Supporting Information

[Cu$_{18}$H$_3$(S-Adm)$_{12}$(PPh$_3$)$_4$Cl$_2$]: fusion of Platonic and Johnson solids through a Cu(0) center and its photophysical properties

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Experimental

Materials

Tetrakis(acetonitrile)copper(I) tetrafluoroborate (Cu(CH$_3$CN)$_4$BF$_4$), triphenylphosphine (PPh$_3$), 1-adamantane thiol (Adm-SH), sodium borohydride (NaBH$_4$), tetra-n-butylammonium hexafluorophosphate (TBAPF$_6$), β-cyclodextrin were procured from Sigma-Aldrich. HPLC grade solvents- chloroform, dichloromethane, acetonitrile, methanol, and n-hexane were purchased from Spectrochem. Milli-Q water was utilized throughout the experiments.

Synthesis of Cu$_{18}$ NC

Initially, 50 mg of Cu(CH$_3$CN)$_4$BF$_4$ and 50 mg of PPh$_3$ were dissolved in the mixture solution of 2 mL acetonitrile and 0.5 mL chloroform at room temperature. After 5 min of stirring, 20 mg of Adm-SH was added to the reaction mixture and continued stirring. After the addition of 50 mg NaBH$_4$ dissolved in 2.5 mL methanol, the color of the solution becomes red from colorless. The reaction was kept for another 1 h under continuous stirring. After completion, the reaction mixture was centrifuged and collected the red precipitate. After drying properly, the precipitate was dissolved in the solvent mixture of chloroform/hexane (volume ratio 1:1). The final clear solution was kept for crystallization at ambient conditions. After 7 days, red-colored cubic crystals were obtained.

The synthesis of atomically precise Cu NCs is much more challenging compared to the Ag NCs and Au NCs due to the low reduction potential and the high reactivity of the Cu with respect to Ag and Au. Hence, the synthesis of Cu NCs containing zero-valent Cu atoms in the core experiences more complications. In the synthesis of reported [Cu$_{32}$(PET)$_2$H$_8$Cl$_2$][PPh$_4$]$_2$, it had been shown that tetramethylethylenediamine was an important reagent for the synthesis where in the first step Cu(I) complex was formed, followed by the reduction of the complex was occurred under Ar atmosphere, though the tetramethylethylenediamine is not attached in the final product.$^{31}$ Doubly charged Cu$_{32}$ NCs stabilized by PPh$_4^+$ were formed where no Cu(0) is present. In the synthesis of [Cu$_{25}$H$_{10}$(SPhCl)$_{18}$]$^3$, Cu(II) salt was used as a precursor and after reduction by NaBH$_4$, ended up with the anionic NCs with again all Cu is in +1 state.$^{32}$ In both cases, the single crystals were obtained at low temperatures. In the synthesis of reported [Cu$_{61}$S(Bu)$_{26}$S$_6$Cl$_6$H$_{14}$]$^+$, a mild
reducing agent borane tert-butylamine complex was used instead of the strong reducing agent NaBH₄ to make the largest Cu(0)-containing core-shell copper NCs. In the synthesis of [Cu₁₅(PPh₃)₆(PET)₁₃]²⁺, [Cu₃₆H₁₀(PET)₂₄(PPh₃)₁₆Cl₂], and [Cu₈₁(PhS)₄₆(‘BuNH₂)₁₀(H)₃₂]³⁺, a one-pot direct reduction strategy had been followed. In the case of Cu₁₅ NC and Cu₃₆ NC, NaBH₄ was used and in the case of Cu₈₁ NC, ‘BuNH₂·BH₃ was used as reducing agents, though in all cases, Cu(I) salts were taken as a metal precursor. It has been observed that in the case of the mild reducing agent which gives rise to high-nuclearity Cu NC compared to the strong reducing agent under ambient conditions. In both cases, there is no Cu(0) atom. But in this work, Cu₁₈ NC was synthesized by a facile one-pot synthetic strategy. This synthetic procedure is almost the same as the procedure of Cu₃₆ NC. Only we have changed the PET ligand with the bulky adamantane thiol ligand in our synthesis and that bulkiness of the ligand may induce the stability of the Cu(0) atom at the center of the Cu₁₀ core.

