Self-Assembly

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Supramolecular Organic–Inorganic Hybrid Assemblies with Tunable Particle Size: Interplay of Three Noncovalent Interactions**

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Supramolecular structures involving inorganic nanoparticles are currently of great interest in areas ranging from sensing to cancer therapy and energy conversion.[1] Self-assembly allows the design of complex structures in a facile manner,[2] while inorganic metal and semiconductor nanoclusters possess unique optic, magnetic, and electric properties. Therefore, high potential lies in structures that combine both features. Different approaches for the noncovalent connection of inorganic nanoclusters in solution exist.[3] An established method is the supramolecular association through DNA base pairing.[4] Nanoparticles have also been connected by hydrogen bonds or ionic interaction with other polymers.[5] Aggregation with oppositely charged colloids yields so-called "super crystals".[6] The shape of the resulting aggregates can be controlled when using amphiphilic building blocks that form micelles and vesicles.[7] From a functional perspective, examples with high potential are semiconductor quantum dots combined with dyes or conjugated polymers.[8] However, controlling the assembly size in solution is a challenge.[9] Kinetic control and a step-growth "polymerization" process have been discussed.[10] Yet possibilities are limited and it is desirable to develop further concepts for the formation of nanoscale hybrid assemblies. Of particular interest are approaches that rely on a combination of general interaction forces rather than the synthesis of specific binding motifs.

Recently, we have shown that "electrostatic self-assembly" of organic macroions and multivalent organic counterions leads to well-defined supramolecular assemblies of various sizes and shapes in aqueous solution.[11] The concept is based on the combination of ionic and π–π interactions and thus can be applied to a wide variety of chemically and structurally different building blocks. This has also led to light-switchable, host-triggerable, and catalytically active assemblies,[12] although in all cases with organic molecules as building blocks.

Herein, we present the formation of a new type of organic–inorganic hybrid particles through self-assembly driven by the interplay of ionic, π–π, and Hamaker interactions: well-defined gold–dendrimer–dye and cadmium sulfide–dendrimer–dye assemblies of up to several hundred nanometers in size can form in aqueous solution. The supramolecular reaction path is shown in Scheme 1: First, gold colloids are formed in generation 8 (G8) poly(amidoamine) (PAMAM) dendrimers through the established procedure of electrostatic nanotemplating.[13] Subsequently, and for the first time, the gold-containing dendrimers, which are again positively charged, are interconnected by ionic dye molecules where ionic interaction, mutual π–π interaction of dye molecules, and Hamaker interactions between gold colloids play a role.

In the first step, gold-containing G8 dendrimer is prepared: the cationic dendrimer is loaded 1:1 with $AuCl_4^-$-ions, that is, theoretically 1024 gold ions per dendrimer; chemical reduction results in 3 nm-size gold nanoparticles inside an 11 nm-sized G8 dendrimer.[13c,14] These hybrid particles are then mixed with the ionic dye Ar26 at pH 11 and the solution is then set to pH 7, so that the primary amine groups of the dendrimer become protonated again: The Au-G8 dendrimer carries 1024 positive charges and the anionic Ar26 is divalent. Substantial interconnection into larger assemblies occurs for charge ratios (molar ratio of dye sulfonate to protonated dendrimer amine groups) $l \geq 0.3$, as can be seen from the static light scattering intensity (see the Supporting Information). Figure 1 shows transmission electron microscopy (TEM) images of the resulting structures: Gold-containing dendrimers have become interconnected into large assemblies with diameters of about 120 nm. In the inset the crystalline structure of the 3 nm gold nanoparticles in the dendrimer is visible. Dynamic light scattering allows measurement of the size distribution of these assemblies directly in solution (Figure 2). Results for a charge ratio of $l = 0.38$ as shown in Figure 2a reveal narrow monomodal distributions

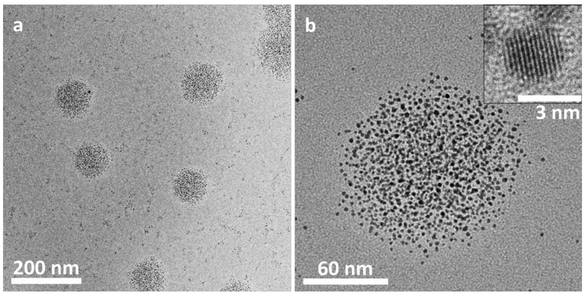

Figure 1. Transmission electron microscopy at different scales of supramolecular gold–dendrimer–dye assemblies (l (Ar26/G8) = 0.35).

