

## Supporting Information

### **[Ag<sub>67</sub>(SPhMe<sub>2</sub>)<sub>32</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>3+</sup>: Synthesis, Total Structure, and Optical Properties of a Large Box-Shaped Silver Nanocluster**

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## Characterization

### UV-vis optical absorption spectroscopy (UV-vis)

UV-vis absorption measurements were done using a Cary 5000 UV-Vis-NIR (Varian Inc.) spectrophotometer.

### Photoluminescence spectroscopy (PL)

PL measurements were carried out on a Fluoromax-4 (Horiba Jobin Yvon) spectrofluorometer.

### Electrospray ionization mass spectrometry (ESI-MS)

ESI-MS of nanoclusters (NCs) was carried out using a Bruker MicroTOF-II mass spectrometer. As-prepared and purified Ag<sub>67</sub> NCs were dissolved in DCM and then centrifuged to discard the insoluble solids. The diluted solutions of the supernatants were injected into the instrument at a flow rate of 500-600 µL/h in both positive and negative modes. Other instrumental parameters were maintained as following: mass range: 100-10000 Da, capillary voltage: 4.0-4.5 kV, nebulizer gas: 0.0-0.4 bar, dry gas: 0.0-4.0 L/min, and temperature 70-150 °C. Note that at soft ionization conditions (nebulizer gas: 0.0-0.1 bar and dry gas: 0.0-1.2 L/min), the Ag<sub>67</sub> with all the eight phosphines was observed, while at moderately harsh conditions (nebulizer gas: 0.2-0.4 bar and dry gas: 2.0-4.0 L/min), Ag<sub>67</sub> was observed with a sequential loss of PPh<sub>3</sub>.

## Analytical ultracentrifugation (AUC)

AUC of Ag<sub>67</sub> NCs in DCM was performed using a Beckman Coulter XL-A analytical ultracentrifuge in sedimentation velocity (SV) mode. A standard 12 mm path length cell with titanium centerpieces and sapphire windows and a 4-hole An60Ti rotor (Beckman Coulter) was used for the SV run. The experiment was conducted at 40,000 revolutions per minute at 6 °C and scans were acquired in intensity mode at 490 nm. At least 90 scans were acquired for each sample and data analysis was performed with Ultrascan 3.3 (Revision 2046) using the 2-dimensional spectrum analysis model.<sup>1</sup> Sedimentation velocity data was also subjected to van Holde-Weichet analysis to assess the monodispersity of the sample.

## Nuclear magnetic resonance (NMR)

The sample was prepared by dissolving the purified Ag<sub>67</sub> NCs in 700 µl of deuterated CD<sub>2</sub>Cl<sub>2</sub> and then 600 µl of the solution was transferred to 5 mm NMR tubes. The <sup>1</sup>H NMR spectra were recorded by collecting 256 scans with a recycle delay time of 5 s using Bruker 700 MHz AVANAC III spectrometer equipped with Bruker CP TCI multinuclear *CryoProbe* (BrukerBioSpin, Rheinstetten, Germany). The free induction decay (FID) data were collected with spectral width of 15243 Hz digitized into 64k data points. The FID signals were zero-filled and amplified by exponential line-broadening factor of 1 Hz before Fourier transformation.

The <sup>31</sup>P NMR spectra were acquired at 298 K using Bruker 600 AVANAC III spectrometer equipped with Bruker BBO multinuclear probe (BrukerBioSpin, Rheinstetten, Germany). To achieve a sufficient signal-to-noise ratio, the <sup>31</sup>P NMR spectra were recorded by collecting at least 1k scans with a recycle delay time of 5 s. The <sup>31</sup>P NMR spectra were recorded using 1D pulse sequence with proton power-gate decoupling using zgpg30 program from Bruker pulse library.

Topspin 2.1 software (BrukerBioSpin) was used in all experiments to collect and to analyze the data.

## Single crystal X-ray diffraction (SCXRD)

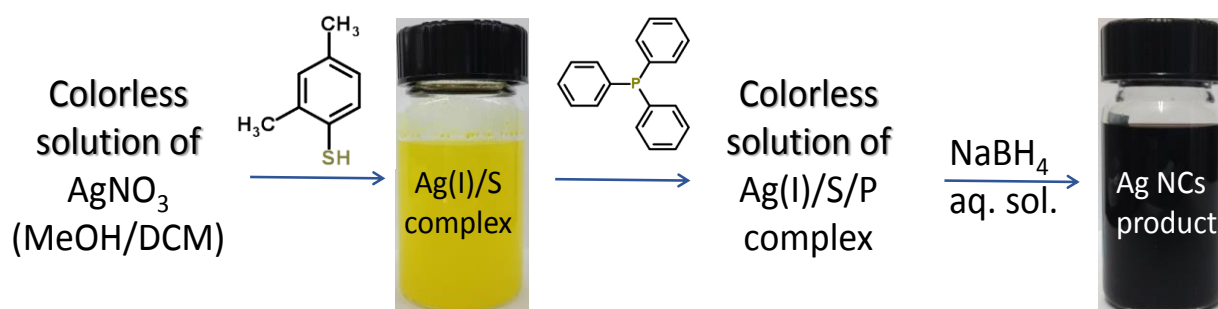
**SCXRD data** were collected using Bruker X8 PROSPECTOR APEX2 CCD diffractometer using CuKα ( $\lambda = 1.54178 \text{ \AA}$ ). Indexing was performed using APEX2 (Difference Vectors method).<sup>2</sup> Data integration and reduction were performed using SaintPlus 6.01.<sup>3</sup> Absorption correction was performed by multi-scan method implemented in SADABS.<sup>4</sup> Space group was determined using XPREP implemented in APEX2. Structure was solved using Direct Methods (SHELXS-97) and refined using SHELXL-97 (full-matrix least-squares on  $F^2$ ) contained WinGX v1.70.01.<sup>5</sup> Crystal data and refinement conditions are shown in Table S1.

