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COMMUNICATION

Dual Emitting Ag₃₅ Nanocluster Protected by 2-Pyrene Imine ThiolArijit Jana^{a,b}, Papri Chakraborty^a, Wakeel Ahmed Dar^a, Sourov Chandra^b, Esma Khatun^a, M. P. Kannan^a, Robin H. A. Ras^{b,c}, Thalappil Pradeep^{a*}Received 00th January 20xx,
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In this communication, we present the synthesis of 2-pyrene imine thiol (2-PIT)-protected Ag₃₅ nanoclusters using a ligand exchange-induced structural transformation reaction. The formation of the nanocluster and its composition were confirmed through several spectroscopic and electron microscopic studies. UV-vis absorption spectrum showed a set of characteristic features for the nanocluster. This nanocluster showed blue emission under UV light due to pyrene to metal core charge-transfer, and a NIR emission due to charge-transfer within the metal core. This is the first report of dual emitting pyrene protected atomically precise silver nanocluster.

Ligand protected metal nanoclusters (NCs) are an emerging class of quantum materials connecting the gap between atoms and bulk metallic materials.^[1-2] Owing to their unique electrical, optical and other spectroscopic properties such as luminescence^[3-5], chirality^[6], etc., they are important in applications such as catalysis,^[7] CO₂ reduction,^[8] bioimaging,^[9] etc. The surface ligand environment not only stabilizes the fragile metal core but also determines their electronic properties.^[10-11] Literature suggests that small organic thiol and phosphine co-protected silver nanoclusters such as Ag₆,^[12] Ag₁₄,^[13] Ag₂₅,^[14] Ag₂₉,^[15] Ag₆₇,^[16] etc., are more promising compared to bulky DNA,^[17-18] and dendrimer^[19] protected NCs in making structure-property correlations. From our group, we have reported silver NCs such as Ag₁₆, Ag₁₇,^[20] Ag₂₂,^[21] Ag₄₀, Ag₄₆,^[22] etc., and their crystal structures as a step toward understanding their various functional properties. Generally, light sensitivity and chemical instability of the Ag core limit their practical applications. In view of such limitations, designing new multidentate ligands that can stabilize Ag NCs is important. In contrast to the conventional organic thiols and phosphines used for protecting silver NCs, in this work we have used 2-pyrene imine thiol, a polycyclic aromatic hydrocarbon (PAH)-based ligand for Ag NC synthesis. Atomically precise silver NCs

protected with electron dense pyrene ligands are a new class of functional hybrid nanomaterials, which show electronic, optical with other physical properties, due to a combination of both ligand and the cluster core.

Pyrene is a good candidate among other PAHs, due to its multiple absorption and emission properties.^[23] Due to their high emission quantum yield and excimer stability, pyrene functionalised nanoparticles (NPs) and dendrimers are widely used for optoelectronic,^[24-25] molecular labelling,^[26] and fluorescence sensing applications^[27]. There are some reports of functionalised pyrene protected gold NPs, where the NPs show erratic emission of pyrene.^[28] Due to the resonance energy transfer from the chromophore to the metallic core, the emission quenches significantly. Distance from the nanoparticle core to pyrene has a significant role for this energy transfer process.^[29] Generally increasing the distance from the metallic core to the pyrene center decreases quenching. In case of a cluster, which has a molecular core, quenching is expected.

To obtain a highly stable silver NC, appended with PAHs, we have used 2-PIT and triphenylphosphine (TPP) as ligands. The synthesis of 2-PIT ligand was through a high-temperature condensation reaction between pyrene aldehyde and 2 amino thio-phenol. Fig. 1a shows the schematic representation of the synthesis of 2-PIT ligand. In brief, pyrene aldehyde was mixed with 2 amino thio-phenol in argon atmosphere in methanol-ethanol solvent mixture, under refluxed (60 °C) conditions. After 4 hour reaction, a yellow colored ligand was filtered using a Whatman 42 filter paper and washed several times with methanol-ethanol, solvent mixture to remove the excess starting materials. The as-prepared 2-PIT ligand was confirmed using ¹H, and ¹³C{¹H} NMR (shown in the Fig. S1 and S2 respectively) and mass spectral studies.

