

Self-Limiting Cation Exchange for Ternary Nanoclusters

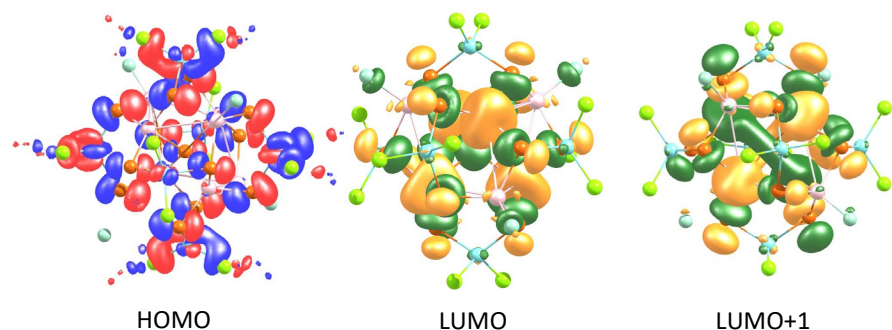
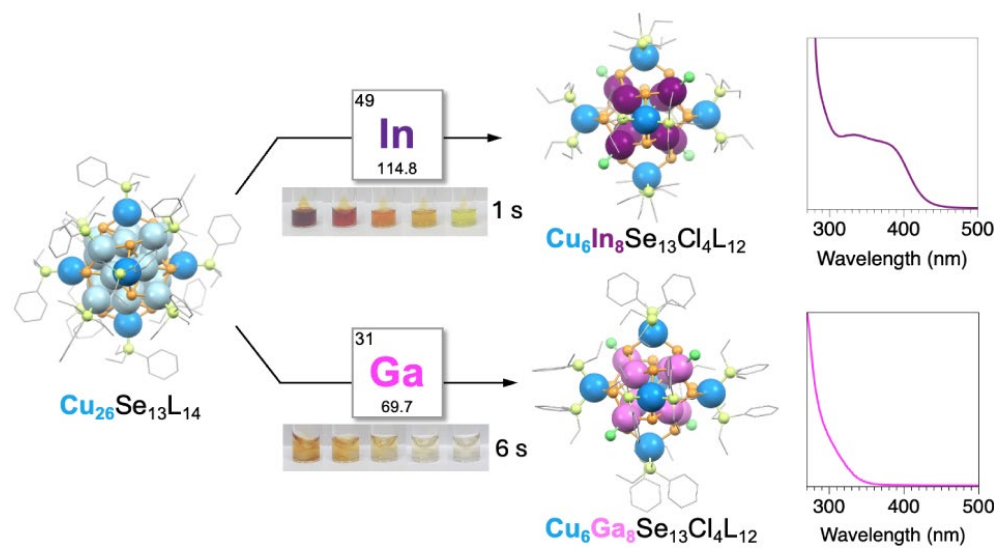


Figure: Rapid In/Ga exchange gives atomically defined products; DFT/TDDFT assigns the broad absorption to charge-transfer frontier orbitals from HOMO to LUMO and LUMO+1.

Scientific Achievement

A CINT User Team shows that multinary semiconductor composition of large clusters, their structure, surface coordination, and optical response can be programmed at the single-cluster level.

Significance and Impact

Self-limiting cation exchange converts $\text{Cu}_{26}\text{Se}_{13}$ molecular cluster template into atomically defined $\text{Cu}_6\text{M}_8\text{Se}_{13}\text{Cl}_4(\text{PR}_3)_{12}$ ($\text{M}=\text{In}, \text{Ga}$) clusters in high purity and near-unity yield.

Research Details

- In/Ga exchange preserves Se_{13} framework and locks cations into a *pseudo-core/shell* motif: Inner/facet M^{3+} , outer-edge Cu^+ .
- Surface coordination completes the self-limit: Phosphines passivate Cu^+ while Cl^- binds inner M^{3+} sites.
- DFT/TDDFT links spectra to orbital composition: Cu/Se-rich occupied states $\rightarrow$ In/Ga-centered acceptor states, giving broad charge-transfer absorption.
- Thermolysis leads to thin films of CuInSe_2 semiconductor solids.

Ma, F.; Ivanov, S. A.; Mishra, I.; Zeng, C. Precision Synthesis of I–III–VI Ternary Semiconductor Nanoclusters via Self-Limiting Cation Exchange. *JACS* 2026

Work was performed, in part, at the Center for Integrated Nanotechnologies.