The structure was refined as a 2-component inversion twin with component relationship as 65:35. Only two of three [B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sup>1-</sup> anions were localized. The third one is probably disordered in the crystal at (0, ½, 0.344) and (½, 0, 0.582) as well as some amount of solvent (each cavity of 6577 Å<sup>3</sup> contains 1693 ē). Geometry of the benzene rings was constrained by AFIX 66. SIMU 0.02 restraint was applied to the most of [S(C<sub>6</sub>H<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub>]<sup>1-</sup> anions (molecules 2, 3, 4, 6, 7, 9, 11, 12, 13, 14, 15 and 16). Single C–C bonds between benzene rings and methyl groups were slightly restrained to 1.51(2) Å (bonds C74–C78, C92–C97, C94–C98 and C124–C128). Hydrogen atoms are placed at calculated positions and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{sp}2})$  or  $1.2U_{\text{eq}}(\text{C}_{\text{sp}3})$ . Strongly delocalized electron density (3830 ē per unit cell) was found in the voids with total pore volume equals to 15936 Å<sup>3</sup> (28.0% of the unit cell volume) and omitted from the refinement using the PLATON's SQUEEZE procedure.

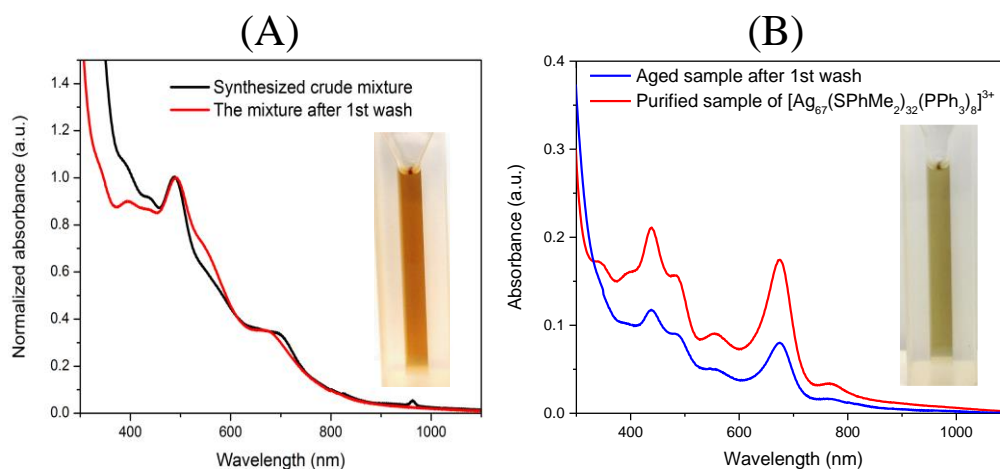
**Table S1.** Crystal data and structure refinement for Ag<sub>67</sub>(SPhMe<sub>2</sub>)<sub>32</sub>(PPh<sub>3</sub>)<sub>8</sub>.

Identification code	Ag <sub>67</sub> (SPhMe <sub>2</sub> ) <sub>32</sub> (PPh <sub>3</sub> ) <sub>8</sub>
Empirical formula	C <sub>472</sub> H <sub>466</sub> Ag <sub>67</sub> B <sub>3</sub> P <sub>8</sub> S <sub>32</sub>
Formula weight	14671.82
Crystal system, space group	Orthorhombic, <i>Ccc2</i>
Unit cell dimensions	$a = 46.195(1) \text{ \AA}$ , $b = 48.069(1) \text{ \AA}$ , $c = 25.6424(8) \text{ \AA}$
Volume	56941 (3) $\text{\AA}^3$
Z, calculated density	4, 1.711 Mg m <sup>-3</sup>
$F(000)$	28376
Temperature (K)	100.0(1)
Radiation type	Cu $K\alpha$
Absorption coefficient	19.62 mm <sup>-1</sup>
Absorption correction	Multi-scan
Max and min transmission	0.145 and 0.274
Crystal size	0.09 × 0.10 × 0.12 mm
Shape, color	Prism, black
$\theta$ range for data collection	3.7–65.1°
Limiting indices	$-54 \leq h \leq 50$ , $-56 \leq k \leq 28$ , $-30 \leq l \leq 28$
Reflection collected / unique / observed with $I > 2\sigma(I)$	105002 / 43399 ( $R_{\text{int}} = 0.031$ ) / 39625
Completeness to $\theta_{\text{max}} = 65.08^\circ$	99.4 %
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	43399 / 581 / 2126
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.054$ , $wR_2 = 0.144$
Final $R$ indices (all data)	$R_1 = 0.061$ , $wR_2 = 0.152$
Weighting scheme	$[\sigma^2(F_o^2) + (0.0777P)^2 + 804.5305P]^{-1*}$
Goodness-of-fit	1.07
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.35(1)
Largest diff. peak and hole	1.65 and -1.45 e $\text{\AA}^{-3}$

