A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

International Edition

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201906740
Angew. Chem. 10.1002/ange.201906740

Link to VoR: http://dx.doi.org/10.1002/anie.201906740
http://dx.doi.org/10.1002/ange.201906740

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Angewandte Chemie International Edition

10.1002/anie.201906740

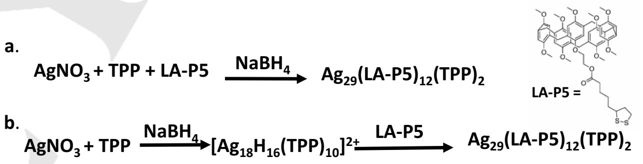
Pillar[5]arene Stabilized Silver Nanoclusters: Immense Stability and Luminescence Enhancement Induced by Host-Guest Interactions

Madathumpady Abubaker Habeeb Muhammed, Laila Khalil Cruz, Abdul-Hamid Emwas, Ahmed M. El-Zohry, Basem Moosa, Omar F. Mohammed and Niveen M. Khashab*

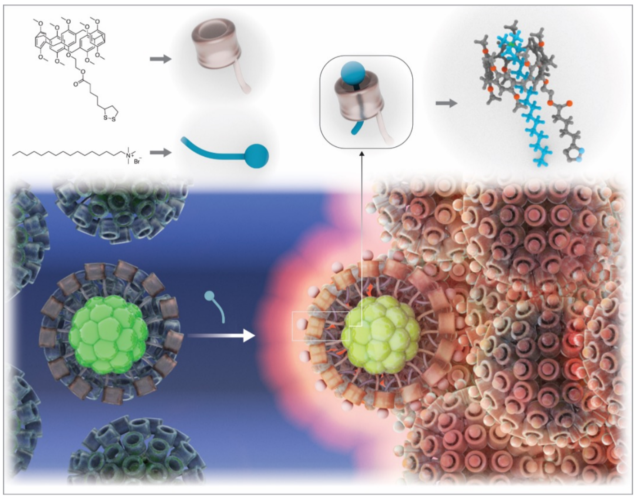
Abstract: Herein, we report the synthesis of a new class of functional silver nanoclusters (AgNCs) capped with pillar[5]arene (P5) based host ligands. These NCs are readily prepared via direct synthesis or ligand exchange synthesis and are stable at room temperature for over 4 months. The pillar[5]arene stabilized NCs ($Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$) endorse reversible host-guest interactions with neutral alkylamines and cationic quaternary ammonium guests. This results into the formation of spherical assemblies with unparalleled changes in their optical properties including an astonishing ≈2000-fold luminescence enhancement. This is the highest luminescence enhancement ratio reported so far for such atomically precise NCs. Our synthetic protocol paves the way for the preparation of a new generation of metal nanoclusters protected by macrocyclic ligands with molecular recognition and selectivity toward specific guests.

Ligand protected atomically precise metal nanoclusters (NCs) have generated great interest due to their unique physical and chemical properties.[1] They are used in several areas including catalysis,[2] sensing,[3] imaging[4] and drug delivery.[5] Most of the NCs have a core-shell structure consisting of a metal atom core surrounded by a shell of metal-ligand staple motifs.[1a] Hence, surface ligands play a vital role in determining the stability, atom packing as well as shaping the electronic properties of the NCs.[1b] Several ligands including alkane thiols,[6] aromatic thiols,[7] peptides,[8] DNA,[9] proteins,[10] dendrimers,[11] polymers,[12] and phosphines[13] have been used extensively for cluster synthesis. Additional functionality can be introduced to NCs by either ligand exchange[14] with functional ligands or by ligand conjugation.[15] More recently, functional metal NCs were prepared by employing macrocycle-based ligands such as thia- and diphenyphosphine-calixarenes.[16] Macrocycles can host a variety of guest molecules bringing new and diverse properties to the NCs. The hydrophobic nature and cone-like conformation of calixarenes however, drastically limits the nature of guests that could be accommodated in the cavity as well as critically decreases the accessibility to the metallic cluster.[16a]

Pillararenes are interesting macrocycles composed of hydroquinone units linked by methylene ($-CH_2-$) bridges at the para positions resulting in a symmetric pillared structure that can be easily functionalized.[17] Although pillararene functionalized gold and silver nanoparticles have been reported in literature,[18] the synthesis of pillararene functionalized NCs has not been explored thus far, to the best of our knowledge. Pillararenes would bring valuable functionalities to the NCs as they can host electron-poor and neutral species since many electron-rich hydroquinones are in close proximity.[19] This is extremely valuable for imparting changes in the optical properties such as photoluminescence (PL) of NCs. Many of the reported NCs are weakly luminescent and thus suffer from low PL quantum yield.[20] The common practices to increase the PL of NCs include doping to form alloy NCs,[21] aggregation induced emission (AIE) process,[22] solvent induced aggregation[23] and enhancement by rigidifying the ligand shell.[24]



Scheme 1. Synthetic routes of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ via direct synthesis and ligand exchange.



