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Electronic Supplementary Information

Dynamic Evolution of Supramolecular Chirality Manipulated by H-Bonded Coassembly and Photoisomerism

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Experimental section

Materials

Solvents were purchased from Guoyao Chemical Reagent Co. Ltd, Shanghai. 4-Hydroxybenzyl cyanide (Aladdin, 98%, Shanghai), *p*-Dimethylaminobenzaldehyde (Aladdin, 98%, Shanghai) 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, Heowns, 98%, Tianjin), Ethyl bromoacetate (Mreda, 98%, Beijing), L-Alaninemethylester hydrochloride (Aladdin, 98%, Tianjin), L-Valine methyl ester hydrochloride (Bidepharm, 97%, Shanghai), L-Phenylalanine methyl ester hydrochloride (Bidepharm, 97%, Shanghai), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, Bidepharm, 98%, Shanghai), 4-Dimethylaminopyridine (DMAP, Bidepharm, 98%, Shanghai), L-Hydroxybenzotriazole (HOBT, Heowns, 98%, Tianjin). Both chemicals and solvents were used without further purification. The water used in experiment is deionized (DI) water.

Characterizations

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AVANCE III HD 400 MHz (Switzerland) spectrometer at room temperature with tetramethylsilane (TMS) as reference and dimethyl sulfoxide-d (DMSO-d_6) as solvent, respectively. High-resolution mass spectrometry (HR-MS) was performed on Agilent Q-TOF 6510 MS spectrometer (America). Transmission electron microscope (TEM) images were measured by a HITACHI JEM-100CX II electron microscope (Japan). The samples for TEM detection were dropped in the copper grid and air-dried. Scanning electron

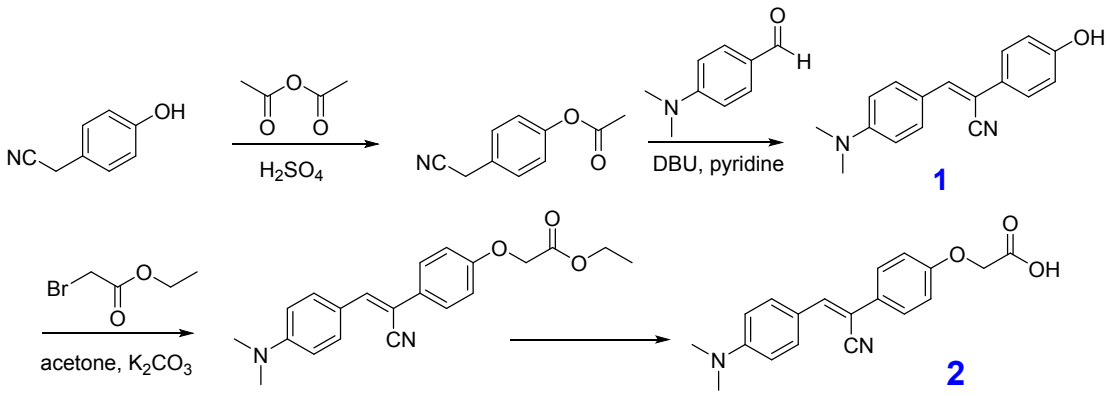
microscope (SEM) images were measured by a Zeiss scanning electron microscope. The samples for SEM detection were dropped in the silicon pellet, dried and then sprayed by the gold before detection. AFM testing was conducted with a Bruker Bioscope Resolve and operated in tapping mode at ambient temperature (America). Specification of the tip is OMCL-AC160TS-R3. The AFM sample was dropped on the mica wafer and air-dried. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku SmartLab polycrystall X-ray diffraction (Japan) with Cu Kα radiation (λ = 0.15406 nm, voltage 45 KV, current 200 mA, power 9 KW). The samples were casted onto cover glasses (18 mm × 18 mm) and dried to form thin films. FT-IR spectra were characterized on a Bruker Tensor II (America), and KBr was used as the disperse media. FL and UV-Vis spectra were recorded via RF-6000 and UV-1900 from SHIMADZU (Japan), respectively. A certain concentration of solution was poured into a quartz cuvette (3 mm path-length) to detect the absorption peaks and fluorescent emission. Circular dichroism (CD) and circularly polarized luminescence (CPL) spectra were measured with Applied Photophysics Chirascan V100 (England).

Self-assembly

Target molecules (Ala-CS, Val-CS and Phe-CS) were dissolved into DMSO as 0.1 M stock solutions, respectively. A self-assembly system of Ala-CS was achieved (3×10^{-3} M) by injecting certain volume stock solution (30 μl for instance) into bulky DI water (970 μl for instance), which was followed by aging at ambient conditions for at least 8 h before testing. MA was dissolved into DI water as 2×10^{-2} M stock solution. Ala-CS/MA coassembly systems with various ratios were achieved by mixing certain volume MA stock solution with target molecular stock solution which concentration was fixed as 3×10^{-3} M and the adding moderate amount of DI water. TPMA was dissolved into DMSO as 0.1 M stock solution. Ala-CS/TPMA coassembly systems with various ratios were achieved by mixing certain volume TPMA stock solution with target molecular stock solution which concentration was fixed as 3×10^{-3} M and the adding moderate amount of DI water. The self-assemble and coassemble systems of Val-CS and Phe-CS were formed via the same method.

Synthesis of Ala-CS, Val-CS and Phe-CS

A precursor, N,N-dimethyl-4-hydroxy cyanostilbene (**1**) was prepared according to references[S1]. Then K_2CO_3 (1.38 g, 10 mmol) and ethyl bromoacetate (200 mg, 1.2 mmol) were added into the solution. And the mixture was reflux overnight with N_2 protection. The resultant solution was filtered and subjected to rotary evaporation to remove all solvents. The product was hydrolyzed in THF/H_2O = 1:1 mixed solvent with LiOH (300 mg). The mixture was extracted via CH_2Cl_2, dried via anhydrous sodium sulfate and subjected to rotary evaporation to remove all solvents to obtain precursor **2**.



