

Supporting Information

Luminescent [CO₂@Ag₂₀(SAdm)₁₀(CF₃COO)₁₀(DMA)₂] nanocluster: synthetic strategy and its implication towards white light emission

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Experimental

Materials

1-Adamantane thiol (AdmSH), silver nitrate (AgNO_3), silver trifluoroacetate (CF_3COOAg), β -carotene, and Nile Blue were procured from Sigma-Aldrich. HPLC grade solvents-triethylamine (Et_3N), *N,N*-dimethylacetamide (DMA), and methanol (MeOH) were purchased from Spectrochem.

X-ray Crystallography Details

Data collections were performed at the X-ray diffraction beamline (XRD2) of the Elettra Synchrotron (Trieste, Italy).^{S1} The crystals were dipped in NHV oil (Jena Bioscience, Jena, Germany) and mounted on the goniometer head with nylon loops (MiTeGen, Ithaca, USA). Complete datasets were collected at 100 K (nitrogen stream supplied through an Oxford Cryostream 700). Data were acquired using a monochromatic wavelength of 0.6198 Å through the rotating crystal method on a Pilatus 6M hybrid-pixel area detector (DECTRIS Ltd., Baden-Daettwil, Switzerland). The diffraction data were indexed and integrated using XDS.^{S2} Using Olex2,^{S3} the structure was solved with the SHELXT^{S4} structure solution program using Intrinsic Phasing and refined with the SHELXL^{S5} refinement package using Least Squares minimisation.

Computational Details

All the structure optimizations have been done using the DFT method in Gaussian 09 software.^{S6} The B3LYP functional with Pople's 6-31G* basis set^{S7,S8} and LANL2DZ effective core potential (ECP)^{S9,S10} were used for the nonmetallic elements (S, F, O, N, C, and H) and metal (Ag), respectively. The TD-DFT has been performed for electronic absorption spectra with the scanning of 300 excited states. We have used DMA as conductor-like polarizable continuum solvent model for all the considered NC.^{S11} The non-covalent interaction (NCI) plot 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).^{S12,S13} Besides, the Kohn-Sham orbital analysis has been performed for the understanding of core and ligands orbital contribution in the frontier molecular orbitals using Multiwfn program.^{S12}

The projected density of states (PDOS) calculation for the compound at the bulk level is carried out using Vienna Ab-Initio Simulation Package (VASP) for the NC by using Generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) functional.^{S14,S15} Projector augmented wave (PAW) method has been applied for the consideration of interaction between core and valence electrons.^{S15} The energy cut-off of 470 eV has been implemented for geometry optimization. The ionic relaxations have been carried out using a conjugate gradient algorithm with convergence criteria of 10^{-5} eV/Å for minimum energy and ≤ 0.05 eV/Å for Hellmann-Feynman forces on atoms. Due to the large size of the unit cells of the compounds, the Brillouin zone was sampled at the Gamma point of (1×1×1). For the PDOS calculation, a higher (2×2×2) K-point is used.

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 (DMA) 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 Nova NANOSEM 450 (with EDS) was used for the Scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) measurements have been done using the Omicron Nano tech instrument (MgK α radiation at 1253.6 eV). All binding energies were referenced to the neutral C 1s peak at 284.8 eV. The thermo-gravimetric analysis (TGA) was done on SDT Q600 (Shimadzu) instrument with a heating rate of 10 °C min⁻¹ under N₂ atmosphere. Zeta potential were carried out by dynamic light scattering (DLS) experiments using a Malvern Zetasizer Nano ZS.

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 Ag₂₀-SAdm crystals were dissolved in DMA (1 mg/mL) and diluted by acetonitrile (1:1). The

solution was infused at 20 $\mu\text{L}/\text{min}$ for positive mode. The spectrometer was operated in the mass range of m/z 1800–6000 for positive mode.

Instrument parameters	ES+ (positive mode)
Capillary (kV)	3.500
Sampling Cone	120.0000
Source Temperature ($^{\circ}\text{C}$)	70
Source Offset	34
Desolvation Temperature ($^{\circ}\text{C}$)	110
Cone Gas Flow (L/Hr)	147
Desolvation Gas Flow (L/Hr)	280

Overlap integral calculation

The calculation of overlap integral, $J(\lambda)$ by using the following relation

$$J(\lambda) = \frac{\int_0^{\infty} I_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda}{\int_0^{\infty} I_D(\lambda) d\lambda} \quad (\text{S1})$$

Where, $I_D(\lambda)$ = the normalized PL emission intensity of the donor component within the spectral range of λ to $(\lambda + d\lambda)$

$\epsilon_A(\lambda)$ = the molar extinction coefficient of the acceptor at wavelength λ

First Energy Transfer

In the first energy transfer process, donor molecule is Ag₂₀-SAdm NC and acceptor molecule is β -carotene.

So, the overlap integral, $J(\lambda)$

$$\begin{aligned} J(\lambda) &= \frac{1}{2 \times 10^{-6}} \frac{7.4394 \times 10^{11}}{54.4685} \text{M}^{-1} \text{cm}^{-1} \text{nm}^4 \\ &= 6.83 \times 10^{15} \text{M}^{-1} \text{cm}^{-1} \text{nm}^4 \end{aligned}$$

Where, concentration of the acceptor molecule, $C_A = 2 \times 10^{-6} \text{M}$

Path length of the cuvette, $l = 1 \text{cm}$

Also, absorbance of the acceptor, $A = \epsilon_A \times C_A \times l$

$$\text{Hence, } \epsilon_A = \frac{A}{C_A \times l}$$

Second Energy Transfer

In the second energy transfer process, donor molecule is (Ag₂₀-SAdm NC + β -carotene) composite and acceptor molecule is Nile Blue.

So, the overlap integral, $J(\lambda)$

$$J(\lambda) = \frac{1}{2 \times 10^{-6}} \frac{9.7456 \times 10^{11}}{73.13075} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$$
$$= 6.66 \times 10^{15} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$$

Where, concentration of the acceptor molecule, $C_A = 2 \times 10^{-6} \text{ M}$

Path length of the cuvette, $l = 1 \text{ cm}$

Energy transfer efficiency calculation

Energy transfer efficiency (Φ_{ET}) is calculated by the following equation

$$\Phi_{ET} = 1 - \frac{\tau_{DA}}{\tau_D} \quad (S2)$$

Where, τ_{DA} = emission lifetime of donor emission in presence of acceptor

τ_D = emission lifetime of donor emission in absence of acceptor

First Energy Transfer

In the first energy transfer process, donor molecule is Ag₂₀-SAdm NC and acceptor molecule is β -carotene.

Here, τ_{DA} = emission lifetime of Ag₂₀-SAdm NC emission in presence of β -carotene at 425 nm

$$= 1.23 \text{ ns}$$

τ_D = emission lifetime of Ag₂₀-SAdm NC emission in absence of β -carotene at 425 nm = 5.29 ns

Φ_{ET} = Fractional energy transfer efficiency

$$\Phi_{ET} = 1 - \frac{1.23}{5.29} = 1 - 0.23 = 0.77$$

Second Energy Transfer

In the second energy transfer process, donor molecule is (Ag₂₀-SAdm NC + β -carotene) composite and acceptor molecule is Nile Blue.