Scheme 2. Schematic representation of host-guest interaction between $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ and CTAB resulting in NCs host-guest assembly and a vast luminescence enhancement.

Herein, pillar[5]arene-based host ligands were successfully employed to prepare extremely stable AgNCs (Ag_{29}(LA-

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10.1002/anie.201906740

P5)$_{12}$(TPP)$_2$) with drastically enhanced lumiescence upon host-guest interactions. NCs with Ag$_{29}$ core but different surface functionality are well known in literature.[25] Lipoic acid (LA) ligands, for example, produce water dispersible, red luminescent Ag$_{29}$(LA)$_{12}^{3-}$ NCs.[25c-e] Ag$_{29}$(BDT)$_{12}$(TPP)$_4^{3-}$ (BDT=1,3-benzenedithiol) were also successfully prepared when TPP is used as a co-ligand to the main BDT ligand.[25a] These NCs exhibit luminescence with an emission maximum around 670 nm. Functionalizing NCs with macrocycles such as pillararene makes them readily accessible to an extended variety of guest molecules, which can consequently tune their optical properties. Both direct synthesis and ligand exchange synthesis can reproducibly induce Ag$_{29}$(LA-P5)$_{12}$(TPP)$_2$ (Scheme 1). Tuning the nature of the guest molecule provoked unprecedented changes in the optical properties of Ag$_{29}$(LA-P5)$_{12}$(TPP)$_2$ including a dramatic ≈2000-fold PL enhancement when cetrimonium bromide surfactant (CTAB) was used as the guest molecule (Scheme 2).

A dithiolate lipoic acid (LA) terminated copillar[5]arene (LA-P5) ligand was synthesized by DCC coupling of monoethanol substituted P5 and LA (Scheme S1). The ligand was characterized by ^{1}H NMR spectroscopy (Figure S1) and MS spectrometry (Figure S2). The presence of LA with two thiols offer stronger anchoring than monothiol ligands.[26] Synthesis of NCs was first carried out by direct synthesis starting from an Ag precursor that was reduced in the presence of LA-P5 and triphenylphosphine (TPP) ligands (Scheme 1a). ESI-MS measurements to assign a molecular formula for the cluster were not successful and thus matrix-assisted laser desorption ionization (MALDI) mass spectrometry (MS) was employed using *trans*-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix. It should be noted that some NCs do not ionize by electrospray and so MALDI MS is the most suitable option. [1a, 27] In this case, an intense peak centered around 15207 Da is displayed at the threshold laser power supporting a molecular formula of ~Ag$_{29}$(LA-P5)$_{12}$(TPP)$_2$ (theoretical mass 15283 Da) (inset, Figure S3). Additionally, twelve other peaks are seen at lower m/z values with varying intensity (Figure S3). All the reported Ag$_{29}$ cores have twelve thiol ligands bound to it.[25] These peaks are separated by a fixed m/z value of ~932. This is due to the loss of a single LA-P5 ligand as a result of S-C bond cleavage, which is consistent with previous reports on loss of ligands under laser irradiation.[1a, 28] Our cluster is two phosphines short when compared to Ag$_{29}$(BDT)$_{12}$(TPP)$_4^{3-}$.[25a] This may be due to the fact that the geometry and size of LA-P5 ligand are completely different than that of BDT and phosphines are labile and are known to dissociate during ionization. MALDI-MS of NCs at various laser powers were also measured where fragmentation of the NCs is more pronounced at higher powers (Figure S4). A bunch of peaks due to Ag$_m$S$_n$ clusters with a spacing of 248 Da (assigned to the loss of Ag$_2$S) between the major peaks of the adjacent group of peaks were observed. The formation of Ag$_m$S$_n$ peaks at higher laser power is typical for NCs.[1a, 28] Expanded view of an Ag$_m$S$_n$ peak exhibited a spacing of 32 Da corresponding to the loss of S. XPS measurements were performed to understand the oxidation state of Ag as well as the binding nature of LA-P5 ligand on the NC (Figure S5). XPS survey spectrum revealed the presence of the important elements Ag, S and P in the purified NCs. The expanded region of Ag displayed the binding energy (B.E.) for Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ at 368 and 374 eV, respectively. This suggests zerovalent state of most of Ag in the NC. The B. E. value for S 2p$_{3/2}$ at 161.7 eV suggests thiolate binding to the NCs. Binding energy for unbound thiol/disulfide occurs at 163.5 -164 eV.[29]

