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Self-assembly of gold nanoparticles through tandem hydrogen bonding and polyoligosilsequioxane (POSS)–POSS recognition processes

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Diaminopyridine-functionalized polyhedral oligomeric silsequioxanes (POSS-DAP) self-assemble with complementary thymine-functionalized Au nanoparticles (Thy-Au) into well-defined spherical aggregates, providing highly structured nanocomposites.

Fabrication of nanocomposite materials with controlled structure is a key component in the development of new technologies.[1] Self-assembly through non-covalent interactions (*e.g.* hydrogen bonding, acid/base proton transfer, and specific electrostatic forces) is an effective technique that has previously been proven successful in forming different nanoparticle assembly motifs.[2] Application of this methodology to mixed monolayer protected clusters (MMPCs)[3,4] extends the utility of this method, providing access to materials possessing unique optical,[5] electronic,[6] and magnetic[7] properties.

Ease of functional group manipulation as well as recent advances using both noble metal and other core materials such as iron oxide, cadmium selenide, cobalt, make MMPCs important building blocks for functional materials and composites. Polyoligosilsequioxane (POSS) units are another nanoscopic building block (~1.5 nm diameter) that has found multiple applications as polymer modifiers and in hybrid organic–inorganic nanocomposites, imparting thermal stability as well as resistance to oxidation and other chemical degradation pathways.[8] Covalently bound silsequioxane modified gold clusters have shown interesting physical, chemical, and electronic behaviour, but produced amorphous structures.[9]

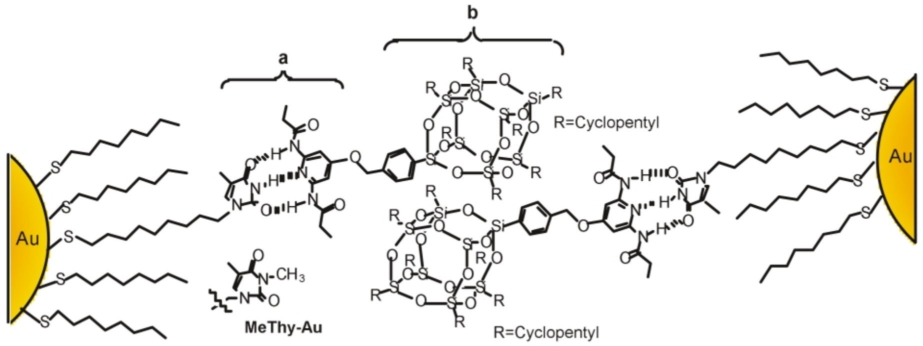
An intriguing aspect of POSS derivatives is their strong tendency to crystallize into two-dimensional structures, making them potential 'recognition elements' for supramolecular assembly processes. For example, Coughlin *et al.* have shown that POSS units attached as pendant side-chains on polyethylene copolymers aggregate and crystallize as nanocrystals.[10] To apply this methodology to the assembly of nanoparticles, we have developed a two-stage assembly strategy coupling hydrogen bond-mediated MMPC–POSS interactions with POSS–POSS self-assembly. In this communication, we report the formation of well-defined spherical aggregates (~250 nm–1.5 μm) with uniform internal spacing using diaminopyridine-functionalized POSS nanoparticles (**POSS-DAP**[11])† and thymine functionalized Au MMPCs (**Thy-Au**).

The **Thy-Au**[12] nanoparticles used in this study were made through place displacement[4] of a thymine functionalized thiol into octanethiol-protected gold nanoparticle prepared by Brust-Schiffrin[3] methodology to provide a monolayer with ~10% thymine coverage. To provide a control system that cannot participate in hydrogen bonding, **MeThy-Au** control was prepared in analogous fashion (Scheme 1).

Transmission electron microscopy (TEM) was used to characterize the POSS–MMPC aggregates. Solutions of **POSS-DAP** (10 mg ml^{-1} in $CHCl_3$) and MMPCs **Thy-Au** and **MeThy-Au** (2 mg ml^{-1} in $CHCl_3$) were dropcast onto 300 mesh Cu TEM grids. Microscopy of the resultant **POSS-DAP**/**Thy-Au** grids revealed the presence of large, discrete, well-defined spherical aggregates (Fig. 1b–c), whereas **MeThy-Au**/**POSS-DAP** images showed complete lack of aggregation (Fig. 1a). This difference in behavior demonstrates that the aggregation observed upon addition of **POSS-DAP** with **Thy-Au** is the result of specific three-point hydrogen bonding between the thymine and diaminopyridine recognition units.

To determine the assembly motif produced using POSS–POSS interactions, small angle X-ray scattering (SAXS) studies were performed on the **POSS-DAP–Thy-Au** aggregates (Fig. 2). SAXS studies reveal two distinct features within these large aggregates. The peak at 0.402 q, provides an average Au diameter of 15.6 Å (1.56 nm), consistent with expected particle size. The peak at 0.175 q, corresponds to an average **Au-POSS**/**POSS-Au**, center-to-center distance range of 3.65 ± 0.08 nm, corresponding to an interparticle distance of 2.09 ± 0.08 nm. The 2.1 nm surface to surface distance indicates that side to side POSS–POSS packing interactions are occurring (Scheme 1), rather than a face-to-face which would clearly lead to a substantially larger particle–particle spacing (~4.5 nm). The relatively tight range of the interparticle spacing indicates that the POSS nanoparticles (~1.5 nm) are packing uniformly around each other in a nanocrystalline fashion, templating the Au nanoparticles into a well-spaced structure (Fig. 3).