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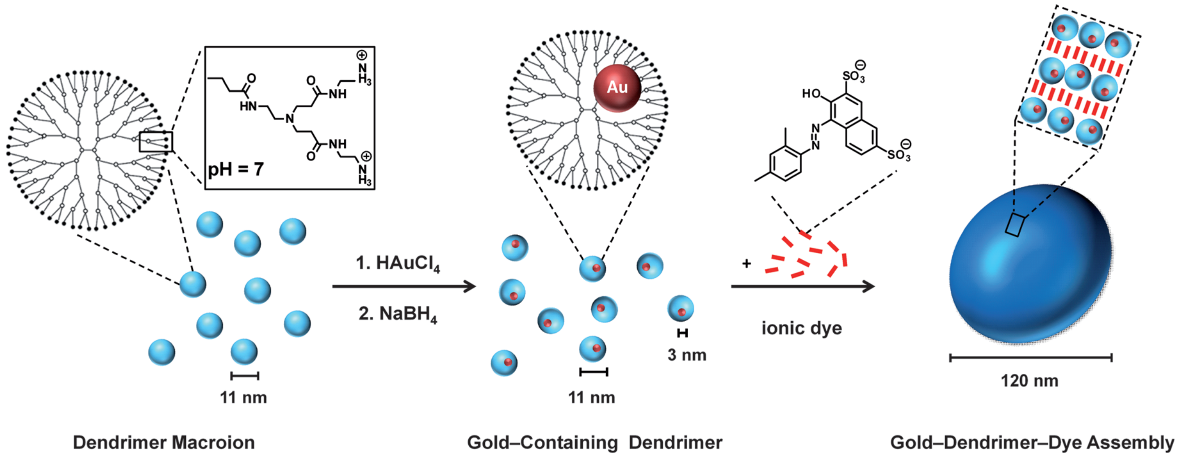

Scheme 1. Representation of the supramolecular structure formation investigated in this study.

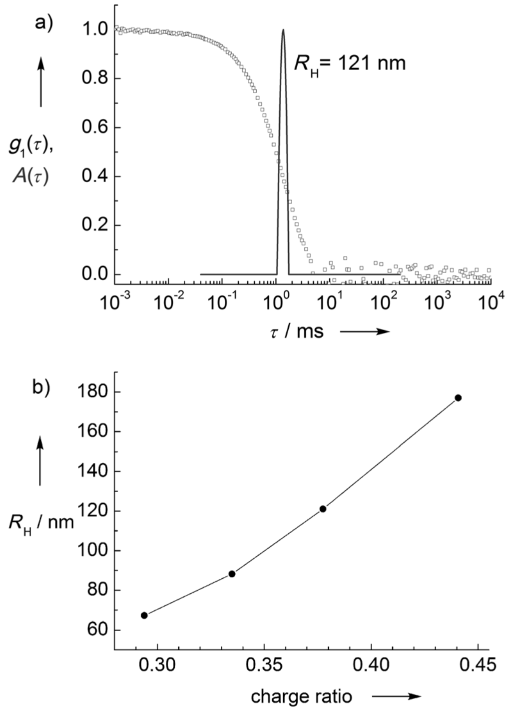

Figure 2. a) Dynamic light scattering on gold–dendrimer–dye assemblies: electric field autocorrelation function $g_1(\tau)$ and distribution of relaxation times $A(\tau)$ at a scattering angle of $\theta = 90°$, l (Ar26/G8) $= 0.38$; b) dependence of hydrodynamic radius R_H on Ar26/G8 charge ratio.

(width of the relaxation time distribution: $\sigma = 0.11$). Therefore, hybrid assemblies of very well-defined size form. These are stable in aqueous solution with a constant size and they also remain stable when varying the temperature between 5 °C and 60 °C. The average aspect ratio as measured from TEM is 1.2; that is, particles are slightly ellipsoidal, which is in agreement with the light scattering results.[15] Through choice of the dye/hybrid particle loading ratio, the size of the assemblies can further be tuned between hydrodynamic radii of $R_H = 65$ nm and $R_H = 180$ nm (Figure 2b). For smaller loading ratios, no significant (light scattering detectable) assembly formation occurs while precipitation is observed for loading ratios $l \geq 0.45$. (For factors controlling the size in the tunable stable range, see below). The hybrid particles of varying size in solution are stable for at least some months.

