ssPNA templated assembly of oligo(p-phenylenevinylene)s†

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A single-stranded oligothymine peptide nucleic acid (PNA) was used as a template for the assembly of a chiral oligo-(p-phenylenevinylene) diaminotriazine derivative (OPV) in methylecyclohexane (MCH) revealing nanostructures in which the size is controlled by the template.

In nature, templates with specific binding sites are used to efficiently form assemblies and polymers with definite size or sequence.1 This behavior has inspired many researchers to exploit templated polymerization2–5 as a tool to control the size and sequence of synthetic polymers via a ‘bottom-up’ approach.4–8 Especially oligonucleotides are interesting building-blocks, since they can be obtained monodisperse, functionalized and used to create predefined nanosized structures via sticky-end cohesion.9

In a previous study, we showed that the single-stranded desoxyribonucleic acid (ssDNA) oligothymine can act as a template for the assembly of complementary diaminotriazine equipped guest molecules in water.7 In this construct, the single DNA strand templates a supramolecular strand of chromophores held together by π–π, hydrophobic and hydrogen bond interactions. The efficiency of this templated assembly depends on the host–guest and guest–guest interactions and can be described by a templated assembly model based on a one-dimensional Ising model.10 The use of DNA as template requires water as solvent10 and therefore the variety of guest molecules is limited. In order to broaden the scope of this templated approach to organic solvents, we now report on the use of a single-stranded peptide nucleic acid (ssPNA), consisting of 10 thymine residues (pT10, Scheme 1), as a template for the assembly of a chiral π-conjugated oligo-(p-phenylenevinylene) diaminotriazine derivative11 (OPV, Scheme 1) in MCH. PNA12 is an achiral and uncharged analogue of DNA in which the phosphate backbone is replaced by an N-(2-aminoethyl)glycine backbone, making it soluble in a range of organic solvents. We have previously shown that OPV forms hydrogen bonded hexamers that subsequently self-assemble into helical fibers in heptane.11a Here, we describe the non-templated self-assembly and pT10 templated assembly process of OPV studied by means of temperature-dependent UV-vis absorption and CD spectroscopy. The assemblies were visualized with atomic force microscopy (AFM).

The synthesis of OPV11a and pT1013 were performed according to literature procedures. We have first investigated the non-templated self-assembly of OPV. In chloroform, OPV is molecularly dissolved and has an absorption maxima \( \lambda_{\text{max}} \) at 430 nm. In MCH at 323 K, OPV (100 μM) is molecularly dissolved since a similar absorption maximum is found. Upon cooling to 263 K, hypochromicity, a red shift of the onset of the absorption, and an absorption maximum shifting from \( \lambda_{\text{max}} = 430 \) to 440 nm (Fig. 1a) are observed.15 Simultaneously, at low temperatures, a positive Cotton effect is observed with a zero-crossing at \( \lambda_{z} = 434 \) nm,16 indicating that OPV self-assembles into right-handed helical aggregates, similar as earlier observed in heptane.11 The non-templated self-assembly process has been studied in more detail by monitoring the UV absorption at \( \lambda = 500 \) nm as a function of temperature at different concentrations. The self-assembly is fully reversible and the observed exponential transition is indicative of a cooperative non-templated self-assembly process.11,17 By fitting both the concentration- and the temperature-dependent self-assembly data to the cooperative self-assembly model,17 the enthalpy of binding (\( \Delta H_{b} \approx -75 \pm 8 \) kJ mol\(^{-1}\)) was determined (Fig. 1e and f).17

To visualize the OPV assemblies, a MCH-solution has been drop-cast onto graphite (HOPG). AFM micrographs show the

Scheme 1  Molecular structures of the host template pT10 and the guest OPV and a schematic representation of ssPNA templated self-assembly (in blue and red OPV, and in black and red the PNA template).
Fig. 1 Absorption and CD spectra at temperatures between 323 and 263 K for OPV (a and c, respectively) and pT10–OPV (1 : 10) (b and d, respectively) mixtures in MCH. (e) The self-assembled fraction upon cooling of OPV and OPV–pT10 (10 : 1) mixtures and the fits to the cooperative self-assembly model\(^{17}\) and templated assembly model\(^{7,40}\) respectively. [pT10] = 10 \(\mu\)M, [OPV] = 100 \(\mu\)M. (f) \(T_c\) and \(T_e\) (inverted scale) as a function of [OPV] (logarithmic scale) for OPV and pT10–OPV (1 : 10) mixtures.

formation of fibers with a 4–6 nm height (Fig. 2a, c). This height corresponds well with the diameter of the fibers consisting of hexameric H bonded rosettes earlier reported for OPV in heptane.\(^{11a}\)

To investigate the PNA templated assembly of OPV, a base-equivalent of pT10 was added to a 200 \(\mu\)M solution of OPV in chloroform at 263 K. No Cotton effect and spectral changes were observed in the OPV absorption region indicating that there is no interaction between OPV and pT10. To increase the host–guest and guest–guest interaction in the templated PNA assembly, MCH was used as a solvent. In this solvent OPV itself already forms self-assembled fibers (vide supra) which have to be less stable than the proposed OPV–pT10 constructs. When OPV is mixed with a base-equivalent of pT10 in MCH at 323 K and cooled down to 263 K, hypochromicity is accompanied by a blue shift of \(\lambda_{\text{max}}\) to 425 nm and a red shift of the onset (Fig. 1b). Compared to the non-templated OPV self-assembly, the OPV–pT10 mixture has a lower intensity of the Cotton effect (Fig. 1d). Furthermore, the zero-crossing of the Cotton effect \(\lambda_{0}^{\text{c}}\) is 410 nm\(^{16}\) for the pT10–OPV mixture, while for the OPV, \(\lambda_{0}^{\text{c}}\) is 434 nm (Fig. 1b, c). This indicates that OPV is differently organized when the template pT10 is present.\(^{18}\)

