Unexpected aggregation induced circular dichroism, circular polarized luminescence and helical assembly from achiral hexaphenylsilole (HPS)

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Supporting Information:

Fig. S1. The UV-vis absorption spectrum (A) and circular dichroism spectra (B) of HPS and HPS-MR in THF solution with a concentration of 100 μM and from cast films.

Fig. S2. AFM images of the self-assembled helical fibers formed by HPS-MR on the evaporation of its different THF-water solution. The water content is 0%(A), 50%(B), 80%(C) and 90%(D), respectively, concentration: 10μM.

Fig. S3. TEM images of self-assembled fibers of HPS (A、B) and HPS-MR (C、D) formed upon the evaporation of THF-water solution (The water content is 80%)

Fig. S4. Comparison between crystal packing mode and the best packing mode identified by the proposed algorithm.

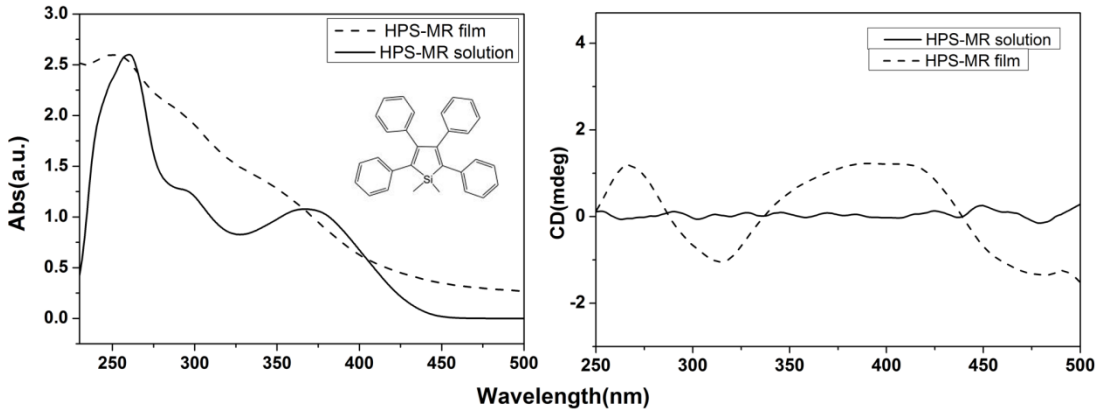

Fig. S1 The UV-vis absorption spectrum (A) and CD spectra (B) of HPS and HPS-MR in THF solution with a concentration of 100 μM and drop cast films.