Here, τ_{DA} = emission lifetime of (Ag₂₀-SAdm NC + β -carotene) composite emission in presence of Nile Blue at 540 nm = 0.27 ns

τ_D = emission lifetime of (Ag₂₀-SAdm NC + β -carotene) composite emission in absence of Nile Blue at 540 nm = 0.65 ns

Φ_{ET} = Fractional energy transfer efficiency

$$\Phi_{ET} = 1 - \frac{0.27}{0.65} = 1 - 0.41 = 0.59$$

Förster distance calculation

The calculation of Förster distance, R_0 by using the following relation which is the specific distance between donor and acceptor for which energy-transfer efficiency is 50%

$$R_0 = 0.211 \times [k^2 \theta_D J(\lambda) / \eta^4]^{1/6} \quad (S3)$$

Where, $k^2 = 2/3$, θ_D , and η , are the orientation factor, PLQY of the donor, and refractive index of the medium, respectively

First Energy Transfer

In the first energy transfer process, donor molecule is Ag₂₀-SAdm NC and acceptor molecule is β -carotene.

θ_D = quantum yield of Ag₂₀-SAdm NC = 0.32

the overlap integral, $J(\lambda) = 6.83 \times 10^{15} \text{ M}^{-1}\text{cm}^{-1}\text{nm}^4$

η = refractive index of the DMA solvent = 1.4375

So, $R_0 = 55.77 \text{ \AA} = 5.58 \text{ nm}$

Second Energy Transfer

In the second energy transfer process, donor molecule is (Ag₂₀-SAdm NC + β -carotene) composite and acceptor molecule is Nile Blue.

θ_D = quantum yield of (Ag₂₀-SAdm NC + β -carotene) composite = 0.39

the overlap integral, $J(\lambda) = 6.66 \times 10^{15} \text{ M}^{-1}\text{cm}^{-1}\text{nm}^4$

η = refractive index of the DMA solvent = 1.4375

So, $R_0 = 57.40 \text{ \AA} = 5.74 \text{ nm}$

Calculation of distance between donor and acceptor molecule

The distance between donor and acceptor molecule, r is calculated by using the following relation

$$\Phi_{ET} = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6} \quad (S4)$$

Φ_{ET} = energy transfer efficiency

R_0 = Förster distance

First Energy Transfer

In the first energy transfer process, donor molecule is Ag₂₀-SAdm NC and acceptor molecule is β -carotene.

Φ_{ET} = energy transfer efficiency = 0.77

R_0 = Förster distance = 55.77 Å

So, the distance between Ag₂₀-SAdm NC and β -carotene, $r = 45.59 \text{ Å} = 4.56 \text{ nm}$

Second Energy Transfer

In the second energy transfer process, donor molecule is (Ag₂₀-SAdm NC + β -carotene) composite and acceptor molecule is Nile Blue.

Φ_{ET} = energy transfer efficiency = 0.59

R_0 = Förster distance = 57.40 Å

So, the distance between (Ag₂₀-SAdm NC + β -carotene) composite and Nile Blue, $r = 54.03 \text{ Å} = 5.40 \text{ nm}$

Energy transfer rate (k_T) calculation

Energy transfer rate (k_T) is calculated by using the following relation

$$k_T = \frac{1}{\tau_D} \left(\frac{R_0}{r}\right)^6 \quad (S5)$$

τ_D = emission lifetime of the donor molecule

R_0 = Förster distance

r = the distance between donor and acceptor molecule

First Energy Transfer

In the first energy transfer process, donor molecule is Ag₂₀-SAdm NC and acceptor molecule is β -carotene.

τ_D = emission lifetime of the Ag₂₀-SAdm NC at 425 nm = 5.29 ns

$R_0 = \text{Förster distance} = 55.77 \text{ \AA}$

$r = \text{the distance between Ag}_{20}\text{-SAdm NC and } \beta\text{-carotene} = 45.59 \text{ \AA}$

So, Energy transfer rate, $k_T = 6.33 \times 10^8 \text{ s}^{-1}$

Second Energy Transfer

In the second energy transfer process, donor molecule is (Ag₂₀-SAdm NC + β -carotene) composite and acceptor molecule is Nile Blue.

$\tau_D = \text{emission lifetime of the (Ag}_{20}\text{-SAdm NC + } \beta\text{-carotene) composite at 540 nm} = 0.65 \text{ ns}$

$R_0 = \text{Förster distance} = 57.40 \text{ \AA}$

$r = \text{the distance between (Ag}_{20}\text{-SAdm NC + } \beta\text{-carotene) composite and Nile Blue} = 54.03 \text{ \AA}$

So, energy transfer rate, $k_T = 2.21 \times 10^9 \text{ s}^{-1}$

Table S1. Crystal data and structure refinement parameters.

Identification code	Ag ₂₀ -SAdm
CCDC number	2210204
Empirical formula	C ₁₂₉ H ₁₆₂ Ag ₂₀ F ₃₀ N ₂ O ₂₄ S ₁₀
Formula weight	5172.60
Temperature/K	100.0
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> /Å	15.085(3)
<i>b</i> /Å	19.980(4)
<i>c</i> /Å	27.634(6)
α /°	90
β /°	96.34(3)
γ /°	90
Volume/Å ³	8278(3)
<i>Z</i>	2
ρ_{calc} g/cm ³	2.075
μ /mm ⁻¹	1.745
F(000)	5024
Crystal size/mm ³	0.1×0.05×0.02
Radiation	Synchrotron (λ = 0.6199)
2 Θ range for data collection/°	1.099 to 24.056
Index ranges	-19 ≤ <i>h</i> ≤ 19, -26 ≤ <i>k</i> ≤ 26, -36 ≤ <i>l</i> ≤ 36
Reflections collected	120474
Independent reflections	12245
Data/restraints/parameters	19534/1849/734
Goodness-of-fit on F ²	1.503
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	R ₁ = 0.1333, wR ₂ = 0.3906
Final R indexes [all data]	R ₁ = 0.1625, wR ₂ = 0.4158
Largest diff. peak/hole / e Å ⁻³	4.146/ -2.493

Table S2. The obtained radiative, nonradiative rate constants, quantum yield and lifetime of Ag₂₀-SAdm NC.

Temperature (K)	Relative quantum yield (ϕ)	Lifetime (τ_{av}) (ns)	k_r (s⁻¹)	k_{nr} (s⁻¹)
298	0.32	5.29	6.05×10^7	1.29×10^8
343	0.004	0.93	4.30×10^6	1.07×10^9