Synthesis of Ala-CS

L-alanine methyl ester hydrochloride (417 mg, 1 mmol), **2** (322 mg, 1 mmol), EDC (400 mg, 2 mmol), HOBT (0.1 mmol), DMAP (0.1 mmol) and triethylamine (0.2 mL) were added into the mixture. After 24 h reaction, crude products were extracted by DCM/water for three times. The combined DCM solution was washed by saturated NaCl aqueous solution, which was subjected to column purification to obtain the pure product Ala-CS. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ = 8.39 (d, 1H), 8.14 -7.49 (m, 5H), 7.06 (d, 2H), 6.81 (d, 2H), 4.58 (s, 2H), 4.31 (p, 1H), 3.02 (s, 6H), 1.39-1.31 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ = 174.29, 167.69, 158.13, 151.95, 141.78, 131.27, 128.36, 126.79, 121.58, 119.85, 115.78, 112.10, 102.74, 67.21, 47.79, 30.89, 17.61. HRMS (TOF) m/z $[M+H]^+$, calcd for $C_{22}H_{23}N_3O_4$, 394.1689; found, 394.1859. Val and Phe were fabricated via the same method. Val-CS: ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ =12.79 (s, 1H), 8.16 (d, 1H), 7.84 (d, 2H), 7.70 (s, 1H), 7.61 (d, 2H), 7.04 (d, 2H), 6.80 (d, 2H), 4.66 (s, 2H), 4.23 (m, 1H), 3.01 (s, 6H), 1.36 (s, 1H), 0.90 (d, 6H). ^{13}C NMR (100 MHz, DMSO-d_6, 273 K) δ = 173.20, 168.13, 158.23,

151.95, 141.74, 131.27, 128.29, 126.78, 121.59, 119.85, 115.65, 112.10, 102.75, 67.00, 57.38, 30.32, 19.60, 18.45. HRMS (TOF) m/z $[M+H]^+$, calcd for $C_{24}H_{27}N_3O_4$, 422.2002; found, 422.2163. Phe-CS: ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ = 8.27 (d, 1H), 7.91-7.78 (m, 2H), 7.69 (s, 1H), 7.63-7.50 (m, 2H), 7.28-7.18 (m, 5H), 6.99-6.90 (m, 2H), 6.85-6.77 (m, 2H), 4.58-4.45 (m, 3H), 3.02 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ = 173.13, 167.83, 158.05, 151.96, 141.75, 138.10, 131.28, 129.72, 129.64, 128.66, 128.34, 126.86, 126.79, 121.59, 119.84, 115.69, 112.11, 111.75, 102.77, 67.49, 67.16, 53.70, 36.96, 34.86, 30.89, 25.60. HRMS (TOF) m/z $[M+H]^+$, calcd for $C_{28}H_{27}N_3O_4$, 470.2002; found, 470.2167.

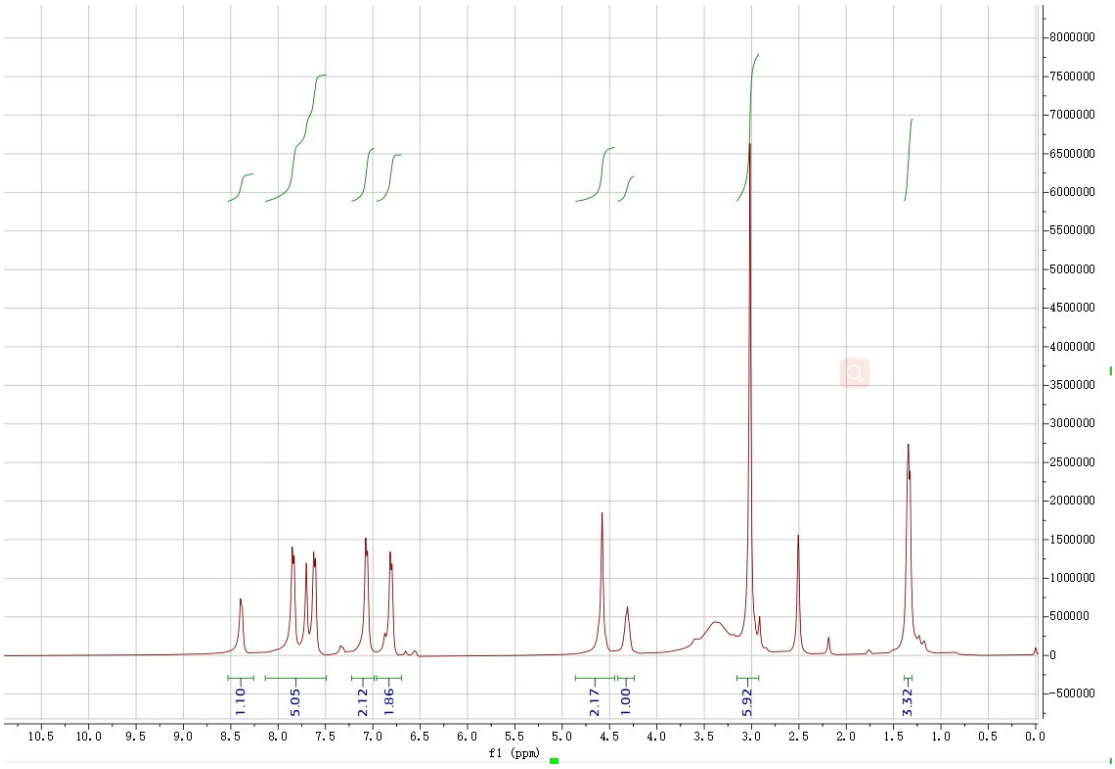


Figure S1. ^1H NMR spectrum of Ala-CS.

