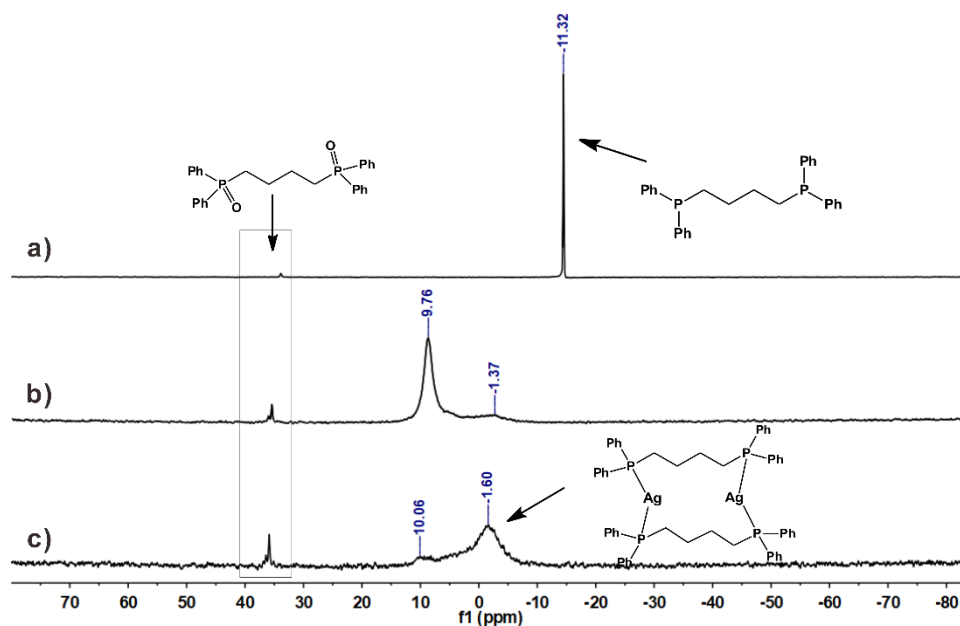


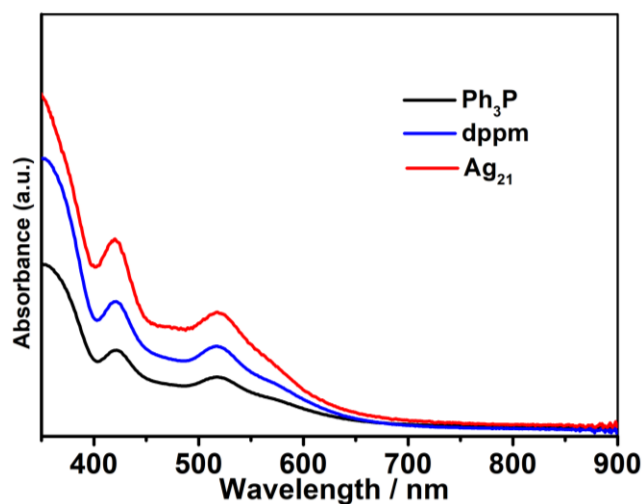
## **Supporting Information**

### **Solvent-triggered reversible interconversion of all-nitrogen-donor-protected silver nanoclusters and their responsive optical properties**