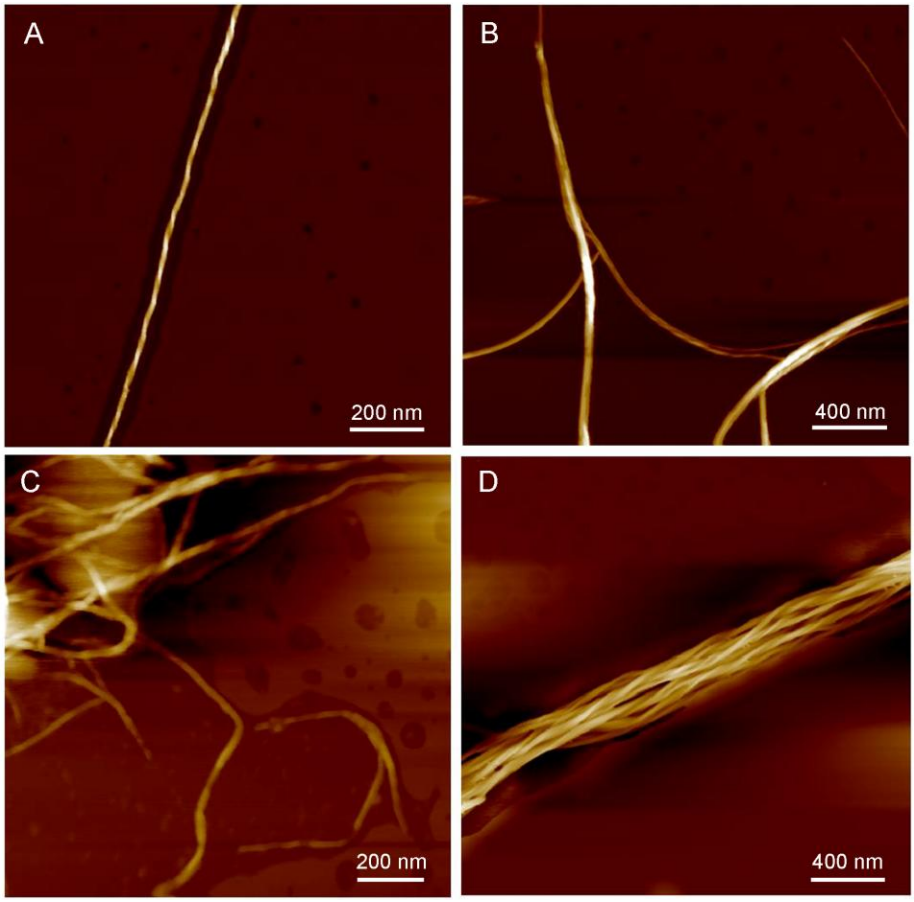

Fig. S2 AFM images of the self-assembled helical fibers formed by HPS-MR on the evaporation of its different THF-water solution. The water content is 0%(A), 50%(B), 80%(C) and 90%(D), respectively, concentration: 10μM.

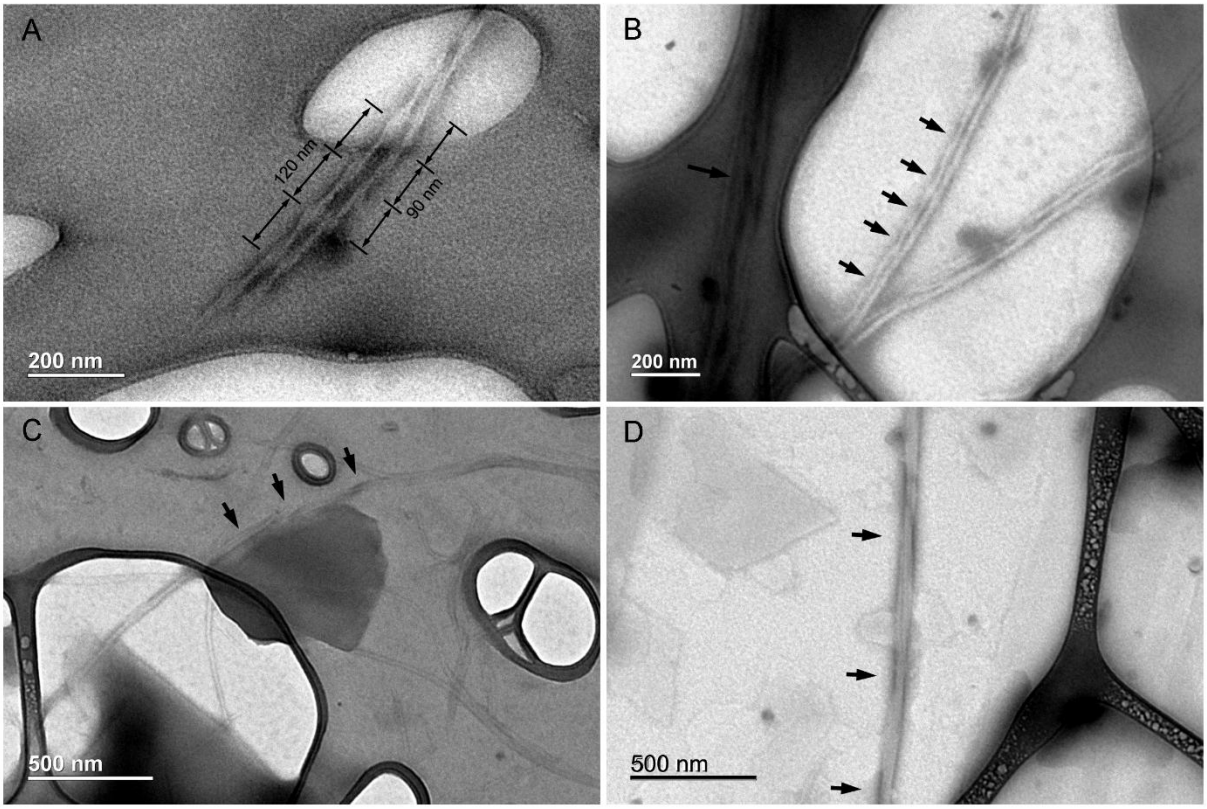

Fig.S3 TEM images of self-assembled fibers of HPS (A、B) and HPS-MR (C、D) formed upon the evaporation of THF-water solution (The water content is 80%)

Details in modeling process

(1) Sample the structures of HPS molecules in solution with molecular dynamics (MD) simulations.