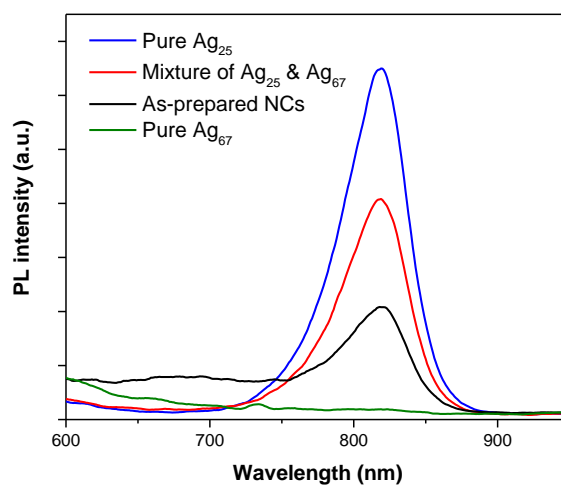
$$*P = (F_o^2 + 2F_c^2)/3$$



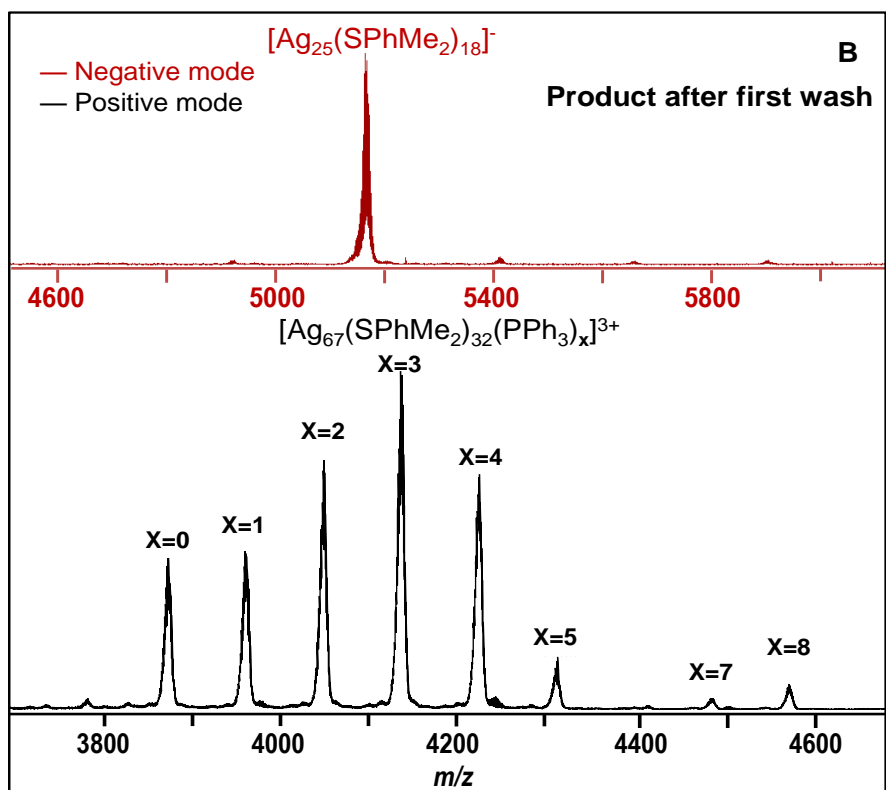
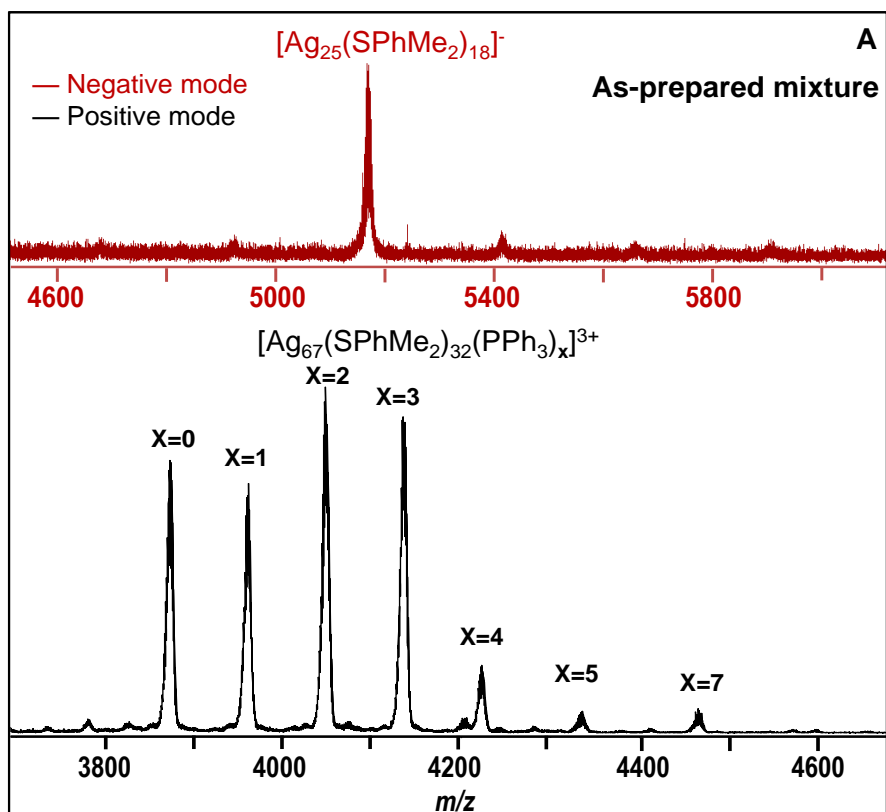
**Scheme 1:** Synthesis steps of  $[\text{Ag}_{67}(\text{SPhMe}_2)_{32}(\text{PPh}_3)_8]^{3+}$  nanocluster.

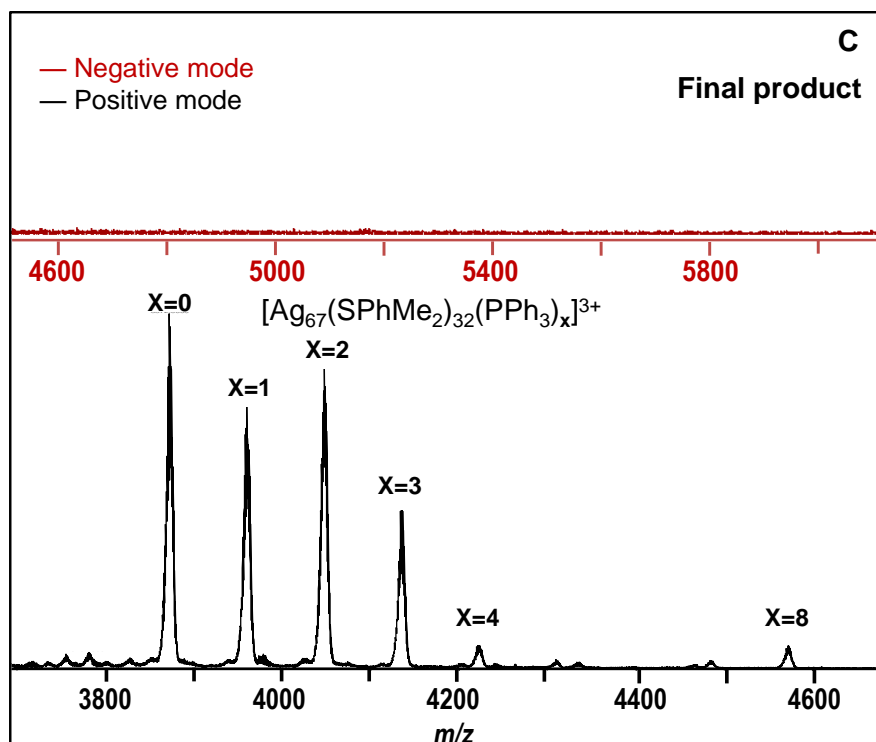


**Figure S1.** UV-vis spectra of the evolution of  $\text{Ag}_{67}$  NCs. (A) The as-synthesized NCs product in a DCM/MeOH mixture and immediately after first wash. (B) After aging overnight at room temperature and the final purified product of  $\text{Ag}_{67}$  NCs.