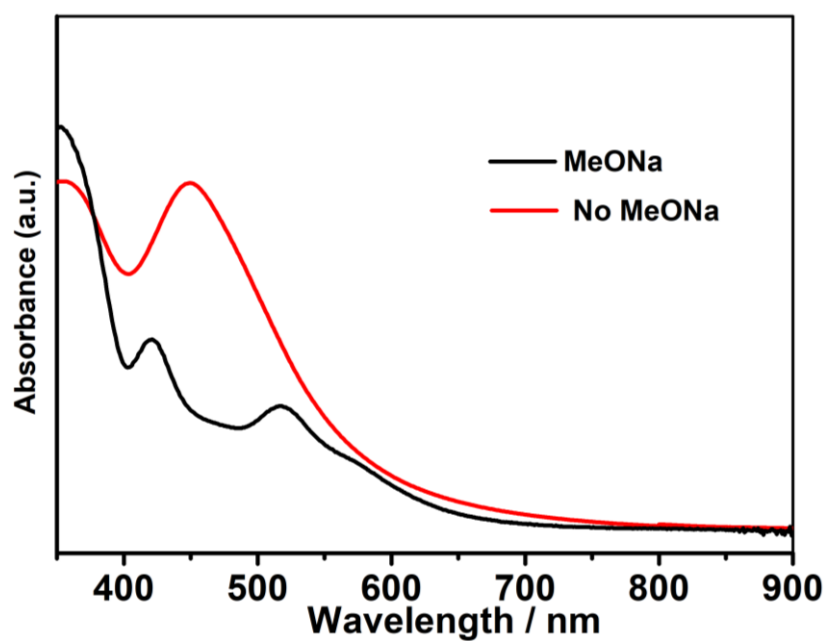
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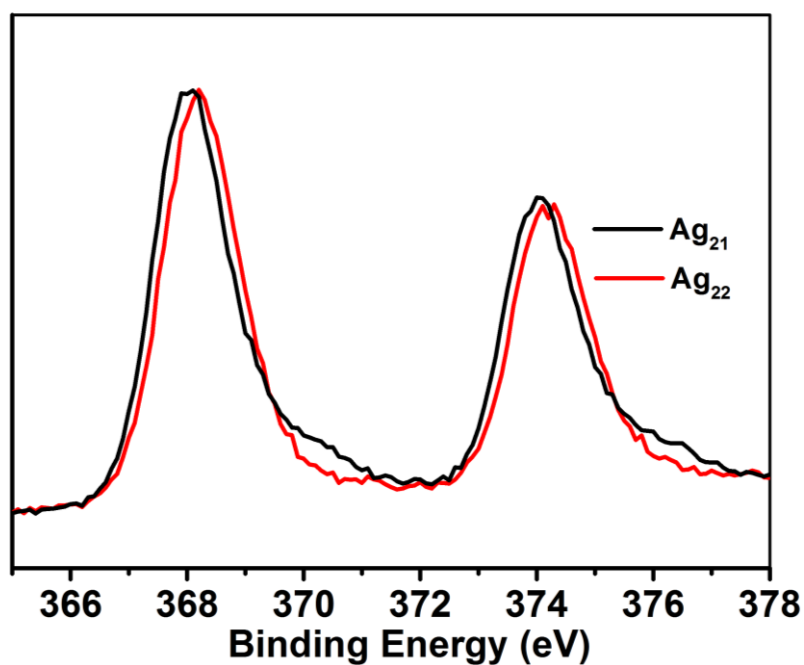
**Supplementary Figure 1. Trace of phosphine ligands with  $^{31}\text{P}$  NMR in solution.** (a) Free dppb in  $\text{CH}_2\text{Cl}_2$ . The result solution before (b) and after adding  $\text{NaBH}_4$  overnight (c) in the synthesis of **Ag<sub>22</sub>**. Note, the weak signal of dppb oxide were observed, which were oxidized by air.



