Supporting Information

π-π Stacking Mediated Chirality in Functional Supramolecular Filaments

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S.1 The Starting Structure of a Pre-assembled mCPT-buSS-Tau Filament

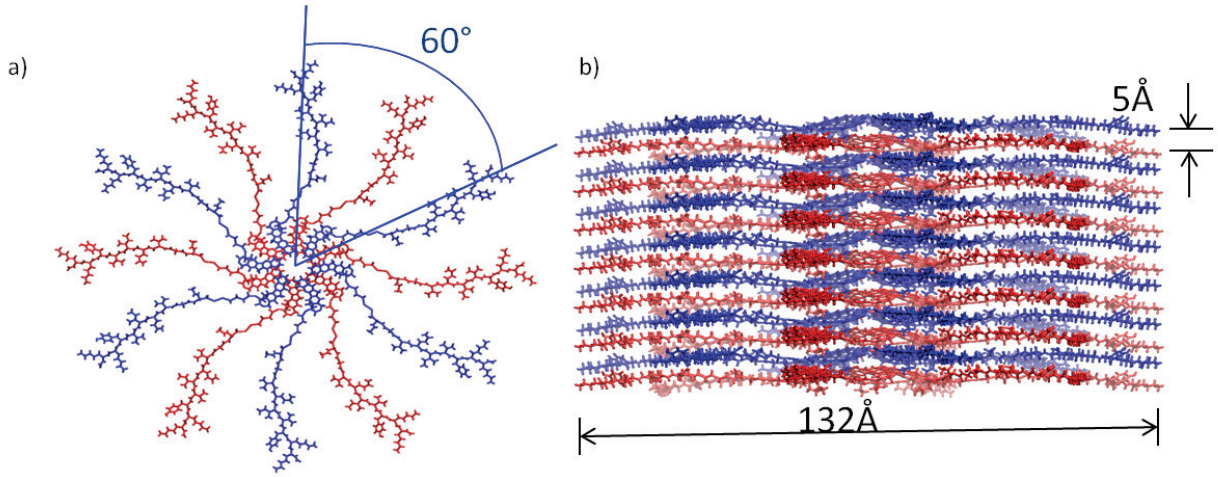

Figure S 1. The starting structure of a pre-assembled mCPT-buSS-Tau filament for molecular dynamics simulation. a) Six DAs are placed radially in the first layer (blue). The CPT tails are pointing inward and the angle between neighboring DAs is 60°. The second layer also has 6 DAs (red) and is rotated by 30° relative to the first layer. b) The alternate first and second layers are placed along the filament axis to form 9 layers in total, resulting in 54 (6 x 9 =54) mCPT-buSS-Tau molecules. The distance between the layers is 5 Å.