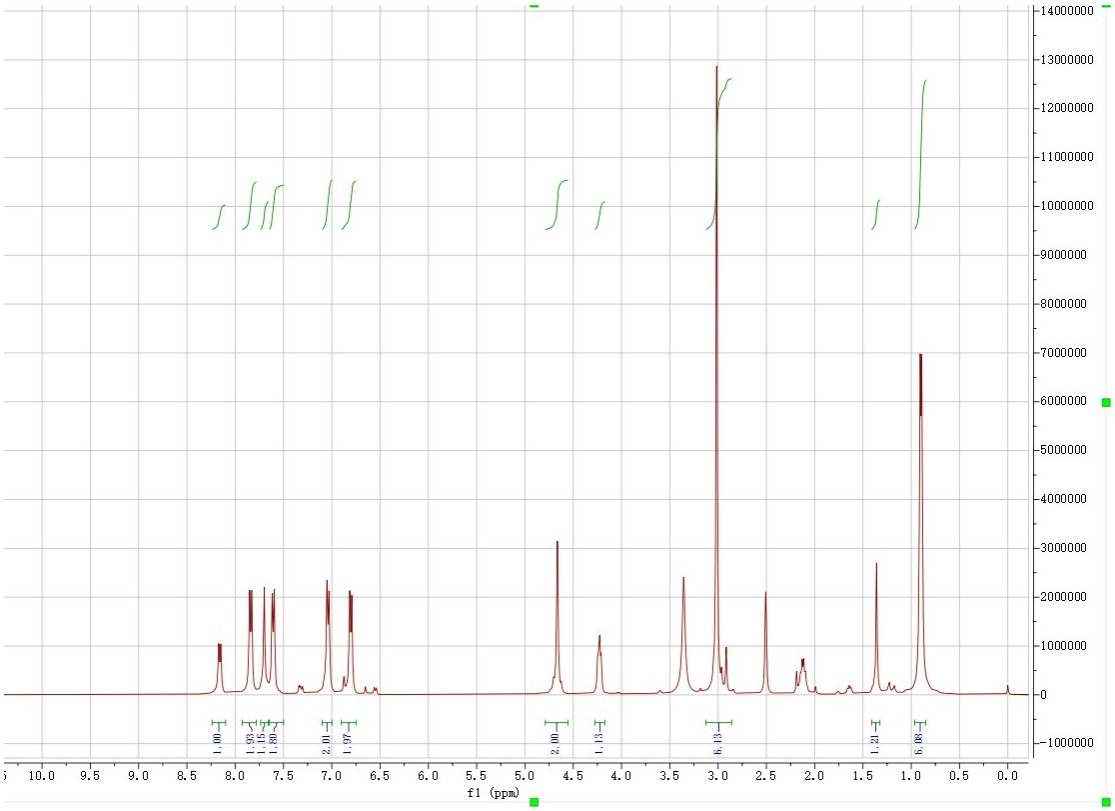


Figure S2. ^{1}H NMR spectrum of Val-CS.

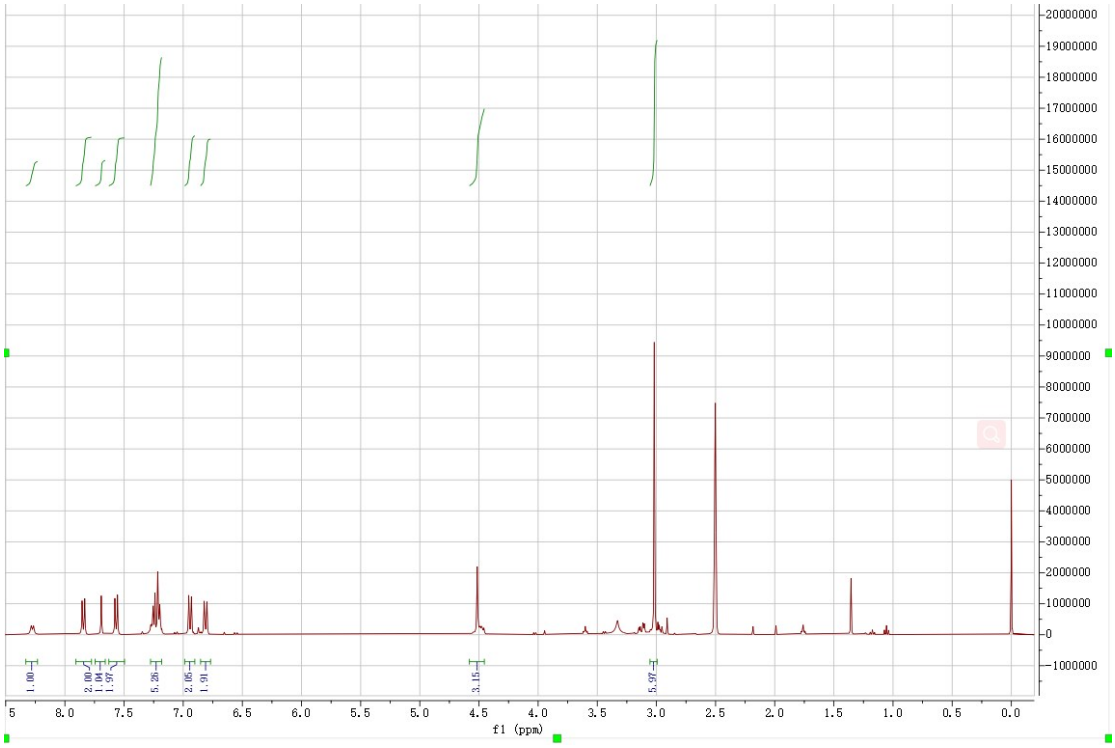


Figure S3. ^{1}H NMR spectrum of Phe-CS.