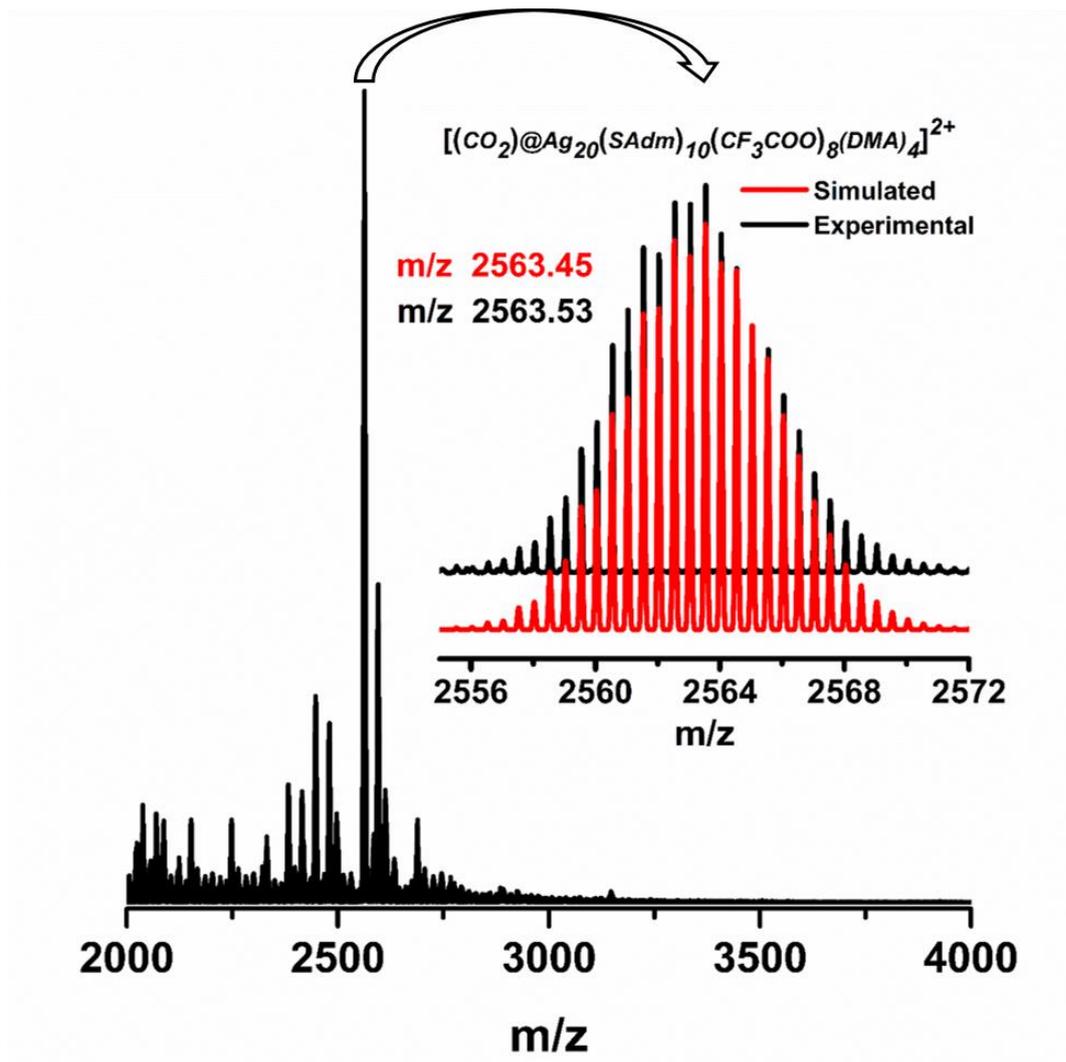


Fig. S1 ESI-MS spectrum of unstable cationic $[(\text{CO}_2)@\text{Ag}_{20}(\text{S-Adm})_{10}(\text{CF}_3\text{COO})_8(\text{DMA})_4]^{2+}$ NC.

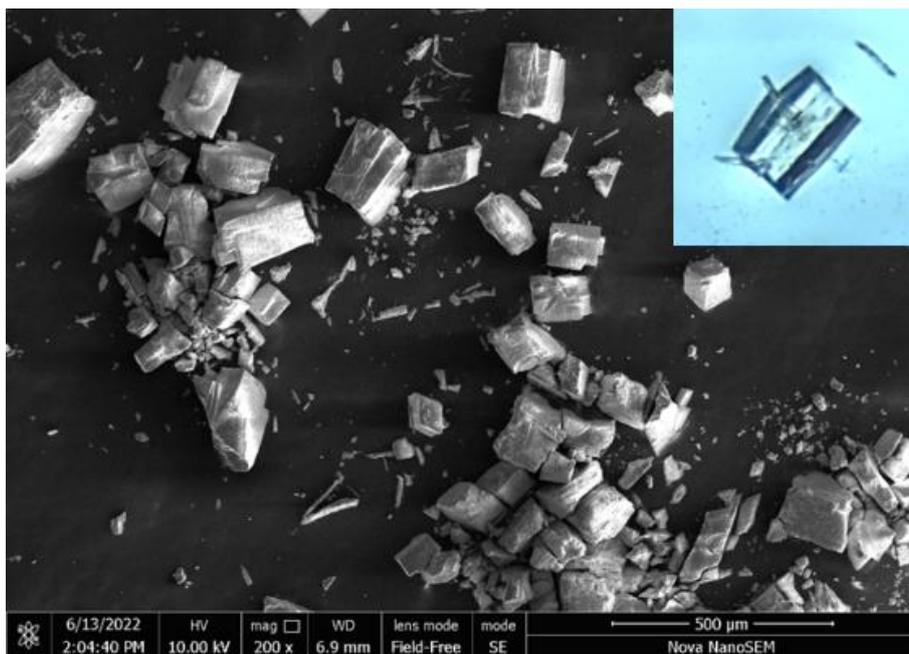


Fig. S2 SEM micrograph of the as-synthesized crystal, inset showing the optical microscopic image of the crystal.

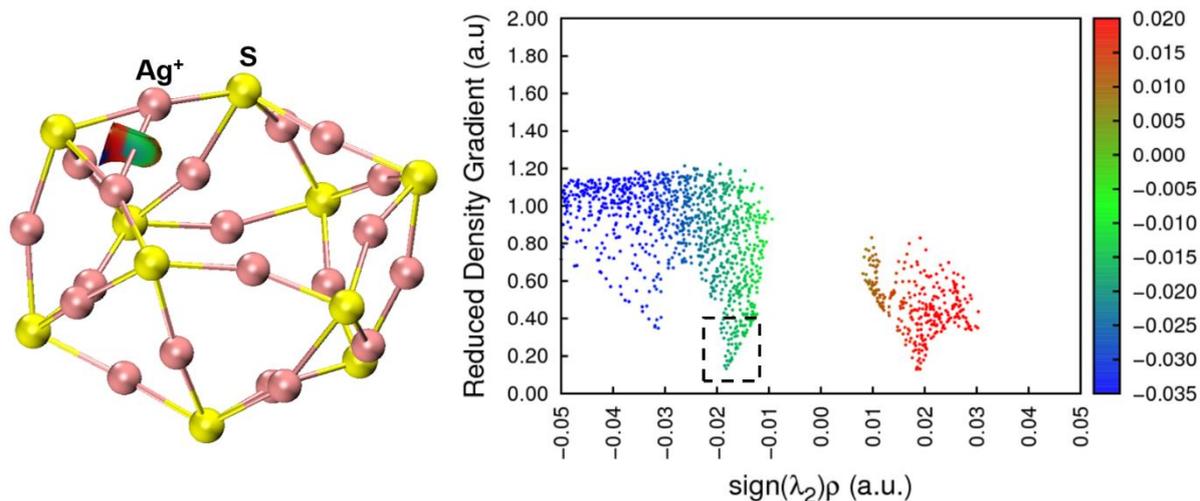


Fig. S3 The Reduced Density Gradient (RDG) isosurface of argentophilic interaction and the associated corresponding scatter plot of (RDG vs. $\text{sign}(\lambda_2)\rho$) of $\text{Ag}_{20}\text{-SAdm NC}$. Where the green color in the plot indicates the presence of nonbonding interaction.