S.2 Distribution of Components in the Assembly

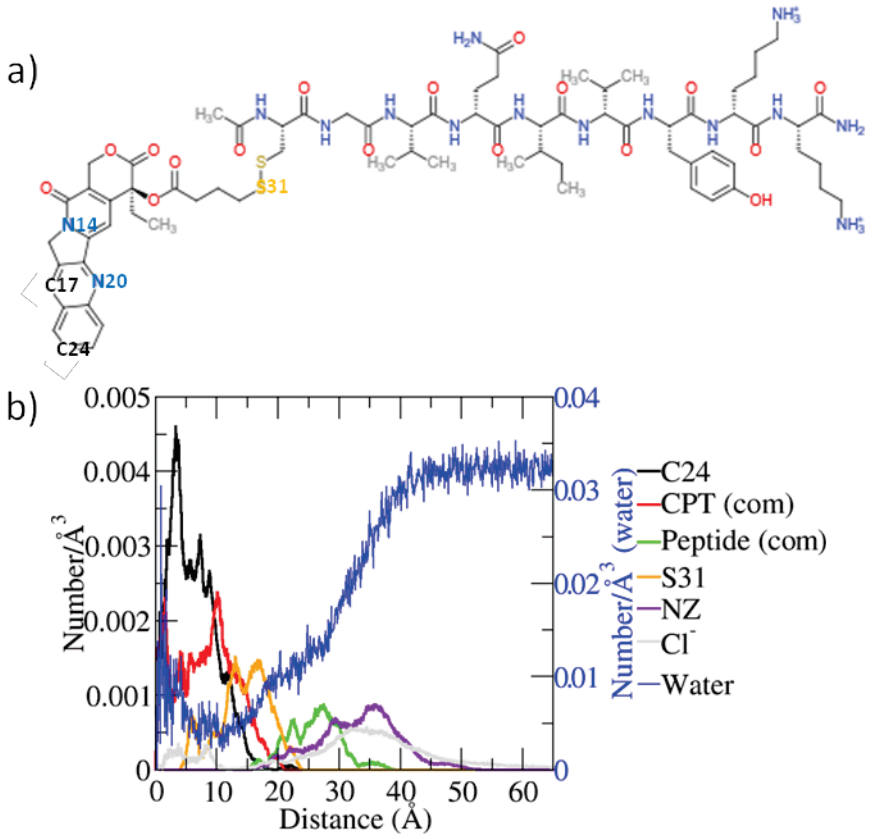

Figure S 2. Distribution of components in the assembly of mCPT-buSS-Tau nanofilament. a) Structure of mCPT-buSS-Tau. b) Radial distributions in the pre-assembled mCPT-buSS-Tau nanofilament after 210 ns. The center of mass of the selected atoms is counted and averaged in the last 2ns (1000 frames, except for water (10 frames)). The atom at the end of CPT, C24, is deviated from the center. CPTs (center of CPT, red) remain buried in the core of the assembly, while the peptides (center of peptide, green) wrap around the core, forming the outer shell. CPTs and peptides are conjugated via disulfide bonds (S31, orange). The positively charged side chains of two Lysine residues at the end of the peptides (NZ, purple) populate the outermost layer, forming an interface with water, where they are neutralized by Cl^- ions (grey). A small number of water molecules (blue, alternate y axis) are observed in the core: ~0.01/Å^3 at 2Å from the core.

