Supporting Information

An atomically precise silver nanocluster for artificial light-harvesting system through supramolecular functionalization

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**Experimental**

**Materials**

Adamantane thiol (AdmSH), silver nitrate (AgNO₃), silver trifluoroacetate (CF₃COOAg), tetraphenylphosphonium chloride (PPh₄Cl), tetra-n-butylammonium hexafluorophosphate, β-cyclodextrin were procured from Sigma-Aldrich. HPLC grade solvents- triethylamine (Et₃N), dimethylformamide (DMF), dichloromethane (DCM), acetonitrile (ACN), methanol (MeOH) were purchased from Spectrochem.

**X-ray Crystallography Details**

Bruker Axs Kappa Apex II SCXRD (single crystal X-ray diffractometer) with CCD detector (MoKα radiation, λ= 0.71073 Å) was used here. The crystal structure was solved by SHELXT 2014 and refined by the full matrix least-squares method using SHELXL 2018 present in the program suite WinGX (version 2014.1). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were (positioned geometrically) refined isotropically using an olex2.

**Computational Details**

All the DFT calculations have been performed using Gaussian 09 software. The B3LYP functional with Pople’s 6-31G* basis set and LANL2DZ effective core potential (ECP) were used for the nonmetallic elements (S, F, O, N, C and H) and metal (Ag), respectively. The electronic absorption spectra were performed using the time-dependent density functional theory (TD-DFT) with the scanning of 300 excited state. DCM solvent has been considered with a conductor-like polarizable continuum solvent model in TD-DFT calculation. The non-covalent interaction (NCI) and critical points were performed through the reduced density gradient (RDG) using the quantum theory of atoms in molecules (QTAIM) method implemented in the Multiwfn program (version-3.8). Also, the Kohn-Sham orbital analysis has been performed for the understanding of core and ligands orbital contribution in the frontier molecular orbitals.

The binding energies (BE) of β-cyclodextrin (β-CD) and adamantane group of Ag₁₆ NC are performed using Vienna Ab-Initio Simulation Package (VASP) implementing the generalized gradient approximation method in PBE functional. The Projector augmented wave (PAW) method has been implemented for the consideration of the interaction between core and
valence electrons. The energy cutoff of 470 eV has been employed. A conjugate gradient algorithm has been implemented for the ionic relaxation with energy criterion of $10^{-5}$ eVÅ$^{-1}$ and Hellmann-Feynman force criterion of $\leq 0.05$ eVÅ$^{-1}$. The van der Waals corrections of Grimme’s DFT-D3 method has considered in our calculation. During optimization the Brillouin zone was sampled at the $\Gamma$-centered K-point of (1x1x1), due to possesses of large unit cell of $\beta$-CD encapsulated Ag$_{16}$ NC (Ag$_{16}$ NC $\cap$ $\beta$-CD$_n$, n = 1, 2) structures. The binding energy can be calculated using the following equation,

$$BE = \frac{E_{Ag_{16} NC \cap \beta-(CD)n} - nE_{\beta-CD}}{n}$$

(S1)

Where, $n$ denotes the number of $\beta$-CD molecules get encapsulated, the $E_{Ag_{16} NC \cap \beta-(CD)n}$, $E_{Ag_{16} NC}$ and $nE_{\beta-CD}$ are the total energies of the $\beta$-CD encapsulated Ag$_{16}$ NC inclusion complex, individual Ag$_{16}$ NC and the free $\beta$-CD molecules, respectively.

