

Supporting Information

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

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Molecular modeling

Molecular modeling studies of the templated single-stranded peptide nucleic acid (ssPNA, **pT10**) - oligo(*p*-phenylenevinylene)s (**OPV**) assemblies (Scheme 1) were carried out by means of Molecular Mechanics (MM) and Molecular Dynamics (MD) simulations. To build the **pT10** template structure, the crystal structure of an oligomeric PNA derivative was extracted from '1hzs' referenced in the Protein Data Bank (X-ray diffraction data).¹ The geometry of **pT10** was optimized, leading to an extended structure where thymine bases are almost parallel to each other. For the chiral OPV molecules, the geometry was also optimized. In order to build the **pT10-10OPV**, the diaminotriazine moiety of each OPV was positioned in front of thymine bases of **pT10** (yielding in total 30 H-bonds), with adjacent OPV molecules in a helical arrangement (around 1 turn/10 units), parallel to each other and their planes almost perpendicular to the axis of the **pT10** template. The molecular modeling simulations were carried out using the CHARMM force field for nucleic acids, which was previously tested for other ssPNA oligomers.² The temperature is set to 263 K at equilibration; MD timescale is 10 ns (with 1 fs time step) and the dielectric constant is set to 2.0, i.e. the dielectric constant value of methylcyclohexane (MCH).

Starting from a relatively extended right-handed PNA helix, MD leads to a relatively disordered aggregate: the relaxed structures show that the each thymine is not anymore bonded to one OPV unit. As an example, Figure SI-1 shows an extracted snapshot at the end of the 10 ns MD, depicting such a disordered aggregate. Remarkably, multiple H-bonded patterns are observed: e.g., OPV diaminotriazine units hydrogen-bonded to the thymine bases and amide linkages of **pT10** (see Figure SI-1b). The thymine units, as well as the OPV planes, are not parallel to each other and the OPV molecules are distorted, giving rise to a large number of π - π interactions patterns (T-shape and parallel displaced adjacent phenyl groups). The structure depicted in Fig. SI-1 shows 13 intermolecular H-bonds (as estimated with a maximum distance criterion of 2.5 Å, and D-H...A angle criterion from 0°-180°): 7 are associated to thymine-diaminotriazine H-bonds, and 6 to **pT10** backbone-diaminotriazine H-bonds. The estimated number of π - π interactions in this structure is 22

(as estimated with a maximum distance criterion of 4.5 Å), mainly between the phenyl groups of neighbouring OPVs. Although the stacking of adjacent OPV molecules is not regular, local helical arrangements can be observed (see dimer in Figure SI-1c). The MD simulation over a 10 ns timescale is enough to probe many **pT10** folding conformations, and Figure SI-1 shows only one of these. The Root-Mean Square deviation of atoms and the radius of gyration of the complex are stable over the last 5 ns of the simulation (with an average of 1.8 nm for the radius of gyration).

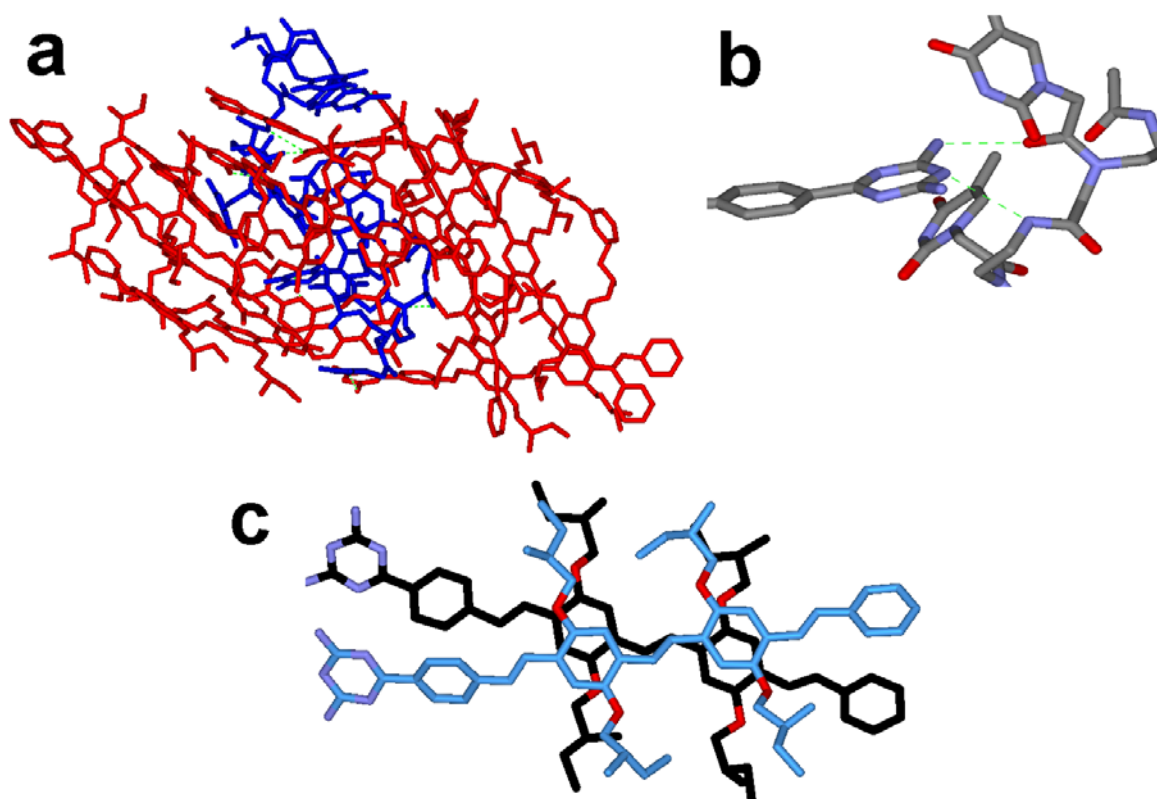


Figure SI-1: a) Stick representation of a snapshot at the end of the 10 ns MD run of the **pT10-OPV** assembly. **pT10** is shown in blue, and **OPV** is depicted in red (the alkyl end-groups of OPV and all the hydrogen atoms are omitted for the sake of clarity). b) and c) are parts of the structure shown in a), displaying some characteristic interactions: b) H-bonds between the diaminotriazine unit of OPV and the peptide backbone of **pT10** (H-bonds in green); c) π -stacking of adjacent OPV molecules in the complex.

- 1 A.B. Eldrup, B.B. Nielsen, G. Haaima, H.Rasmussen, J.S.Kastrup, C. Christensen, and P.E. Nielsen, *Eur. J. Org. Chem.* 2001, **9**, 1781.
- 2 S. Sen and L. Nilsson, *J. Am. Chem. Soc.* 2001, **123**, 7414.