**Figure S2.** PL emission spectra of the as-prepared NCs product and pure  $\text{Ag}_{67}$  compared with pure  $\text{Ag}_{25}$  and a mixture of  $\text{Ag}_{25}$  and  $\text{Ag}_{67}$  (excitation at 490 nm). These data suggest that the PL peak of as-prepared NCs most likely corresponds to  $\text{Ag}_{25}$ , which is a byproduct.

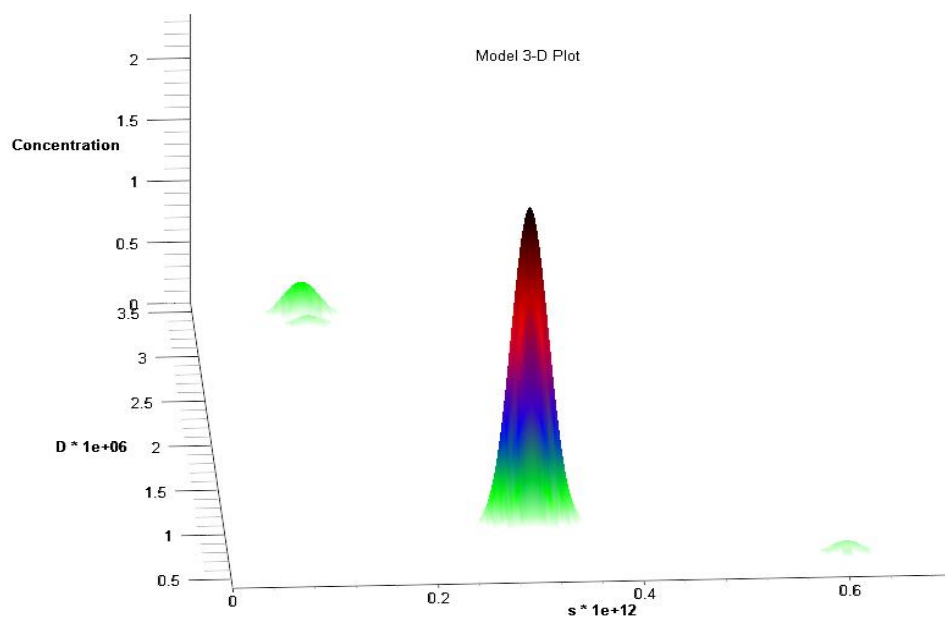




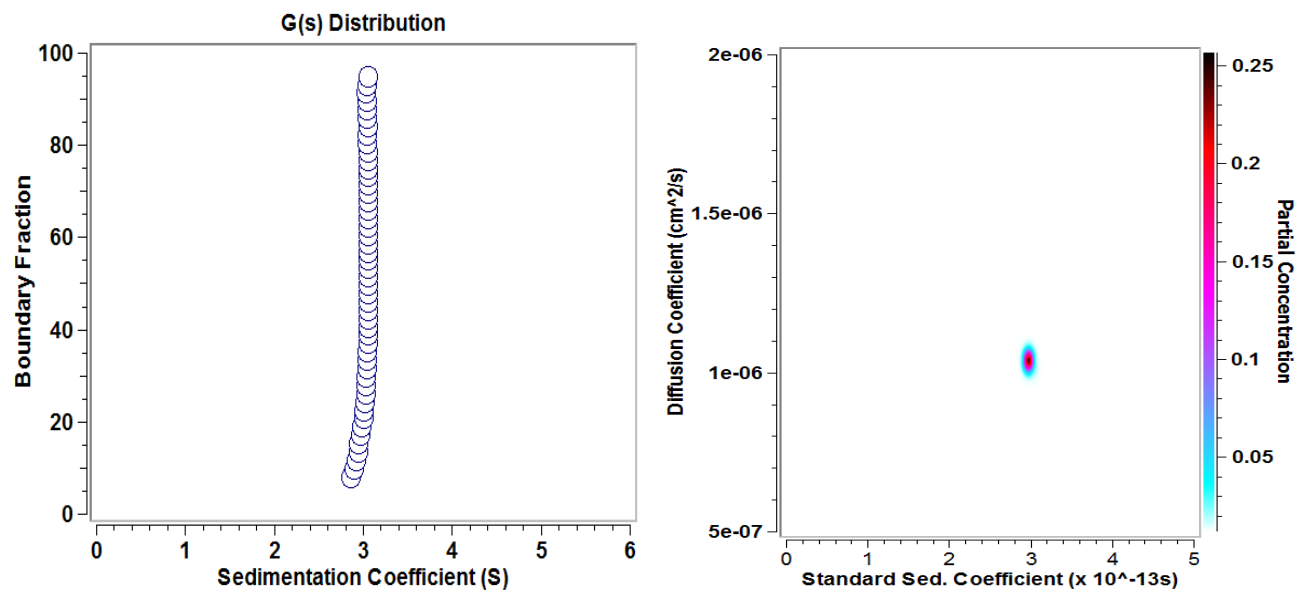
**Figure S3.** ESI-MS in the negative (dark red) and positive (black) modes of  $\text{Ag}_{67}$  NCs. (A & B) As-prepared NCs mixture and first wash product, respectively, show the presence of both  $[\text{Ag}_{25}(\text{SPhMe}_2)_{18}]^-$  and  $[\text{Ag}_{67}(\text{SPhMe}_2)_{32}(\text{PPh}_3)_8]^{3+}$  NCs. (C) The cleaned final product of  $\text{Ag}_{67}$  NCs that does not contain  $\text{Ag}_{25}$ . It is worth noting that the number of phosphine ( $\text{PPh}_3$ ) ligands was varying from 0 to 8 (in the range of  $m/z$  ~3872-4572) during the electrospray ionization. This fragmentation of peaks is due to the sequential loss of  $\text{PPh}_3$  from  $\text{Ag}_{67}$  under given experimental conditions.

