

Supplemental information for

Hierarchical chirality transfer in the formation of chiral silica fibres with DNA-porphyrin co-templates

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Experimental section

Materials

DNA sodium salt from Herring testes (D1626, Type XIV) is from Sigma. meso-tetra(4-sulfonatophenyl) porphyrin (TPPS) is from Fisher Scientific,

N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (50% in methanol, TMAPS) is from TCI, Japan. Tetraethyl orthosilicate (TEOS), HCl (37%), NaOH, from Sinopharm Chemical Reagent Co. Ltd. All the reagents are used as received and used as received without further purification.

Synthesis

Synthesis of DTHF composite fibers

DNA stock solution (10 mg/mL) was sonicated for 2.5 h by a cell crusher in ice bath to get the uniform short DNA solutions. Then 1 mL this DNA solution was added into 8 mL deionized water and followed with the addition of TPPS water solution (2

mg/mL) of an amount of 400 uL (for molar ratio DNA/TPPS = 1/0.024) or 800 uL (for molar ratio DNA/TPPS = 1/0.056). Then 120 uL TMAPS solution (75% in methanol) and 100 uL TEOS were added into the solution followed by pH adjusting to 4.3 with 0.01 M HCl solution. Then the whole reaction mixture was stirred for 15 min and steric react at 25° for 3 days. The products were formed as light green cotton-like powders and centrifuged for collection.

Characterization

The macroscopic features of the samples were observed with SEM (JEOL JSM-7800) with an accelerating voltage of 1.0 kV. TEM was performed with a JEOL JEM-2100 microscope operating at 200 kV (Cs = 1.0 mm, Point resolution 2.3 Å), the samples were dispersed in ethanol and dropped on a carbon thin film on a Cu grid. Powder X-ray diffraction patterns were recorded on a Rigaku X-ray diffractometer D/ MAX-2200/PC equipped with Cu K α radiation. The CD spectra and DRCD spectra were taken on a JASCO J-815 spectropolarimeter fitted with DRCD apparatus.