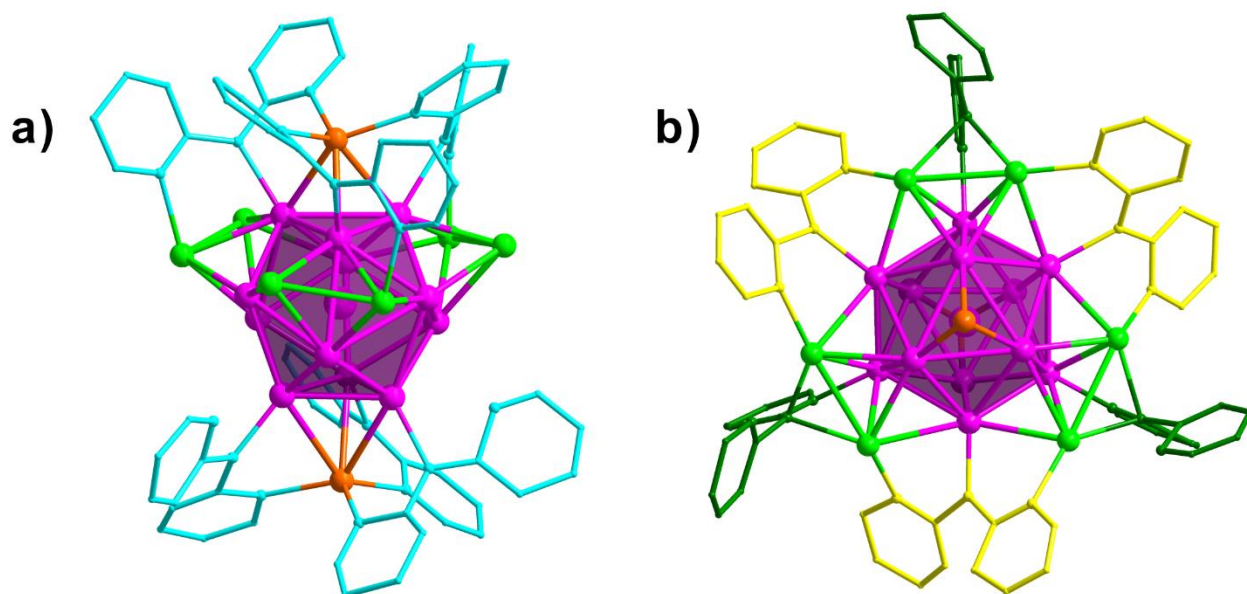
**Supplementary Figure 2. Comparison of optical absorption spectra of the  $\text{Ag}_{21}$  crystal sample prepared by dppb and the crude products in the presence of other different phosphine ligands.**



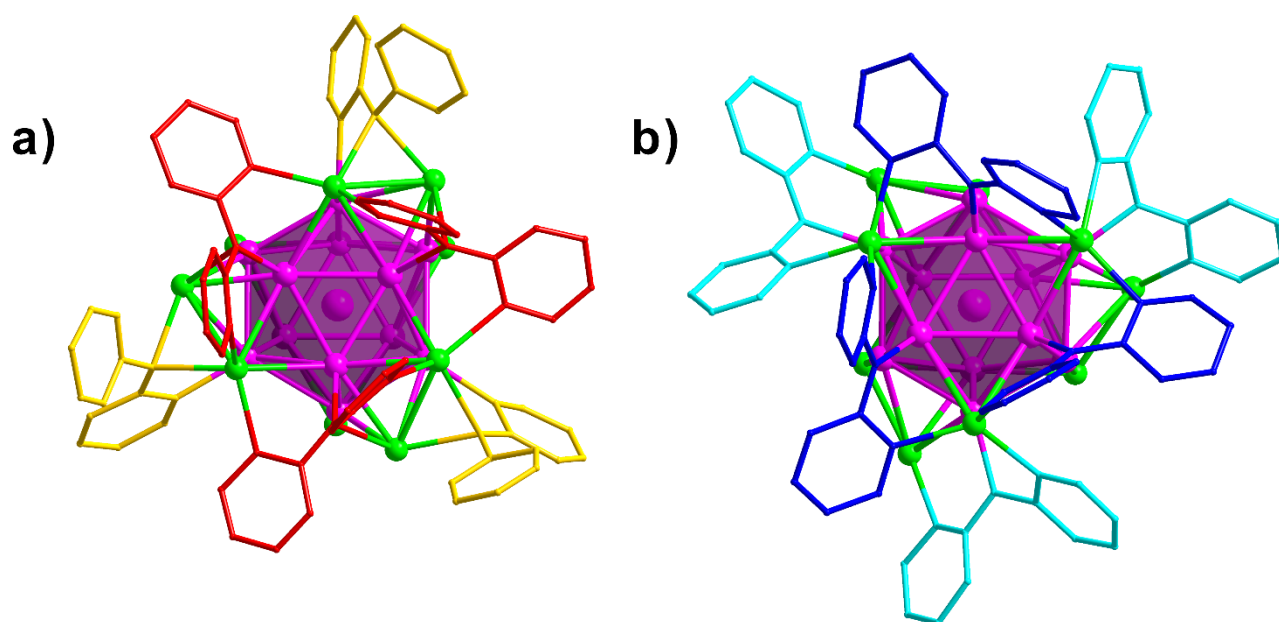
**Supplementary Figure 3.** Comparison of optical absorption spectra of the crude products with and without MeONa.



