

# Facile Route to Supramolecular Structures: Self-Assembly of Dendrimers and Naphthalene Dicarboxylic Acids

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Inspired by natural materials with excellent properties, the synthetic design of nanoscale structures has become highly interesting. The easiest way to create such structures is by self-assembly, that is, by the association of building blocks in solution.<sup>[1]</sup> While the self-assembly of amphiphilic molecules is a classical field, the formation of supramolecular structures by ionic interaction has been much less investigated. Self-assembly with ionic surfactants can yield well-organized solid materials in the case of both polyelectrolyte–surfactant complexes<sup>[2]</sup> and dye–surfactant complexes,<sup>[3]</sup> and a variety of applications from coatings to optical devices have been considered. Examples that produce solid state structures by using ionic building blocks other than classical surfactants also exist.<sup>[4]</sup> However, only a few studies deal with the corresponding polyelectrolyte–surfactant supramolecular structures in solution.<sup>[5]</sup> The combination of two polyelectrolytes has been intensively investigated and is usually kinetically driven as a result of the high number of charges on both components.<sup>[6]</sup> It is desirable to use ionic building units that assemble into defined equilibrium supramolecular structures in solution. Extending the classical self-assembly of amphiphiles to multivalent organic ions may open a versatile field of supramolecular structures and functionalities.

In this study, we used the electrostatic self-assembly of macroions and organic counterions to form supramolecular architectures. We have chosen a simple model system. Poly-(amidoamine) dendrimers, which are well defined and characterized,<sup>[7]</sup> serve as the macroions and 1,4- or 2,3-naphthalene dicarboxylic acid (NDC) as the divalent counterions. In methanolic solution, the carboxylic acid can directly protonate the dendrimer and can potentially connect multiple dendrimers.

Figure 1 shows samples of the fifth generation (G5) dendrimer combined with the two different counterions at different counterion/dendrimer ratios. Herein we denote the

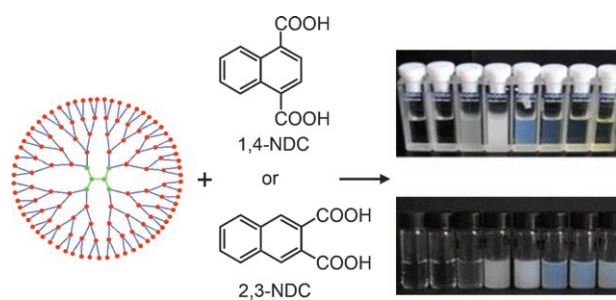


Figure 1. Electrostatic self-assembly: schematic representation of a poly-(amidoamine) dendrimer, formulas of the counterions, and photographs of the resulting samples. Top: 1,4-NDC:G5, bottom: 2,3-NDC:G5, with increasing amounts of NDC (1:8 to 4:1) from left to right.

molar ratio of carboxylic acid groups to dendrimer primary amine groups as the “loading ratio”. It is already evident from the opalescence of some of the samples that larger aggregates had formed. 1,4-NDC and 2,3-NDC show a different dependence on loading ratio, as can be seen in Figure 1. Up to a loading ratio of 1:4, all solutions were clear. Above a ratio of 1:4, the counterion structure and dendrimer generation determined whether clear solutions, opalescence, or precipitation were observed. Dynamic light scattering gave initial information on the structures.<sup>[8]</sup> In particular, for the mid-generation dendrimers (G4–G6), stable aggregates with monomodal size distribution can be formed. The sizes range from several 10s of nanometers to 100 nm. Thus, multiple G5 dendrimer molecules with a diameter of about 5.4 nm become connected by the counterions.

