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seminar

Wednesday, 12th January, 9.30am, Online

Host: Prof. Luis M. Liz-Marzán

Magic from Magic-Sized Clusters: Reversible Isomerization and Centimeter-Length Hierarchical Self-Organization

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Because magic-sized clusters (MSCs) are smaller than nanoparticles, they can provide insight into molecular-level processes and assume novel properties. In this talk I will highlight two recent MSC discoveries from my group. The first is on inorganic isomerizations. Structural transformations are ubiquitous at all length scales, spanning from isomerization reactions of small molecules to solid-solid transformations in bulk crystals. Despite attempts to merge understanding of these disparate regimes by reducing domain size, bulk-like solid-solid transformation behavior still predominates at nanocrystal (>2 nm) length scales. Here we show that MSCs, which are smaller than nanocrystals, can possess essential characteristics of both solid-solid transformations and molecular isomerization reactions. These MSC isomers interconvert reversibly, with a 140 meV shift in their excitonic energy gap. The diffusionless reconfiguration of the inorganic core is evidenced by our reconstruction of the atomic pair distribution function (PDF) from total x-ray scattering. The first order kinetics of the transformation are driven by a distortion of the ligand binding motifs. This reversible transformation of MSCs presents the missing bridge between molecular isomerization and solid-solid transformations.

The MSCs small size and high ligand/core ratio, gives them “softer” inter-particle interactions, with access to a richer phase diagram beyond the classical close packed structures (fcc, bcc) seen with larger particles. We have recently found remarkable hierarchical assembly behavior of these MSC nanomaterials. These 1.5 nm CdS MSCs can self-assemble into highly aligned structures, which span over six orders of magnitude in length scale. The MSCs assemble into filaments with hexagonal interparticle geometry, which bundle into larger fibers, and into centimeter-length superstructures of highly ordered thin films patterns. The thin films have long-range periodicity and interesting optical properties that emanate from the MSC core and/or the organic interconnections, such as light diffraction and dichroism. The multiscale self-organization behavior of these MSC patterned films displays similarities to biosystems, providing a new platform for the design and study of advanced materials.