S.3 Water Molecules in the Core

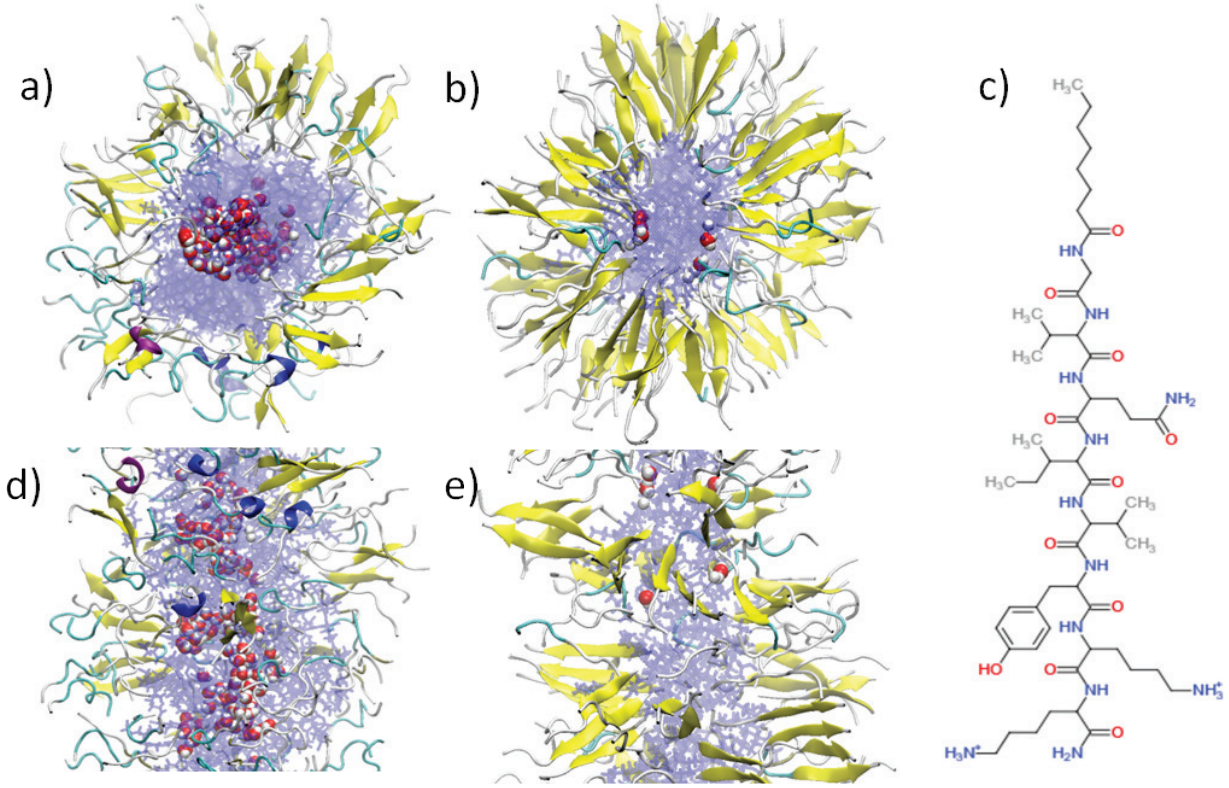

Figure S 3. Water in the core of the nanostructure of mCPT-buSS-Tau (a, d) and C8-Tau (b, e). (c) Structure of C8-Tau. Water molecules in the CPT core (within 10 Å from the center) of mCPT-buSS-Tau are shown in red and white VDW representations in the top (a) and the side (d) view of the filament of mCPT-buSS-Tau. Small clusters of water molecules are scattered throughout the core, making a loose water ribbon. The CPT is displayed in transparent blue licorice. The secondary structures of the peptide are shown: β sheet, α helix, 3-10 helix, turn, isolated bridge, and coil in yellow, magenta, blue, cyan, gold, and white, respectively. Water molecules in the core of the C8-Tau fiber (within 7 Å from the center) are shown in (b) and (e). Cryo-TEM of C8-Tau fiber at 1 mM shows the width of 9.0±1.2 nm and their widths vary at 50 μM[1]. The width of the C8-Tau fiber at 227 mM after the simulation is 8.7±0.2 nm. The C8-Tau fiber has no water in the core except at the edge of the hydrophobic core. The flexible hydrocarbon C8 facilitates the water-tight packing and formation of comparably more β sheets. Meanwhile, the rigidity of bulky CPT leads to the loose packing and disturbs the arrangements of the peptide tails inhibiting or slowing down the kinetics of the formation of β sheet of the peptide to some extent.

S4. Helical Stacking of CPTs

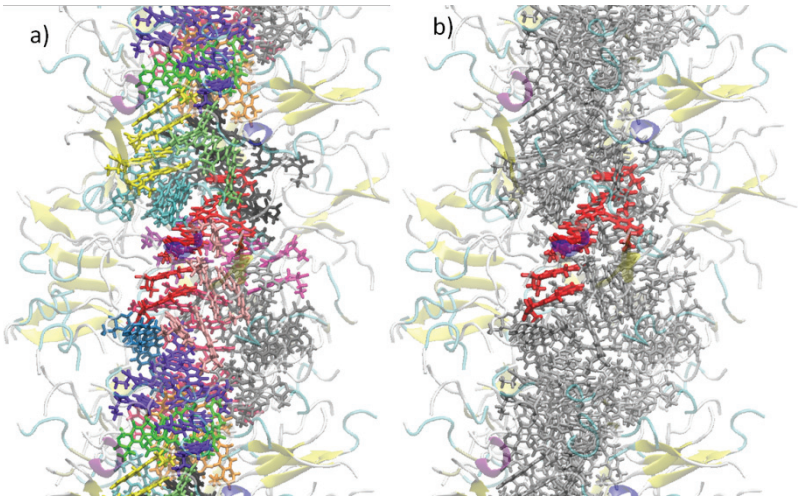

Figure S 4. Helical stacking of CPTs in the core of the mCPT-buSS-Tau filament. a) The parallel CPTs are displayed in the same colors. The peptides are shown in transparent secondary structures. b) One of the short helical CPT strands is highlighted in red to show its right-handedness.

References

(1) Cheetham, A. G.; Zhang, P. C.; Lin, Y. A.; Lock, L. L.; Cui, H. G. *J. Am. Chem. Soc.* **2013**, *135*, 2907.