In the first step, Gromacs package(version 4.6.5)[1] was adopted to perform MD simulation to sample the conformations. Only one trajectory of 20ns is generated with the saving interval of 2ps. A cutoff of 12Å was applied for both the vdw and

short-range electrostatic interactions. The long-range electrostatic was calculated with Particle-Mesh Ewald (PME) method[2, 3]. The HPS molecule was incubated in a water box(with the size of 3nm*3nm*3nm) filled by 859 water molecules with TIP3P model[4]. The system was then optimized with the steepest gradient algorithm, followed by a 100-ps simulation to relax the solvent conformation with the restraint potential on atoms in HPS molecule. Finally the MD simulation was performed under NPT ensemble. The time step was set to be 2fs and the non-bonded pair-list was updated every 20 fs. All the bonds with hydrogen atoms were constrained using LINCS algorithm[5]. For Silicon atom, σ=4.5773Å and ε=1.254kJ/mol are adopted to describe the Lennard-Jones 12-6 potential.

(2) Select representative conformations of HPS molecule from the generated trajectories of MD simulation.

The trajectory generated by MD simulation contains 10000 frames with one conformation for each frame. To select representative conformation, K-center algorithm was first applied to cluster all the conformations into 300 clusters with RMSD as the distance metric. Central conformations from these clusters were then selected as representative ones for further modeling.

(3) Construct packing units for aggregates from representative conformations.

In each packing unit, two constrains are satisfied: packing unit consisted of two molecules are centrosymmetric and the interaction energy between two molecules are optimized considering the relative position and orientation. The first constraint is adopted to keep the symmetry of packing unit and the second constraint is applied to decrease the energy of the packing unit, making the packing unit stable. From each conformation, multiple packing units can be obtained because of the existence of different potential basins in conformational space. In this part, only vdw energy is considered in the energy calculation. As a result, a total number of 2187 packing units are identified from 300 conformations.

(4) Search different packing modes with different packing units and identify the best one by considering the total energy of system.

Similarly to construct packing unit from conformation, finding packing modes needs to sample different lattice parameters to optimize the total energy (only vdw interaction considered) between the unit and its neighbor images. All the packing modes generated by 2187 packing units are filtered with energy. The one with lowest energy is selected as the best packing mode.

Validation of the method

Among the four steps proposed in the manuscript, the first two steps are designed to choose different conformations that may be adopted in aggregates, which is widely used in the sampling of other systems. The last two steps are performed to identify the best packing mode from the possible ones with the selected conformations. To validate the robustness of last two steps, we choose the conformations of two HPS molecules from the unit cell in the crystal structure as the building block to reproduce the lattice parameter in crystal structures. As a result, the packing mode identified by our method is almost identical with that in crystal(see Fig S4). To quantity the difference between them, two aggregate blocks with 27 packing units for each are constructed. The root-mean-square deviation (RMSD) between two blocks are only 0.35Å, much smaller than the length of one chemical bonds.

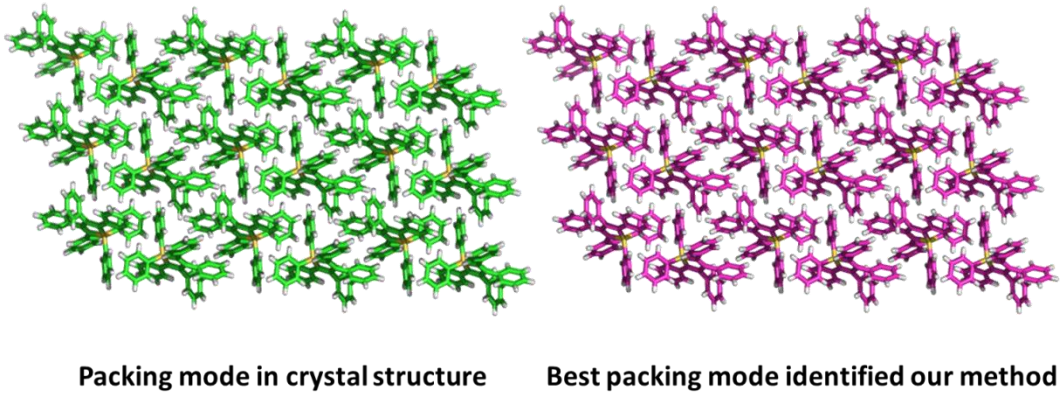

Figure S4. Comparison between crystal packing mode and the best packing mode

identified by the proposed algorithm.

References

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