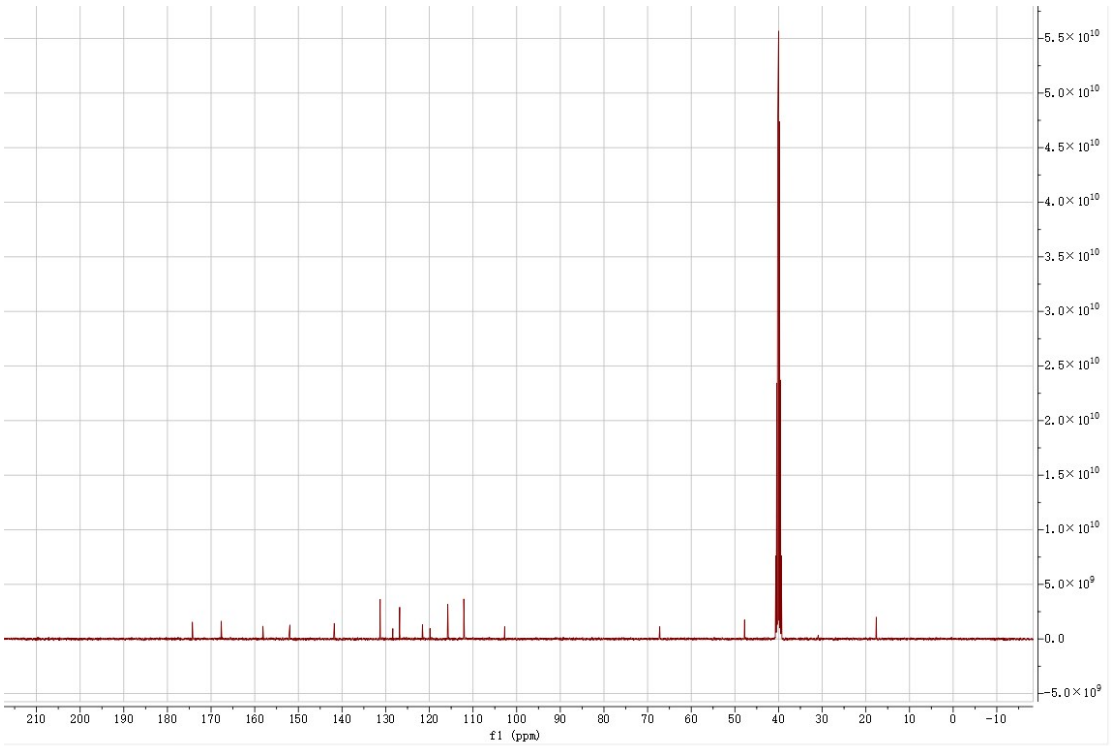


Figure S4. ^{13}C NMR spectrum of Ala-CS.

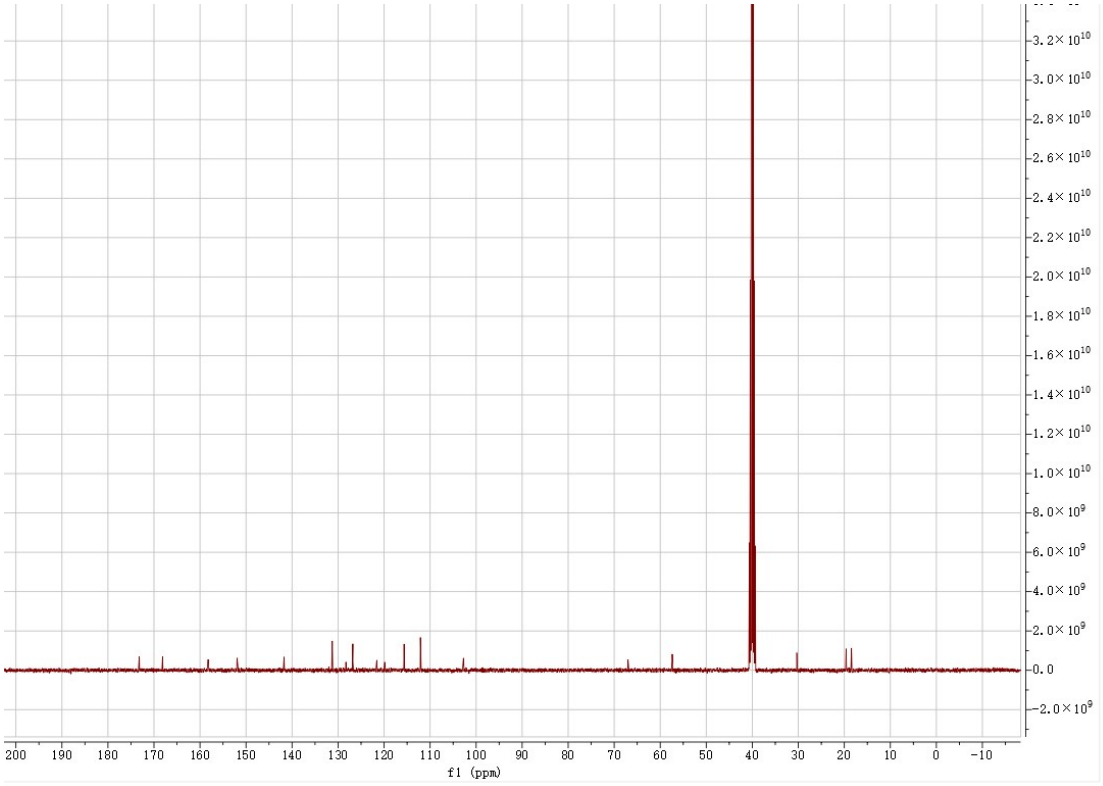


Figure S5. ^{13}C NMR spectrum of Val-CS.

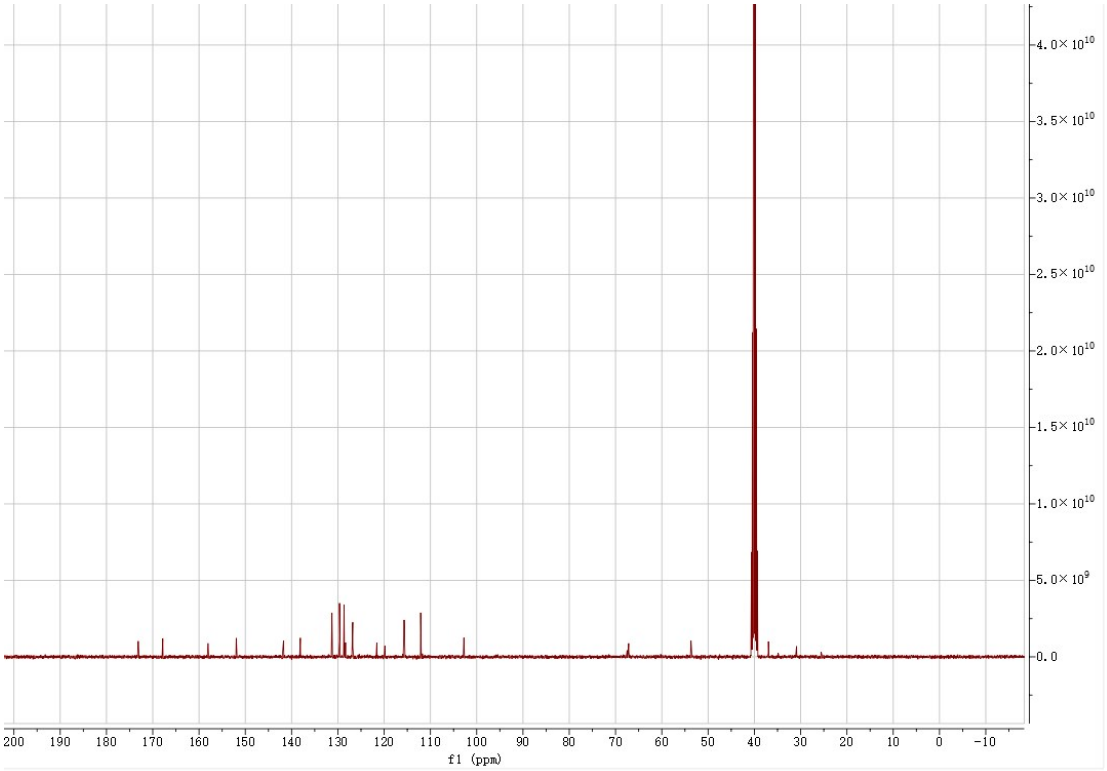


Figure S6. ^{13}C NMR spectrum of Phe-CS.