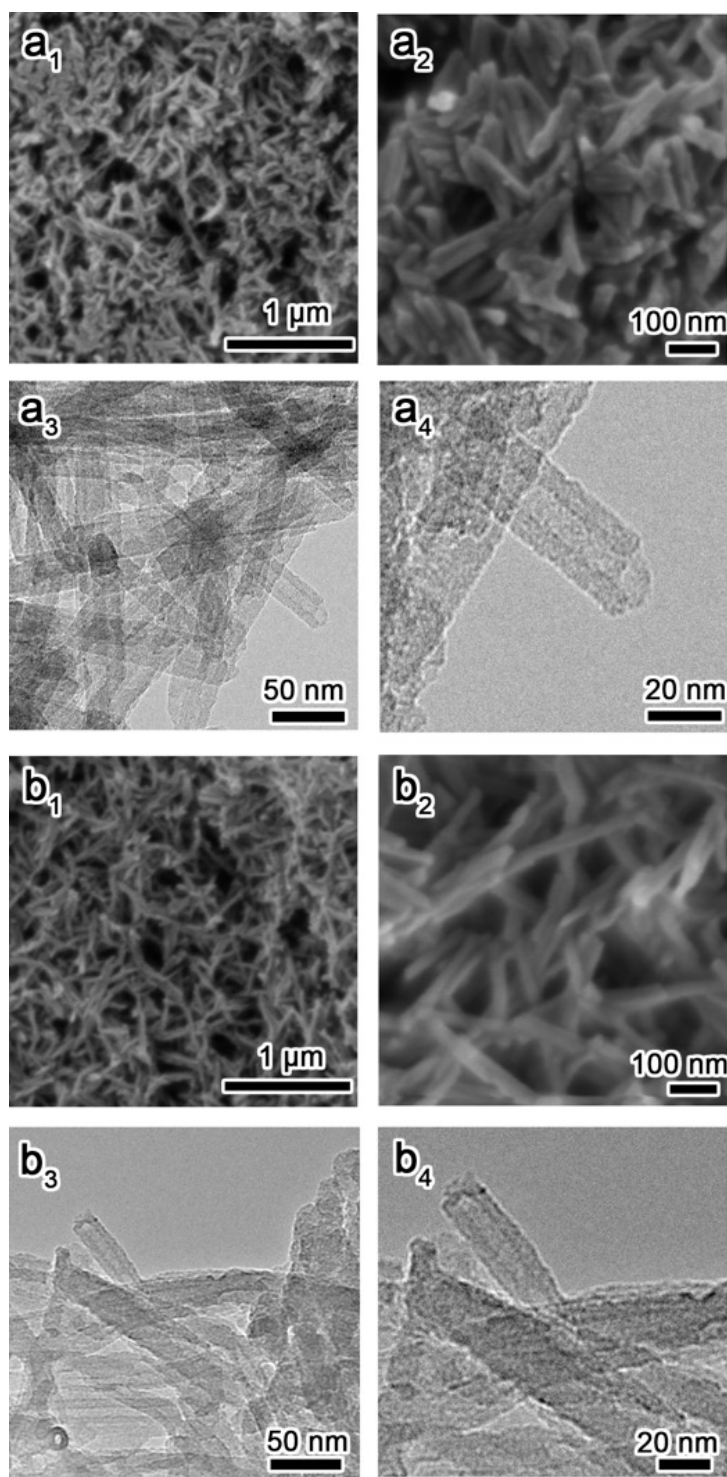


Fig. S1. SEM images a₁, a₂, b₁, b₂) and TEM images a₃, a₄, b₃, b₄) of the TPPS-rods. The molar ratio of the reactants is TPPS:TMAPS:TEOS:H₂O=x:7.2:15:18000. Here x is 0.028 a) and 0.056 b). The reaction pH is 4.3 and the temperature is 25°C.

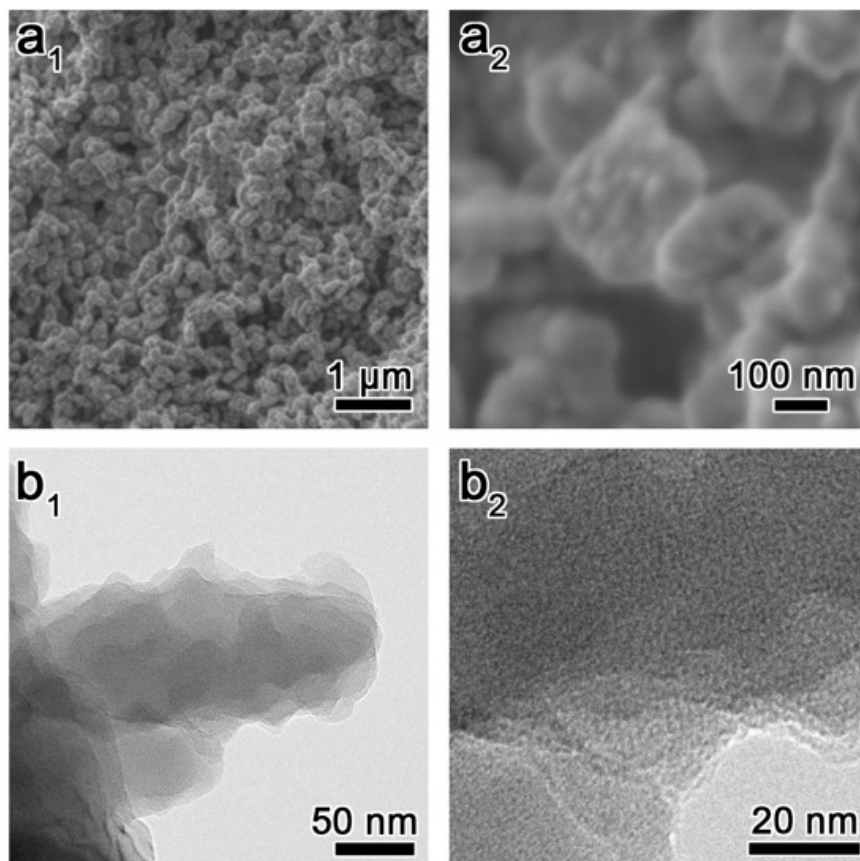


Fig. S2. SEM images (a₁) and (a₂) and TEM images (b₁) and (b₂) of the DNA-plate, The molar ratio of the reactants is DNA:TMAPS:TEOS:H₂O=1:7.2:15:18000. The reaction pH is 4.3 and the temperature is 25°C.