**Table S2.** Summary of AUC results.

Molecular. Weight.	Sedimentation coefficient in DCM ( $s_{\text{apparent}}$ )	Standard Sedimentation coefficient ( $s_{20,W}$ )	Diffusion coefficient in DCM ( $D_{\text{apparent}}$ )	Standard Diffusion coefficient ( $D_{20,W}$ )	Frictional ratio ( $f/f_0$ )	%
<b>12100 ± 1150</b>	(5.7 ± 0.1) x 10 <sup>-13</sup> s	(3.0 ± 0.1) x 10 <sup>-13</sup> s	(2.4 ± 0.1) x 10 <sup>-6</sup> s	(1.1 ± 0.1) x 10 <sup>-6</sup> s	1.49 ± 0.3	92%

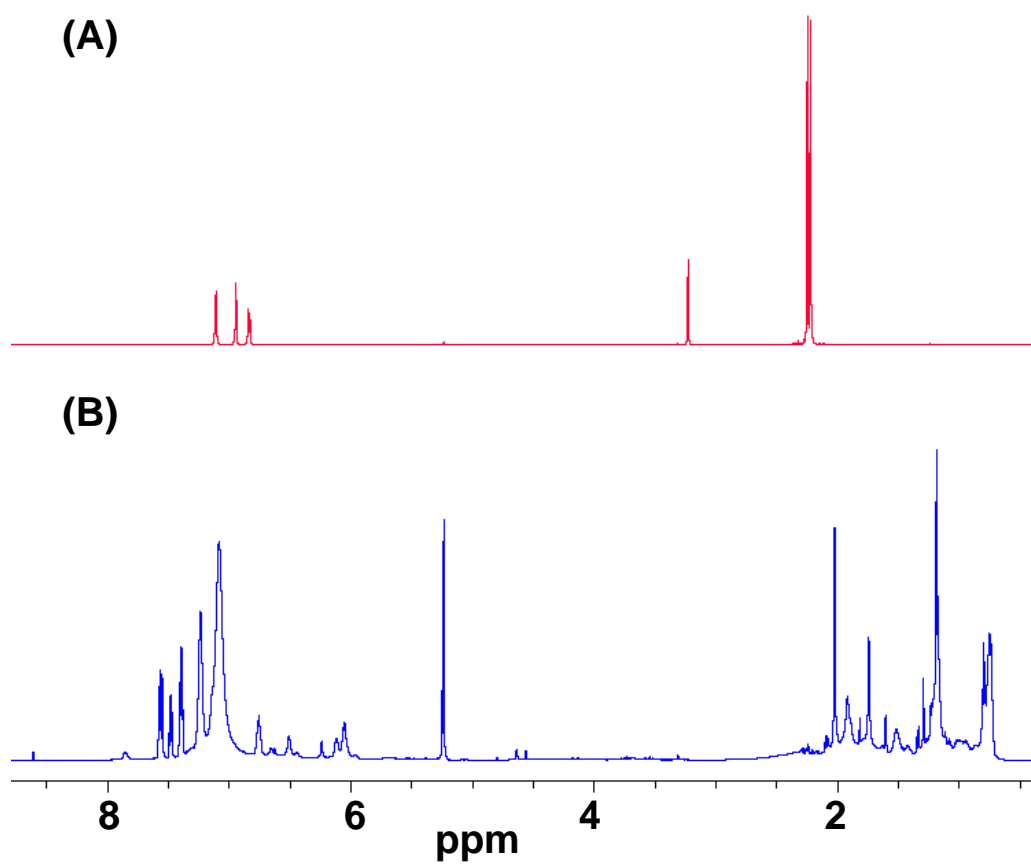


**Figure S4.** 3D representation of sedimentation and diffusion coefficients for the Ag<sub>67</sub> NCs.

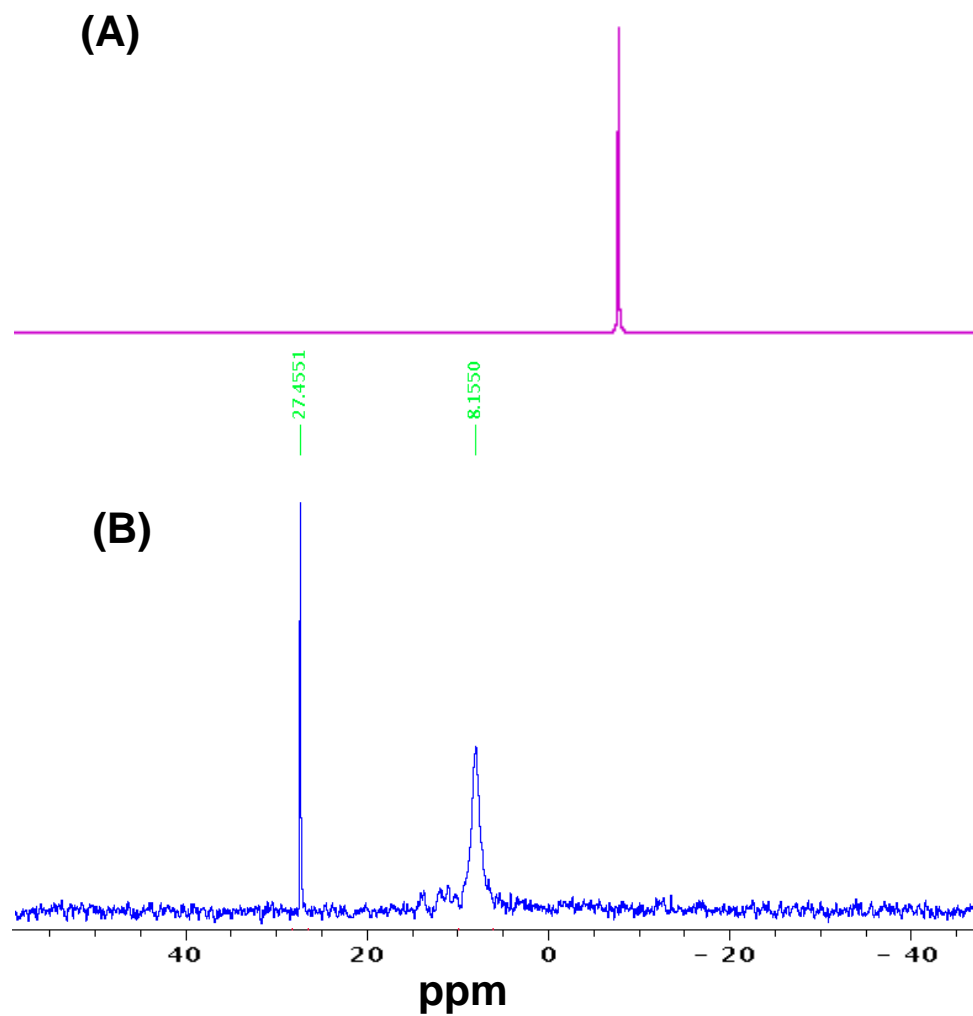