However, the $\text{Ag}^I \dots \text{Ag}^I$ bond distances fall in the range of $3.04 \text{ \AA} - 3.28 \text{ \AA}$, which is revealed by crystallographic analysis also experimentally proving the presence of argentophilic interactions.^{S16}

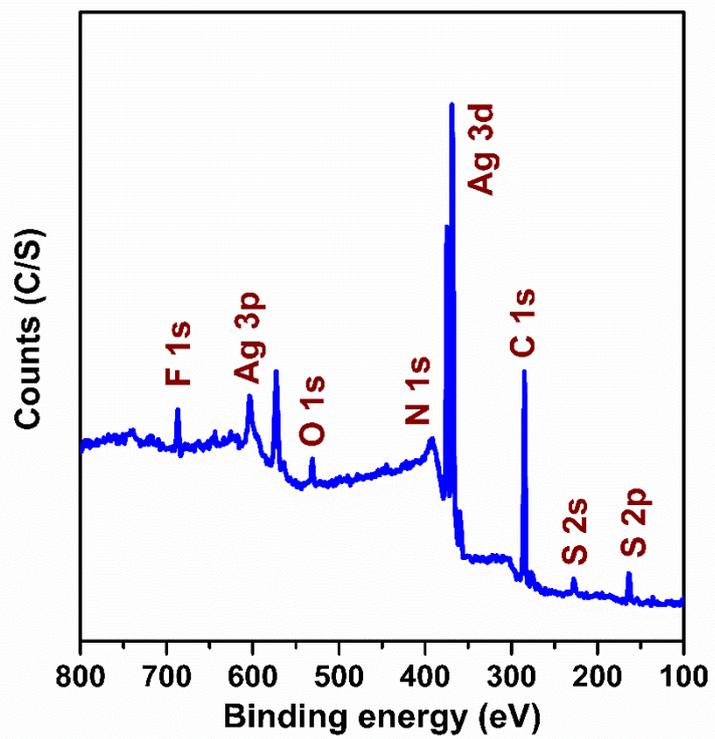


Fig. S4 XPS survey spectrum of Ag₂₀-SAdm NC.

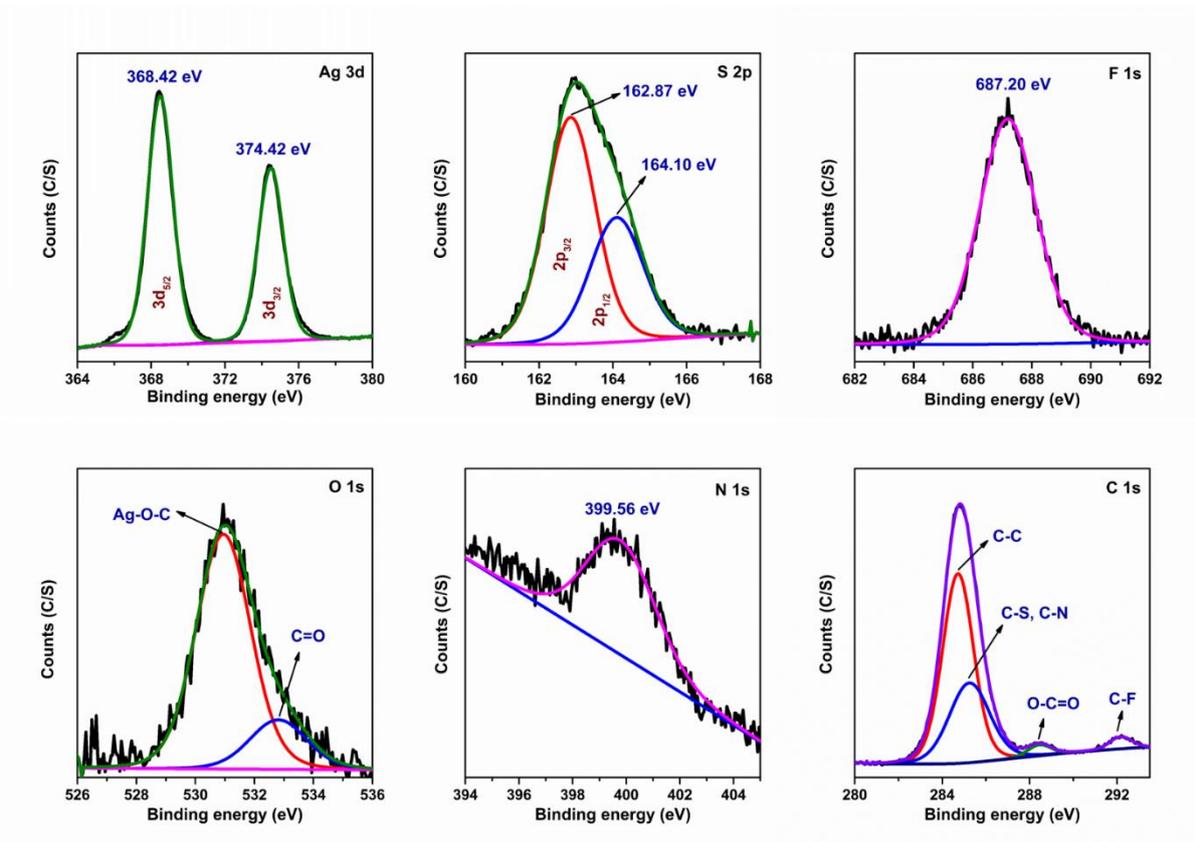


Fig. S5 Binding energy spectra of the corresponding elements. The binding energy spectra of each element confirmed their corresponding oxidation states.

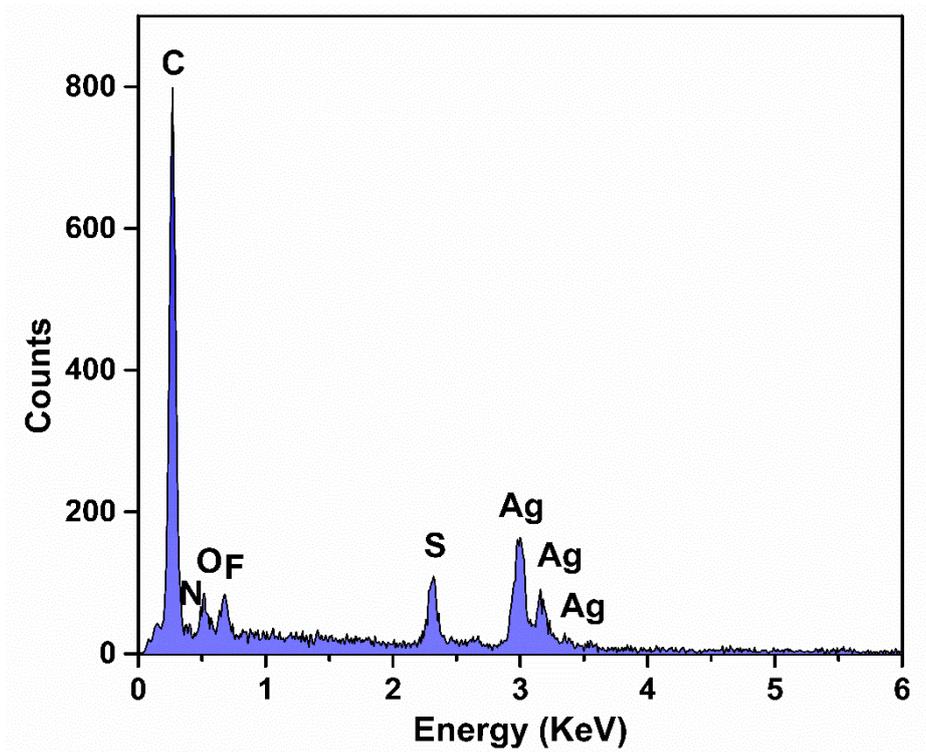


Fig. S6 EDS spectrum of Ag₂₀-SAdm NC.