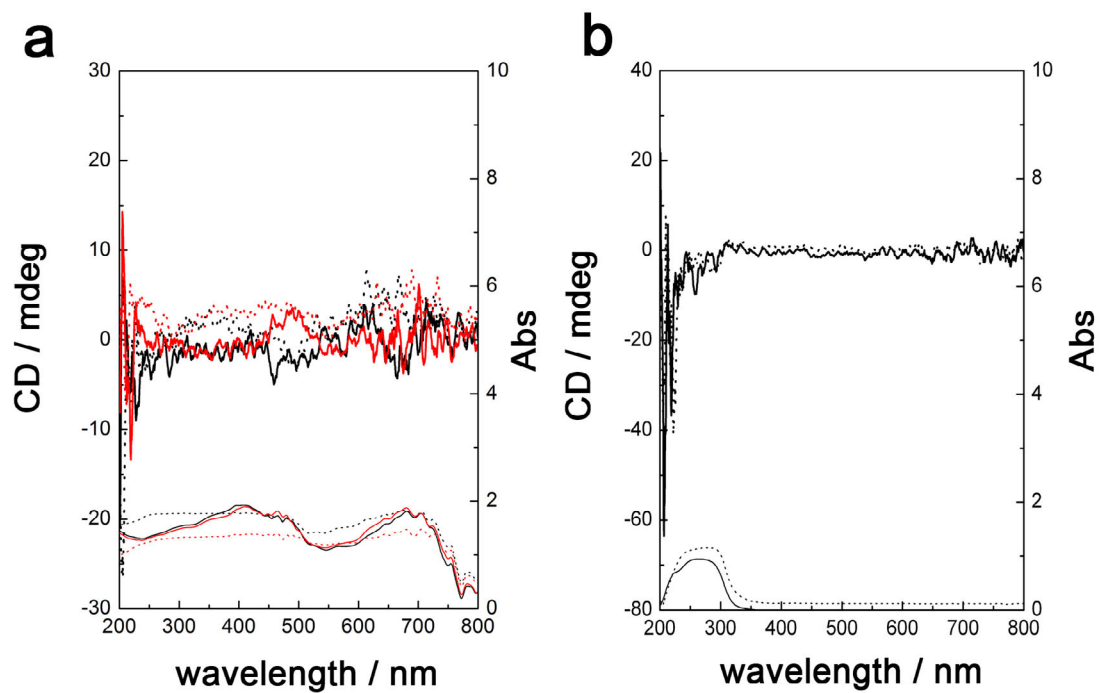


Fig. S3. DRCD spectra of the TPPS-rod in Fig S1 a) (a, black line) and in fig S1 b) (a, red line), and DNA-plate b) measured under dry (solid line) and wet (dotted line) conditions.

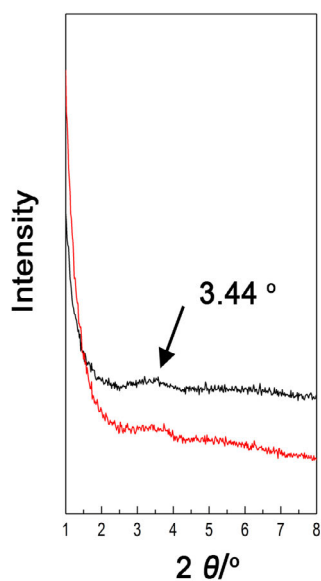


Fig. S4. Small angle XRD of the DTHF-1 (black line) and DTHF-2 (red line). Small weak peak at 3.44° (marked by black arrow) indicates the arranged channels with unit cell parameter around 2.5 nm. There are many possible reasons for the weak signals in the XRD pattern. The DNA molecules have the screw-like packing feature. The chiral distortion would lead to both the ordering of the DNA packing and the repeating units decreased, which the intensity of the XRD would be greatly influenced. Besides, the long-rang regularity is also affected by various factors such as lattice fluctuation, modulation, defects, etc. These factors would also lead to the broaden and weaken of the peaks.