As compared to purely organic dendrimer–dye assemblies,[16] the assembly size differs significantly: $R_H = 48$ nm is found for the dendrimer–dye assembly but $R_H = 121$ nm for the gold–dendrimer–dye assembly. This means that different or additional effects play a role in the assembly size control in the ternary system. The behavior can only be caused by the gold particles. Gold colloids can mutually attract each other through Hamaker interaction (“van-der-Waals interaction on the colloidal scale”). This is a short-range force that in a diluted system can only come into play once particles are brought near to each other through other forces. Thus, it does not play a role in the initial solution at high pH, where the dendrimer is uncharged and no association occurs. When the dendrimer becomes charged through acid addition, oppositely charged dye counterions bind to the polyelectrolyte dendrimer in a cooperative manner (as for the neat dendrimer–dye system[16]) so that they can undergo ionic interaction with the macroion and π–π interaction with each other and interconnect dendrimers owing to their multivalency.[16,17] This brings the dendrimers in close proximity and the gold colloids into a distance of a few nanometers where the Hamaker attraction becomes effective. (Based on the architecture of the gold–dendrimer hybrid particle,[13c] a distance of 1–6 nm is expected.) The different attractive interactions (ionic, π–π, and Hamaker) and repulsive interactions (repulsion of like charges, geometric effects) equilibrate at a certain assembly size and aggregation number. This is why defined hybrid assemblies arise. The formation of “monodisperse” equilibrium assemblies is in analogy to the dendrimer–dye system,[11c,12a–b] but on the attractive side, more free energy contributes than in the pure dendrimer–dye system so that larger assemblies result. The charged nature of the assemblies, as can be detected by ζ-potential measurements, is what stabilizes the assemblies in solution.

Furthermore, it is of major interest whether the concept can also be applied to a wider range of chemical systems. Therefore, we chose an example of semiconductor nanoparticles (specifically, cadmium sulfide particles) to be produced with dendrimer templates prior to the supramolecular structure formation. Importantly, this is a different type of electrostatic nanotemplating, as the chemical reaction that creates the particles here is a “precipitation” rather than a reduction reaction. Here we show the example of a G8 dendrimer containing CdS nanoparticles with a size of predominately 1.4 nm (plus larger sizes up to 3.1 nm particles; for CdS size characterization, see the Supporting Information). The CdS-containing dendrimer is then again combined with the divalent anionic dye molecules. Figure 3 shows TEM images of the CdS–dendrimer particles before and after interconnection with the dye. While the TEM contrast of the nanoparticles within the organic matrix is lower for the CdS than for the gold, it can again be seen that supramolecular interconnected assemblies form. Of course, drying effects may play a role in TEM sample preparation. Dynamic light scattering results of the solution show again a very narrow size distribution ($R_H = 129$ nm, $\sigma = 0.12$; Figure 4). Interestingly, to build CdS containing assemblies in solution of a comparable size as the Au-containing assemblies discussed above requires a larger loading ratio (l (Ar26/G8) = 0.74). For assemblies with CdS with l (Ar26/G8) = 0.36, an $R_H = 59$ nm ($\sigma = 0.10$) results. This is most likely due to the stronger attractive Hamaker interaction in the gold case. The latter is also confirmed by further densification of the Au–dendrimer–dye assemblies upon drying in TEM sample preparation as compared to larger and looser structures seen for the CdS sample.