**Supplementary Figure 4.** XPS spectrum of  $\text{Ag}_{21}$  (black profile) and  $\text{Ag}_{22}$  (red profile) nanoclusters.

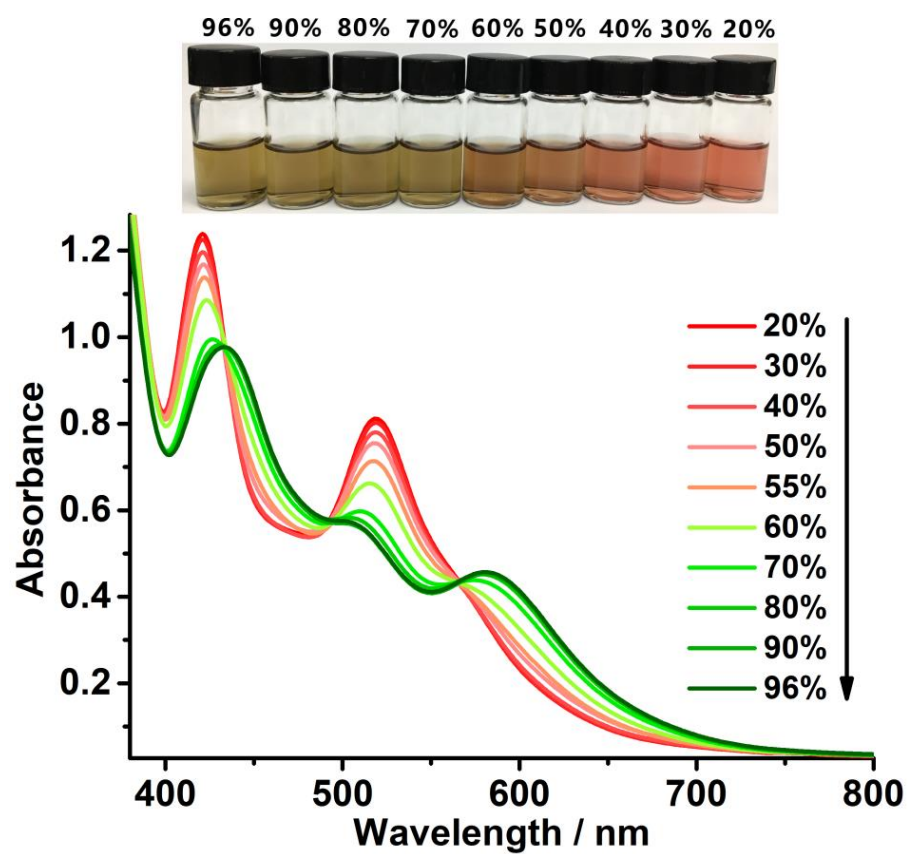


**Supplementary Figure 5.** The surface structures of  $\text{Ag}_{21}$  cluster. (a) Side view and (b) top view of the complex with  $\text{Ag}_{13}$  core and eight faces capped silver atoms. Color codes: purple = Ag atoms of  $\text{Ag}_{13}$  core, bright green = cap Ag atoms; surface dpa ligands are colored blue, green and yellow.