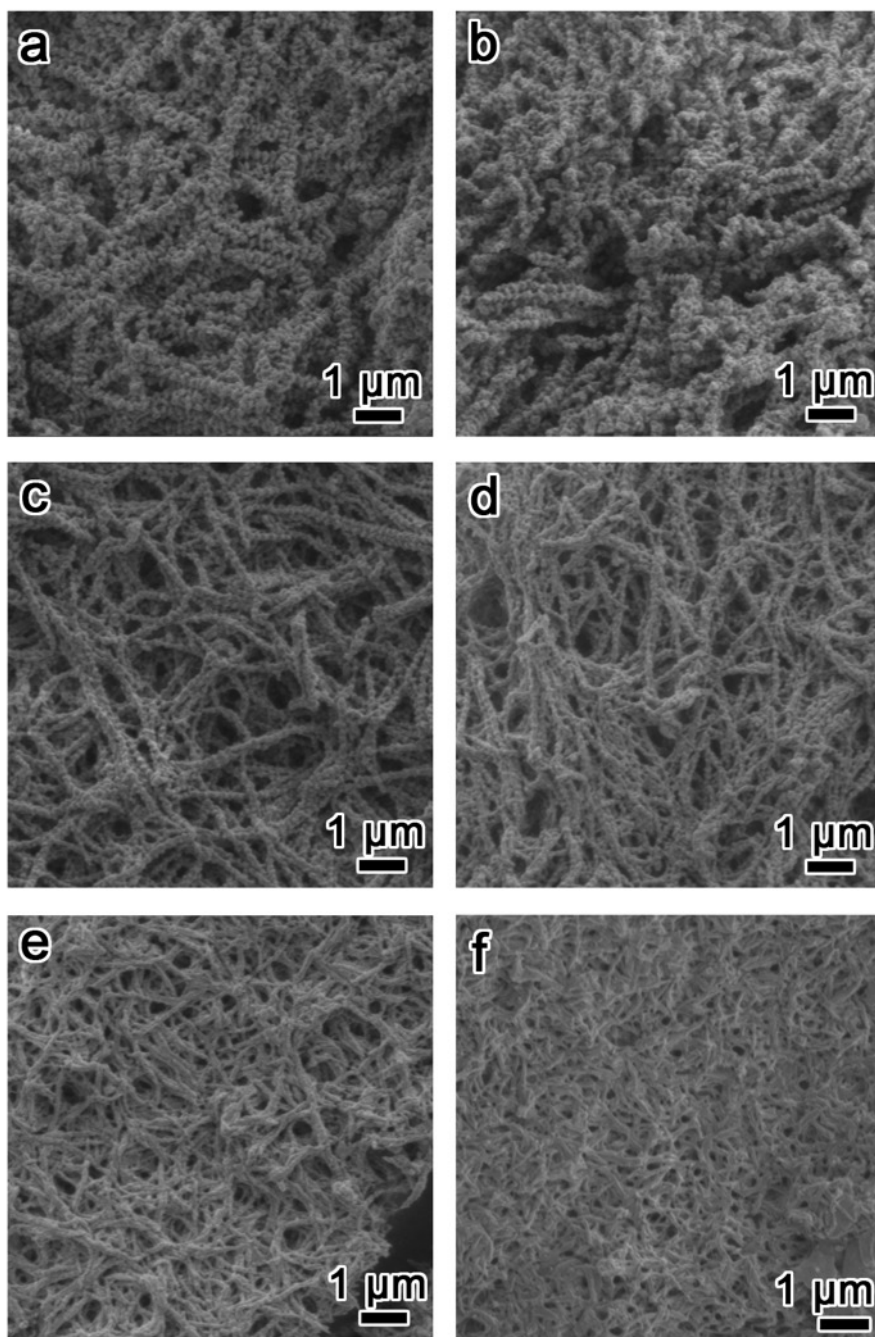


Fig. S5. SEM images of the DTHFs synthesized with different amount of TPPS. The molar ratio of the reactants is DNA:TPPS:TMAPS:TEOS:H₂O=1:x:7.2:15:18000. Here x corresponding to 0.021 a), 0.028 b), 0.042 c), 0.056 d), 0.084 e), 0.14 f). The reaction pH is 4.3 and the temperature is 25°C.

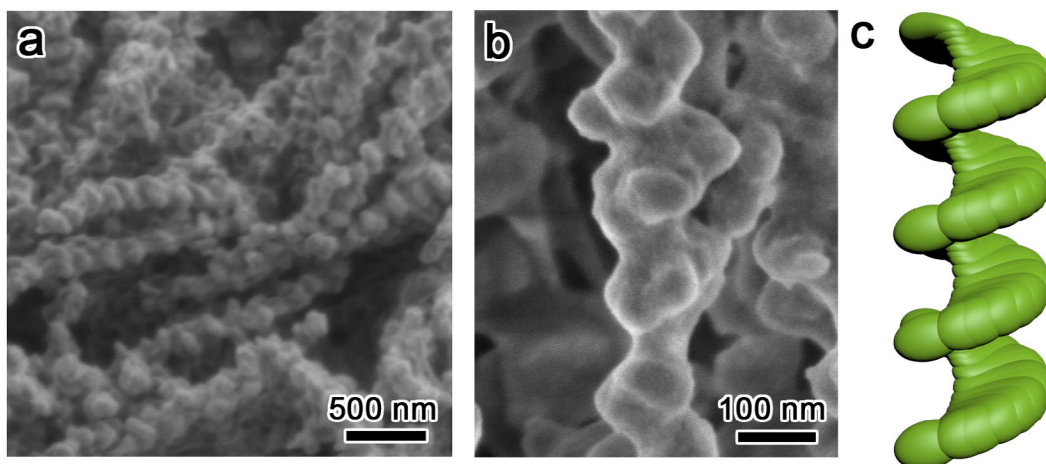


Fig. S6. SEM images of the DTHF-2. The molar ratio of the reactants is DNA:TPPS:TMAPS:TEOS:H₂O =1:0.028:7.2:15:18000. The reaction pH is 4.3 and the temperature is 25°C.