**Figure S5.** Left: Standard sedimentation coefficient distribution of Ag<sub>67</sub> NCs via van Holde-Weichet analysis. The near vertical plot illustrates a predominantly monodisperse NCs solution in DCM. Right: 2D representation of sedimentation and diffusion coefficients for the Ag<sub>67</sub> NCs.

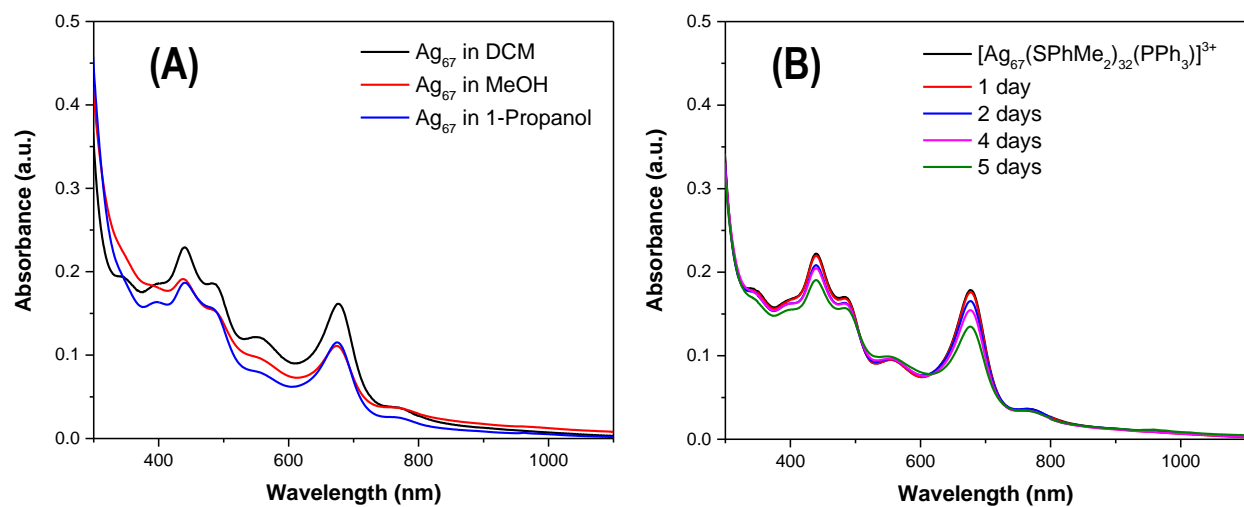




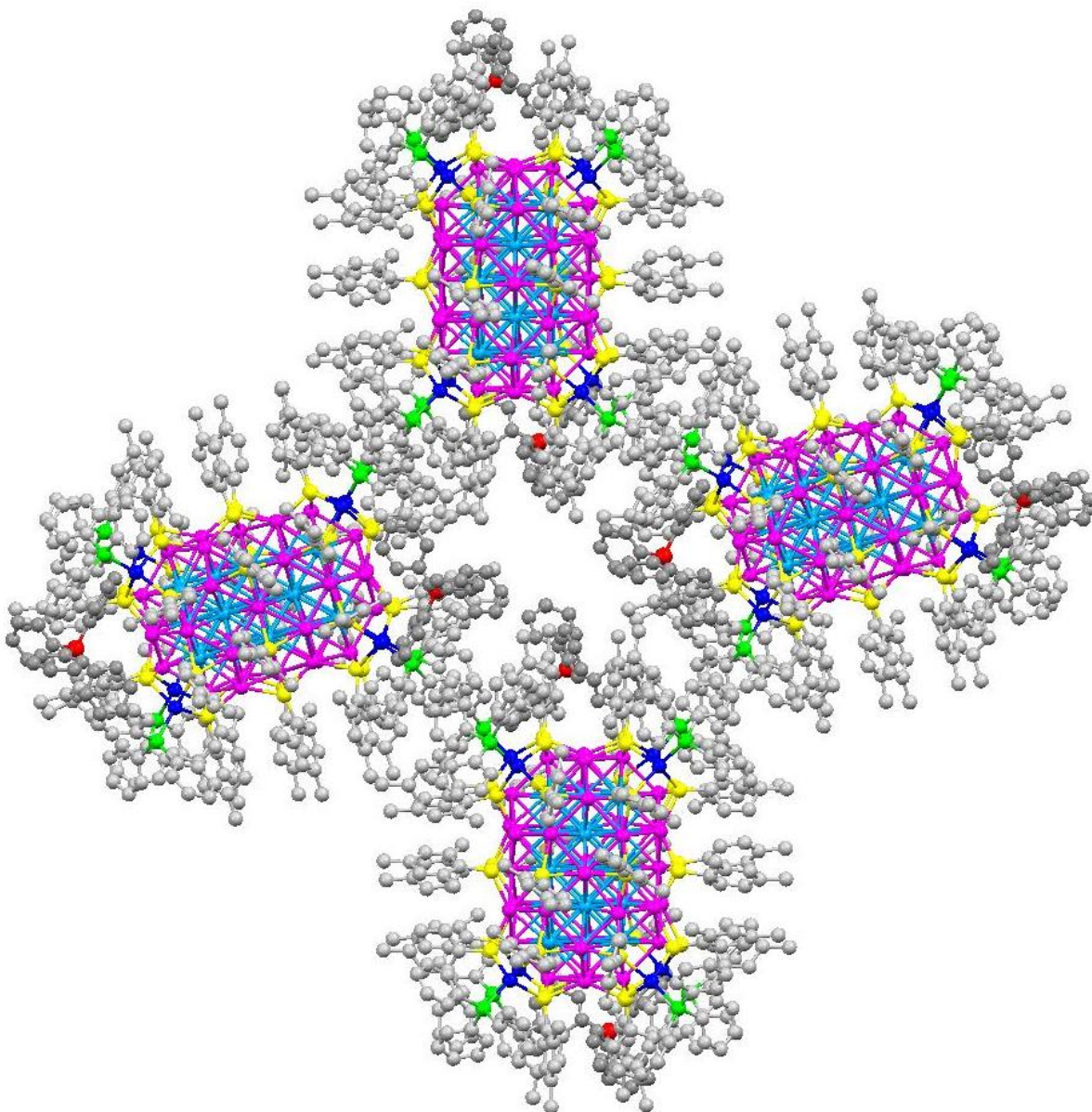
**Figure S6.**  $^1\text{H}$  NMR spectra of (A) 2,4-dimethylbenzenedithiol ( $\text{HSPHMe}_2$ ) ligand, and (B)  $\text{Ag}_{67}$  NCs dissolved in  $\text{CD}_2\text{Cl}_2$ .