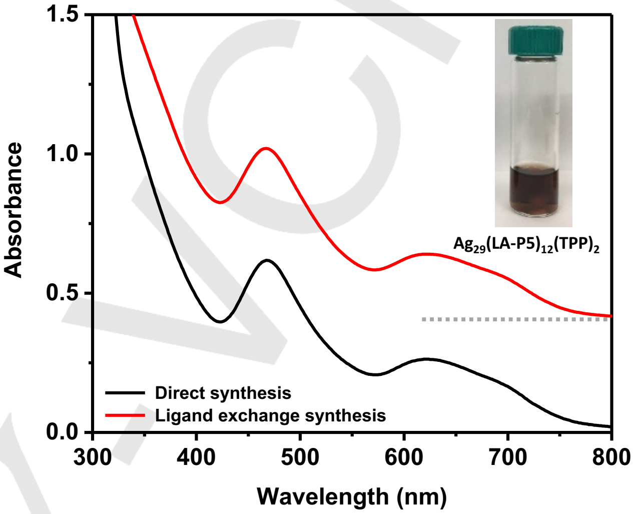

Figure 1. Optical absorption spectra of Ag$_{29}$(LA-P5)$_{12}$(TPP)$_2$ formed via direct synthesis (black trace) and ligand exchange synthesis (red trace). The red trace is shifted vertically for visual clarity. Photograph of the NC dispersion formed via direct synthesis in DCM is given in the inset.

Interestingly, a ligand exchange induced structure/size transformation (LEIST) synthesis afforded the same NCs where pre-synthesized TPP capped AgNCs ([Ag$_{18}$H$_{16}$(TPP)$_{10}$]$^{2+}$) were treated with LA-P5 (Scheme 1b). ESI-MS analysis showed a peak at m/z 2290 that can be assigned to the molecular formula [Ag$_{18}$H$_{16}$(TPP)$_{10}$]$^{2+}$ (Figure S6). The [Ag$_{18}$H$_{16}$(TPP)$_{10}$]$^{2+}$ dispersion in methanol was green in color with two distinctive absorption features at 545 and 614 nm and a shoulder peak at 444 nm as reported previously (black trace, Figure S7).[13a] When LA-P5 dissolved in DCM was added to the solution under stirring, a clear color change from green to dark brown was observed after 5 minutes. Optical absorption spectroscopy exhibited molecule-like and highly structured absorption spectrum confirming the formation of NCs (Figure S7). It is worth mentioning that no spectral features for larger particles (i.e plasmonic) were detected in our steady-state absorption spectra, providing a clear indication for the high purity of the NCs. The absorption spectra of the NCs prepared by direct synthesis (scheme 1a) and ligand exchange synthesis (Scheme 1b) are identical which supports the formation of Ag$_{29}$(LA-P5)$_{12}$(TPP)$_2$ (Figure 1). The absorption spectrum of NCs exhibited two well resolved peaks at 468 and 623 nm and a shoulder around 700 nm (Figure 1). Upon comparison, the absorption profile of the reported Ag$_{29}$ NCs looks the same as Ag$_{29}$(LA-P5)$_{12}$(TPP)$_2$ with the peaks appearing at lower wavelengths. While, Ag$_{29}$(LA)$_{12}^{3-}$ NCs[25d] exhibit absorption features at 425 and 500 nm with a shoulder around 330 nm, Ag$_{29}$(BDT)$_{12}$(TPP)$_4^{3-}$ NCs[25a] exhibit absorption

10.1002/anie.201906740

peaks at 447 and 513 nm. The difference in the absorption features can be attributed to the difference in the surface ligand chemistry. Moreover, pillararene capped NCs can only be formed when both LA-P5 and TPP are used as ligands. When LA-P5 was solely used as a ligand for NCs direct synthesis, a reddish brown dispersion with a broad plasmon-like band centered at 455 nm appeared (Figure S8) suggesting the possibility of formation of tiny nanoparticles instead of NCs (Figure S9).