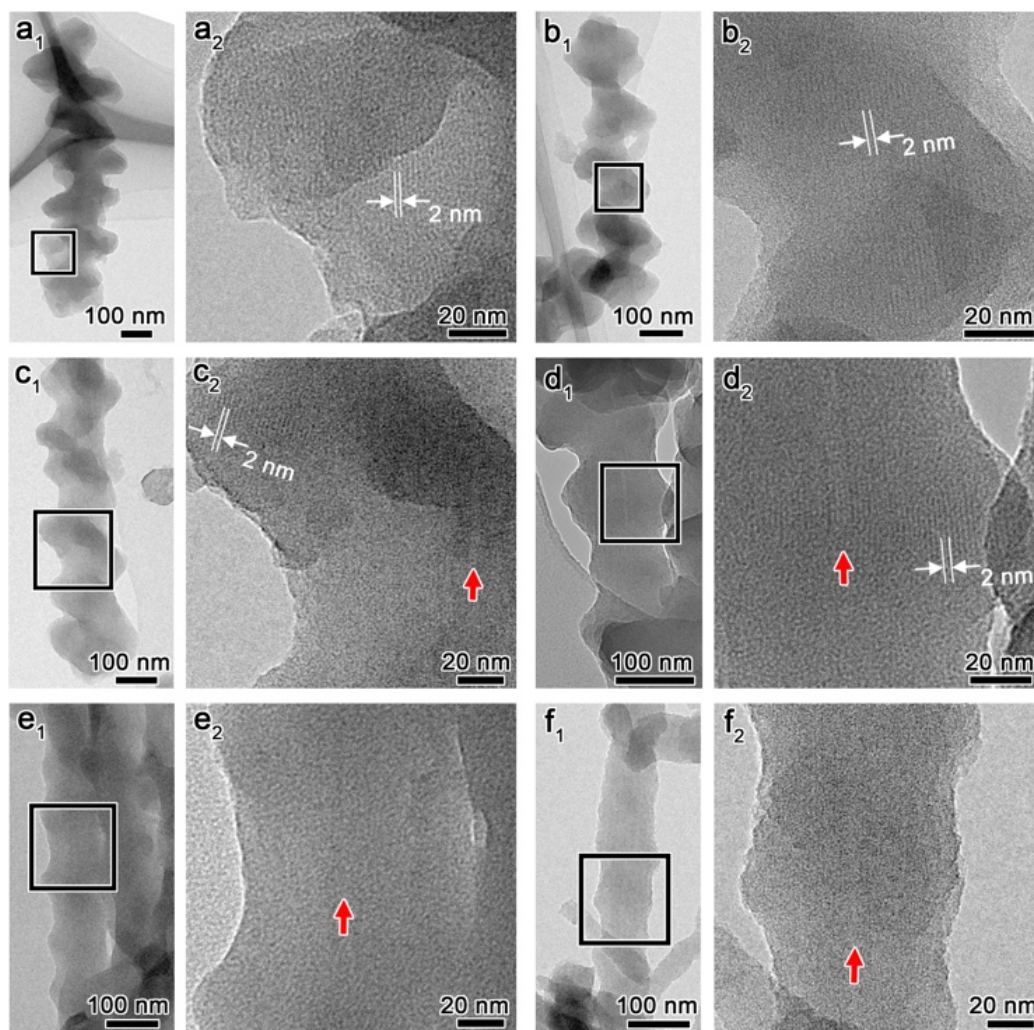


Fig. S7. TEM images of series of DTHFs synthesized with different amount of TPPS. The molar ratio of the reactants is DNA:TPPS:TMAPS:TEOS:H₂O=1:x:7.2:15:18000,, where x = (a) 0.021, (b) 0.028, (c) 0.042, (d) 0.056, (e) 0.084 and (f) 0.14. The channels of DNA assemblies are marked by white arrow and the nanotube assembled by TPPS is marked by red arrow.