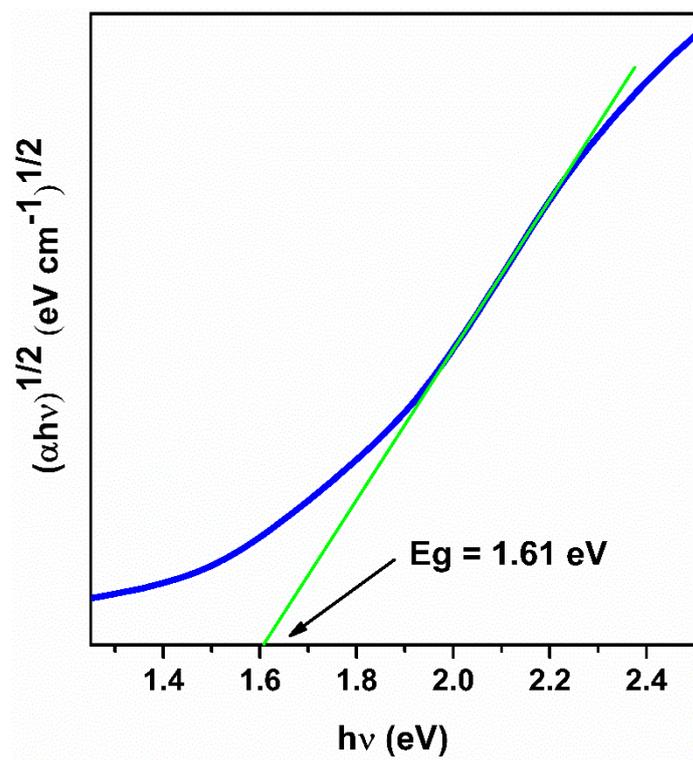


Fig. S7 Bandgap calculation of $\text{Ag}_{20}\text{-SAdm NC}$.

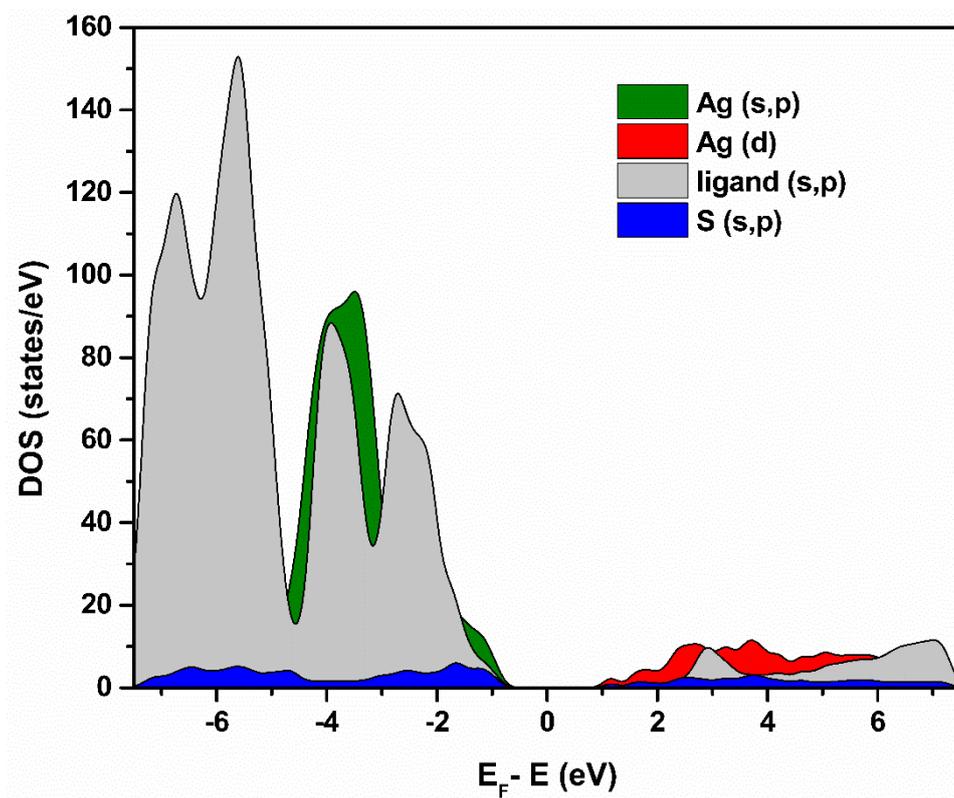


Fig. S8 PDOS calculation of the as-synthesized Ag₂₀-SAdm NC.

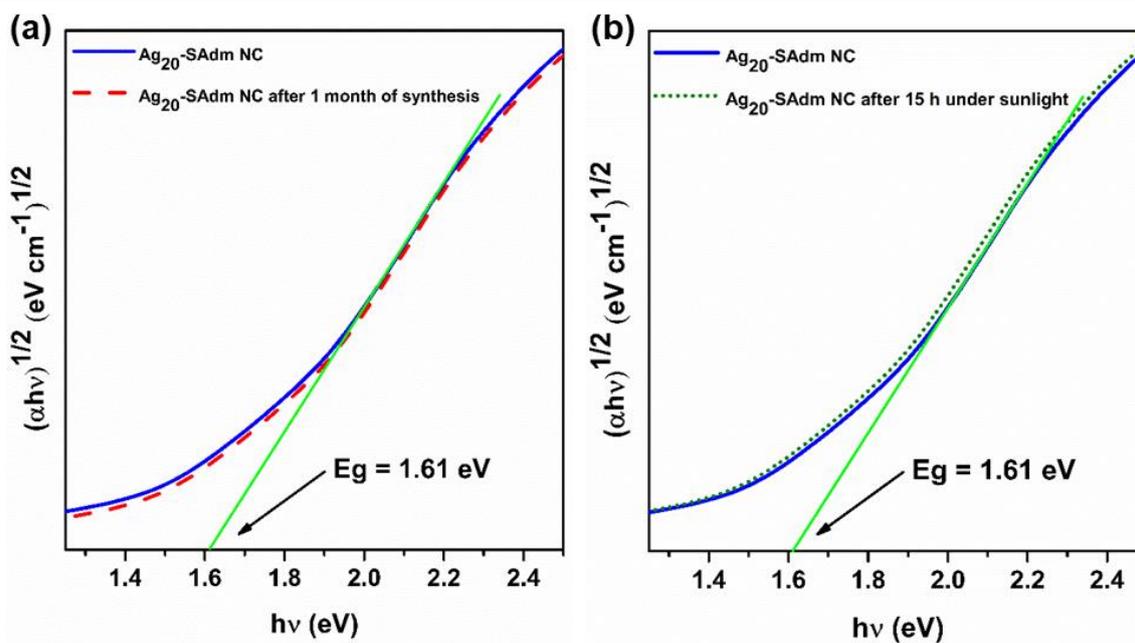


Fig. S9 (a) Bandgap energy values of the as-synthesized NC and after 1 month of synthesis. Note: It signifies the stability of the cluster over time. (b) Bandgap energy values of the as-synthesized NC and after exposure for 15 h (5 h per day for 3 days) under sunlight. Note: It further signifies the photostability of the cluster over time.