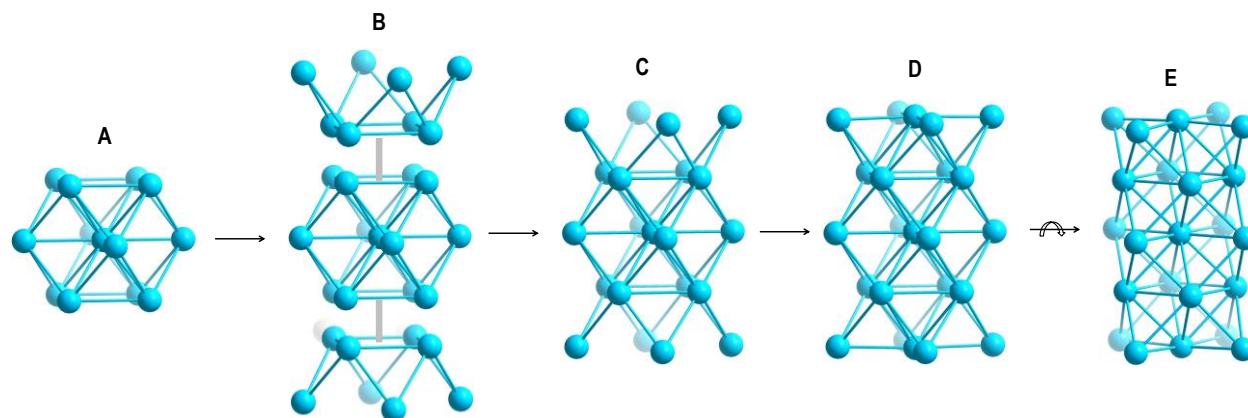
**Figure S7.**  $^{31}\text{P}$  NMR spectra of (A) triphenylphosphine ( $\text{PPh}_3$ ), which shows only one sharp peak at -7.3 ppm, and (B)  $\text{Ag}_{67}$  NCs dissolved in  $\text{CD}_2\text{Cl}_2$ .



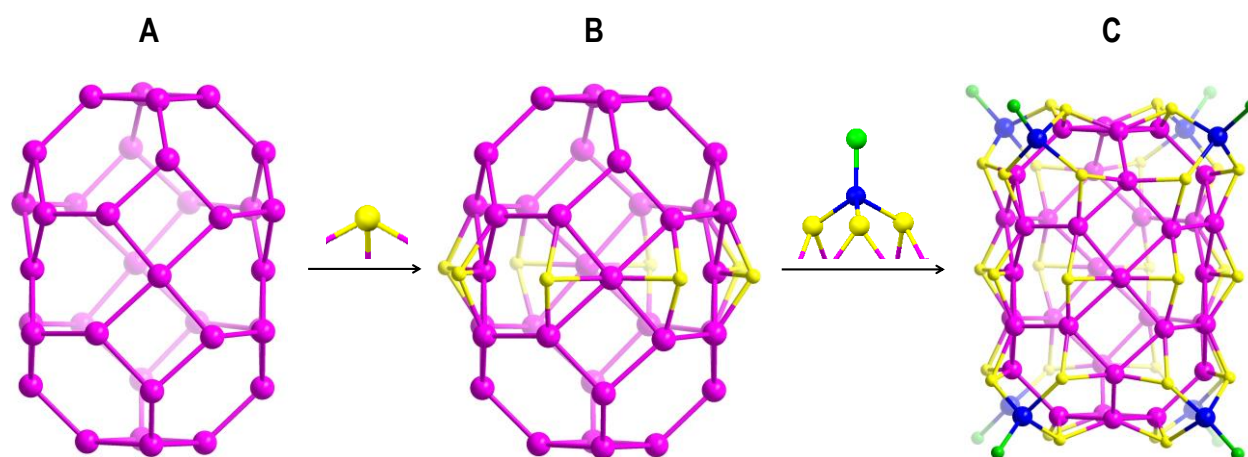
**Figure S8.** (A) UV-vis spectra of  $\text{Ag}_{67}$  NCs in different solvents. (B) Monitoring the stability of  $\text{Ag}_{67}$  NCs in DCM at 5 °C.