The formation of the 2-PIT ligand was confirmed through single-crystal structure studies. Fig. 1b shows the crystal structure of the ligand, which crystallized in a monoclinic P2₁/c crystal system. From the crystal structure, we observed that the C-H proton of the imine group and the S-H proton combined themselves and formed a five-membered ring. The distance of S and imine carbon is 1.77 Å compared to 1.72 Å distance of C-S bond with benzene ring, which indicate a weak bonding with the imine carbon.

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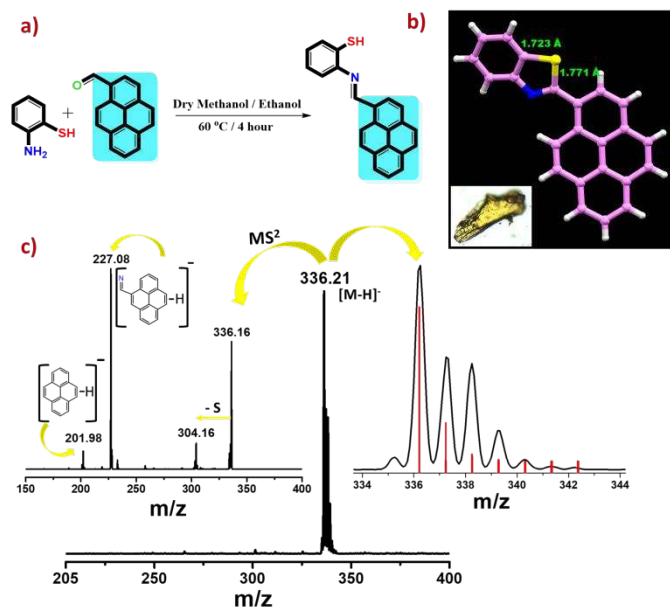


Fig. 1 a) Schematic representation of the synthesis of 2-pyrene imine thiol ligand; b) crystal structure of the ligand (inset shows the optical image of the single crystal); c) mass spectrum and MS/MS fragmentation data of the ligand. (color codes of the atoms: violet = carbon; blue = nitrogen; yellow = sulphur; gray = hydrogen).

Several C-H \cdots π intermolecular interactions in the intermolecular packing of the ligands are shown in Fig. S3; four molecules packed inside the unit cell in a lamellar fashion are visible in it. Negative mode electrospray ionisation mass spectrum (ESI-MS) in DCM showed the $[M-H]^-$ ion peak at m/z 336.21, which indicated the existence of the molecule in the thiol (SH) form in solution. Proton NMR spectrum shown in Fig. S1 with a single peak at 3.45 ppm confirmed the thiol form in solution. Furthermore, we confirmed the formation of the imine thiol form through MS/MS fragmentation studies, showing the loss of S, pyrene imine and pyrene moieties from the molecular ion peak, by varying the collision energy.

Ag_{35} NC was prepared using ligand exchange-induced structural transformation (LEIST) reaction from Ag_{18} nanocluster. Fig. 2a shows a schematic representation of the synthetic procedure employed in the LEIST reaction. The product clusters were also formed by a controlled co-reduction reaction of metal thiolates in presence of TPP. Detailed characterization of the Ag_{18} NCs through UV-vis absorption and MS studies are shown in Fig. S4. Conversion of Ag_{18} NC to Ag_{35} NC through several intermediates was reflected in the changing color of the reaction mixture. Changes in the UV-vis absorption features of these intermediates are shown in Fig. S5. A dark violet color appeared at the end of the reaction after 48 h. Fig. 2b shows the UV-vis absorption features of the purified NC. The nanocluster has well defined sharp absorption features at 557 and 497 nm. Absorption features of the Ag_{35} NC remain unchanged after two months, indicating the good stability of the NC. A uniform particle size distribution of the NC was also confirmed using TEM imaging. TEM images show small cluster particles <2 nm in diameter (Fig. 2d).