Synthesis of Cu₁₈D NC

The same procedure was adopted whatever was mentioned for the synthesis of the Cu₁₈ NC. Instead of NaBH₄, we have used NaBD₄ as a reducing agent.

Synthesis of Cu₁₈ ∩ β-CD₁

Initially, 3 mg of Cu₁₈ NC was dissolved in 5 mL of tetrahydrofuran and then a 2 mL aqueous solution of β-CD (2 mg/mL) was added. The resultant reaction mixture was then sonicated for 15 min and kept for stirring for 1 h with a recurrent sonication for 2 min at every 15 min intervals. The obtained solution was washed several times with water. Finally, the aqueous phase was removed and the organic phase was dried.

X-ray Crystallography details

Single-crystal data of Cu₁₈ NC was collected on a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector operating in shutter less mode and an Oxford Cryosystems Cryostream 800 Plus at 173 K using Cu Kα (λ = 1.54184 Å) from PhotonJet micro-focus X-ray Source. Data were processed using the CrystAlisPro software suite. The structure was solved using the charge-flipping algorithm, as implemented in the program SUPERFLIP and refined by full-matrix
least-squares techniques against Fo² using the SHELXL program⁹ through the OLEX2 interface.¹⁰

**Computational details**

The DFT calculations were done using Gaussian 09 D.01 program.¹¹ B3LYP functional with Pople’s 6–31G* basis set¹²,¹³ was used for non-metal elements, and LANL2DZ-ECP (effective core potential)¹⁴,¹⁵ was employed for Cu atoms, respectively. Chloroform solvent was considered to simulate the experimental non-polar solvent scenario. The TD-DFT calculations considered 300 singlet-to-singlet excitation energies. The -PPh₃ ligand is simplified to -PMe₃ during the calculation. Kohn-Sham orbital analysis has been performed for identifying the orbital contribution in molecular orbitals and corresponding energies by using the multi wave function 3.6 program.¹⁶,¹⁷ The NMR spectrum is simulated by using the GIAO method implemented in Gaussian 09 D.01 program.¹⁸

The projected density of states (PDOS) calculation for the compounds at the bulk level is carried out using Vienna Ab-Initio Simulation Package (VASP) by using Generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) functional.¹⁹,²⁰ Projector augmented wave (PAW) method is used for treating ion-electron interactions.²¹ The ionic relaxations have been carried out using a Conjugate gradient algorithm with convergence criteria of 10⁻⁴ eV for minimum energy and 0.05 eV Å⁻¹ 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 (1×1×1). For the PDOS calculation, a higher (2×2×2) K-point is used. The atomic charges are calculated using Bader charge analysis.²²

**Instrumentation**

A SHIMADZU UV-3800 spectrometer was used for measuring the absorbance spectra. Emission measurements were performed using a Fluorolog-3 spectrofluorimeter from Horiba Jobin Yvon. The relative quantum yield was determined by the best match of the excitation wavelength of a well-known chromophore such as pyrene with the NC and the excitation was fixed at 317 nm. The concentration of the chloroform solutions was fixed by adjusting the absorption 0.05 OD and measured the quantum yield at room temperature. A picosecond time-correlated single photon counting (TCSPC) system (Horiba Jobin Yvon-IBH) was utilized for
the measurement of emission lifetime. Transmission electron microscopy (TEM; FEI Tecnai G2 F30 S-Twin; 300 kV), scanning electron microscope (SEM), and energy-dispersive X-ray spectroscopy (EDS; FEI Nova NANOSEM 450) were used. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements have been done by using the Omicron Nanotech instrument (MgKα 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. Cyclic Voltammogram was done by using a CH instrument with a three-electrode system where glassy carbon was used as a working electrode, graphite electrode served as a counter electrode and silver wire was used as a reference electrode in dichloromethane solvent. In this organic solvent, 0.5 M [(n-Bu)₄N]PF₆ salt was added as a supporting electrolyte. We have calibrated against the standard reference electrode (Ag/Ag⁺). Bruker Avance III, 500 MHz, NMR was used for the ¹H and ³¹P studies. Electron paramagnetic resonance (EPR) spectrum was recorded using MiniScope MS 5000 Magmetech EPR spectrometer. Waters Q-TOF mass spectrometer equipped with a Z-spray source was used for the electrospray ionization (ESI) mass spectrometry measurement in positive mode. Samples were dissolved in chloroform (1 mg/mL) and diluted by acetonitrile (1:1). The solution was infused at 20 µL/min. The spectrometer was operated in the mass range of m/z 1500–6000, capillary voltage was 2.9 kV, sampling cone 60, source temperature 70 °C source offset 28, desolvation temperature 100 °C, cone gas flow 20 L/Hr, desolvation gas flow 244 L/Hr. The chloroform solution of the synthesized NCs is drop-casted between the patterned gold electrodes deposited on the ceramic plate to form a thin layer of the material. The electrical and photoresponse measurements were observed using a Keithley 6712 electrometer using a laser of 360 nm wavelength and 10 mW.

