Chapter 6

Conclusions and perspectives

The work presented in this thesis is aimed at the development of a method to prepare two-component assemblies of nanoparticles. The key idea in the design of a model system was to manipulate the mutual interactions of the nanoparticle components. Preferably, this should lead to the controlled manufacture of ordered aggregates. Thus, a system was studied consisting of functionalised gold clusters that aggregate in solution due to hydrogen-bonding interactions.

A set of ligands was prepared – MOT and DTOT – that preferentially forms complementary dimers, by the formation of an array of three hydrogen bonds. Threefold H-bonding moieties provide a synthetically accessible way to accomplish selectivity by molecular recognition, but with a relatively weak interaction (compared to fourfold or manyfold binding, like in DNA). The binding strength plays an important role in the reversibility of the process, which is one of the prerequisites in the formation of ordered structures. The ligands (MOT and DTOT) were attached to Au$_{55}$ clusters, yielding Au$_{55}$–M and Au$_{55}$–D, respectively. These clusters are small compared to other nanoparticles. Therefore ligand–ligand interactions are of increased importance in the overall intercluster interaction. Moreover, these clusters are monodisperse. This is a second prerequisite for obtaining macroscopically ordered assemblies of clusters. Nevertheless, it was shown that Au$_{55}$ clusters are relatively labile in solution, compared with larger gold nanoparticles. Retention of their structural integrity during all experiments demands working at low concentrations and limits the useful shelf life of cluster (stock) solutions to a few days.

It was shown that these clusters can form both homo- and hetero-aggregates. The aggregation process could be adjusted to selectively lead to the formation of hetero-aggregates by the choice of aggregation medium. This was achieved by using mixtures of solvents, providing a balance between cluster solvation and effectively attractive intercluster interactions.

It was proved that complementary MOT–DTOT interactions are necessary to immobilise the clusters on two-dimensional self-assembled monolayers that contain
MOT or DTOT. This strongly suggests that complementarity is also decisive in the formation of 3D aggregates (of Au$_{55}$–M and Au$_{55}$–D) in media of similar composition. Moreover, the adsorption experiments indicate that the *cooperative* formation of multiple MOT–DTOT pairs is required to immobilise a single cluster. Therefore, it is likely that cooperativity also plays a role in the solution-based formation of 3D aggregates. This provides an explanation why the aggregation process is irreversible under the investigated conditions, despite the fact that single MOT–DTOT pairing is reversible. This irreversibility impedes the formation of ordered aggregates. Here, it should be noted that the much weaker (and non-selective) MOT–MOT interaction did lead to ordering of Au$_{55}$–M clusters.

As a result of irreversibility, the morphology of hetero-aggregates is determined by a combination of kinetic and thermodynamic factors that favours the formation of elongated strand-like aggregates. This morphology – and the way it varies with varying medium composition – was explained by the Bending Ligand Model (BLM). This model states that the flexibility of the ligands facilitates the formation of multiple MOT–DTOT pairs between two clusters. Thus, surfaces with higher curvature (i.e. protrusions) will have more ‘dangling’ ligands and therefore are more likely to capture unbound clusters. In this way, the observed morphology is directly related to the design of the ligands, that combines flexible alkyl chains and multiply hydrogen-bonding headgroups. Hence, this may provide a more general principle for the formation of aggregates with a strongly anisotropic (pseudo-1D) morphology.

The method that is presented here may be developed further in two directions. One can pursue either the formation of *ordered* assemblies or exploit the *anisotropy* of the aggregation mechanism. These two directions impose different demands on system design (*vide infra*). Increasing the applicability of the Au$_{55}$ system itself mainly requires improvement of the thermal and chemical stability of the ligand-protected Au$_{55}$ clusters. The latter may be achieved by incorporating e.g. H-bonding groups in or along the alkyl-spacers of the ligands, since intra-layer H-bonding makes the ligand shells more rigid [1, 2].

Improved control over the aggregation process is necessary for any further development of the technique. This will be facilitated by a more quantitative description of the process described here, by further systematic variation of the parameters that were discussed in the preceding chapters (cluster concentration, DMSO/dioxane ratio, functional group density of the SAMs).

The formation of ordered assemblies, requires that the growth process is more (pseudo-) reversible, whereas the growth of anisotropic structures depends on its irreversibility. Modifying the strength of the effective interparticle interaction will lead to a shift in either direction. Such modifications may be accomplished in the following ways:

1. The effective interaction can be influenced by the temperature or by temperature variations since H-bonding equilibria are temperature sensitive [3].
2. Media composed of different combinations of solvents that have H-bonding
properties similar to DMSO/dioxane may yield different aggregate morphologies. This will allow quantification of the relationship between morphology and solvent parameters. (Pseudo-) reversibility may also be reached by changes in the solvent mixing during the destabilisation of cluster solutions.

3. (Slight) changes to the ligand headgroups (e.g. the number of hydrogen bonds or their strength by substituent effects) can be used to increase or decrease the strength of the complementary interaction [4], without loss of selectivity. Such changes can also lead to a greater similarity in solubility properties of the complementary particles. This will facilitate the variation of other parameters, since it will reduce the undesired formation of homo-aggregates.

4. The number of functional groups per cluster may be varied to tune their overall H-bonding capability. The most straightforward way to achieve this is the use of a mixed ligand shell. However, this will also lead to an intrinsic spread in cluster shell composition.

The BLM suggests that increasing the rigidity of the ligand shell facilitates the formation of ordered structures, since it would make the cluster-interactions more isotropic. On the other hand, increasing the ligand flexibility (possibly in combination with stronger hydrogen bonding) may yield more or different anisotropy in the aggregate morphology. Hence, validation of the BLM and exploitation of its consequences may be accomplished by variation of the length and stiffness of the ligand spacers.

Finally, the aggregation method based on molecular recognition with our model system, may be applied to control the assembly of nanoparticles of different composition. Such nanoparticles may be chosen for their (intrinsic) physical properties or expected collective properties. Notably, it should be possible to prepare composites of particles of different core composition. ligand-protected nanoparticles have been made from many different (transition) metals or semiconductor materials [5]. The main limitation of the application of a complementary ligand system is that ligand exchange between particles should not occur on the time-scale of the aggregation process. Therefore, it depends on the availability of sufficiently strongly binding ligands. Alternatively – when different core materials are used – exchange may be prevented by the application of ligands with different particle-bonding substituents that have a high binding affinity for only one of the materials. Another limitation will be formed by the size of the nanoparticles. Above a certain size, interparticle Van der Waals interactions will dominate the hydrogen-bonding interactions and specificity will be lost.

The possibility to immobilise clusters on a functionalised surface also allows for several further developments. For instance, patterned two-dimensional assemblies of clusters may be brought about using patterned self-assembled monolayers. The latter can be manufactured with micro-contact printing [6]. Multi-layered two-dimensional assemblies, consisting of alternating monolayers of complementarily functionalised particles may also be attainable, yet this requires the formation of compact monolayers of a single cluster component on a SAM, by complementary interactions.
References