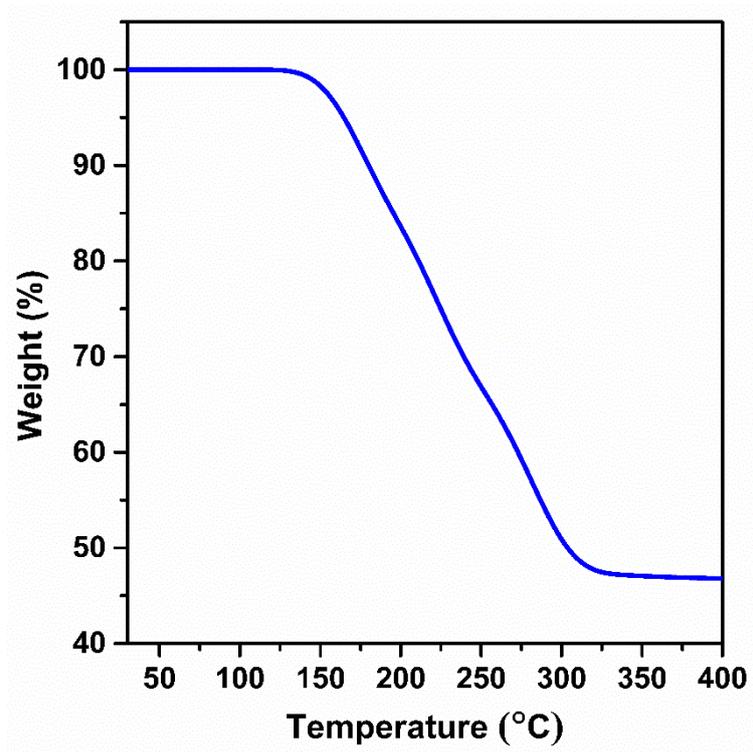


Fig. S10 TGA of Ag₂₀-SAdm NC.

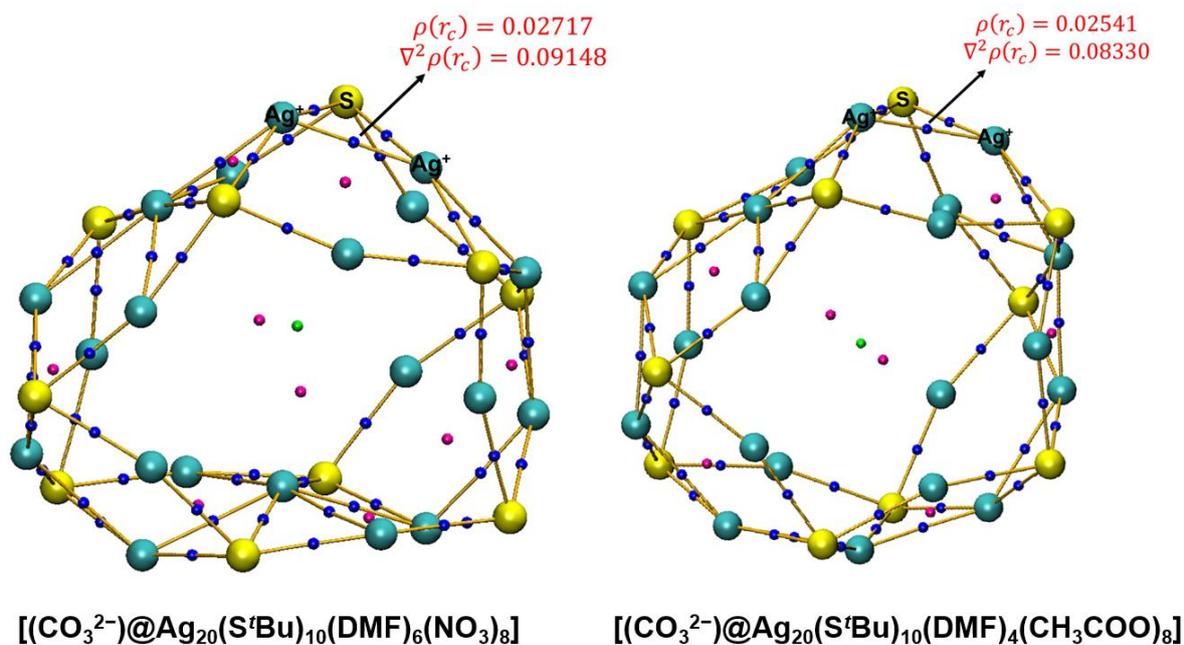


Fig. S11 QTAIM molecular plot of the bond critical point (BCP), ring critical point (RCP), and cage critical point (CCP) for considering the Ag---Ag noncovalent interaction of reported Ag₂₀-based nanoclusters (ligands were omitted for clarity).^{S17,S18}

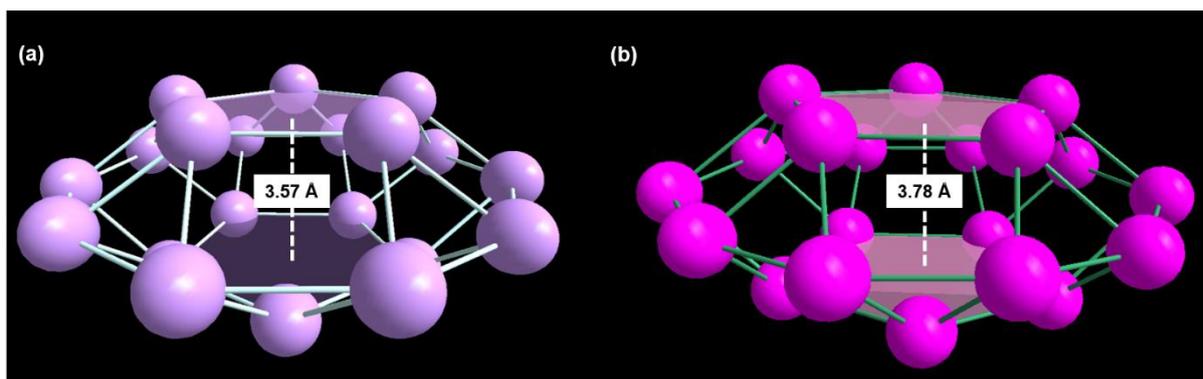


Fig. S12 Diameter of the Ag_{20} cluster nodes (a) as-synthesized Ag_{20} -SAdm NC and (b) reported Ag_{20} NC, (part of this figure is reproduced with permission from reference S17, Royal Society of Chemistry, copyright 2013).

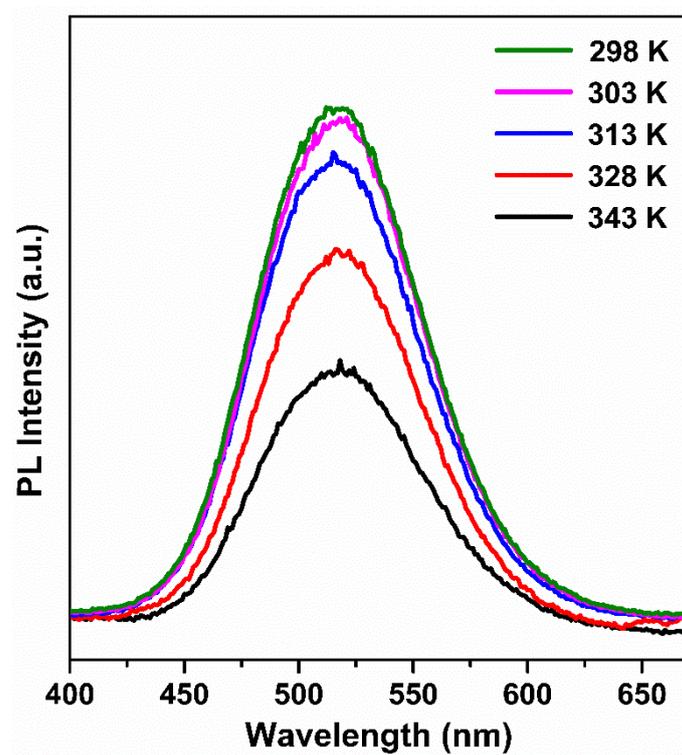


Fig. S13 Temperature-dependent PL studies of the as-synthesized NC in the solid-state.