**The radiative and nonradiative rate constants calculation**

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

\[
k_r = \frac{\phi}{\tau_{av}} \quad (S1)
\]

\[
k_{nr} = \frac{(1-\phi)}{\tau_{av}} \quad (S2)
\]

where, \( \phi \) = Quantum yield; \( \tau_{av} \) = Average emission lifetime.
Table S1. Crystal data and structure refinement parameters.

| Identification code       | Cu18 NC |
|---------------------------|---------|
| CCDC number               | 2132516 |
| Empirical formula         | C_{192}H_{242}Cl_{2}Cu_{18}P_{4}S_{12} |
| Formula weight            | 4273.06 |
| Temperature               | 173 (2) K |
| Wavelength                | 1.54184 Å |
| Crystal system            | monoclinic |
| Space group               | P2_1/c (No. 14) |
| Unit cell dimensions      | a = 19.2184 (2) Å; b = 47.4362 (6) Å, c = 24.0097 (3) Å; α = 90°; β = 100.5215 (12)°; γ = 90° |
| Volume                    | 21520.4 (5) Å³ |
| Z                         | 4 |
| Density                   | 1.319 mg/m³ |
| Absorption coefficient    | 3.783 mm⁻¹ |
| F(000)                    | 8808 |
| Crystal size              | 0.15 × 0.06 × 0.04 mm³ |
| Theta range for data collection | 2.517 to 67.079° |
| Limiting indices          | -16 ≤ h ≤ 22, -56 ≤ k ≤ 56, -28 ≤ l ≤ 26 |
| Reflections collected     | 136476 |
| Independent reflections   | 37748 [R(int) = 0.0579] |
| Completeness to theta = 67.079° | 98.3 % |
| Refinement method         | Full-matrix least-squares on F² |
| Data / restraints / parameters | 37748 / 36 / 2065 |
| Goodness-of-fit on F²     | 1.016 |
| Final R indices [I > 2sigma(I)] | R₁ = 0.0534, wR₂ = 0.1127 |
| R indices (all data)      | R₁ = 0.0722, wR₂ = 0.1199 |
| Largest diff. peak and hole | 1.307 and -0.629 e. Å⁻³ |
Table S2. List of reported thiolate protected Cu NCs.

| Sr. No. | Formula of Crystals | Presence of Cu(0) | Emission Property | Ref.  |
|---------|---------------------|-------------------|-------------------|-------|
| 1       | [Cu_{15}(PPh_3)_6(SCH_2CH_2Ph)_13]^{2+} | -                 | NIR emission     | S4    |
| 2       | [Cu_{25}H_{10}(SPhCl_2)_{18}]^{3-}  | -                 | -                | S2    |
| 3       | [Cu_{32}(SCH_2CH_2Ph)_{24}H_8Cl_2][PPh_4]_2 | -                 | -                | S1    |
| 4       | [Cu_{36}H_{10}(SCH_2CH_2Ph)_{24}(PPh_3)_6Cl_2] | -                 | -                | S5    |
| 5       | [Cu_{61}(S'Bu)_{26}S_6Cl_6H_{14}]^+ | Partial Cu(0)     | -                | S3    |
| 6       | [Cu_{81}(PhS)_{46}('BuNH_2)_{10}(H)_{32}]^{3+} | -                 | -                | S6    |
| 7       | [Cu_{18}H_3(S-Adm)_{12}(PPh_3)_4Cl_2] | One isolated Cu(0) | Violet emission  | This work |
Table S3. The obtained radiative, nonradiative rate constants, quantum yield and emission lifetime.