Most of the organic soluble AgNCs reported so far lack long term stability so while the majority disintegrates within several minutes, some stay stable for few days.[1a] Producing NCs with long term stability is a major goal of prospective NCs research. We checked the stability of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ against that with just TPP protection ($[Ag_{18}H_{16}(TPP)_{10}]^{2+}$). Both samples were stored at room temperature protected from light. The characteristic absorption features of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ remained the same after 4 months of storage while those of $[Ag_{18}H_{16}(TPP)_{10}]^{2+}$ disappeared after just 3 days of storage (Figure S10). Moreover, our NCs were stable upto 7 days with light exposure, which makes them applicable for imaging and photocatalytic activites. This long term stability of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ is ascribed to the dithiol binding of LA-P5 as well as the presence of the bulky pillararene rings.

The luminescence of the as-prepared $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ was extremely weak and broadly centered at 745 nm under 468 nm excitation (Figure S11). We reasoned that host-guest interactions with a suitable guest molecule may lead to enhancement in the PL of the NCs. Tuning the surface functionality of an atomically precise gold cluster have been successfully demonstrated in literature using specific host–guest interactions between β-cyclodextrin (CD) and the ligand anchored on the cluster.[30] Primed by this prospect, the host-guest interactions of the pillararene functionalized NCs were explored. Since P5 can host neutral and cationic guest molecules, neutral alkylamines and cationic quaternary ammonium salts were chosen as guests for the study. Linear alkylamines and diamines form host-guest interaction with P5 due to the hydrogen bonding between the amino group of the guest and the methoxyl groups of the host.[31] On the other hand, quaternary ammonium salts form host-guest interaction with P5 due to the cation/π interactions.[32] Both OA[31] and CTAB (Figure S12a) are threaded through the P5 cavity forming a pseudo rotaxane structure with 1:1 stoichiometry.

The host-guest interactions between P5 and the chosen guests were studied first by ^1H NMR titration before incorporation onto NCs. The data of ^1H NMR titration of octylamine (OA, the selected alkylamine) with P5 is presented and explained in Figure S13. The association constant (K_a) between P5 and n-octylamine is 20±2 M^{-1} as reported in literature.[31] The data of ^1H NMR titration of cetrimonium bromide (CTAB, the selected quaternary ammonium salt) with P5 is presented and explained in Figure S14 and Figure S15. The K_a value of CTAB with pillar[5]arene was calculated to be 863±28 M^{-1} using curve-fitting analysis (Figure S12b).

The host-guest interaction between $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ and CTAB is presented in Scheme 2. The NCs precipitate was redispersed, after centrifugation, in DCM containing CTAB or OA and incubated overnight. The changes in the absorption features are shown in Figure 2a. While the absorption peak at 623 nm blue shifted to 580 nm, the peak at 468 nm became sharper and more prominent for OA treated NCs (brown trace, Figure 2a). In addition, the dispersion color changed from greenish brown to brown. The changes in absorption features were more drastic for CTAB treated NCs. The absorption peaks at 623 and 468 nm are shifted to 490 and 430 nm respectively, with the appearance of an additional peak at 330 nm (red trace, Figure 2a). The dispersion color change was more visible as it turned to light yellow from greenish brown. We reason that the dispersion color change and modifications in absorption features are due to the charge redistribution on NCs after the strong host-guest interactions.

Surprising modifications in the PL of the NCs was observed after host-guest interactions as shown in Figure 2b. A remarkable 30 times PL enhancement was observed for OA treated NCs with peak maximum at 810 nm. On the other hand, an astonishing approximately 2000-fold PL enhancement was observed for CTAB treated NCs with peak maximum at 650 nm (Figure 2b). This is the highest luminescence enhancement ratio reported to date for atomically precise NCs. The emission was so strong that it was perceived by the naked eye under UV irradiation (Figure 3). The corresponding excitation spectra are given Figure S16. The quantum yield of the NCs after host-guest interactions with CTAB was an impressive 17%. A mixture of LA-P5 and OA/CTAB did not show any red emission proving that the emission originates from the NCs (Figure S17). Also, the TRPL data (Figure S18) for the NCs in the presence of guest molecules (CTAB and OA) show similar emission decays to the pristine NCs. Despite the fact that more photons are detected on the photodiode in the presence of guest molecules, mainly with the CTAB, all the kinetic traces could be fitted with bi-exponential equations with corresponding lifetimes of 0.7 ns (85 %) and 4.5 ns (15%). Thus, we propose that this huge emission increase is due to the host-guest interactions with CTAB.This has also resulted in increasing the absorption coefficient of the clusters after adding the CTAB.