**Instrumentation**

UV-vis spectroscopy was carried out on a UV-3800 SHIMADZU UV–vis/NIR spectrometer. Emission measurements were performed using a Fluorolog-3 spectrofluorimeter from Horiba Jobin Yvon. The relative quantum yields were determined by the best match of the excitation wavelength of a well-known chromophore such as perylene with the crystals and the excitation was fixed at 380 nm. The concentration of the solutions (DCM) was fixed by adjusting the absorption 0.05 OD and the quantum yield was measured at room temperature. A picosecond time-correlated single-photon counting (TCSPC) system (Horiba Jobin Yvon-IBH) was utilized for the measurement of emission lifetime. Solutions were excited at 375 nm using a pulsed diode laser. FEI Tecnai G2 F30 S -Twin transmission electron microscope (TEM) 300 KV and FEI Nova NANOSEM 450 (with EDS) were used for the microscopic characterization. X-ray photoelectron spectroscopy (XPS) measurements have been done using the Omicron Nano tech instrument (MgKα radiation at 1253.6 eV). All binding energies were referenced to the neutral C 1s peak at 284.8 eV. The powder X-ray diffraction was recorded on Bruker D8 Advance X-ray diffractometer in the 20 range 5–30°. Differential pulse voltammogram (DPV) and cyclic voltammogram (CV) were measured on a CH instrument with a three-electrode system where glassy carbon electrode (GCE) was used as a working electrode, graphite electrode served as a counter electrode and silver wire was used as a reference electrode in DCM with 0.05 M tetra-n-butylammonium hexafluorophosphate salt was added as an electrolyte. We have calibrated against the standard reference electrode (Ag/Ag$^+$). A Bruker
Avance III, 500 MHz, NMR was used. DCM solution of the NC, β-carotene and their composites are drop-casted between the patterned gold electrodes deposited on the ceramic plate to form a thin layer of the material. The electrical and photoresponse measurement was observed using a Keithley 6712 electrometer using sunlight.

**ESI-MS measurement**

Waters Q-TOF mass spectrometer equipped with a Z-spray source was used for the electrospray ionization (ESI) mass spectrometry measurement with positive mode. The Ag_{16} crystals were dissolved in DCM (1 mg/mL) and diluted by acetonitrile (1:1). The solution was infused at 20 µL/min for positive mode. The spectrometer was operated in the mass range of m/z 1000–6000 for positive mode.

| Instrument parameters       | ES+ (positive mode) |
|-----------------------------|---------------------|
| Capillary (kV)              | 3.0600              |
| Sampling Cone               | 88.0000             |
| Source Temperature (°C)     | 70                  |
| Source Offset               | 24                  |
| Desolvation Temperature (°C)| 150                 |
| Cone Gas Flow (L/Hr)        | 53                  |
| Desolvation Gas Flow (L/Hr) | 213                 |

The Ag_{16} \(\beta\)-CD_{1} was dissolved in DCM (1 mg/mL) and diluted by acetonitrile (1:1). The solution was infused at 25 µL/min for positive mode. The spectrometer was operated in the mass range of m/z 1000–6000 for positive mode.

| Instrument parameters       | ES+ (positive mode) |
|-----------------------------|---------------------|
| Capillary (kV)              | 2.8000              |
| Sampling Cone               | 54.0000             |
| Source Temperature (°C)     | 70                  |
| Source Offset               | 24                  |
| Desolvation Temperature (°C)| 150                 |
| Cone Gas Flow (L/Hr)        | 53                  |
| Desolvation Gas Flow (L/Hr) | 213                 |
The Ag_{16} \beta-\text{CD}_{2} was dissolved in DCM (1mg/ml) and diluted by acetonitrile (1:1). The solution was infused at 25 µL/min for positive mode. The spectrometer was operated in the mass range of m/z 1000–6000 for positive mode.

| Instrument parameters          | ES+ (positive mode) |
|--------------------------------|---------------------|
| Capillary (kV)                 | 1.9000              |
| Sampling Cone                  | 54.0000             |
| Source Temperature (°C)        | 70                  |
| Source Offset                  | 24                  |
| Desolvation Temperature (°C)   | 150                 |
| Cone Gas Flow (L/Hr)           | 53                  |
| Desolvation Gas Flow (L/Hr)    | 213                 |

The radiative and nonradiative rate constants calculation

The radiative rate \((k_r)\) and nonradiative rate \((k_{nr})\) constants are calculated using the following equations

\[
k_r = \frac{\phi}{\tau_{av}} \tag{S2}
\]

\[
k_{nr} = \frac{(1-\phi)}{\tau_{av}} \tag{S3}
\]

Where,

\(\phi = \text{Quantum yield}\)

\(\tau_{av} = \text{Avg. lifetime}\)
Förster radius ($R_0$) calculation from the experimental data

$$R_0 = d \left( \tau_{\text{pure}} \times k_{ET} \right)^{1/6} \quad \text{(S4)}$$

Where, $d = 2$ nm calculated from the theoretical optimized structure of the donor-acceptor system.