| Compound          | Relative Quantum yield (\(\phi\)) | Emission Lifetime (\(\tau_{av}\) (ns)) | \(k_r\) (s\(^{-1}\)) | \(k_{nr}\) (s\(^{-1}\)) |
|-------------------|------------------------------------|----------------------------------------|------------------------|------------------------|
| \(\text{Cu}_{18}\) | 0.0032                              | 0.26                                   | \(1.23 \times 10^7\)   | \(3.83 \times 10^9\)   |
| \(\text{Cu}_{18} \cap \beta\text{-CD}\_1\) | 0.012                              | 0.97                                   | \(1.23 \times 10^7\)   | \(1.02 \times 10^9\)   |
**Fig. S1** The optical images of the Cu$_{18}$ NC with cubic shape.
Fig. S2 (a) The attachment of two $\mu_3$ bridged hydrides, and (b) one $\mu_5$ bridged hydride with the core. (c) Attachment of two chloride atoms by $\mu_2$ bridging mode at the two opposite positions of the square edges of the Cu$_6$ octahedron. Color legend; Cu, light and deep orange; Cl, green; H, white.
Fig. S3 DFT optimized structure of the Cu$_{18}$ NC.
Fig. S4 GIAO $^1$H NMR spectrum of the Cu$_{18}$ NC.
Fig. S5 $^1$H NMR spectra in CDCl$_3$ of (a) Cu$_{18}$ NC and (b) Cu$_{18}$D NC.
Fig. S6 $\mu_3$ bridging mode of S (a) bonding between two Cu atoms of the motif and one Cu atom of the Cu$_6$ octahedron, and (b) bonding with two Cu atoms of the motif and one Cu atom of the Cu$_5$ distorted square pyramid. Color legend; Cu, light and deep orange; S, yellow.
Fig. S7 $\mu_3$ bridging mode of S (a) bonding between one Cu atom of the motif and two Cu atoms of the Cu$_6$ octahedron, and (b) bonding with one Cu atom of the motif and two Cu atoms of the Cu$_5$ distorted square pyramid. Color legend; Cu, light and deep orange; S, yellow.
Fig. S8 (a) $\mu_3$ bridging mode of S which are making connection among Cu$_6$ distorted octahedron, Cu$_5$ distorted square pyramid, and motif shell, and (b) $\mu_2$ S atoms in the metal-ligand motifs. Color legend; Cu, light and deep orange; S, yellow.
**Fig. S9** Attachment of four P atoms with the four Cu atoms of the metal-ligand motifs. Color legend; Cu, light and deep orange; P, magenta.
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Fig. S11 The herringbone pattern of the Cu$_{18}$ NC caused by the hydrophobic interactions between the adamantane moieties along the x-axis.
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Fig. S18 Survey spectrum and deconvoluted XPS spectra of each element of the Cu$_{18}$ NC.
Fig. S19 Cyclic voltammogram data of the Cu_{18} NC.
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Fig. S21 Localized density of states (LDOS) of different types of Cu atoms in the Cu$_{18}$ NC. Representative atoms from each category are analysed.
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Fig. S28 Temperature-dependent PL property of the Cu$_{18}$ NC and Cu$_{18}$ NC with β-CD.
Fig. S29 Cyclic voltammogram data of Cu$_{18}$ NC with β-CD.
Fig. S30 I-V characteristic plot of the Cu$_{12}$ NC.
**Fig. S31** UPS data of the Cu$_{18}$ NC.
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