Figure 2 shows sedimentation coefficient distributions obtained by analytical ultracentrifugation for three samples that contained G5 dendrimer; it can be seen that the distribution width varies. 1,4-NDC:G5 = 2:1 and 2,3-NDC:G5 = 2:1 are narrowly distributed whereas 2,3-NDC:G5 = 1:1

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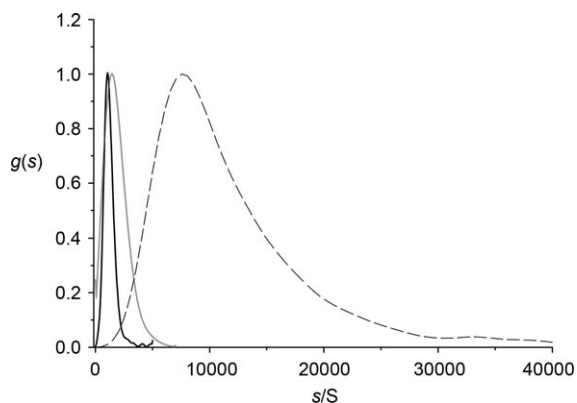


Figure 2. Sedimentation coefficient distribution for selected samples. —: 1,4-NDC:G5=2:1, - - -: 2,3-NDC:G5=2:1, and - · - ·: 2,3-NDC:G5=1:1.

shows a much broader distribution. In the following we focus on the two narrowly distributed aggregates.

The shape of the particles was elucidated by small-angle scattering. Results for the two afore-mentioned samples with both counterions are shown in Figure 3. As is already evident from the scattering curves, the aggregate architecture differs. Data were analyzed by Fourier transformation into the pair distance distribution function  $P(r)$ . The shape of the  $P(r)$  curve indicates the particle shape.<sup>[9]</sup> 2,3-NDC:G5=2:1 forms spherical aggregates with a diameter of  $D=105$  nm, whereas the aggregates of 1,4-NDC:G5=2:1 have a cylindrical shape. The cylinders have a diameter of  $d=35$  nm and a length of  $l=180$  nm. The diameter is

very well defined, as is evident from the form-factor minima in the  $I(q)$  scattering curve. Further data analysis of the cross-section  $P(r)$  shows a homogeneous scattering contrast for the cylindrical particles, which means that they are not hollow (but can be swollen with solvent throughout). The dimensions from  $P(r)$  analysis are consistent with the cross-section radius of gyration and the location of the form factor minima in the  $I(q)$  curves. The absolute scattering intensity yields an “apparent molecular weight”, which indicates that about 800 dendrimer molecules and the corresponding number of dye molecules are associated in one particle.<sup>[10]</sup> The assembly, and in particular the dendrimers, are also expected to be swollen with solvent in the aggregated state. In a simplified view, in such an aggregate the distance between dendrimer molecules could be assumed to be the dendrimer diameter plus the length of a dye molecule, that is, about 6 nm. Based on this, the volume of a cylinder of the found dimensions would be filled with about 800 dendrimer molecules, which is in accordance with the experimentally determined number and thus confirms that cylinders are “homogeneous” but swollen with solvent.

Regarding the well-defined size and shape of the assemblies, it was interesting to see whether they represent equilibrium structures or are kinetically controlled. We reproducibly found the same particle shape independent of the order in which the components were mixed or how the sample was prepared. This indicates that the assembly structures represent equilibrium structures in which the morphology is determined by the counterion architecture and the ratio of the components. This is in contrast to complexes

formed by the aggregation of two oppositely charged polyelectrolytes, in which structures often depend on the preparation method and are kinetically trapped.<sup>[6d]</sup> No change in morphology was observed after several weeks (determined by using small-angle X-ray scattering).

To obtain further information on the nature of the aggregates, the 1,4-NDC:G5=2:1 sample was prepared in solutions that contained different amounts of KBr. For salt concentrations above  $10^{-3}$  mol l<sup>-1</sup>, a time-dependent increase in turbidity was observed. We concluded that the aggregates still carry charges and behave as charged colloids that can be “salted out”. The charged nature of the aggregates was confirmed by zeta-potential measurements, which revealed their overall positive charge.

