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## Supramolecular Polymerization of SOPV Monomers: A Molecular Dynamics Study of Dimerization/Tetramerization Mechanism

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### [Introduction]

Supramolecular systems characterized by complex kinetic pathways has been receiving much attention recently as a new class of materials. [1-3] S-chiral oligo (phenylene-vinylene) known as SOPV is one of the examples of such systems [2,3], which is capable of making supramolecular polymers via kinetically metastable pathways and produce various polymorphic self-assembled structures. [5] In particular, it was experimentally shown that under specific temperature and concentration, SOPV can form nanofibers with different helicity (referred to as P-SOPV and M-SOPV) (Fig.1). Upon heating the kinetically formed aggregates (P-SOPV), which is a metastable state, was found to slowly transform to a thermodynamically more stable one (M-SOPV). Based on this observation it has been claimed that SOPV polymerization involves two distinct aggregation pathways, namely off-pathway (leading to P-SOPV) and on-pathway (leading to M-SOPV). The choice of solvent is also known to be crucial for nucleation processes and product yields. It is therefore imperative to study the underlying mechanism of SOPV polymerization, and here we study the initial stage of polymerization (namely, dimerization/tetramerization) as the basis for understanding the subsequent elongation processes.

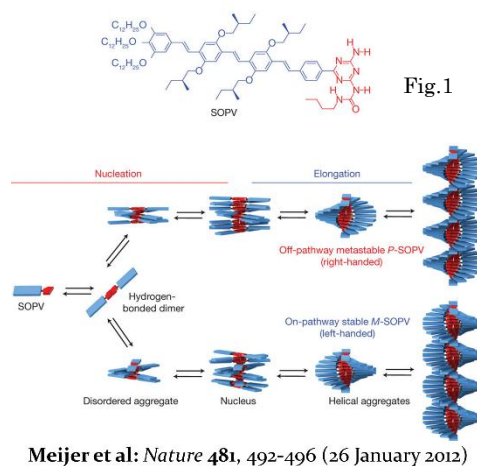
### [Method]

We performed molecular dynamics (MD) simulation of the aggregation process of SOPV monomers using the Gromacs program package. The system consists of SOPV monomers solvated in methylcyclohexane (MCH) in a cubic box of about 120 Angstroms (totaling about 50000 atoms). The solute and solvent were modeled with the General Amber Force Field (GAFF) and OPLS-UA, respectively. By using GPU and hydrogen mass repartitioning, we ran several tens of trajectories up to a few microseconds starting from various initial conditions and performed statistical analysis to obtain atomistic insights into characteristic binding modes of dimers and tetramers in MCH.

### [Results]

1. From the comparison of dimerization in the gas phase and in MCH solution, it was found that the solvent effect is crucial for the final structure of a single dimer: [Fig.2]

- a. The dimer in the gas phase takes a compact stacked form, which is due to the dominant  $\pi$ - $\pi$  interactions between the main aromatic chains.



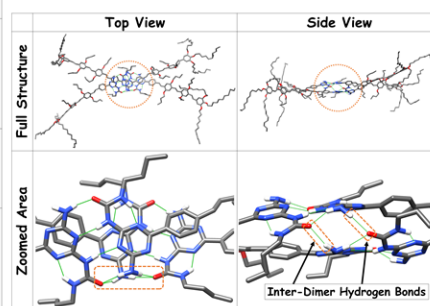
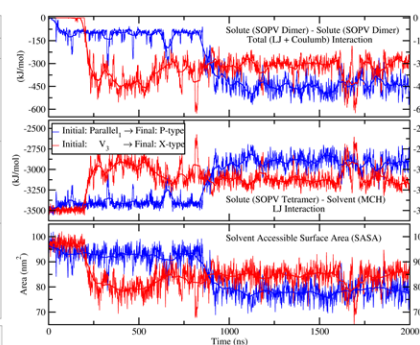
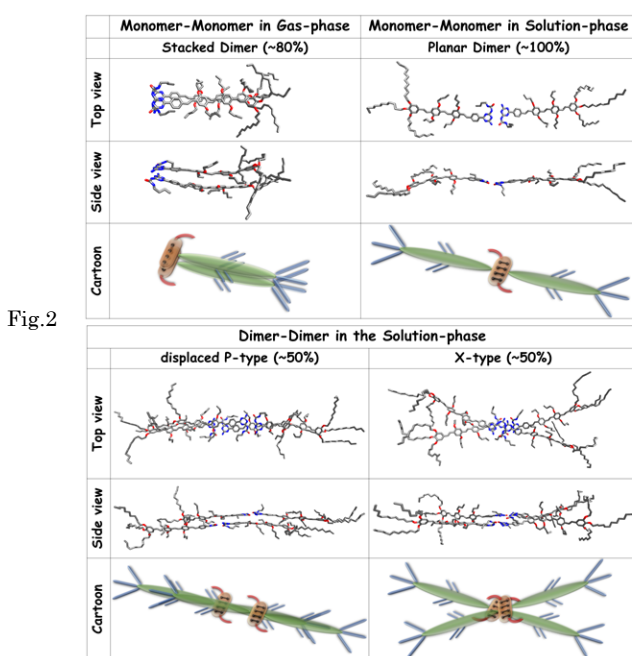
b. In MCH, solute-solvent van der Waals (vdW) interactions win over the  $\pi$ - $\pi$  stacking interactions, resulting in an open extended structure of the single dimer.

2. The assembly of four SOPV monomers in MCH (starting from 22 different initial configurations) all reduced to either (a) displaced parallel dimers (called P-type) or (b) cross-shaped dimers (called X-type). The crossing point was located at the hydrogen bonding interfaces (HBIs) of the two dimers [Fig.2]

3. Energy decomposition analysis showed that there is a competition between the solute-solute and solute-solvent interactions. The X-type configuration tries to maximize the solute-solvent interactions by taking an extended cross shape, while the P-type configuration tries to maximize the intra-solute  $\pi$ - $\pi$  stacking. It was also observed that structural interconversions occur in time between X and P-type configurations, thus exhibiting a bistable feature. [Fig.3]

4. Although both structures have almost equal chance of occurrence, the X-type configuration was found to appear more frequently than P-type counterpart. [Fig.3]

5. The X-type configuration shows double hydrogen bonds that connect two dimers [Fig.4]. This is in contrast to P-type structures for which no hydrogen bond was observed between dimers.



## [References]

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