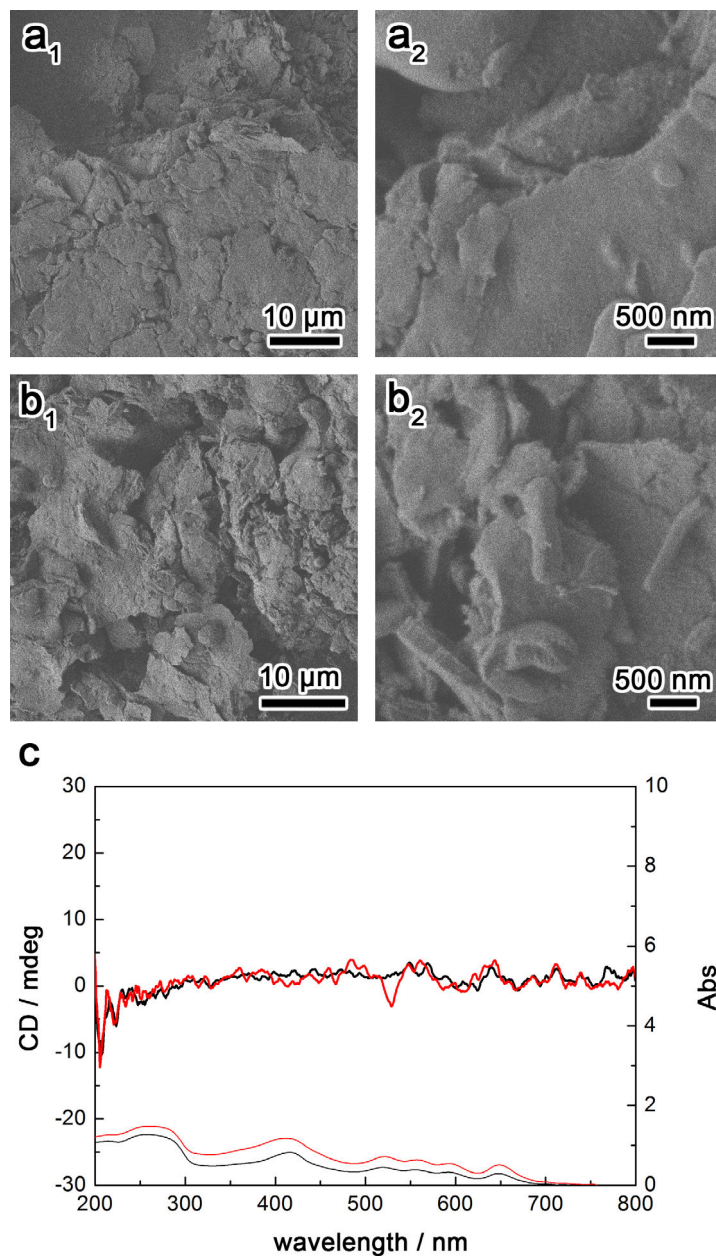


Fig. S8. SEM images and the corresponding DRCD and UV/Vis spectra of the DNA-TPPS silica composition synthesized under pH of 6.2. The molar ratio of the reactants is DNA:TPPS:TMAPS:TEOS:H₂O=1:x:7.2:15:18000. Here x corresponding to 0.028((a) and black line in c)), 0.056 ((b) and red line in c)).

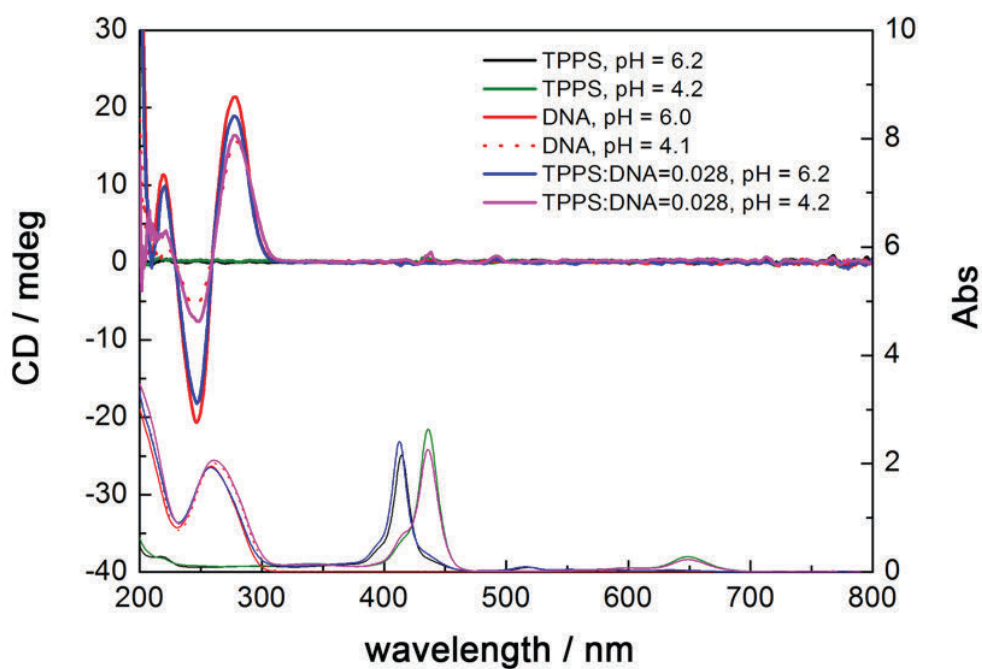


Fig. S9. CD and UV/Vis spectra of aqueous solutions of TPPS (black line, pH = 6.2 and green line, pH = 4.2), DNA (red line, pH = 6.0 and red dotted line, pH = 4.1), TPPS/DNA mixture solution with molar ratio of TPPS/DNA = 0.028 (blue line, pH = 6.2 and pink line, pH = 4.2).