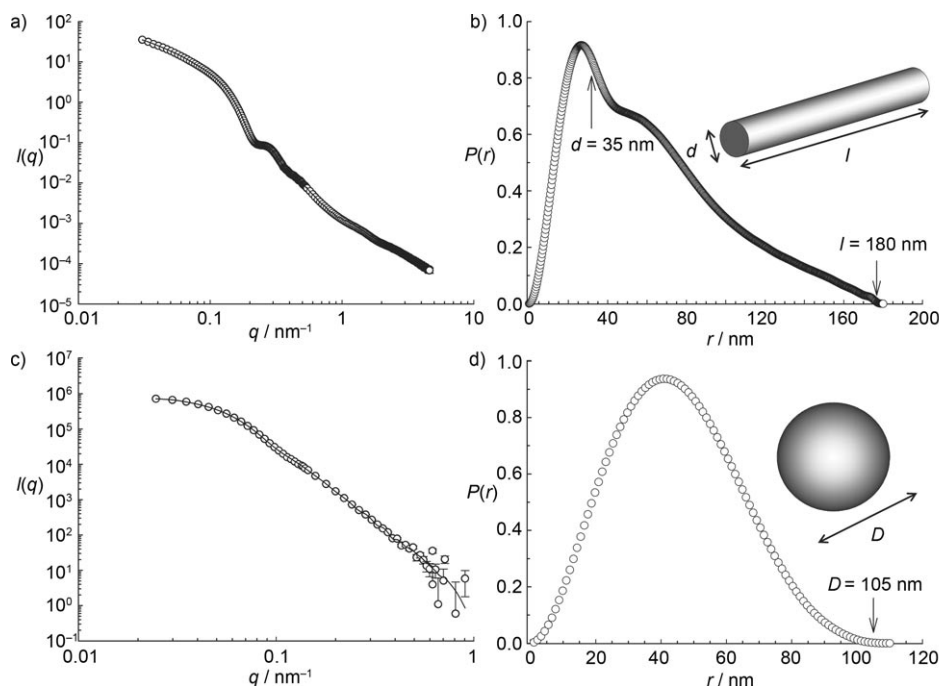


Figure 3. Small-angle scattering characterization of supramolecular assemblies of 1,4-NDC:G5=2:1 and 2,3-NDC:G5=2:1. Scattering curves  $I(q)$  ( $\circ$ ) and fitted data (—) for a) 1,4-NDC:G5 and c) 2,3-NDC:G5 are presented. The corresponding  $P(r)$  curves for b) 1,4-NDC:G5 and d) 2,3-NDC:G5 are also shown.  $I(q)$  and  $P(r)$  are in arbitrary units.

Thus the complex may contain a slight excess of dendrimer amine groups that are, in part, positively charged and which provide the overall charge of the complex. Correspondingly, analysis of the sedimentation scans from analytical ultracentrifugation showed that 10% of the naphthalene dicarboxylic acid was unaggregated. The remaining charge causes a repulsive force between the growing aggregates, and may be the factor that determines the size at which growth ceases. Once the assemblies exist, interparticle attraction may be weak in comparison to an internally hydrophobic colloid. However, as the length of cylinders produced in self-assembly processes usually cannot be controlled, the narrow size distribution is quite remarkable and certainly requires future investigation.

UV/Vis spectra of the samples and the corresponding counterions are shown in Figure 4. 1,4-NDC shows a shift in its absorption maximum upon addition of dendrimer, which

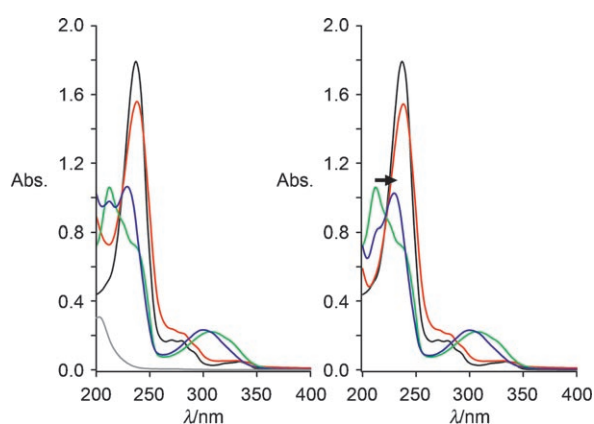


Figure 4. UV/Vis spectra of a) the components and samples and b) after subtraction of the dendrimer spectrum for better comparison. —: 2,3-NDC, —: 2,3-NDC:G5=2:1, —: 1,4-NDC, —: 1,4-NDC:G5=2:1, and —: G5.