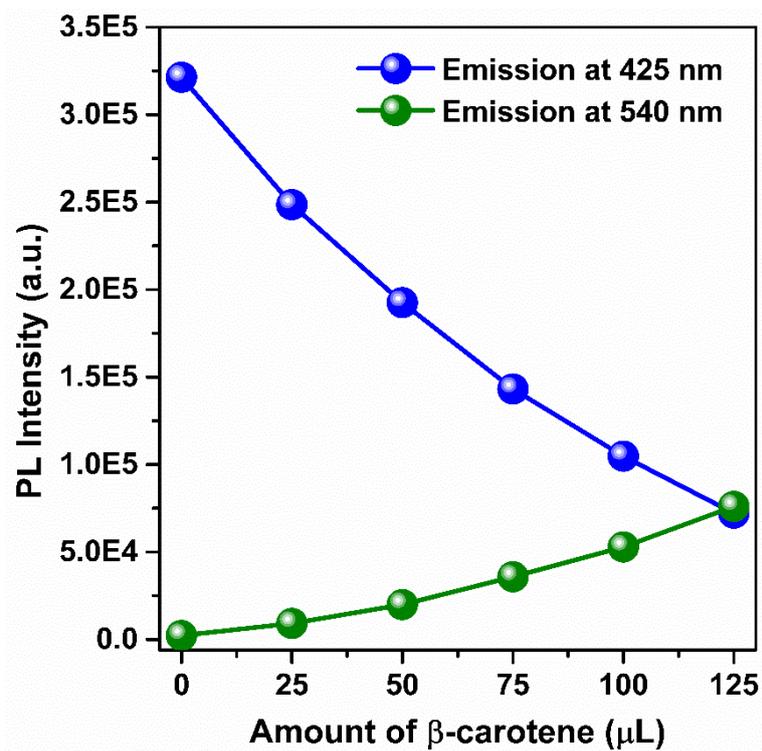


Fig. S14 Change in emission intensity of the donor molecule, $\text{Ag}_{20}\text{-SAdm NC}$ with respect to the gradual addition of the acceptor molecule, β -carotene. PL intensity of the donor molecule is gradually decreasing with the increase of PL intensity of the acceptor molecule.

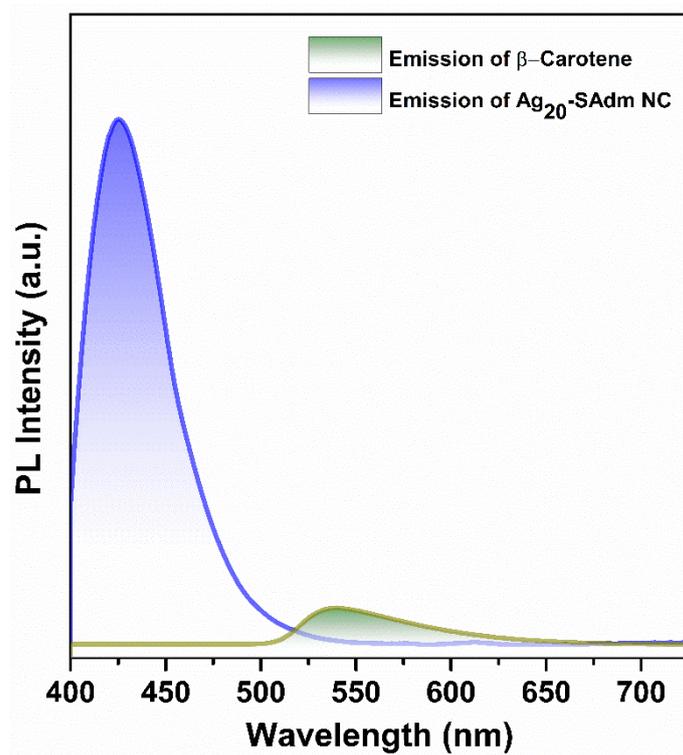


Fig. S15 Comparison of the emission of pure β -carotene with the emission of the Ag_{20} -SAdm NC under the same excitation (385 nm) in DMA.

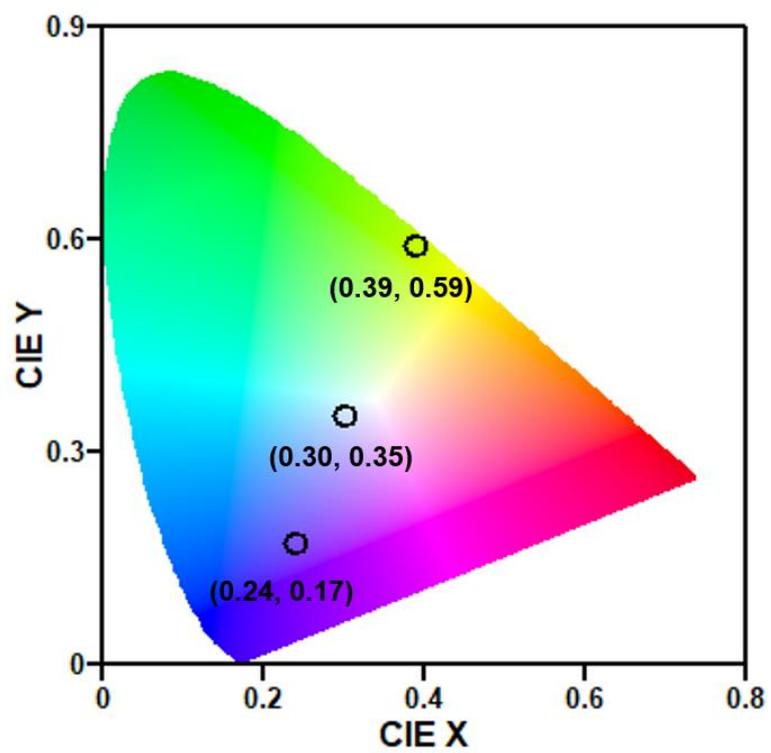


Fig. S16 CIE plot obtained from the mixing of Ag₂₀-SAdm NC and β-carotene.