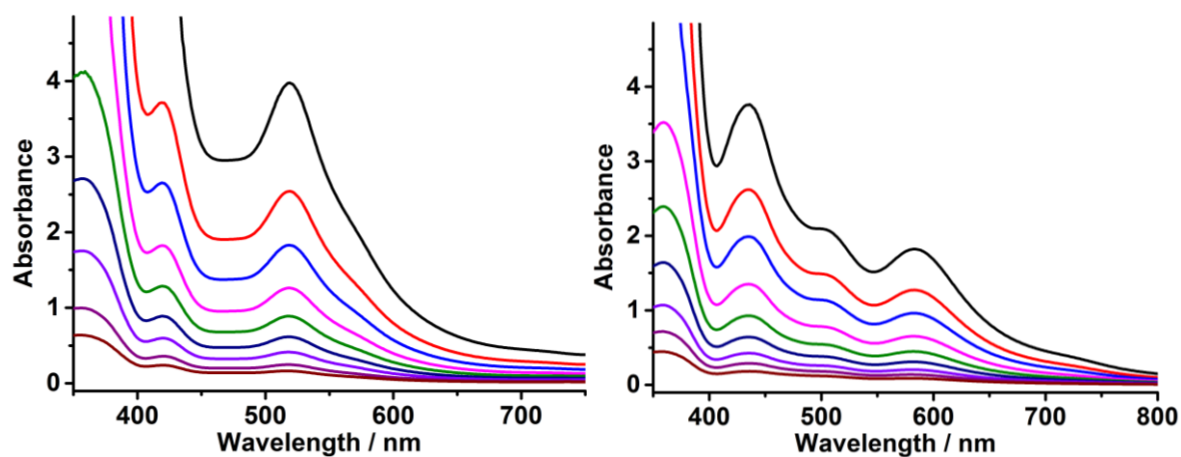


**Supplementary Figure 6.** The surface structures of  $\text{Ag}_{22}$  cluster. (A) Top view and (B) down view of the complex with  $\text{Ag}_{13}$  core and nine faces capped silver atoms. Color codes: purple = Ag atoms of  $\text{Ag}_{13}$  core, bright green = cap Ag atoms; surface dpa ligands are colored blue, light blue, red and yellow.