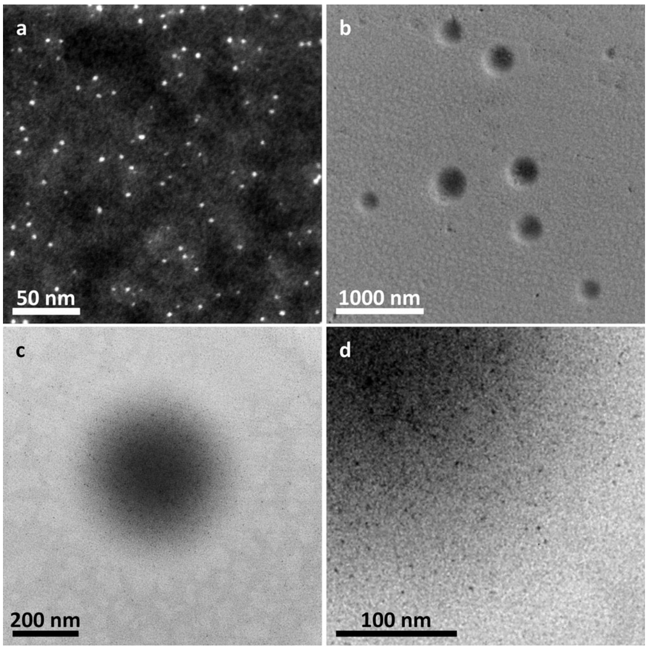

Figure 3. Transmission electron microscopy of a) CdS nanoparticles in dendrimer templates (STEM mode, mean CdS diameter 2.6 nm) and b),c) supramolecular CdS–dendrimer–dye assemblies; d) enlargement of (c) with CdS particles visible in the outer part of the aggregate (l (Ar26/G8) = 0.74, c(G8) = 2×10^{-7} mol L^{-1}).

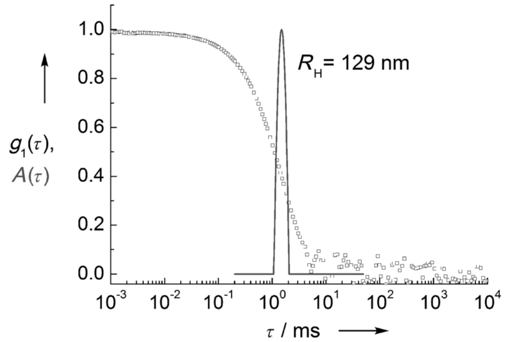

Figure 4. Dynamic light scattering on CdS–dendrimer–dye assemblies: electric field autocorrelation function $g_1(\tau)$ and distribution of relaxation times $A(\tau)$ at a scattering angle of $\theta = 90°$ (l (Ar26/G8) = 0.74, c(G8) = 2×10^{-7} mol L^{-1}).

Figure 5 shows photographs before and after supramolecular structure formation through dye addition. Clearly, the fluorescence of the CdS quantum dots becomes quenched. Thus, the dye and the quantum dot “talk to each other”, despite the presence of the dendrimer.[18] This is important, as it is the key for producing a wide variety of potentially functional nanoparticle–dye systems in which the macromolecular component provides connectivity, structural control, and stability. As the concept is based on the delicate interplay of general noncovalent interactions rather than the specific design of certain binding motifs, it can be widely exploited using various building block chemistries and architectures. Resulting hybrid structures may for example be of interest for solar energy conversion or for nanoscale devices in optoelectronics.

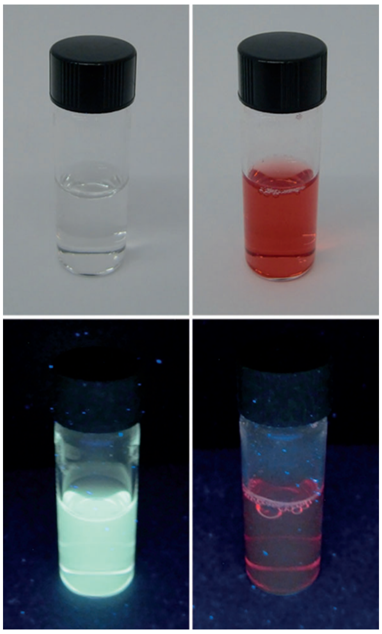

Figure 5. Photographs of a CdS–dendrimer solution (left) and a CdS–dendrimer–dye assembly solution (right), both in daylight (top) and upon UV irradiation (bottom); l (Ar26/G8) = 0.1.

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[14] This has been shown in analogy to previous studies by TEM, SAXS and SANS.[13c]

[15] The ratio of the radius of gyration from static light scattering and the hydrodynamic radius from dynamic light scattering is $R_G/R_H = 1.1$, which thus indicates slightly elongated particles.

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[17] The π–π interaction between the initially molecularly dissolved dye molecules that is induced upon binding to the polyelectrolyte is evident from UV/Vis absorption spectra; see the Supporting Information and Ref. [16].

[18] The quenching is not due to a re-absorption of the emission of CdS nanocrystals of a different size in close proximity, as is evident from the remaining fluorescence of a dried neat CdS–dendrimer sample (film) in which nanocrystals are even closer.