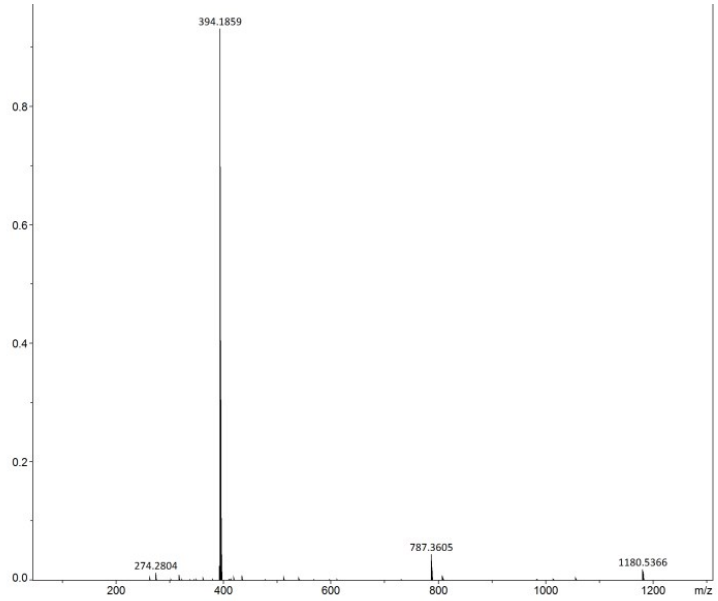


Figure S7. HRMS of Ala-CS.

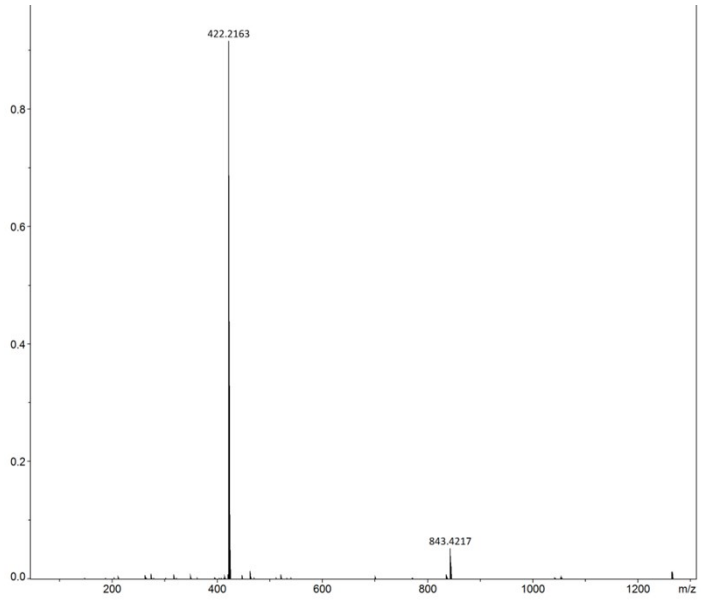


Figure S8. HRMS of Val-CS.

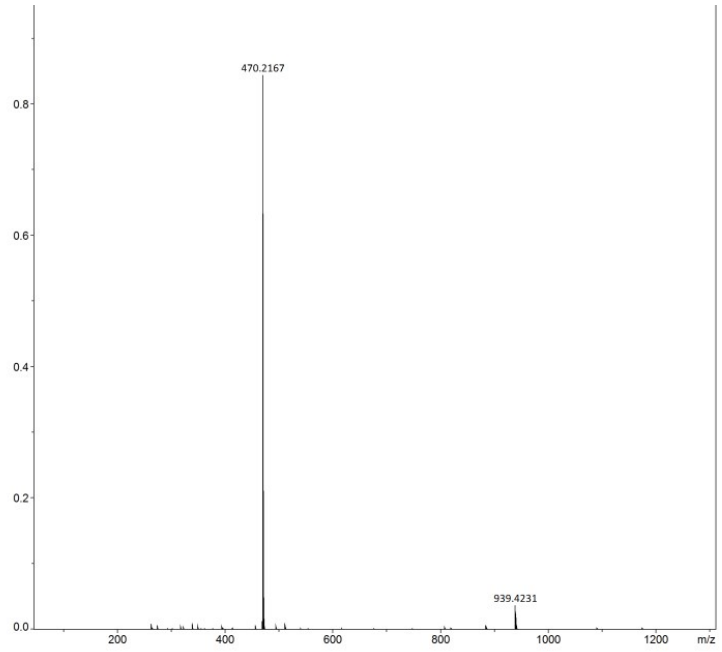


Figure S9. HRMS of Phe-CS.

MD simulation

The native structures of Ala-CS, Val-CS, Phe-CS, MA and TPMA were built from the GaussView6.0 program. The obtained configurations of Ala-CS, Val-CS, Phe-CS, MA and TPMA were initially optimized and the electrostatic potential (ESP) was simultaneously calculated by Hartree-Fork method, respectively. The 6-31G(d) basis set was employed in Gaussian 16 program. The Antechamber program was used to fit the restrained electrostatic potential (RESP) charge, and then the general Amber force

field (GAFF) was adopted to parameterize the bonded interaction of Ala-CS, Val-CS, Phe-CS, MA and TPMA for subsequent MD simulations. All MD simulations were implemented with the GROMACS 2020 program. The water solvent simulated was the SPC216 model. The organic molecules and solvent were coupled to temperature in 298K. The long-range electrostatic interaction was calculated by the particle mesh Ewald (PME) method. The cut-off distance for non-bonded interactions was set to 1 nm. Energy minimization was conducted using the steepest descent algorithm before performing dynamic simulations. MD simulations for two systems were carried out for 50 ns with a time step of 0.001 ps per integration step under the ensemble conditions of T = 298 K. All simulations were visualized using VMD program.

