Tuning Solid-State Photoluminescence of AuCu14 Nanoclusters: Influence of Dendron-Shell Spacing and Dynamics

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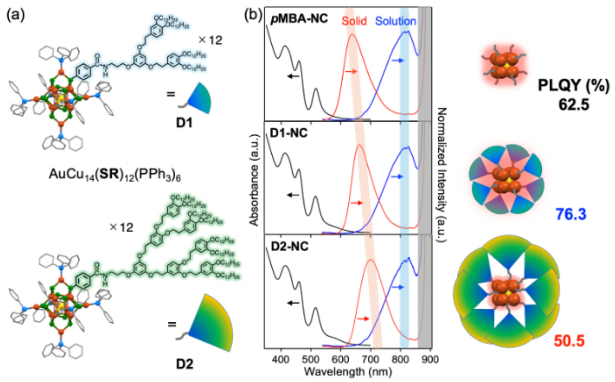
Atomically precise metal nanoclusters exhibit unique optical properties, where intercluster interactions play a crucial role in determining their photophysical behavior in the solid state. Controlling the local packing environment is therefore essential for tuning the emission properties. Ligand-shell engineering offers a promising strategy for modulating the packing and interactions of nanoclusters in the condensed phase. In this study, dendron-functionalized clusters were prepared via post-synthetic modification of a *para* -mercaptobenzoic acid (*p* MBA)-protected AuCu14 nanocluster ([AuCu14(*p* MBA)12(PPh3)6]$^{+}$, ***p* MBA-NC**). Amide coupling between *p* MBA carboxylic acid groups and amine-terminated dendrons (D1-NH2, D2-NH2) yielded two dendronized clusters (**D1-NC** , **D2-NC** ; Figure a) bearing first- and second-generation dendrons (D1 and D2). These systems enable investigation into how dendron generation influences intercluster separation and the photophysical properties of nanocluster solids.

Photoluminescence measurements revealed a significant solid-state blue shift relative to the solution phase, with its magnitude decreasing in the order: ***p* MBA-NC** > **D1-NC** > **D2-NC** (Figure b). This trend suggests that closer intercluster proximity in the solid state induces structural constraints that suppress excited-state relaxation, thereby elevating the emission energy. Bulky dendron layers function as effective spacers to modulate the local packing environment. By increasing intercluster separation and alleviating these constraints, the dendrons allow the clusters to exhibit solid-state photophysical behavior more consistent with their intrinsic, solution-like properties. Interestingly, the solid-state photoluminescence quantum yield (PLQY) showed a different trend. The **D1-NC** exhibited the highest PLQY (76.3%), exceeding both the ***p* MBA-NC** (62.5%) and the bulkier **D2-NC** (50.5%) (Figure b). This result suggests that emission efficiency is governed not only by intercluster separation but also by the dynamic characteristics of the surrounding ligand shell. The D1 dendron presumably restricts ligand-shell motions and suppresses nonradiative pathways, whereas the larger, more flexible D2 dendrons introduce conformational freedom and facilitate vibrational energy dissipation, thereby promoting non-radiative decay as a more significant pathway for excited-state relaxation.

These findings demonstrate that generation-dependent dendronization enables simultaneous modulation of intercluster separation and ligand-shell dynamics, providing a systematic strategy for controlling the solid-state photophysical properties of ligand-protected metal nanoclusters, addressing a common challenge in the design of functional hybrid nanomaterials.

Keywords:
Ligand-protected metal nanoclusters, Dendronized ligand shell, Intercluster interactions, Ligand-shell dynamics, Solid-state photoluminescence



(a) Schematic illustrations of dendron-functionalized AuCu14 nanoclusters (top: D1-NC, bottom: D2-NC). (b) UV-vis absorption (black) and PL spectra in the solid state (red) and solution phase (blue) for AuCu14 nanoclusters.

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