In summary, we have developed a two-stage self-assembly process in which recognition element functionalized **POSS-**



Scheme 1 (a) POSS nanoparticles showing three point hydrogen bonding recognition, **Thy-Au** and diaminopyridine. **MeThy-Au** shown to illustrate disruption of hydrogen bonding interaction by methyl group. (b) Crystalline packing of the non-polar **POSS-DAP** encapsulated **Thy-Au** MMPCs to form larger aggregates with equal spacing between Au nanoparticles.

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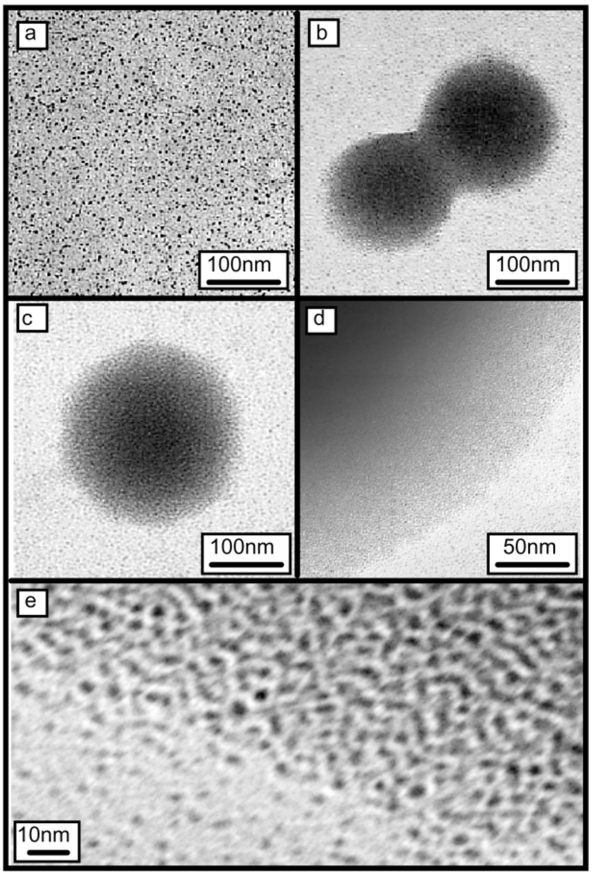

Fig. 1 (a) **MeThy-Au** control with **POSS-DAP** showing no aggregation. (b–c) Different spherical morphologies formed by assembly of **POSS-DAP** with **Thy-Au**. Closer TEM examination of the **POSS-DAP**/**Thy-Au** aggregates gives an overall size distribution, while images of the aggregate's corona reveals evidence of defined spacing around the **Thy-Au** MMPCs (d–e).

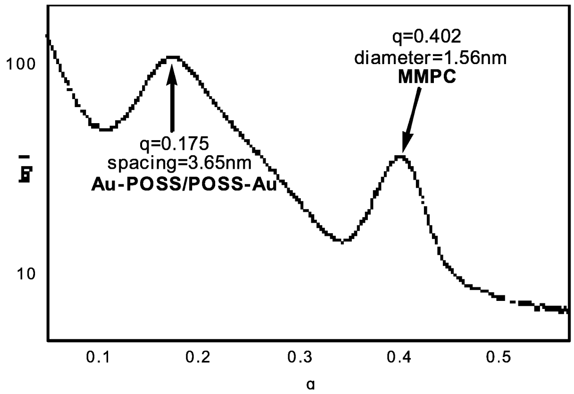

Fig. 2 Small-angle X-ray scattering (SAXS)[13] plot of **POSS-DAP**/**Thy-Au** aggregates.

DAP units self-assemble with complementary **Thy-Au** nanoparticles into structured and discrete aggregates. Initial three-point hydrogen bonding of **POSS-DAP** with complementary **Thy-Au** MMPCs followed by subsequent aggregation and crystallization of the POSS moieties produces well-defined, spherical, hybrid aggregates of varying sizes featuring uniform interparticle spacings. Further characterization of the **POSS-DAP**/**Thy-Au** aggregates, as well as possible applications for these aggregates is currently being investigated.

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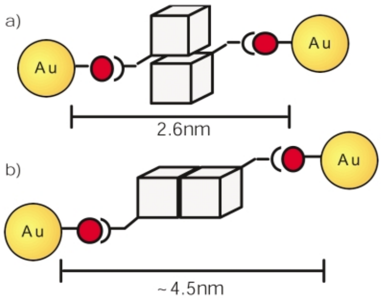

Fig. 3 (a) Schematic illustration showing POSS–POSS, side-to-side packing interactions are preferred to (b) POSS–POSS, face-to-face packing interactions.

Notes and references

† For **POSS-DAP**: δ_H ($CDCl_3$, 200 MHz): 7.80–7.55 (m, 4H), 7.50–7.3 (m, 4H), 2.00–1.3 (m,46H), 1.18 (t, 6H), 0.94 (brq, 6H). MALDI MS: $(M + H)^+$ 1226. FT–IR (neat): 2949, 2864, 2360, 1697, 1584, 1438, 1111, 668 cm^{-1}. Mp > 350 °C.

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