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Formation and manipulation of supramolecular structures of oligo(*p*-phenylenevinylene) terminated poly(propylene imine) dendrimers

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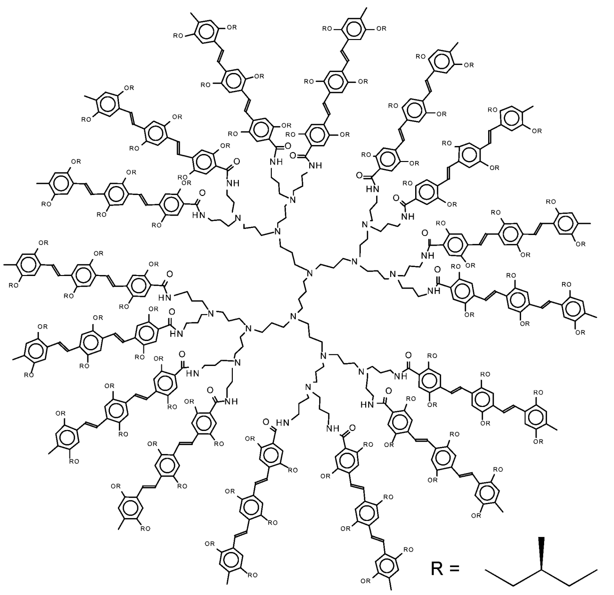
A third generation poly(propylene imine) dendrimer modified with π-conjugated oligo(*p*-phenylenevinylene)s forms spherical and rod-like aggregates that can be manipulated by optical tweezers.

Control of mesoscopic order in π-conjugated systems is a subject of great importance because it enables the tuning of macroscopic properties of electro-optical devices. Furthermore, if shape, dimension and size can be manipulated in a controlled fashion, these materials can presumably be used in nano-sized devices that are small, fast and can store information with high density.[1] Nanoarchitectures can be built-up through self-assembly.[2] Dendrimers are ideal building blocks for creating such structures because they have a well-defined architecture and can easily be modified with functional endgroups.[3] An exciting number of functional assemblies that exploit unique dendritic properties have been reported.[4]

Recently, we have described that poly(propylene imine) dendrimers decorated with palmitoyl- and azobenzene-containing alkylgroups form vesicles in water that could be merged into rod-shaped assemblies.[5] Here, we report that a third generation poly(propylene imine) dendrimer functionalized with π-conjugated oligo(*p*-phenylenevinylene)s[7] (**G3OPV**,† Scheme 1) can also form rod-like and spherical aggregates, which can be manipulated by optical tweezers.

When **G3OPV** was dispersed in decanol a hypsochromic shift of the absorption maximum of $\Delta\lambda = 42$ nm was observed in comparison with dichloromethane ($\lambda_{max} = 417$ nm (CH_2Cl_2) *vs.* $\lambda_{max} = 375$ nm (decanol), data not shown). At the same time, the onset of the spectrum shifts bathochromically from $\lambda = 480$ to 500 nm. This behavior is typical for H-type aggregated OPV units.[8] Circular dichroism (CD) measurements showed no Cotton effect indicating that no chirality at the supramolecular level was obtained. Transmission electron microscopy (TEM) revealed the formation of whiskers (Fig. 1) with a length on average of 1.9 ± 0.5 µm and having a width of 0.20 ± 0.05 m. The aggregates were further investigated by tapping mode atomic force microscopy (TM-AFM, Fig. 1). Similar structures were observed, however, with slightly different dimensions (lengths around 3.2 m and the width of the smallest part being 0.27 µm).

When **G3OPV** was dispersed in water (pH = 1) again a hypsochromic shift of the absorption maximum was observed (($\lambda_{max} = 402$ nm, data not shown) with a vibronic shoulder at $\lambda = 480$ nm. The fluorescence was slightly quenched and red-shifted in comparison with dichloromethane. CD measurements performed on this dendrimer show a weak Cotton effect with a positive sign at 385 nm. Transmission electron microscopy shows the formation of spherical aggregates with an average



Scheme 1 G3OPV.