is caused by  $\pi$ - $\pi$  interactions between the naphthalenes.<sup>[11]</sup> The main peak shifts towards a longer wavelength, which indicates that J-aggregates with head-to-tail orientation are formed. In contrast, no substantial change and no stacking was detected for 2,3-NDC. In addition, fluorescence spectroscopy on diluted samples showed that both aggregates are fluorescent, as expected with NDC building blocks that either have no mutual interactions or are in J-aggregates. This is opposed to H-aggregates in which fluorescence would be quenched.

The UV/Vis spectroscopic behavior correlates with the aggregate shape. The 1,4-NDC sample, which contains NDC stacks, has an anisotropic structure. It may be that the tendency to form stacked aggregates is the driving force for anisotropic aggregation. The NDC becomes attached to the dendrimer electrostatically (or through hydrogen bonding). Once one NDC molecule is bound, further molecules preferentially bind adjacently rather than randomly because this allows additional  $\pi$ - $\pi$  interactions. This is analogous to spectroscopic investigations of cooperative binding in polyelec-

trolyte-dye complexes and cooperativity in surfactant systems.<sup>[2,3,12]</sup> Therefore, the alignment of dyes and, as a consequence, also of dendrimers may be caused. The cylinder diameter has a narrow distribution around 35 nm, although the diameter of the aggregate consists of multiple dendrimers. This may be due to a delicate interplay of interactions, that is, electrostatic contributions,  $\pi$ - $\pi$  interactions, and geometric constraints. The aggregate contains 128 NDC molecules per dendrimer molecule, which would correspond to a dendrimer surface area of 0.7 nm<sup>2</sup> if the dendrimer was within a spherical volume, which is a reasonable average value. However, it is known that G5 dendrimers can adopt nonspherical shapes under external forces, such as aggregate formation. For example, they have been found to represent “disks” of a cylindrical aggregate, in which the dendrimers were adjacent to each other and all surface groups were directed to the outside of the cylinder.<sup>[9d]</sup> Therefore, it seems likely that columns of dendrimers and NDC molecules are present within the cylindrical aggregate, in which NDC stacks connect multiple dendrimer columns. Furthermore, it should be mentioned that for the 2:1 loading ratio, tertiary amine groups are also likely to play a role in the association with acidic groups. Despite the fact that the structure of the internal aggregate is hypothetical at this point, the results clearly demonstrate that this binding concept yields stable supramolecular structures with different morphologies, for example, fluorescent nanorods.

In contrast with the established electrostatic self-assembly by layer-by-layer deposition, we have herein described the self-assembly of two ionic components in solution to give assemblies of varying shape. This process can also be clearly distinguished from ionic self-assembly that gives solid composites. In comparison with different dye aggregates in solution,<sup>[13]</sup> our concept of combining macroions and counterions may open a field of further structural and functional versatility. Unlike hydrogen-bonded structures,<sup>[13b]</sup> this process is not restricted to nonpolar solvents, and compared with the biszwitterion concept recently described by Schmuck et al.,<sup>[14]</sup> our approach does not rely on synthetically introducing a specific binding motif.

In conclusion, we have demonstrated that the self-assembly of cationic dendrimers and oppositely charged small divalent organic ions in methanol can give stable supramolecular structures, such as fluorescent nanorods. Variation of the building blocks has the potential to lead to versatile functional supramolecular architectures.

## Experimental Section

Small-angle neutron scattering was performed at beamline D11, ILL, and small-angle x-ray scattering was performed at beamline ID2, ESRF, Grenoble. The dendrimer concentration was 0.1%. UV/Vis spectra were measured by using a Perkin-Elmer Lambda 25 spectrometer at a dendrimer concentration of 0.01% and analytical ultracentrifugation was performed by using a Beckman Optima XL-I with UV absorption optics.

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