Three models (denoted as Ala-CS, Ala-CS/MA and Ala-CS/TPMA) solvated in water box were prepared. For the initial configuration of each system, the Ala-CS, Ala-CS/MA and Ala-CS/TPMA) were solvated in SPC216 water boxes. The simulation box sizes were 10×10×10 nm^3 with a total of 150 (Ala-CS), 150/150 or 100/300 (Ala-CS/MA) and 150/50 (Ala-CS/TPMA) molecules in the respective systems. Val-CS and Phe-CS systems were calculated via the same method.

Quantum mechanical calculation of ECD spectrum

ECD spectra of single molecule and partial assembly were calculated with quantum mechanical methods. Absolute configurations were extracted directly from crystal structures. These structures were optimized with the rcam-b3lyp/6-311 g(d) basis set of the Gaussian 16 program to obtain a low-energy conformation. Then, the same basic set and method were utilized to calculate ECD spectra based on time-dependent density functional theory (TDDFT). Finally, over the whole available spectrum range, the experimental absorption/ECD spectra were compared, and the wavelength shift was applied to correct the calculated absorption/ECD spectra considering a systematic over/underestimation of transition energies.

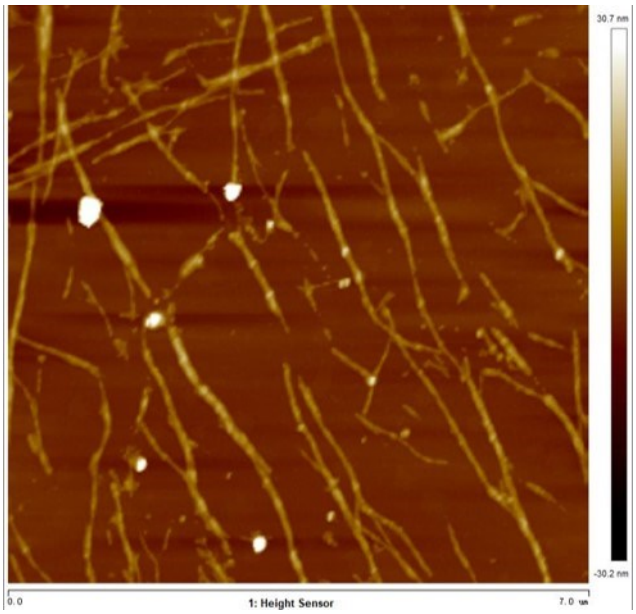


Figure S10. AFM image of Ala-CS/TPMA (3 mM: 3 Mm) in water.

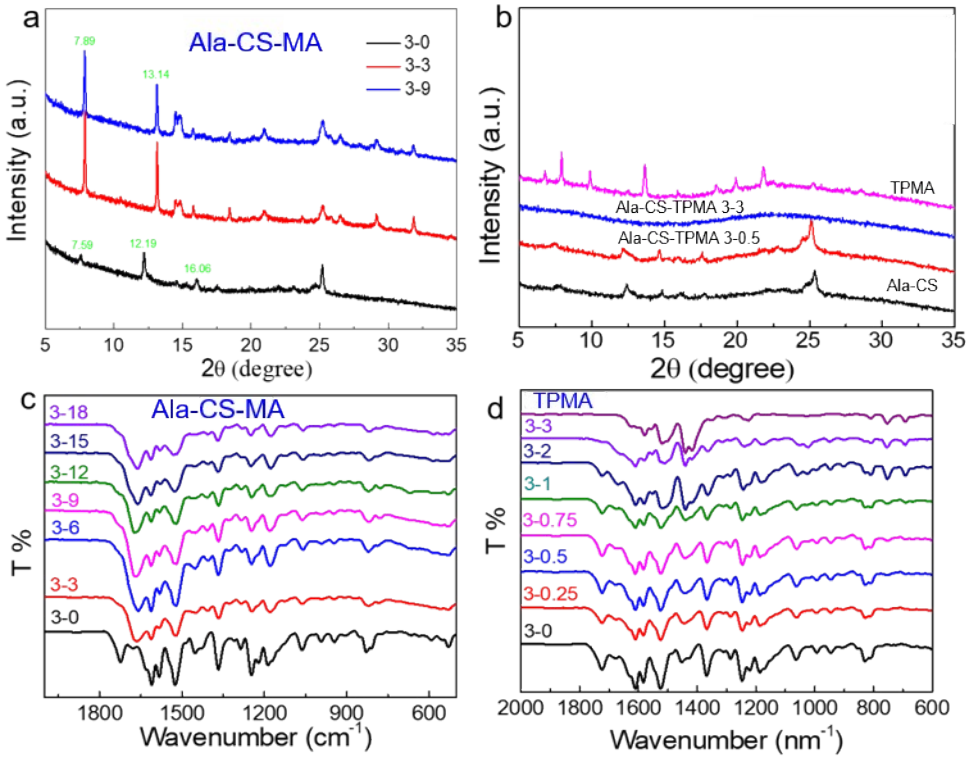


Figure S11. XRD patterns of Ala-CS with variable (a) MA and (b) TPMA molar ratios. FT-IR spectra of (c) Ala-CS/MA and (d) Ala-CS/TPMA assemblies.

