Selective co-aggregation of gold nanoparticles functionalised with complementary hydrogen-bonding groups†

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Molecular recognition between two species of Au_{55} clusters bearing complementary hydrogen-bonding groups provides a facile route to accomplish solution-based assembly of two-component nanoparticle aggregates.

An important challenge in the development of nanotechnology is the preparation of nanoparticle assemblies in which two different types of nanoparticles are intimately mixed.[1] Such assemblies can combine the properties of their components[2] and offer the possibility of new collective properties.[3]

The formation of intimately mixed two-component nanoparticle aggregates requires a means to prevent phase separation (*i.e.* self-association of particles of one type). This may be achieved by promoting specific interactions between the different component particles. Many approaches to nanoparticle assembly are non-specific in nature and for instance make use of Van der Waals interactions,[4] or exploit (symmetric) covalently binding linker molecules.[5] Selective interactions may be obtained by the use of nanoparticles of different diameter,[6] or of opposite charge.[7] A more versatile method is based on selective hydrogen bonding. The strength of this interaction can be selected from a wide range, due to the availability of various complementarily hydrogen-bonding functionalities (with association constants spanning several orders of magnitude),[8] and can be modified by the solvent.[9] Multiple hydrogen bonding forms an important tool in the field of molecular recognition.[10]

Biologically inspired ligands with complementary functionalities (DNA strands, receptor–ligand combinations) have been applied to control nanoparticle interaction.[11] However, the use of selective binding based on (much) smaller synthetic moieties is expected to be more practical in systems chiefly aimed at combining the nanoparticle properties. Thymine and diaminotriazine motifs, for instance, have been used previously to promote particle-polymer interactions[12,13] and interactions between Ag and Au particles.[14] We recently described a very simple pair of synthetic ligands, 1-(8-mercaptooctyl)thymine (***MOT***, **1**) and 8-(4,6-diamino[1,3,5]triazin-2-yl)octane-1-thiol (***DTOT***, **2**), as schematically depicted in Fig. 1, and showed that their triply H-bonded functionalities can be used to bind functionalised gold clusters selectively to gold surfaces with the complementary group.[15]

Here we describe the study of three-dimensional aggregation of Au_{55} clusters functionalised with these ligands, and show that the resulting aggregate morphology can be systematically varied by changes in the composition of the medium, which consists of dimethyl sulfoxide (DMSO) and 1,4-dioxane.

Ligand-functionalised clusters $Au_{55}\boldsymbol{MOT}_{20}[P(C_6H_5)_3]_4$ (**3**)[15] and $Au_{55}\boldsymbol{DTOT}_{15}[P(C_6H_5)_3]_8Cl_4$ (**4**) were prepared from $Au_{55}[P(C_6H_5)_3]_{12}Cl_6$ clusters[16] by ligand exchange with the respective thiolates in dilute (0.25 mg cluster ml^{-1}) CH_2Cl_2–benzene mixtures,[17] thus ensuring retention of the cluster integrity. The clusters were characterised by TEM, XPS, TGA and DSC (ESI†).[15]

Selective co-aggregation experiments were performed by mixing equal amounts of stock solutions of **3** and **4** in DMSO (6.0 mg ml^{-1}) and subsequent dilution with varying amounts of DMSO and 1,4-dioxane. Thus, a series of mixtures was prepared, all with the same particle concentrations (0.06 mg ml^{-1} of each cluster compound) but with a DMSO content varying from 2 to 20% (v/v) in 1,4-dioxane. Under these conditions, *homo*-aggregation does not take place (for **3**) or to a very limited extent (for **4** at the lowest DMSO concentration, *vide infra*). Upon standing at ambient temperature for 13 h, brown flocky deposits had formed in all samples, except the one with the highest DMSO concentration.

TEM micrographs of the aggregates formed from the 10% DMSO mixture (deposited on an amorphous carbon support film) are shown in Fig. 2. The aggregate structure consists of entangled, interconnected strands of remarkably uniform diameter that contain the individual clusters. In Fig. 3(a), micrographs at the same magnification are shown for the various aggregates formed in solvent mixtures with 2–18% (v/v) of DMSO. While the overall morphology stays the same, the average strand diameter increases gradually from 20 ± 6 nm at 2% DMSO to 93 ± 18 nm at 18% DMSO. This is shown in Fig. 3(b).