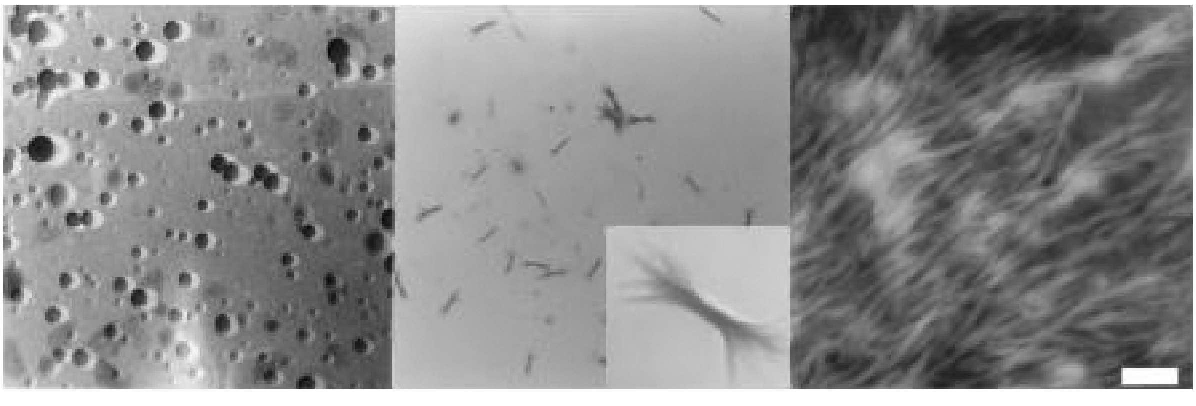


Fig. 1 Transmission electron micrograph of a dispersion of **G3OPV** in water (pH = 1, picture left, bar represents 400 nm). Transmission electron micrograph of a dispersion of **G3OPV** in decanol (picture in the middle; bar represent 5 µm; inset: bar represent 500 nm). Tapping mode atomic force micrograph (picture right; height scale is 22 nm; bar represents 120 nm).

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diameter of 300 nm (Fig. 1). Dynamic light scattering revealed an average particle size distribution of 300 nm. The size of the aggregates strongly depends on the pH of the aqueous solution. For example at pH 5.5 aggregates are present with a sub-micron diameter of up to 3 μm.

The aggregates, which are formed in protic polar media could be built up from bilayers formed by the amphiphilic OPV dendrimers in which the conformation is similar as found previously in the Langmuir layers.[7] In these layers the OPVs are arranged in H-type aggregates. The weak or absence of a Cotton effect found in the CD measurement is presumably due to the branched three-dimensional structure of the dendritic core.

The larger vesicles have been investigated by confocal scanning fluorescence microscopy measurements, which confirmed their globular nature and showed fluorescence in all the nodal planes through the objects. Studies to trap and manipulate these vesicles in water by the aid of optical tweezers have been performed in acidified aqueous solutions (pH = 5.5). By optical trapping, an object is forced to stay near to the focal point of a highly focussed, non-absorbed beam of light.[9] The highly focussed infrared beam forces the vesicles to accumulate near the focus of the beam which results in a very high, local concentration of vesicles in the optical trap (Fig. 2a). Insight into the effect of trapping and the accumulation of vesicles in a small volume, was provided by dual trapping. The dual trap consists of two diffraction limited trapping spots a few μm apart from each other and which can be turned on and off independently.

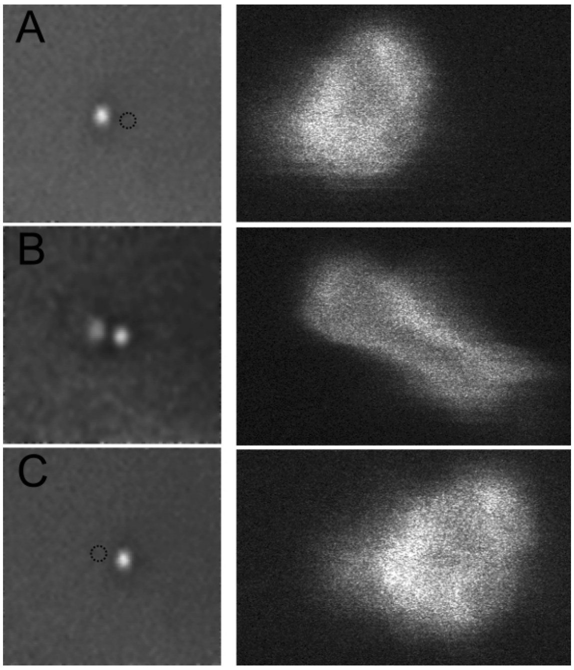

Fig. 2 The ‘switch’ process in the dual trap visualized in transmission (left) and fluorescence (right); the diameter of the formed structures is ~1 μm in both cases. The distance between the traps is ~3 μm. The dashed circles in the transmission images indicate the position of the turned off traps: (A) trap 1 is turned on (B) trap 1 is turned off and trap 2 is turned on (C) trap 2 is turned on.

After releasing the optical beam where the vesicles were trapped originally (Fig. 2A) and turning on the second trap, the gathered vesicles ‘jump’ to the second trap (Fig. 2B), thus demonstrating the attractive interaction between vesicles or the formation of a new assembly, created by the second trap (Fig. 2C).

In summary, oligo(*p*-phenylenevinylene) terminated dendrimers aggregate in protic polar solvents and for the first time π-conjugated assemblies could be manipulated by the aid of optical tweezers resulting in novel architectures. This result shows that micromanupulation is a new and promising tool to gain control over shape and dimensions in π-conjugated assemblies.

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Notes and references

† The aggregates in water were prepared *via* an injection method. **G3OPV** was dissolved in 50 μL methanol and this solution was injected in 5 mL of water.

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