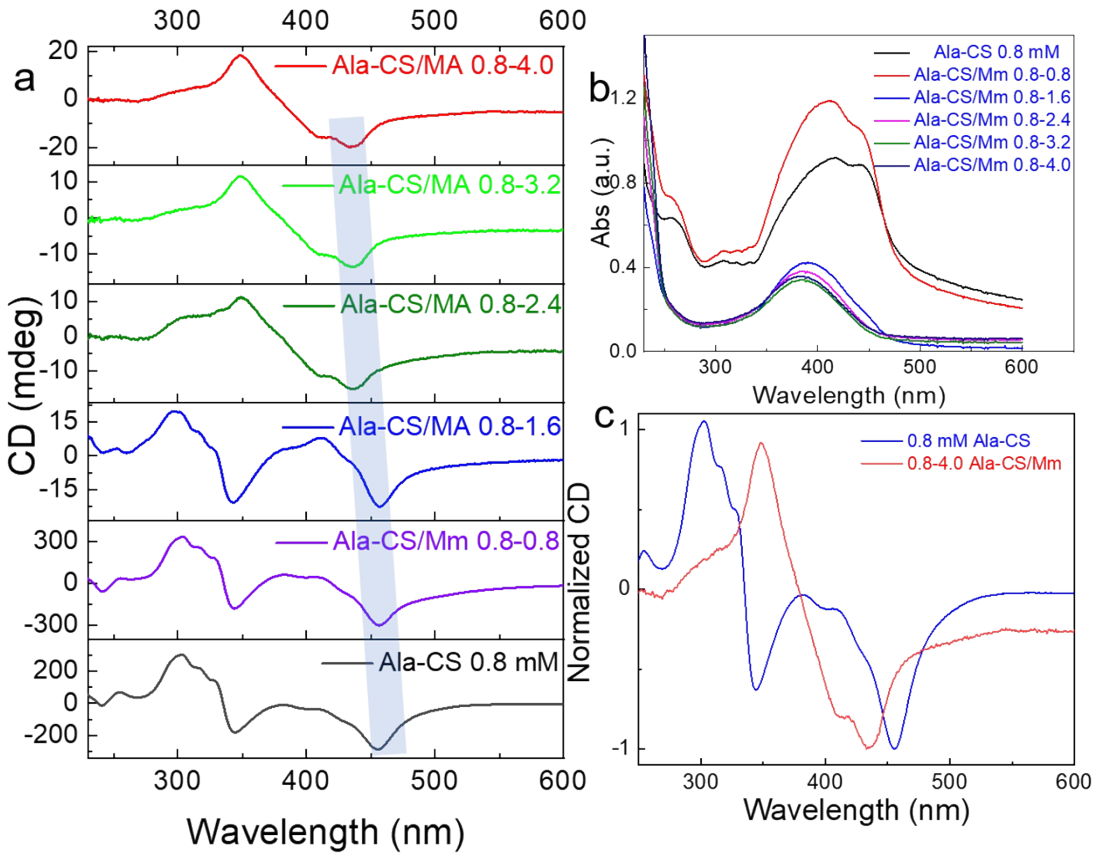


Figure S12. (a) CD spectra and (b) corresponding UV-Vis spectra of Ala-CS with various concentration of MA. (c) CD spectral comparison of self-assembled Ala-CS with coassembled Ala-CS/MA (0.8 mM : 4.0 mM).

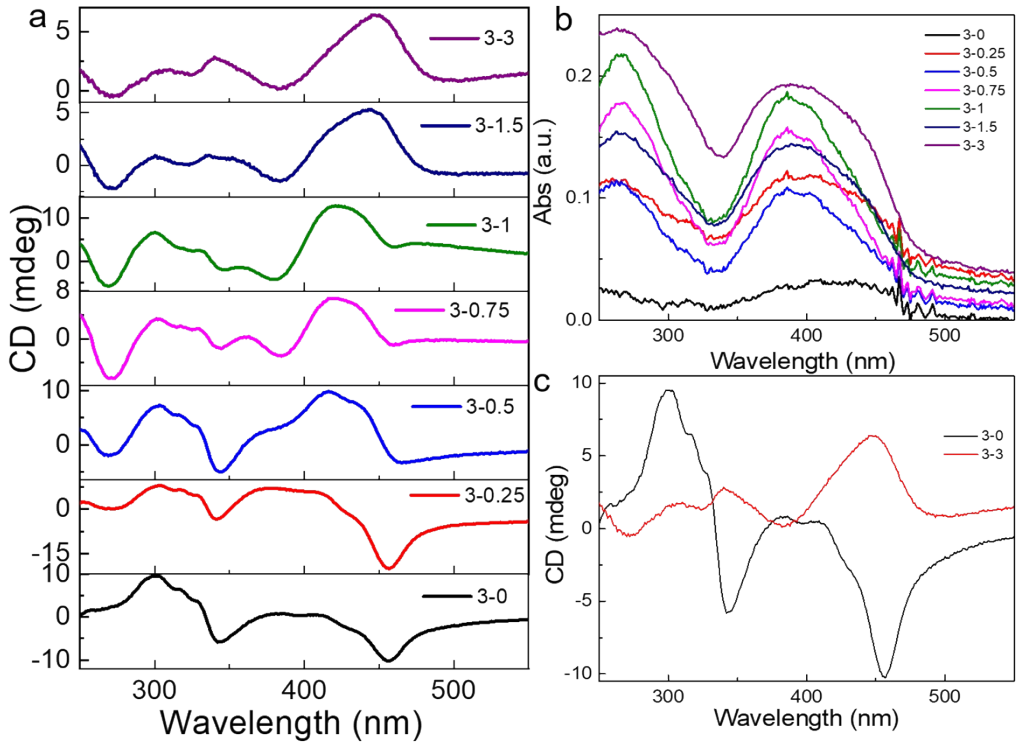


Figure S13. (a) CD spectra and (b) corresponding UV-Vis spectra of Ala with various

concentration of TPMA. (c) CD spectral comparison of self-assembled Ala-CS with coassembled Ala-CS/TPMA (3: 3).

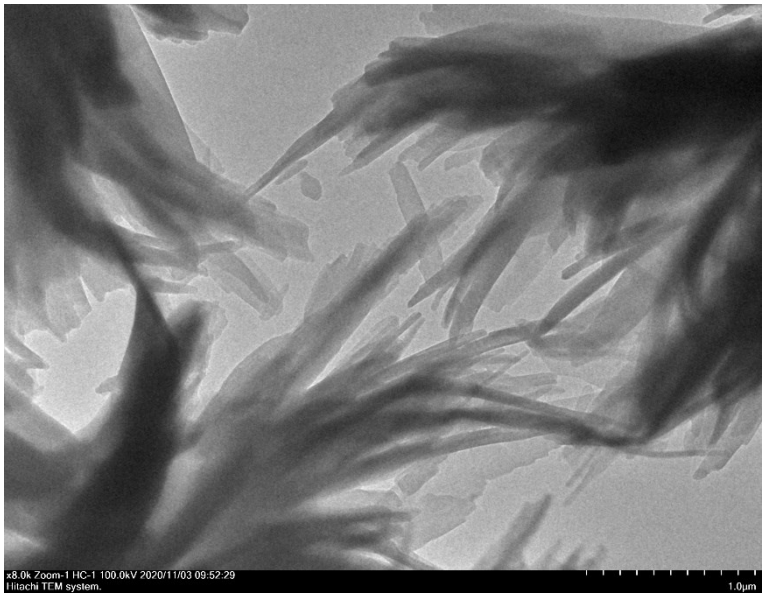


Figure S14. TEM image of Val-CS/TPMA (3:3) in water.

