sub>2</sub>: a novel catalyst with high activity and selectivity for hydrogenation of chloronitrobenzenes. *Chem. Commun.* 5298–5300 (2005).
- S2 Gong, H., Lin, L., Zhao, X., Li, H., Li, D., Xu, Z., Chen, M., Huang, R. & Hou, Z. Atomically precise Ag nanoclusters intercalated in zirconium pyrophosphate for efficient hydrogenation of nitroaromatics. *Appl. Catal., A* **574**, 1–9 (2019).
- S3 Shimizu, K., Miyamoto, Y. & Satsuma, A. Size- and support-dependent silver cluster catalysis for chemoselective hydrogenation of nitroaromatics. *J. Catal.* **270**, 86–94 (2010).
- S4 Mitsudome, T. Mikami, Y., Matoba, M., Mizugaki T., Jitsukawa, K. & Kaneda, K. Design of a Silver–Cerium Dioxide Core–Shell Nanocomposite Catalyst for Chemoselective Reduction Reactions. *Angew. Chem. Int. Ed.* **51**, 136–139 (2012).
- S5 Unglaube, F., Kreyenschulte, C. R. & Mejía, E. Development and Application of Efficient Ag-based Hydrogenation Catalysts Prepared from Rice Husk Waste. *ChemCatChem* **13**, 2583–2591 (2021).
- S6 Crook, R., Deering, J., Fussell, S. J., Happe, A. M. & Mulvihill, S. Enhanced reactivity of silver- and gold-catalysed hydrogenations using silver(I) salts. *Tetrahedron Lett.* **51**, 5181–5184 (2010).
- S7 Brese, N. E. & O’Keeffe, M. Bond-valence parameters for solids. *Acta Crystallogr. Sect.* **B47**, 192–197 (1991).