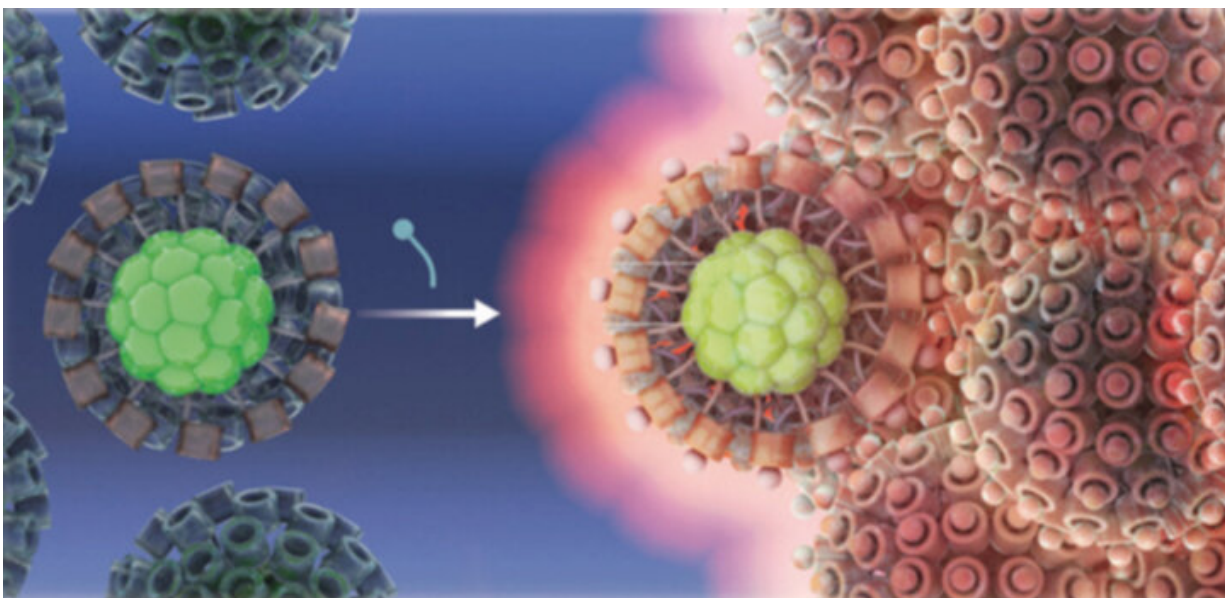


Stabilizing ligands make nanoclusters brighter

November 19 2019



Noncovalent interactions between pillararene-based ligand and cationic cetrimonium bromide generate self-assembled structures that are more stable and better lit. Credit: Wiley-VCH

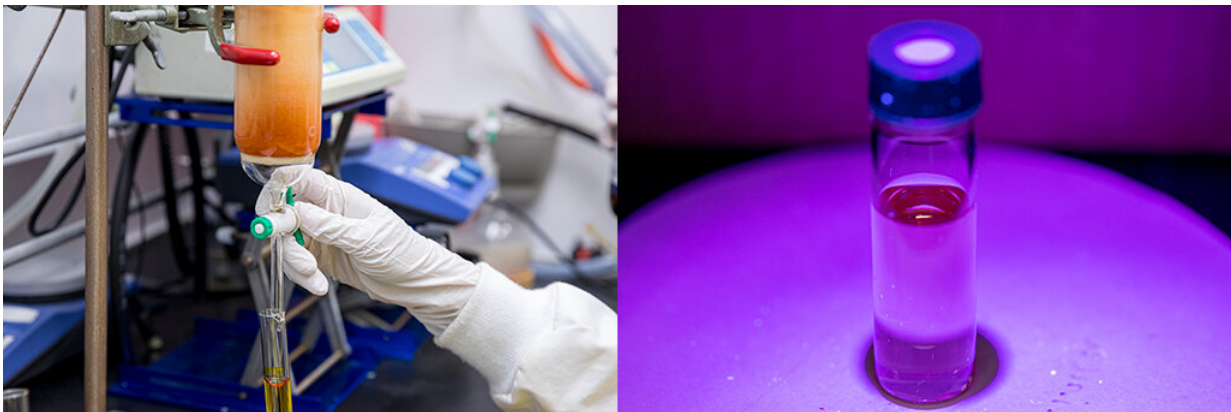
Metal nanoclusters that bear tunable surface ligands could help develop next-generation imaging and photocatalytic approaches, suggests work by KAUST researchers.