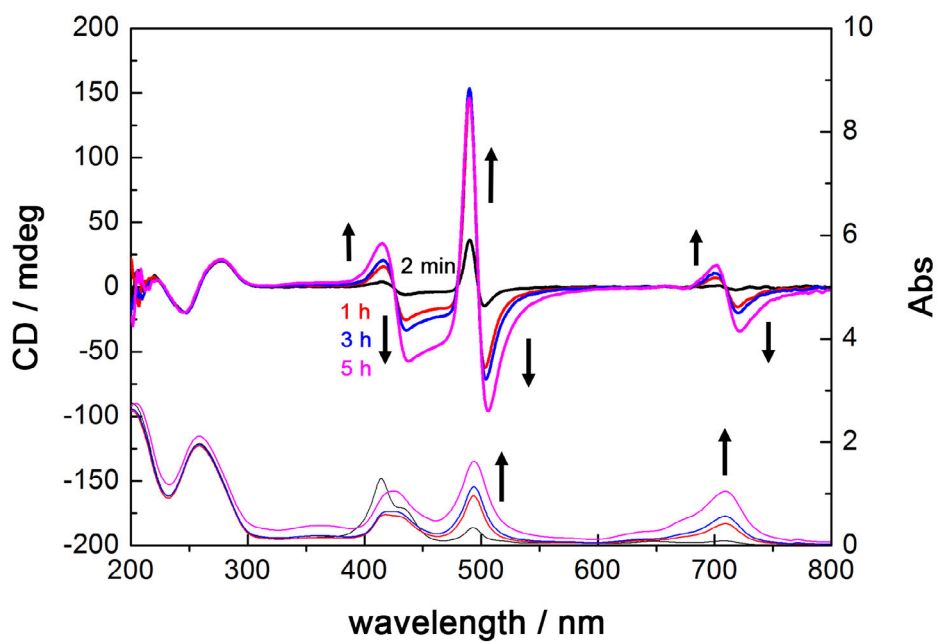


Fig. S10. CD and UV/Vis spectra of the reaction solution at the initial stage of 2 min (black line), 1 h (red line), 3 h (blue line) and 5 h (pink line).