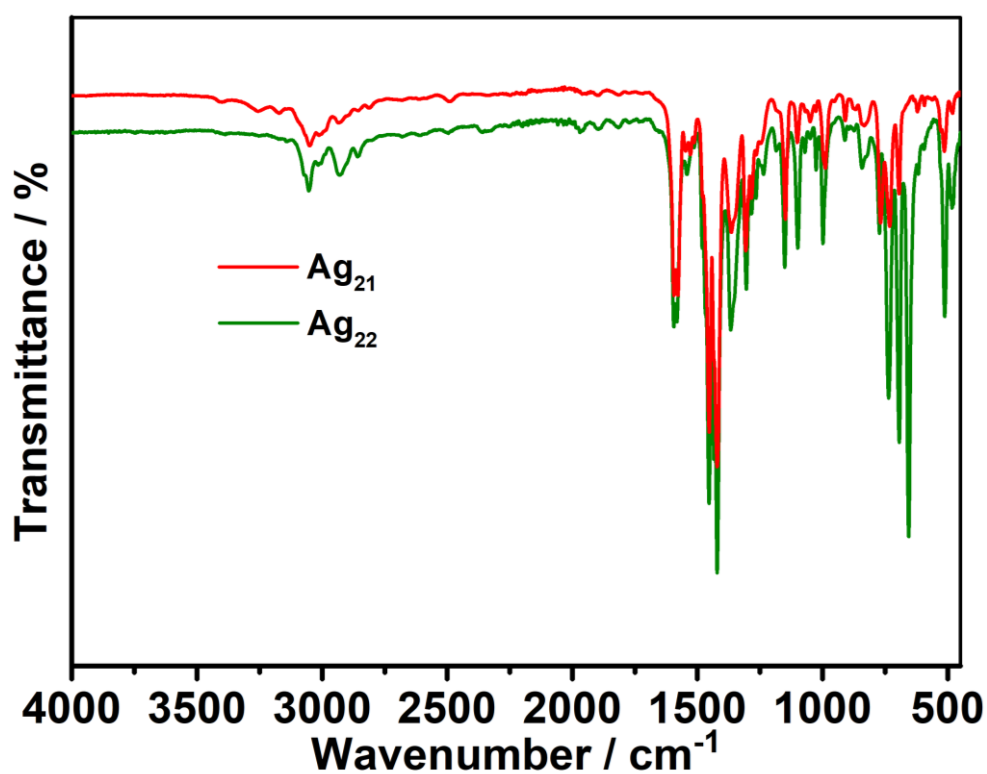




**Supplementary Figure 8.** The optical absorption spectra of the transformation from **Ag<sub>21</sub>** to **Ag<sub>22</sub>** with different volume ratios of EtOH and n-hexane.



**Supplementary Figure 9.** UV/vis absorption spectra of  $\text{Ag}_{21}$  (left) and  $\text{Ag}_{22}$  (right) of various concentrations in EtOH.



**Supplementary Figure 10.** FT-IR spectra of  $\text{Ag}_{21}$  and  $\text{Ag}_{22}$ .

**Supplementary Table1.** Selected bonds lengths of **Ag<sub>21</sub>** and **Ag<sub>22</sub>** clusters.

| Bonds                                | <b>Ag<sub>21</sub></b> (Å) | <b>Ag<sub>22</sub></b> (Å) |
|--------------------------------------|----------------------------|----------------------------|
| Internal Ag-Ag in Ag <sub>13</sub>   | 2.790 (2.757-2.832)        | 2.787 (2.743-2.833)        |
| Peripheral Ag-Ag in Ag <sub>13</sub> | 2.933 (2.770-3.168)        | 2.933 (2.791-3.097)        |
| Capping Ag to Ag <sub>13</sub> core  | 2.867 (2.715-2.975)        | 2.901 (2.767-3.075)        |
| Between capping Ag atoms             | 3.054 (2.971-3.112)        | 2.912 (2.909-2.915)        |
| Amido N to Ag atoms                  | 2.256 (2.042-2.510)        | 2.308 (2.210-2.514)        |
| Pyridyl N to Ag atoms                | 2.242 (2.108-2.371)        | 2.255 (2.165-2.334)        |

**Supplementary Table 2.** Crystal data and structure refinement for **Ag<sub>21</sub>**.

|                                                |                                                                                                                     |
|------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|
| Empirical formula                              | C <sub>250</sub> H <sub>212</sub> N <sub>72</sub> F <sub>12</sub> Cl <sub>20</sub> Ag <sub>42</sub> Sb <sub>2</sub> |
| Formula weight                                 | 9935.94                                                                                                             |
| Temperature/K                                  | 173.4(7)                                                                                                            |
| Crystal system                                 | triclinic                                                                                                           |
| Space group                                    | <i>P</i> 1                                                                                                          |
| Unit cell dimensions                           | $a = 15.6195(7) \text{ \AA}$ $\alpha = 95.839(3)^\circ$                                                             |
|                                                | $b = 18.2852(7) \text{ \AA}$ $\beta = 90.418(3)^\circ$                                                              |
|                                                | $c = 26.5537(9) \text{ \AA}$ $\gamma = 90.042(3)^\circ$                                                             |
| Volume/ $\text{\AA}^3$                         | 7544.3(5)                                                                                                           |
| <i>Z</i>                                       | 1                                                                                                                   |
| Calculated density ( $\text{g/cm}^3$ )         | 2.187                                                                                                               |
| Absorption coefficient / $\text{mm}^{-1}$      | 24.856                                                                                                              |
| <i>F</i> (000)                                 | 4740.0                                                                                                              |
| Crystal size/ $\text{mm}^3$                    | $0.15 \times 0.04 \times 0.03$                                                                                      |
| Radiation                                      | Cu K $\alpha$ ( $\lambda = 1.54178$ )                                                                               |
| 2 $\Theta$ range for data collection/ $^\circ$ | 6.596 to 121.208                                                                                                    |
| Index ranges                                   | $-16 \leq h \leq 17, -19 \leq k \leq 20, -26 \leq l \leq 29$                                                        |
| Reflections collected                          | 39559                                                                                                               |
| Independent reflections                        | 25481 [ $R_{\text{int}} = 0.1233, R_{\text{sigma}} = 0.1819$ ]                                                      |
| Data/restraints/parameters                     | 25481/26/1757                                                                                                       |
| Goodness-of-fit on $F^2$                       | 1.029                                                                                                               |
| Final <i>R</i> indexes [ $I \geq 2\sigma(I)$ ] | $R_1 = 0.1127, wR_2 = 0.2766$                                                                                       |
| Final <i>R</i> indexes [all data]              | $R_1 = 0.1253, wR_2 = 0.3011$                                                                                       |
| Largest diff. peak/hole / $\text{e \AA}^{-3}$  | 4.14/-3.59                                                                                                          |