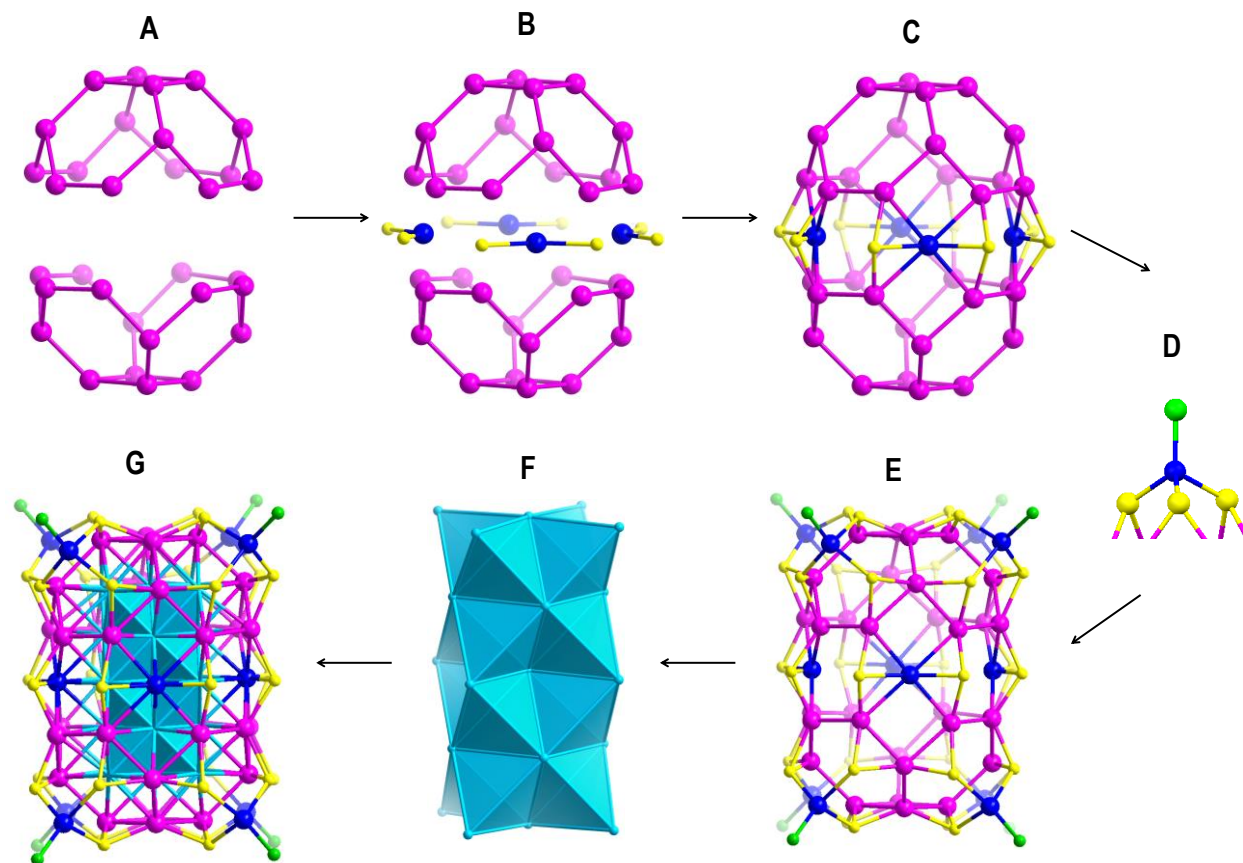
**Figure S9.** Packing of  $[\text{Ag}_{67}(\text{SPhMe}_2)_{32}(\text{PPh}_3)_8]^{3+}$  clusters showing two  $\text{BPh}_4^-$  counterions per cluster. Color legends: gray and dark gray, carbon; blue, magenta, and cyan, silver; yellow, sulfur; green, phosphorous; red, boron. Hydrogen atoms are omitted for clarity.



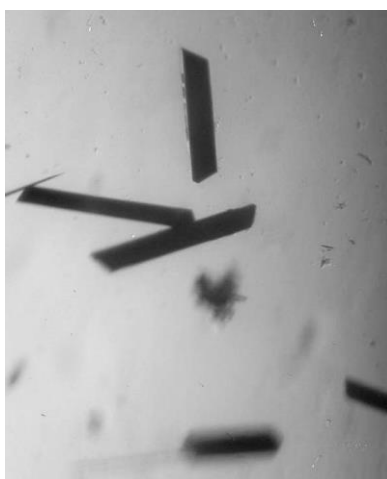
**Figure S10.** Construction of  $\text{Ag}_{23}$  metal core of  $\text{Ag}_{67}$  NC. (A)  $\text{Ag}_{13}$  cuboctahedron. (B) Sharing of two square faces of an  $\text{Ag}_{13}$  cuboctahedron with two  $\text{Ag}_8$  crowns to form  $\text{Ag}_{21}$  metal core as in C. (D) Closing two crowns by two Ag atoms forms  $\text{Ag}_{23}$  core. (E) Structure of D after suitable rotation. Color legend: cyan, silver.



**Figure S11.** Construction of  $\text{Ag}_{44}\text{S}_{32}\text{P}_8$  metal-ligand layer of  $\text{Ag}_{67}$  NC. (A)  $\text{Ag}_{36}$  box. (B) Eight thiols in bridging ligand-motif mode to form  $\text{Ag}_{36}\text{S}_8$ . (C) Protection of eight  $\text{AgS}_3\text{P}$  motifs on  $\text{Ag}_{36}\text{S}_8$  to form  $\text{Ag}_{44}\text{S}_{32}\text{P}_8$ . Color legend: cyan and blue, silver; yellow, sulfur; green, phosphorous.



**Figure S12.** Construction of total structure of Ag<sub>67</sub> NC. (A) Two Ag<sub>16</sub> bowls. (B) Connecting two Ag<sub>16</sub> bowls through four S-Ag-S motifs to form a closed Ag<sub>36</sub>S<sub>8</sub> i.e., (C). (D) AgS<sub>3</sub>P ligand motifs. (E) Eight AgS<sub>3</sub>P motifs sitting on eight hexagonal faces of C to form the structure of Ag<sub>44</sub>S<sub>32</sub>P<sub>8</sub>. (F) The Ag<sub>23</sub> metal core. (G) Ag<sub>23</sub> core encapsulated by E to form the total structure Ag<sub>67</sub>S<sub>32</sub>P<sub>8</sub>. Color legends: blue, magenta, and cyan, silver; yellow, sulfur; green, phosphorous.



**Figure S13.** Photograph of some black crystals grown from the Ag<sub>67</sub> NCs.

## References

- (1) Brookes, E.; Cao, W.; Demeler, B. *Euro. Biophys. J.* **2010**, *39*, 405.
- (2) APEX2 (Bruker AXS Inc, Madison, Wisconsin, USA, 2014).
- (3) SAINT (Bruker AXS. Inc, Madison, Wisconsin, USA, 2014).
- (4) SADABS (University of Gottingen, Germany, 2008).
- (5) Farrugia, L. *J. Appl. Cryst.* **1999** *32*, 837; Sheldrick, G. M. *Acta Cryst.* **2008** *A64*, 112.