Molecular composition of this NC was confirmed using high resolution ESI-MS (HR ESI-MS) technique. During ESI-MS measurements, the ionization of the cluster was enhanced by adding a few drops of methanol. Detailed instrumentations are given in SI. Full range mass spectrum shown in Fig. 3a, indicates a sharp peak at m/z 2659.7 in 3+ charge state. This corresponds to a mass of 7971.1 for the molecular ion species. This peak was assigned as $[Ag_{35}(2-PIT)_7(TPP)_7@H_2O]^{3+}$ by comparing its experimental isotopic distribution with the isotopic distribution of the simulated spectrum. The assignment was further verified using collision induced dissociation (CID) mass spectrometry measurements at different collision-energy (CE), which is in instrumental units of the Waters Synapt G2 Si mass spectrometer. MS/MS fragmentation patterns are shown in Fig. 3b. From MS/MS spectra, we observed that by varying the CE from 0 to 50, there was four sequential mass loss of 262 which indicate four TPP unit detachment from the cluster. Next, by increasing the CE from 50 to 150, further loss of TPP was not observed, which suggested that only 4 TPP molecules are weakly bonded to the outer shell of the cluster. At CE 150, a new peak appeared at 2755.5 with 2+ charge state. The mass loss of 2468.18 indicated the loss of $[Ag_{13}(H_2O)(TPP)_4]$ fragment from the molecular ion peak. Next upon increasing CE from 150 to 175, we observed further loss of three TPP, which indicated that while four TPP molecules are loosely bound to the cluster surface, there were three other strongly bound TPP molecules. Upon further increasing the CE, five sequential mass losses of 124 units due to the loss of aminothiophenol moieties from the NC, generated by the fragmentation of 2-PIT ligand were seen.

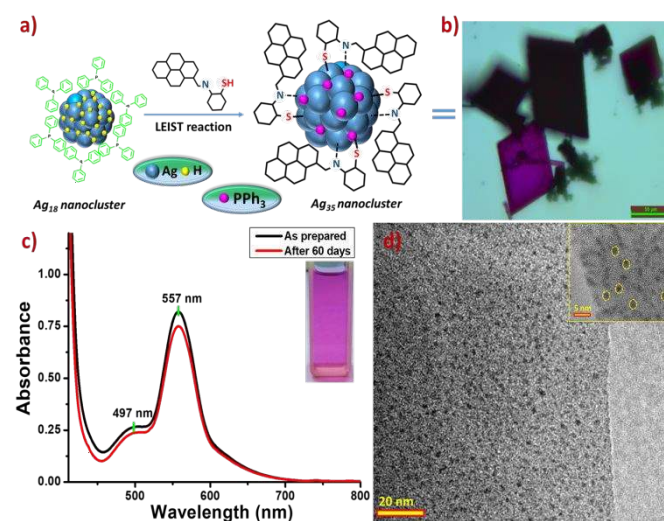


Fig. 2 a) Schematic representation of the synthesis of Ag_{35} NC by LEIST reaction; b) optical microscopic image of the Ag_{35} NC crystals; c) UV-Visible absorption spectrum of Ag_{35} NC showing its stability (inset shows the photographic image of the NC solution in DCM); d) TEM image of the NC showing the uniform particle distribution (inset shows the HRTEM image of the NCs, some particles are encircled).

To further understand the binding of TPP and 2-PIT ligands, we studied ^{13}C , and ^{31}P NMR spectra of the NC. Fig. 3c shows the ^{13}C NMR spectrum of the NCs, which exhibited 23 low intensity signature peaks of carbon in the 120-128 ppm window due to 2-PIT along with TPP signature peaks in the 128-135 ppm region. This clearly suggested the co-protection of 2-PIT and TPP ligands. Multiplet peak

splitting of the ^{13}C spectrum for the TPP region is most probably due to variation in the chemical environment of the TPP outside the NC surface. A broad ^{31}P NMR signal at 9.32 ppm shown in Fig. S6 indicated TPP binding with the cluster. Although there are two sets of TPP molecules on the cluster surface, we were not able to distinguish them through the ^{31}P NMR spectrum. XPS spectra are shown in Fig. S7, and S8 (Table 3) of the ligand and Ag_{35} NC, respectively. Among the four peaks of Ag_{35} NC, two peaks at 284.8 and 286.6 eV are comparable with the two peaks at 284.8 and 286.3 eV of C 1s region of the 2-PIT ligand, which suggests the binding of 2-PIT ligand. Two other peaks of C 1s region at 288.2 and 289.4 eV are due to the two types of TPP ligands. Decrease in the binding energy of N 1s and S 2p regions in the Ag_{35} NC, compared to 2-PIT ligand probably is due to the electron back donation from the metal core to the N and S end of the ligand. Higher electronegativity of N and S compared to Ag is also the reason behind it. The binding energy of 368.4 and 374.5 eV for the Ag 3d region suggests metallic state of silver.