$\tau_{\text{pure}} = \text{Emission lifetime of the donor Ag}_{16} \cap \beta\text{-CD}_2$

$$= 1.03 \text{ µs}$$

$k_{ET} = \frac{1}{N} (k_{\text{mix}} - k_{\text{pure}})$, where $N$ is the number of nearest neighbours, here we are calculating 1:1. $k_{\text{mix}}$ is the total emission decay rate of the donor-acceptor system and $k_{\text{pure}}$ is the total emission decay rate of the donor. The calculated $k_{\text{mix}}$ is $3.9 \times 10^7$ s$^{-1}$ ($k_r = 2.6 \times 10^7$ s$^{-1}$ and $k_{nr} = 1.3 \times 10^7$ s$^{-1}$) and $k_{\text{pure}}$ is $9.7 \times 10^5$ s$^{-1}$.

Energy transfer efficiency calculation

Energy transfer efficiency ($\Phi_{ET}$) is calculated by following equation

$$\Phi_{ET} = 1 - \frac{I_{DA}}{I_D} \quad \text{(S5)}$$

Where,

$I_{DA} = \text{Intensity of donor emission in presence of acceptor}$

$I_D = \text{Intensity of donor emission in absence of acceptor}$

$\Phi_{ET} = \text{Fractional energy transfer efficiency}$

$$\Phi_{ET} = 1 - \frac{12954}{190159} = 1 - 0.068 = 0.93$$

Antenna effect calculation

The antenna effect ($\chi$) is calculated for the certain concentration of donor and acceptor equal to the ratio of emission intensity at 540 nm (for Ag$_{16} \cap \beta$-CD$_2$) upon excitation of the donor which is depicted in Fig. S27.
\[ x = \frac{I_{A+D}^{540\,\text{nm}}(\lambda_{\text{ex}}=380\,\text{nm}) - I_{D}^{540\,\text{nm}}(\lambda_{\text{ex}}=380\,\text{nm})}{I_{A+D}^{540\,\text{nm}}(\lambda_{\text{ex}}=462\,\text{nm})} \]  

\( I_{A+D}^{540\,\text{nm}}(\lambda_{\text{ex}} = 380\,\text{nm}) \) = Emission intensity of (donor + acceptor) at 540 nm upon excitation at 380 nm.

\( I_{D}^{540\,\text{nm}}(\lambda_{\text{ex}} = 380\,\text{nm}) \) = Emission intensity of (donor) at 540 nm upon excitation at 380 nm.

\( I_{A+D}^{540\,\text{nm}}(\lambda_{\text{ex}} = 462\,\text{nm}) \) = Emission intensity of (donor + acceptor) at 540 nm upon excitation at 462 nm.

antenna effect \( (x) = \frac{120345 - 12954}{3142} = 34. \)
### Table S1. Crystal data and structure refinement parameters.