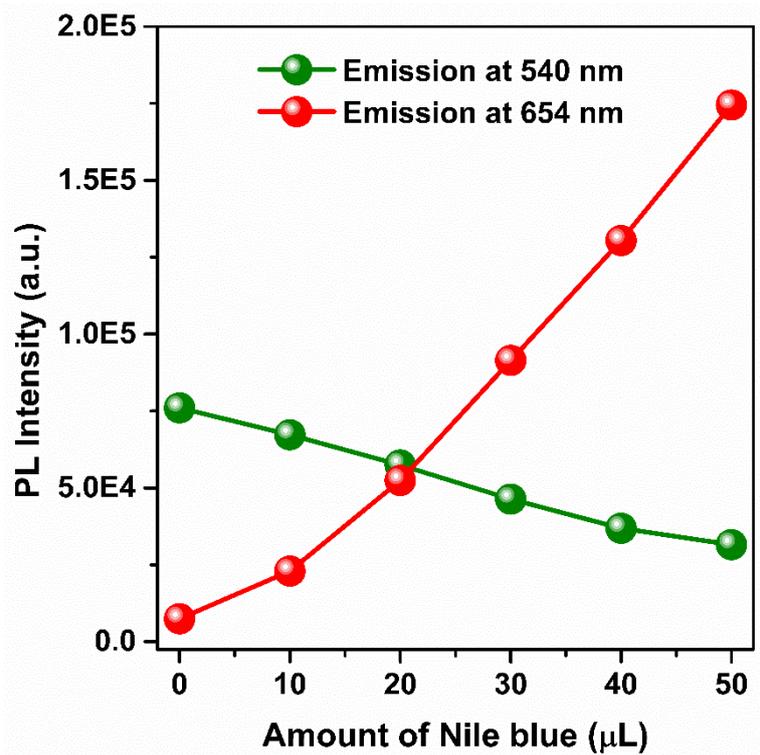


Fig. S17 Change in emission intensity of the donor molecule, Ag₂₀-SAdm NC + β-carotene conjugate with respect to the gradual addition of the second acceptor molecule, Nile Blue. PL intensity of the donor conjugate is gradually decreasing with the increase of PL intensity of Nile Blue.

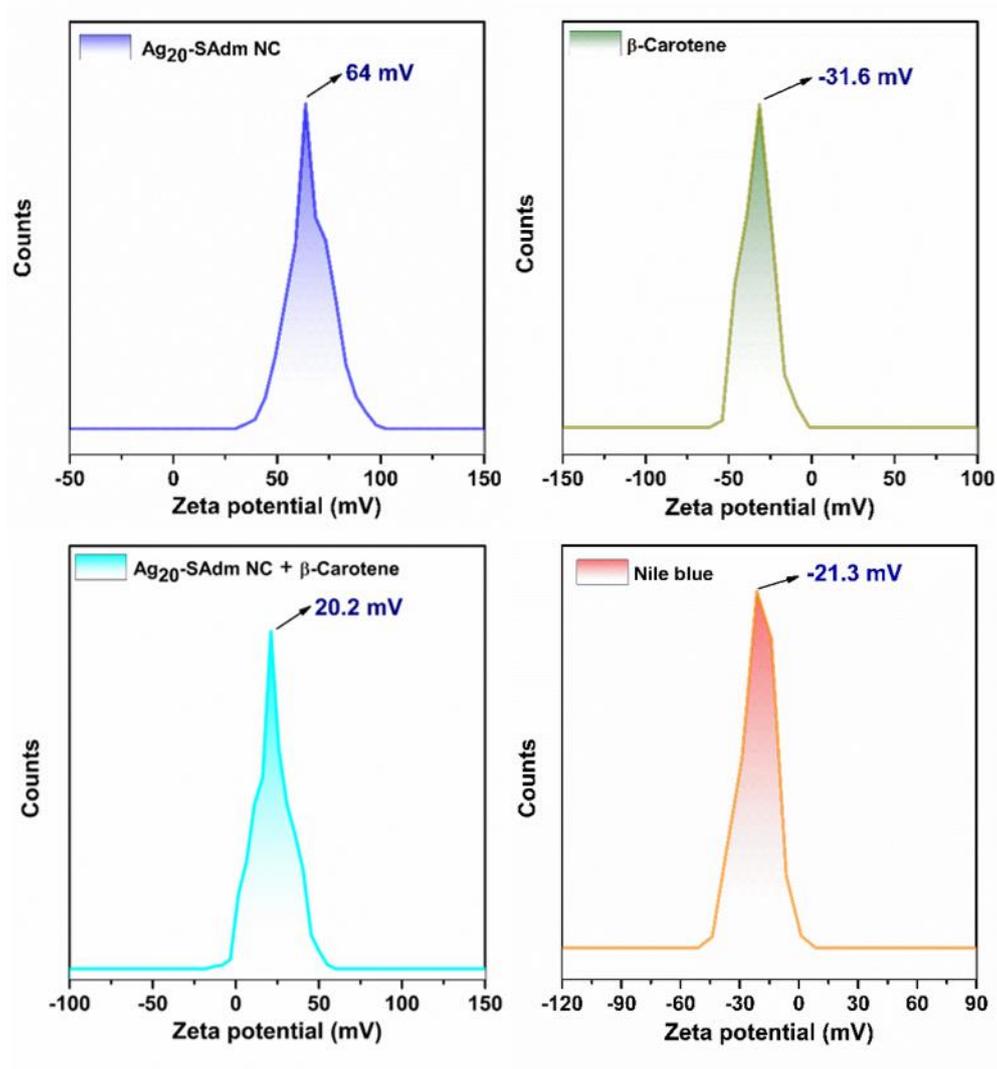


Fig. S18 Zeta potential values of individual and conjugated molecules in DMA medium.

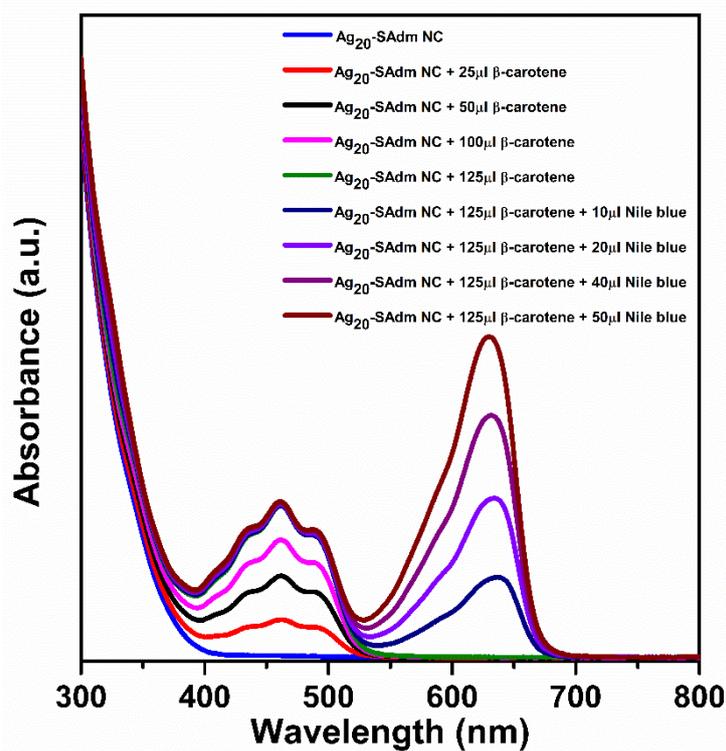


Fig. S19 UV-vis spectrum of Ag₂₀-SAdm NC with the gradual addition of β-carotene followed by addition of second chromophore Nile Blue. 2 mL of 10⁻⁵ M Ag₂₀-SAdm NC in DMA was titrated with 2 × 10⁻⁶ M solution of β-carotene, followed by titrating the obtained solution with 2 × 10⁻⁶ M solution of Nile Blue in DMA. Note: Ag₂₀-SAdm NC is exhibiting peaks below 400 nm. The peaks appear after the addition of respective chromophores signify the presence of the individual components.

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