As control experiments, samples were prepared with only **3** or **4** (with the same *overall* cluster concentration as for the mixed samples, *i.e.* 0.12 mg ml^{-1}) and DMSO concentrations of 2, 10 and 20% (v/v) in 1,4-dioxane. None of these samples showed

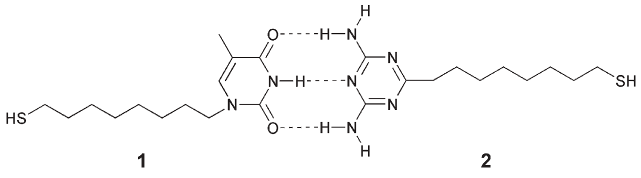

Fig. 1

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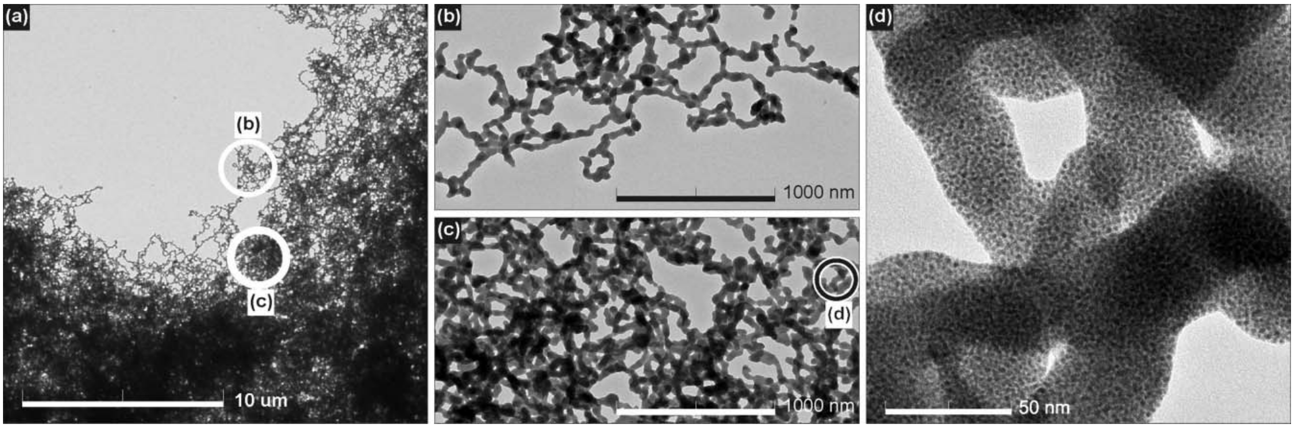

Fig. 2 TEM micrographs at different magnifications of *hetero*-aggregates of **3** and **4** formed by aggregation in 1,4-dioxane containing 10% (v/v) DMSO.

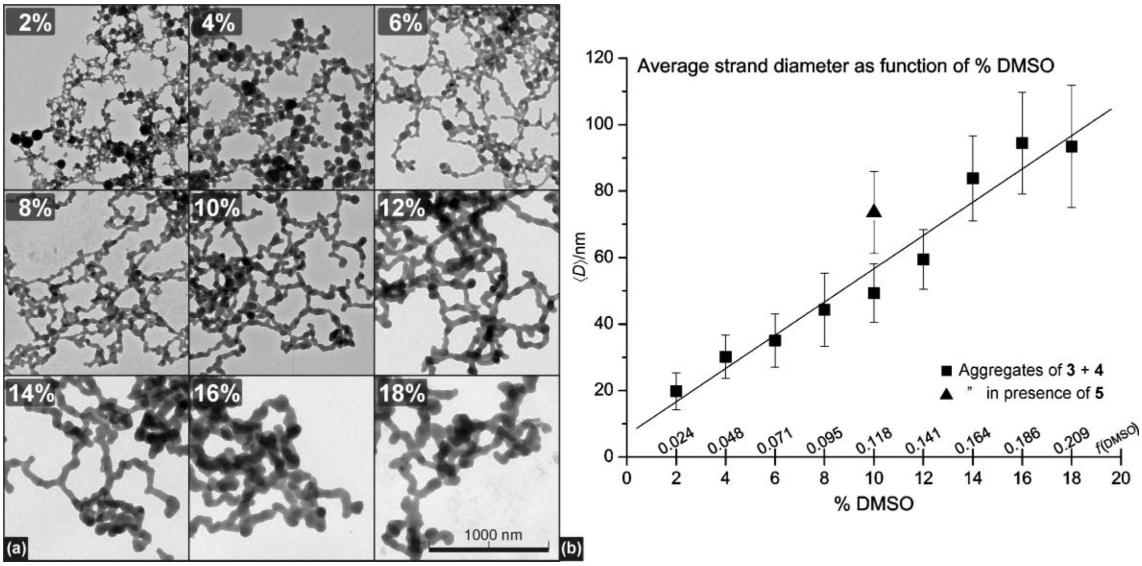

Fig. 3 (a) Details of micrographs of **3**–**4** *hetero*-aggregates, formed in 1,4-dioxane containing the given percentages of DMSO. All micrographs are presented at the same magnification. (b) Aggregate strand diameter as a function of DMSO concentration. Every point is an average of 30 measurements. The error bars represent their standard deviations.

flocculation or sedimentation, except for **4** at the lowest DMSO concentration. TEM analysis on this sample showed some dense spherical aggregates (see ESI†) whereas the other samples showed only isolated clusters. These spherical aggregates of **4** can also be discerned in the TEM micrographs in Fig. 3(a) of the 2 and 4% DMSO mixed cluster samples, but are absent at higher DMSO concentration.