| Parameter                                | Value                                                                 |
|------------------------------------------|----------------------------------------------------------------------|
| Identification code                      | Ag\textsubscript{16} NC                                             |
| CCDC number                              | 2169435                                                             |
| Empirical formula                        | C\textsubscript{102}H\textsubscript{148}Ag\textsubscript{16}Cl\textsubscript{15}N\textsubscript{4}O\textsubscript{16}S\textsubscript{9} |
| Formula weight                           | 4021.15                                                             |
| Temperature                              | 150 (2) K                                                           |
| Wavelength                               | 0.71073 Å                                                           |
| Crystal system                           | Triclinic                                                           |
| Space group                              | P-1 (No. 2)                                                         |
| Unit cell dimensions                     | a = 17.2901(12) Å; \( b = 17.3047(11) \) Å; c = 29.001(2) Å; \( \alpha = 94.002(2)\)°; \( \beta = 97.603(3)\)°; \( \gamma = 119.287(2)\)° |
| Volume                                   | 7410.2(9) Å\(^3\)                                                  |
| Z                                        | 2                                                                   |
| Density                                  | 1.802 mg/m\(^3\)                                                   |
| Absorption coefficient                   | 2.274 mm\(^{-1}\)                                                  |
| F(000)                                   | 3928                                                                |
| Crystal size                             | 0.096 \( \times \) 0.075 \( \times \) 0.045 mm\(^3\)              |
| Theta range for data collection          | 2.512 to 28.633°                                                   |
| Limiting indices                         | -23 \( \leq h \leq 23\), -23 \( \leq k \leq 23\), -38 \( \leq l \leq 38\) |
| Reflections collected                    | 241695                                                              |
| Independent reflections                  | 37175 [R(int) = 0.1401]                                             |
| Completeness to theta = 25.242°          | 99.2 %                                                              |
| Refinement method                        | Full-matrix least-squares on F\(^2\)                              |
| Data / restraints / parameters            | 37175 / 127 / 1485                                                  |
| Goodness-of-fit on F\(^2\)               | 1.018                                                               |
| Final R indices [I > 2sigma(I)]          | R\(_1\) = 0.1059, wR\(_2\) = 0.2692                               |
| R indices (all data)                     | R\(_1\) = 0.2174, wR\(_2\) = 0.3334                               |
| Largest diff. peak and hole              | 3.157 and -1.913 e. Å\(^{-3}\)                                     |
Table S2. Binding energy values of one β-CD encapsulation

| Different encapsulation modes of β-CD | Binding energy (eV) in head configuration | Binding energy (eV) in tail configuration |
|---------------------------------------|------------------------------------------|------------------------------------------|
| S3                                    | -1.57                                    | -0.27                                    |
| S4                                    | -3.30                                    | -2.1                                     |
| S8                                    | -1.60                                    | -0.35                                    |

Table S3. Binding Energy values of two β-CD encapsulation.

| Different encapsulation modes of β-CD | Binding energy (eV) |
|---------------------------------------|---------------------|
| S4-S1                                 | -2.10               |
| S4-S2                                 | -1.06               |
| S4-S3                                 | -1.12               |
| S4-S5                                 | -2.45               |
| S4-S6                                 | -2.66               |
| S4-S7                                 | -2.21               |
| S4-S8                                 | -2.26               |

Table S4. The obtained radiative, nonradiative rate constants, quantum yield and lifetime.