TEM images of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ showed particles with a core size of ~2 nm while TEM images of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ after host-guest interactions with CTAB (Figure 3) and OA (Figure S19) showed several spherical aggregates of 100-300 nm, supporting the host-guest induced emission of NCs. EDX spectrum (Figure S20) of the spherical aggregates showed also the presence of Ag. Thus, the addition of OA or CTAB results in intensive host-guest interactions switching on the emission characters of more clusters than in the absence of guest molecules. Interestingly, the binding of CTAB to $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ is stronger than that of OA (K_a for CTAB is almost 43 times higher than that for OA) causing more drastic enhancement in the PL. An experiment was carried out to check the competitive interaction of CTAB and OA with NCs by treating the NCs with a mixture of CTAB and OA. The changes in the absorption spectrum suggest that CTAB forms host-guest interactions with CTAB over OA (Figure S21a). Similarly, when CTAB was added to a host-guest system of NCs with OA, CTAB replaces OA as suggested by the changes in the absorption spectra (Figure S21b). Finally, when OA was added to a host-guest system of NCs with CTAB, no changes in optical spectra was observed suggesting that OA cannot replace CTAB (Figure

S21c). It is worth noting that the host-guest interactions between $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ and the guest molecules is reversible (Figure 3). For example, when methanol was added to CTAB treated NCs, the optical features reverted back to the original NCs suggesting the extinction of host-guest interactions (Figure S22). It is well known that the cation-л interactions is solvent dependent and is weakened in the presence of polar solvents. Similar changes were observed for OA treated NCs.

Since the addition of guest molecules result only in host-guest interactions with LA-P5 ligands on the NC, we do not anticipate any changes in the cluster stoichiometry. This claim is supported by the fact that the optical features revert back to the original form after methanol addition. It could be hypothesized that the drastic changes to the optical absorption support the possibility of the perturbation to the metal core. In fact, similar observation has been reported for Ag NCs after metal doping.[21] However, the observed changes especially in the PL signal could be also caused by other factors including surface modification via ligand engineering. In addition, surface ligands play crucial role in deciding the optical properties of the NCs and thus the host-guest interaction between LA-P5 and CTAB results in the modification of the ligand chemistry. The addition of positively charged CTAB may lead to a charge redistribution on the surface of NCs, resulting in significant changes in the optical properties. In this regard, there are few reports on the dramatic changes in the color of the dispersion and the optical properties of NCs after the addition of external molecules. For example, weak emission of the water soluble, green emitting 6-aza-2-thiothymine-protected AuNCs (ATT-AuNCs) enhanced 34 fold after introducing L-arginine (Arg) into the capping layer.[33] In our case, we propose that more drastic changes in optical properties occurred after CTAB addition due to the stronger binding between LA-P5 and CTAB.

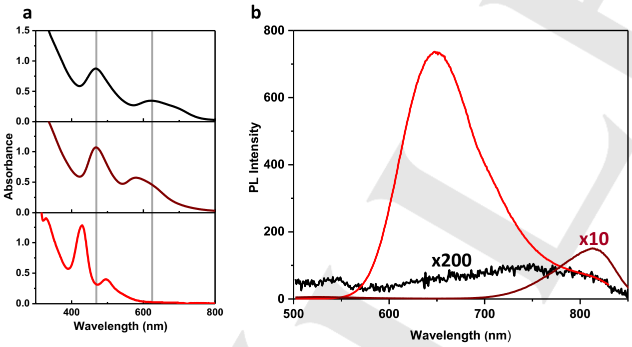

Figure 2. Comparison of the (a) absorption and (b) PL spectra of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ before (black trace) and after host-guest interaction with OA (brown trace) and CTAB (red trace). For visual clarity, PL spectrum of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ has been multiplied by 200 and the PL spectrum of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ treated with OA has been multiplied by 10.