Metal nanoclusters, usually less than two nanometers in size, exhibit unique physical and chemical characteristics that are useful for a

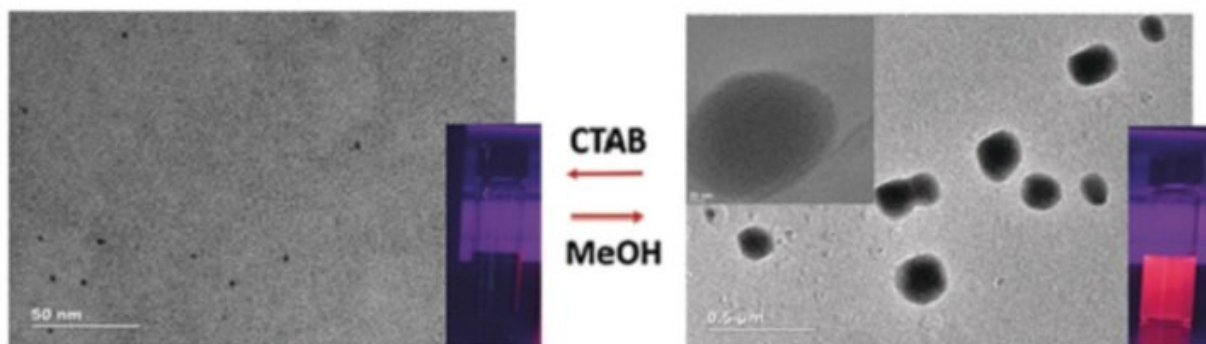
multitude of applications, ranging from catalysis and sensing to imaging and drug delivery. These properties hinge on the size and stability of the nanoclusters. Several ligands have proven effective for stabilizing the nanoclusters and tuning their properties according to specific uses. However, these size-dependent properties remain difficult to harness.

Silver nanoclusters tend to have low stability. Although some of these nanoclusters remain stable over a few days, most disintegrate within minutes, explains Ph.D. student Laila Khalil. This demise highlights the need for stabilizing ligands that can also improve the optical properties of these nanoclusters.

Now, a team led by Niveen Khashab has devised a way to increase stability. They developed sulfur-based ligands with a large cyclic functional group called a pillararene. These ligands can simultaneously stabilize silver nanoclusters. They feature a cylindrical cavity that can accommodate [small molecules](#), or guests, and selectively bind to these guests through noncovalent interactions.



Laila Khalil collects the purified ligand (left). The nanocluster solution is treated with a surfactant and UV light to induce a 2,000-fold increase in luminescence. Credit: KAUST



The nanoclusters form round aggregates in the presence of cetrimonium bromide through reversible host-guest interactions. Credit: Wiley-VCH

"We create and synthesize systems that mimic natural designs," says Khalil to explain why the team decided to produce a macrocyclic thiol [ligand](#). Unlike typical macrocycle-based ligands, such as the hydrophobic and cone-shaped calixarenes, pillararenes are electron-rich cylindrical structures that can be readily modified using various functional groups, which allows them to hold electron-poor and neutral compounds in their cavity. This is expected to widen the range of potential guest molecules and consequently the ability to tailor the properties of the nanoclusters.

The pillararene-functionalized nanoclusters stayed stable for four months when stored in the dark and for up to seven days when exposed to daylight. Their photoluminescence rose 30 times when a neutral amine

was used as a guest molecule. Adding the cationic surfactant cetrimonium bromide induced a 2000-fold increase in photoluminescence that was visible to the [naked eye](#), and it also outperformed other atomically precise nanoclusters. The researchers demonstrated that stronger binding between guest molecules and nanoclusters led to a more pronounced increase in photoluminescence. This suggests that the dramatic increase in emission results from host-guest interactions.

This system could have useful biological applications, especially noninvasive deep-tissue imaging," says Khalil. This will help diagnose diseases, such as skin cancer and brain anomalies.

More information: Madathumpady Abubaker Habeeb Muhammed et al. Pillar[5]arene-Stabilized Silver Nanoclusters: Extraordinary Stability and Luminescence Enhancement Induced by Host-Guest Interactions, *Angewandte Chemie International Edition* (2019). [DOI: 10.1002/anie.201906740](#)

Provided by King Abdullah University of Science and Technology

Citation: Stabilizing ligands make nanoclusters brighter (2019, November 19) retrieved 17 July 2024 from <https://phys.org/news/2019-11-stabilizing-ligands-nanoclusters-brighter.html>

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