Although as-grown cubical blackish-violet crystals of the NC showed optical polarisation, due to the lack of intense electron diffraction spots, we were not able to get the single-crystal structure of the NCs. Fig. 2b and S9 show the optical microscopic images of the single crystals grown after crystallization. EDS elemental images of the single crystals are shown in Fig. 3d. The single crystal showed the existence of Ag, S, P, N and C in the atomic ratio of 3.61: 1.36: 1.47: 1.44: 92.12 in the crystal which indicated the coexistence of 2-PIT and TPP ligands in the NC. FTIR spectra of the 2-PIT ligand and Ag_{35} NC are shown in Fig. S10.

A sharp feature at 3049 cm^{-1} corresponded to the pyrene C-H stretching mode. Similar vibrational features are also there for 2-PIT ligand. A broad O-H vibrational feature centered at 3435 cm^{-1} indicated that H_2O is present in the NC.

Interestingly, the Ag_{35} nanocluster exhibits dual emission features in blue (449 nm) and NIR (896 nm) regions upon excitations at 417 and 530 nm respectively (Fig. 4). Fig. 4a shows the excitation spectrum of the Ag_{35} NCs at 449 nm emission, demonstrating three major excitation peaks at 297, 365 and 417 nm. These low lying excitation maxima resembling with the absorption maxima of 2-PIT ligand, is due to the charge transfer from pyrene to the metal core. The NIR emission peak at 896 nm corresponding to the excitation maxima at 530 and 558 nm is due to metal shell to metal core charge transfer (MMCT) in the NC. Comparing the absorption maximum at 557 nm with the excitation maxima, we can conclude that the NIR emission is due to the charge transfer within the metal core.^[30] Similar type of MMCT leading to NIR emission was reported on the literature.^[31] The Ag_{35} nanocluster shows dual emissive character of ligand as well as metal core and is the first example showing this behavior.

In conclusion, we have shown the synthesis of 2-pyrene imine thiol protected Ag_{35} nanocluster using LEIST reaction. The formation of the NC was confirmed using UV-vis absorption spectroscopy, mass spectrometry, multinuclear NMR, TEM, SEM, EDS, FTIR and XPS measurements. The cluster showed intense blue emission due to pyrene to metal core electron-transfer in the solution phase. There was also a comparable NIR emission, observed due to metal to metal charge transfer.