**Supplementary Table 3.** Crystal data and structure refinement for **Ag<sub>22</sub>**.

|                                                      |                                                                                                                     |
|------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|
| Empirical formula                                    | C <sub>130</sub> H <sub>112</sub> N <sub>36</sub> OF <sub>12</sub> Cl <sub>4</sub> Ag <sub>22</sub> Sb <sub>2</sub> |
| Formula weight                                       | 5180.99                                                                                                             |
| Temperature/K                                        | 173.00(10)                                                                                                          |
| Crystal system                                       | monoclinic                                                                                                          |
| Space group                                          | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                                                  |
| a/Å Unit cell dimensions                             | <i>a</i> = 28.6773(4) Å <i>α</i> = 90 °                                                                             |
|                                                      | <i>b</i> = 16.9550(2) Å <i>β</i> = 96.447(2) °                                                                      |
|                                                      | <i>c</i> = 33.7887(5) Å <i>γ</i> = 90 °                                                                             |
| Volume/Å <sup>3</sup>                                | 16325.0(4)                                                                                                          |
| <i>Z</i>                                             | 4                                                                                                                   |
| Calculated density (g/cm <sup>3</sup> )              | 2.108                                                                                                               |
| Absorption coefficient /mm <sup>-1</sup>             | 24.371                                                                                                              |
| <i>F</i> (000)                                       | 9856.0                                                                                                              |
| Crystal size/mm <sup>3</sup>                         | 0.08 × 0.06 × 0.05                                                                                                  |
| Radiation                                            | CuKα ( <i>λ</i> = 1.54184)                                                                                          |
| 2Θ range for data collection/°                       | 7.41 to 121.996                                                                                                     |
| Index ranges                                         | -27 ≤ <i>h</i> ≤ 32, -18 ≤ <i>k</i> ≤ 19, -38 ≤ <i>l</i> ≤ 37                                                       |
| Reflections collected                                | 77432                                                                                                               |
| Independent reflections                              | 24579 [ <i>R</i> <sub>int</sub> = 0.0849, <i>R</i> <sub>sigma</sub> = 0.0807]                                       |
| Data/restraints/parameters                           | 24579/969/1819                                                                                                      |
| Goodness-of-fit on <i>F</i> <sup>2</sup>             | 1.038                                                                                                               |
| Final <i>R</i> indexes [ <i>I</i> ≥ 2σ ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.1412, <i>wR</i> <sub>2</sub> = 0.3748                                                     |
| Final <i>R</i> indexes [all data]                    | <i>R</i> <sub>1</sub> = 0.1532, <i>wR</i> <sub>2</sub> = 0.3844                                                     |
| Largest diff. peak/hole / e Å <sup>-3</sup>          | 4.96/-3.10                                                                                                          |