These results indicate that the aggregation of the clusters into the strands observed in the material deposited from the **3**/**4** cluster mixtures is due to complementary hydrogen bonding interaction between the ***MOT***-ligands (**1**) on **3** and the ***DTOT***-ligands (**2**) on **4**.

The variation of the aggregate strand diameter with the DMSO concentration in the medium is likely to be associated with partial screening of the hydrogen bonding of the ligands by DMSO (which is a considerable H-bond acceptor[9]). This is supported by an experiment in which 1-*n*-hexylthymine[18] is added, which can compete with cluster **3** in the binding to cluster **4**. The morphology produced in a medium with 10% (v/v) of DMSO and with 1.2×10^3 equivalents of 1-*n*-hexylthymine present (with respect to the total number of cluster-borne ligands **2**) is again similar to that from the other experiments. However, the average strand diameter of 74 ± 12 nm is considerably larger than that obtained in the same medium without added 1-*n*-hexylthymine (49 ± 9 nm, see Fig. 3(b)). Compared with the previously observed trend in strand diameter *vs.* DMSO content, it suggests that the effect of 1-*n*-hexylthymine on aggregate formation is more than 10 times stronger than that of DMSO on a molar basis. This is another indication that molecular recognition processes are involved in aggregate formation. That aggregation takes place despite the presence of an excess of 1-*n*-hexylthymine, shows that even then the aggregate formation is still thermodynamically favourable. This is probably due to entropic reasons (release of 1-*n*-hexylthymine/DMSO molecules) and multiple interligand bonding between the particles.

A tentative explanation of the observed aggregate morphology is based on the irreversibility of the aggregation process under the investigated conditions. If the *overall* process were reversible, the strand-like features would have developed into larger, more spherical aggregates—that allow a larger number of interparticle bonds—by a process resembling the ripening of colloids. If, on the contrary, the interactions between single clusters were completely irreversible, a much more open, fractal-like aggregate structure would have resulted. Therefore we propose that the aggregation proceeds *via* the—*initially* reversible—formation of nuclei of a critical size (larger than a single cluster), while *eventually* the Au_{55} particles become irreversibly attached due to the increasing possibility of binding with neighbouring particles.

The elongation may be caused by the fact that aggregate surfaces with a stronger curvature have more free 'dangling' ligands to interact with incoming particles than less strongly curved surfaces, where a larger fraction of ligands is involved in intercluster interactions. Thus, capture of free Au_{55}-clusters by such aggregates is likely to be faster at more strongly curved surfaces, leading to strand-like growth. This effect may become stronger due to the flexibility of the alkyl chains of the ligands **1** and **2**, which enables them to bend and hence maximise the number of interparticle bonds.

Such a process is favourable if the free energy gained by the triple H-bonding between **1** and **2** outweighs the energy involved in the bending. The formation of H-bonded **1–2** pairs involves desolvation (*i.e.* partial removal of the solvation shell) of their functional groups, so there actually is a balance between bent-and-bound and free-and-solvated states. This balance is expected to depend on solvent composition, as DMSO is much more efficient than 1,4-dioxane in solvating the 'free' ligands.[9] Thus, at higher DMSO concentrations, a larger total amount of 'dangling' ligands will result. This makes the preference for incoming clusters to bind at the aggregate extremities less strong and allows for the growth of aggregates with a larger diameter. This may account for the trend as observed in Fig. 3.

We intend to study the aggregation process in more detail by methods such as dynamic light scattering (DLS), enabling *in-situ* monitoring, and TEM analysis at various aggregation times to test the hypotheses regarding the nucleation and growth processes and their sensitivity to the medium.

In conclusion, we have presented a simple and potentially versatile method to direct two-component nanoparticle aggregation. Although the present study uses two Au clusters that differ only by the functionalisation of their surfaces, the method should be readily applicable to systems containing two different nanoparticle materials. The unusual strand-like growth observed with this aggregation method may also provide a new route towards the formation of nanoparticle assemblies with high aspect ratio, especially since the strand diameter is readily tuned by modification of the used solvent mixture.

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