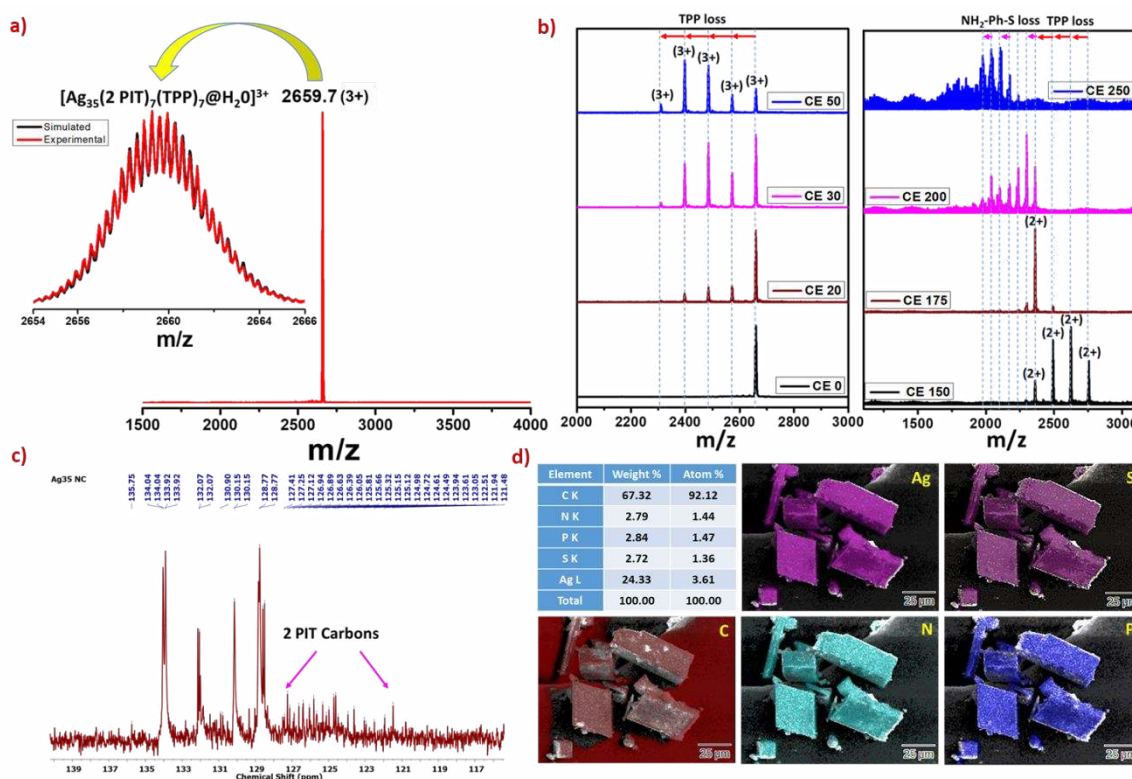


Fig. 3 a) Positive mode ESI- MS spectrum of the Ag_{35} NC in DCM (inset shows the simulated and experimental isotopic distribution patterns of the 2659.7 peak); b) MS/MS fragmentation pattern of the 2659.7 peak using different collision energy; c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of Ag_{35} NC in CDCl_3 ; d) SEM EDS elemental mapping of NC crystals indicating its atomic composition.

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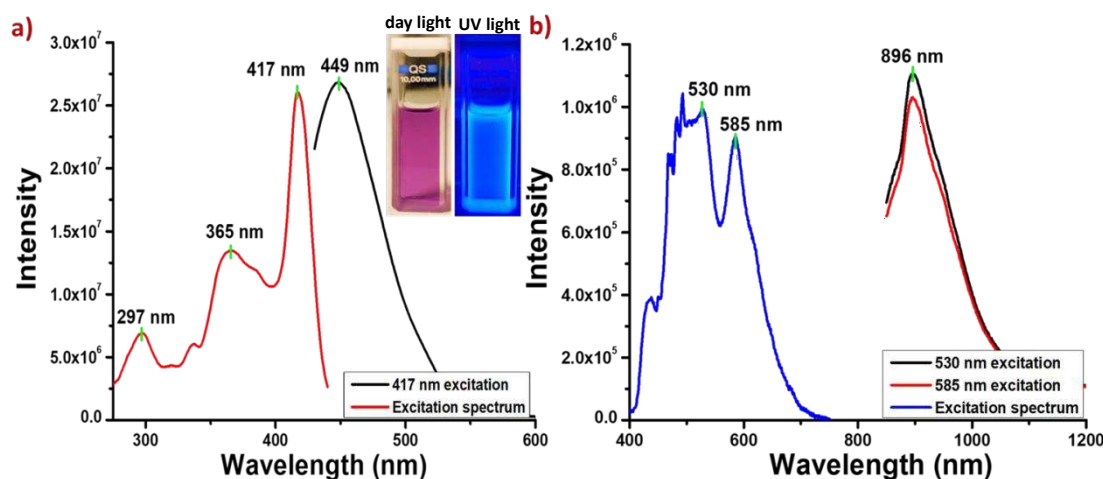


Fig. 4 a) Photoluminescence excitation and emission spectra of the nanocluster (inset shows images of the cluster solution in day light and under UV light); b) NIR emission and corresponding excitation spectra of the nanocluster.

This work is a step toward making silver nanoclusters with a family of electron rich pyrene molecules having composite electronic features. Dual emission in such type of materials may be tuned for desired applications such as ion sensors and for bio imaging.

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Conflicts of interest

There are no conflicts to declare.

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