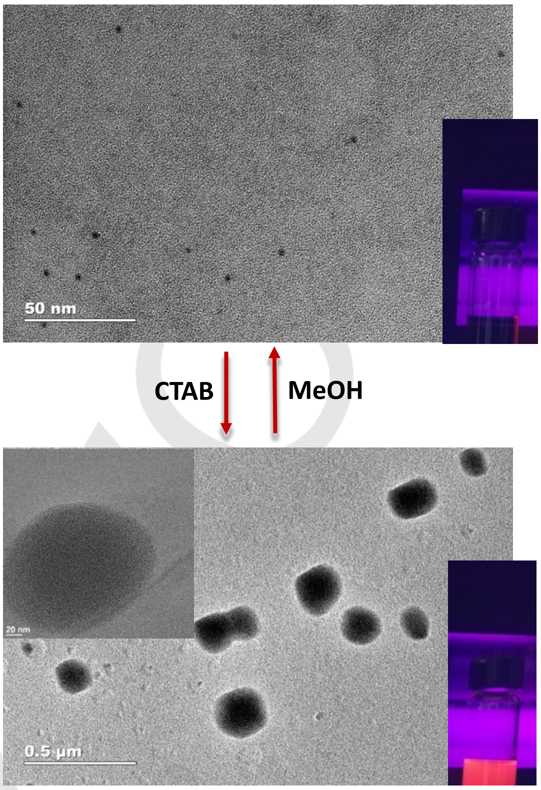

Figure 3. TEM images of $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ before and after host-guest interaction with CTAB. Spherical aggregations of NCs are formed after host-guest interaction. The host-guest interaction is reversible upon MeOH addition. Corresponding NC dispersions in DCM under UV light irradiation are given in the inset.

$Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ were also treated with other alkylamines and diamines such as hexylamine, dodecaneamine, oleylamine, 1,8-diaminooctane and the changes in optical properties were the same as that of OA. Similarly, NCs were mixed with other structurally similar quaternary ammonium salts such as trimethyloctadecylammonium bromide, dodecyltrimethyl-ammonium bromide and trimethyloctyl ammonium bromide. Irrespective of the alkane chain length, they all showed the same dispersion color change, changes in the absorption spectra, and huge PL enhancement in the red region (Figure S23). These observations suggest that CTAB and other structurally similar quaternary ammonium molecules have the perfect size to thread through the P5 cavity and form strong host-guest interactions. On the other hand, when NCs were treated with structurally different quaternary ammonium molecules such as tetrakis(decyl)ammonium bromide and tetraoctylammonium bromide with four bulky alkane chains instead of three methyl groups and one longer alkane chain, the PL enhancement was only one third in comparison to that of CTAB treated NCs (Figure S24).

In conclusion, pillar[5]arene capped AgNCs ($Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$) have been prepared via a tailor-made copillar[5]arene ligand with dithiolate functionality. Unique changes in the optical properties were observed after introducing neutral alkylamine and cationic quaternary ammonium guest molecules to the AgNCs. While alkylamines produced a 30-fold PL enhancement, quaternary ammonium molecules induced an extraordinary ≈2000-fold PL enhancement that can be perceived by the naked eye. The capping by a bulky macrocyclic bidentate ligand resulted in an impressive long-time storage stability of the NCs (4 months). Since $Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$ exhibit strong emission, our next step is to impart water solubility to these NCs for biological applications such as deep-tissue imaging where far red to IR emission is in high demand. We believe this work will motivate further studies of host-guest chemistry on nanoclusters especially that it can be extended to other platforms such as gold, copper, and palladium.

Acknowledgements

We would like to acknowledge Dr. Dalaver Anjum from KAUST Core Labs for HRTEM measurements.

Keywords: nanoclusters • pillararene • host-guest chemistry • molecular recognition • sensors

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10.1002/anie.201906740

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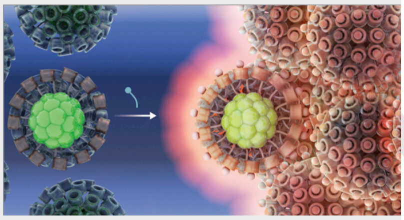
Layout 1:

COMMUNICATION

Host-guest interactions of pillar[5]arene (P5) capped silver nanoclusters ($Ag_{29}(LA\text{-}P5)_{12}(TPP)_2$) with alkylamines and quaternary ammonium guest molecules resulted in the modulation of optical properties of the NCs including an extraordinary ≈2000 fold PL enhancement.



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