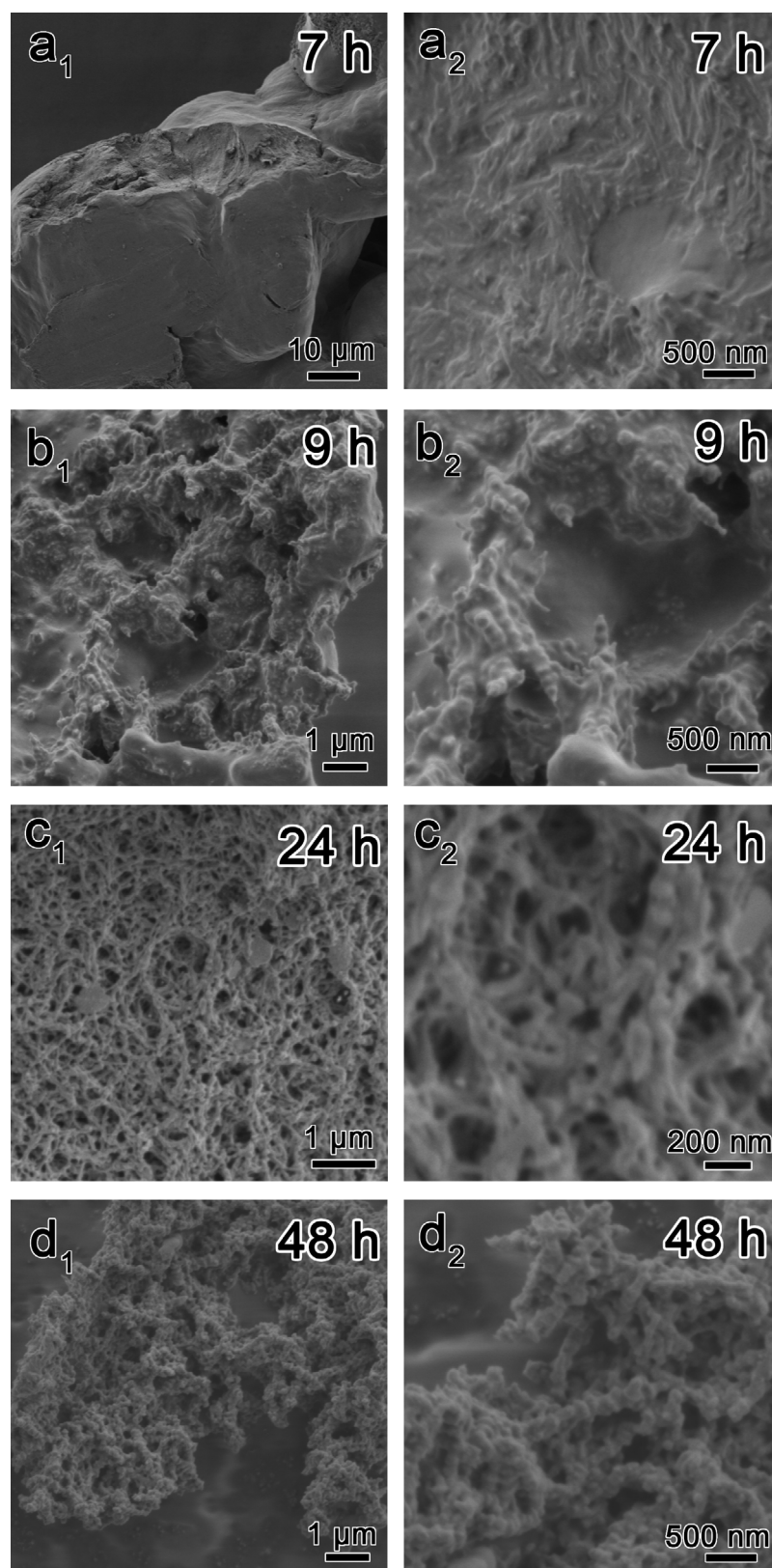


Fig. S11. Low and high magnification SEM images of DTHF at different reaction stage of 7 h (a₁ and a₂), 9 h (b₁ and b₂), 24 h (c₁ and c₂) and 48 h (d₁ and d₂).

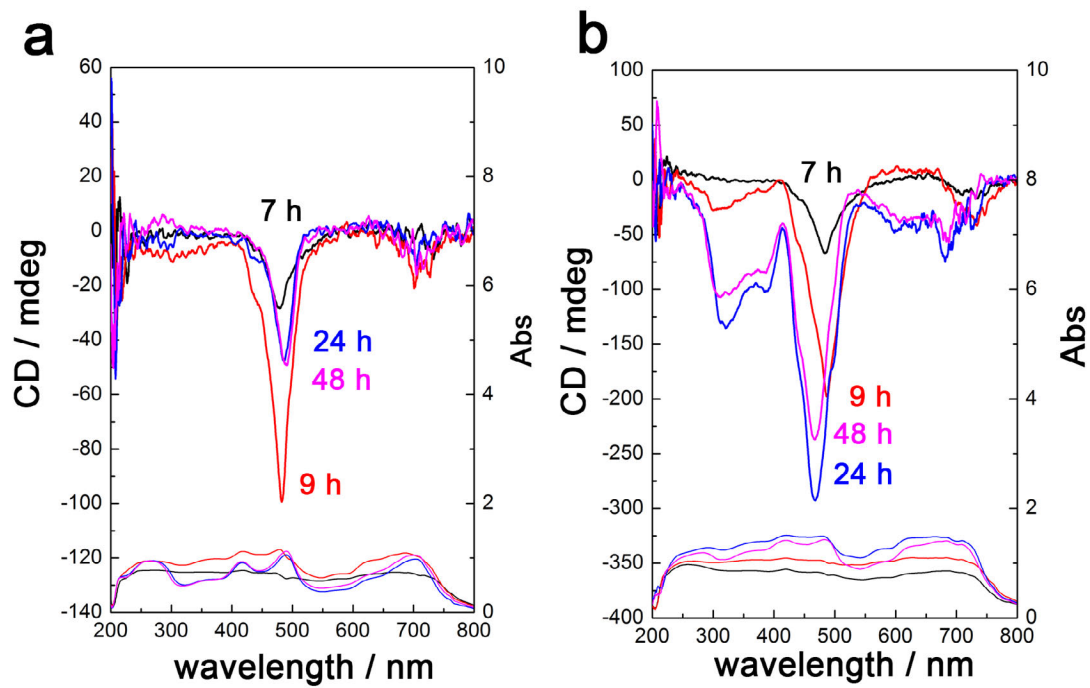


Fig. S12. DRCD and UV/Vis spectra of the DTHF at different reaction stage of 7 h (black line), 9 h (red line), 24 h (blue line) and 48 h (pink line), measured under dry (a) and wet (b) states.