| Inclusion complex       | Relative quantum yield (φ) | Lifetime (τav) (µs) | k_r (s⁻¹)     | k_nr (s⁻¹)  |
|-------------------------|-----------------------------|---------------------|---------------|-------------|
| Ag₁₆ ∩ β-CD₁            | 0.12                        | 0.48                | 2.5 × 10⁵     | 1.83 × 10⁶  |
| Ag₁₆ ∩ β-CD₂            | 0.26                        | 1.03                | 2.52 × 10⁵    | 7.18 × 10⁵  |
Fig. S1 QTAIM molecular plot of bond critical point (BCP), ring critical point (RCP) and cage critical point (CCP) of Ag$_{16}$ NC. In core, we have observed some long-range bond critical point of two Ag atoms. For clarity, we have removed the ligands.
Fig. S2 The Reduced Density Gradient (RDG) isosurface of argentophilic interaction (a), and (b) the scatter plot of (RDG vs. \(\text{sign}(\lambda_2)\rho\)) of Ag\(_{16}\) NC. Where the green color indicates the presence of nonbonding interaction.
Fig. S3 (a) The presence of the eight triangular facets, and among the ten square facets, (b) five square facets from the down side and (c) another five square facets from up side of the square gyrobicupola geometry of the Ag$_{16}$ skeleton, respectively.
**Fig. S4** The three layers of the Ag$_{16}$ skeleton.
Fig. S5 Relation between the top and bottom square facets of Ag$_{16}$ skeleton by rotation of 45°.
Fig. S6 The presence of lattice DMF molecule in Ag$_{16}$ NC.
**Fig. S7** The partial positive mode ESI-MS data of associated fragments along the peak of parent NC where experimental and simulated patterns are well matched.
**Fig. S8** The $^1$H NMR in CDCl$_3$ of (a) as-synthesized Ag$_{16}$ NC and (b) [Ag-Adm]$_n$ complex.
Fig. S9 The $^{19}$F NMR in the CDCl$_3$ of Ag$_{16}$ NC.
Fig. S10 The PXRD data of the Ag$_{16}$ NC.
Fig. S11 EDS spectrum of Ag$_{16}$ NC, inset showing the corresponding SEM micrograph.
Fig. S12 The deconvoluted XPS spectra of the Ag$_{16}$ NC.
**Fig. S13** The generated PL property of Ag$_{16}$ NC after the surface functionalization by the β-CD upon excitation of 380 nm.
Fig. S14 The $^1$H NMR in CDCl$_3$ of (a) β-CD functionalized Ag$_{16}$ NC and (b) the pure β-CD.
**Fig. S15** The UV-vis absorbance spectra of the Ag_{16} NC and β-CD functionalized Ag_{16} NC dissolved in DCM.
Fig. S16 (a) Cyclic-Voltammetry, (b) and (c) DPV of Ag$_{16}$ NC and Ag$_{16}$ NC with β-CD, respectively.
Fig. S17 The partial positive mode ESI-MS data of the Ag$_{16}$ $\cap$ $\beta$-CD$_2^{2+}$ along with its associated fragments.
Fig. S18 The partial positive mode ESI-MS data of the Ag_{16} \cap \beta-CD_{2}^{2+} along with its associated fragments.
Fig. S19 The numbering of the possible β-CD attachment sites on the Ag$_{16}$ NC.
Fig. S20 The binding energy calculation of tail and head configuration of β-CD attachment on the stable S4 position.
Fig. S21 The PL emission of the organic dye β-carotene molecule in DCM upon excitation at 462 nm.
Fig. S22 The zeta potential data of the donor Ag$_{16}$ $\cap$ $\beta$-CD$_2$ and acceptor $\beta$-carotene in DCM.
Fig. S23 UV-visible of Ag$_{16}$ \(\cap\) \(\beta\)-CD$_2$ with the gradual addition of \(\beta\)-carotene in DCM. 2 mL of $10^{-5}$ M Ag$_{16}$ \(\cap\) \(\beta\)-CD$_2$ in DCM was titrated with $2 \times 10^{-6}$ M solution of \(\beta\)-carotene ($\lambda_{\text{max}} = 462$ nm) in DCM.
Fig. S24 The $^1$H NMR in CDCl$_3$ of (a) β-CD functionalized Ag$_{16}$ NC with β-carotene and (b) the pure β-carotene.
Fig. S25 The optimized distance between the donor and acceptor molecules.
Fig. S26 Emission lifetime data of the $\text{Ag}_{16} \cap \beta$-CD$_2$ and $\text{Ag}_{16} \cap \beta$-CD$_2 + \beta$-carotene upon excitation at 375 nm.
Fig. S27 Fluorescence emission intensity of Ag$_{16}$ ∩ β-CD$_2$ ($\lambda_{ex} = 380$ nm), Ag$_{16}$ ∩ β-CD$_2$ + β-carotene {[Ag$_{16}$ ∩ β-CD$_2$] = 10$^{-5}$ M and [β-carotene] = 2×10$^{-6}$ M} ($\lambda_{ex} = 380$ nm) and Ag$_{16}$ ∩ β-CD$_2$ + β-carotene {[Ag$_{16}$ ∩ β-CD$_2$] = 10$^{-5}$ M and [β-carotene] = 2×10$^{-6}$ M} ($\lambda_{ex} = 462$ nm).
Fig. S28 Photocurrent from the donor-acceptor light-harvesting system.
**Fig. S29** 2-D contour plot for differentiating the photocurrent generation ability of the donor-acceptor light-harvesting system with its individual components.
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