The templated assembly process has been studied in more detail by monitoring the UV-vis absorption at \(\lambda = 500\) nm as a function of temperature at different concentrations and compared to the non-templated self-assembly. The transition temperatures, below which the two types of self-assembly set in, are defined as the elongation temperature \(T_{e}\)\(^{17}\) for non-templated self-assembly and as the apparent elongation temperature \(T_{e}^{\text{t}}\) for templated assembly.\(^{7,40}\) For a similar concentration, the \(T_{e}^{\text{t}}\) of the pT10–OPV mixtures is higher than the \(T_{e}\) of OPV (Fig. 1e and f), showing that the pT10–OPV assemblies are more stable than the non-templated self-assemblies of OPV. When fitting the temperature-dependent data to the templated self-assembly model as described previously,\(^{7,40}\) an enthalpy of \(AH_{e}^{\text{t}} \approx -90 \pm 10\) kJ mol\(^{-1}\), a guest–guest interaction energy of \(\varepsilon = -6.2 \pm 0.5\) kT\(_{0}\) was obtained.\(^{19}\)

The enthalpy values extracted for the templated and non-templated assembly processes suggest that the higher stability of the templated assembly as indicated by the higher melting temperature is due to its larger enthalpy gain. A necessary condition for the predominance of templated assembly over self-assembly is that the free-energy change resulting from the combined effects of host–guest and templated guest–guest interaction molecules is larger than the free-energy gain from the stacking of guest molecules in self-assembly. As a consequence, the presence of the PNA template effectively suppresses the self-assembly of OPV unless a large excess of OPV is present in the solution and only then when the pT10 templates are filled.

To visualize the pT10–OPV assemblies, an MCH-solution was drop-casted on graphite (HOPG). In contrast to the sample containing only OPV (Fig. 2a), the AFM micrographs of the pT10–OPV mixture show uniform small particles with a height of 3–4 nm and a deconvoluted width\(^{40}\) of 5–10 nm (Fig. 2b, d).\(^{76}\) The expected dimensions of the pT10–OPV complexes are \(\sim 4 \times 4 \times 4\) nm (the length of pT10 and OPV are 3.6 and \(\sim 4\) nm, respectively) and correspond to the size of the objects observed, revealing that the PNA-template controls the size of the OPV assemblies.

In conclusion, PNA-templated assemblies have been constructed in MCH of which the size is controlled by the PNA template. This PNA-templated approach can in principle be applied to any functional molecule and makes it possible to construct size-controlled functional nanostructures in organic media.
microscopy, 2 dissolve both components and slowly cooled. For atomic force solvent removal and intensive drying, MCH was added to obtain the pT10

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Notes and references


It should be noted that DNA has been used as a template in aqueous solvent mixtures, see for example: (a) A. Furstenberg, M. D. Julliard, T. G. Deligeorgiev, N. I. Gadjev, A. A. Vasilev and E. Vauthy, J. Am. Chem. Soc., 2006, 128, 7661; (b) B. A. Armitage, Top. Curr. Chem., 2005, 253, 55.

10 It should be noted that, though the binding enthalpy is lower, this paradox originates from the fact that although this slope is proportional to the enthalpy shift hypsochromically upon self-assembly, see ref. 11a. It is found that the ratio of these slopes curves is approximately equal to one in our experiments. Calculating the ratio of the two slopes according to this equation gives a value of 1.6 which is comparable to the value 1.67 coming directly from the graphs; S. Jabbari-Farouji and P. van der Schoot, manuscript in preparation.

11 (a) P. Jonkheijm, J. phosphate backbone. Simulations of the CD spectra will be carried out to elucidate the supramolecular structures of DNA and protein backbones. It is found that the ratio of these slopes curves is approximately equal to one in our experiments. Calculating the ratio of the two slopes according to this equation gives a value of 1.6 which is comparable to the value 1.67 coming directly from the graphs; S. Jabbari-Farouji and P. van der Schoot, manuscript in preparation.


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16 Remarkably, preliminary molecular modeling simulations reveal disordered pT10–OPV assemblies (see ESI†). Molecular dynamics hint that the assembly of OPV along pT10 is not only driven by H-bonds of the OPV diaminostriazine unit with the thymine bases of pT10 but also with the peptide backbone. Simulations of the CD spectra will be carried out to elucidate the supramolecular organization of the OPVs in these aggregates, see: F. C. Spano, S. C. J. Meskers, E. Hennebicq and D. Beljonne, J. Am. Chem. Soc., 2007, 129, 7044.

17 It should be noted that a steeper slope for the non-templated self-assembly curve is obtained near the melting temperature, even though the binding enthalpy is lower. This paradox originates from the fact that although this slope is proportional to the enthalpy change, it has different prefactors for each of the two processes. It is found that the ratio of these slopes curves is approximately given by 

\[ \frac{\Delta H^\text{d}{T_1^2}}{\Delta H^\text{s}{T_2^2}} \]

where \( \Delta H^\text{d} \) is the stoichiometric ratio, equal to one in our experiments. Calculating the ratio of the two slopes according to this equation gives a value of 1.6 which is comparable to the value 1.67 coming directly from the graphs; S. Jabbari-Farouji and P. van der Schoot, manuscript in preparation.