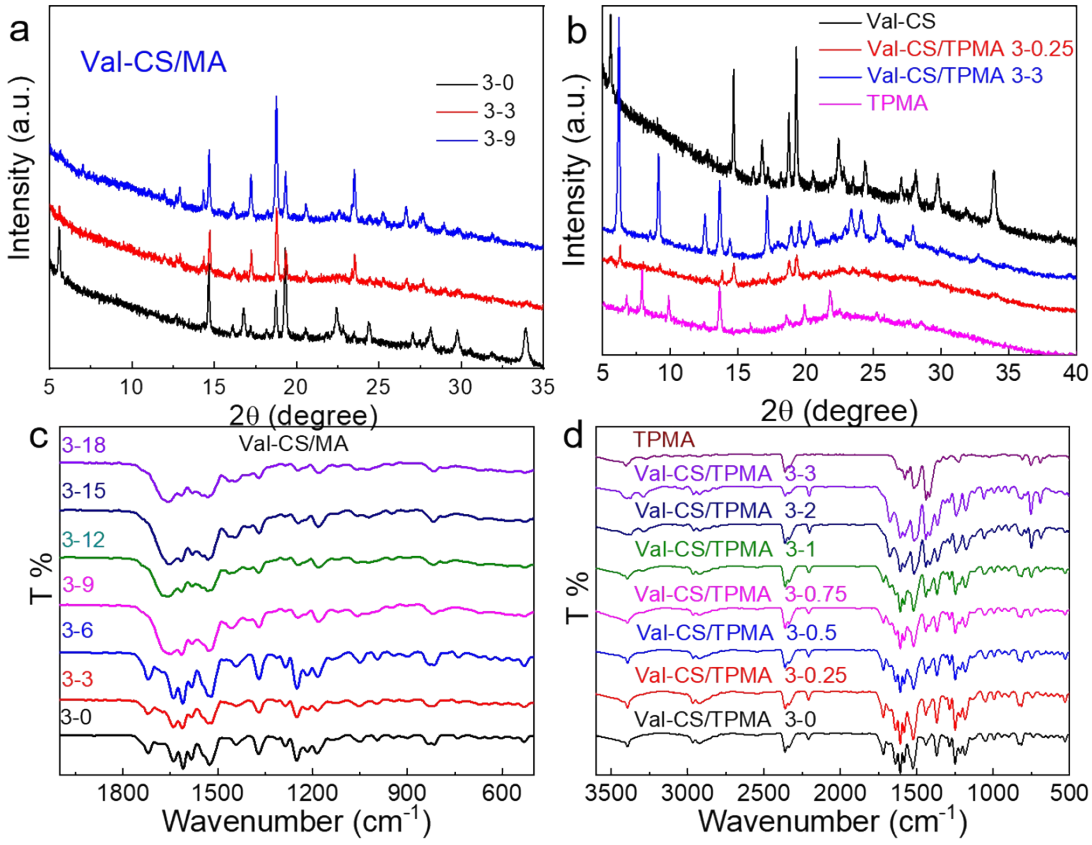


Figure S15. XRD patterns of Val-CS with variable (a) MA and (b) TPMA molar ratios. FT-IR spectra of (c) Val-CS/MA and (d) Val-CS/TPMA assemblies.

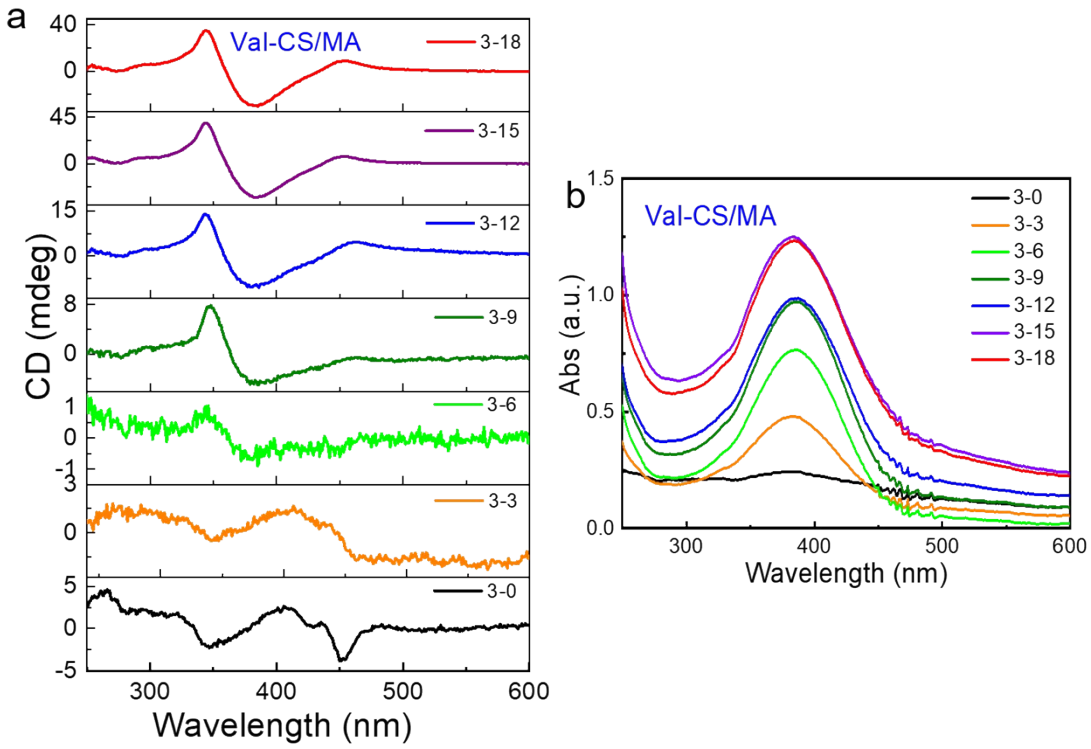


Figure S16. (a) CD spectra and (b) corresponding UV-Vis spectra of Val-CS (3 mM) with various concentration of MA.

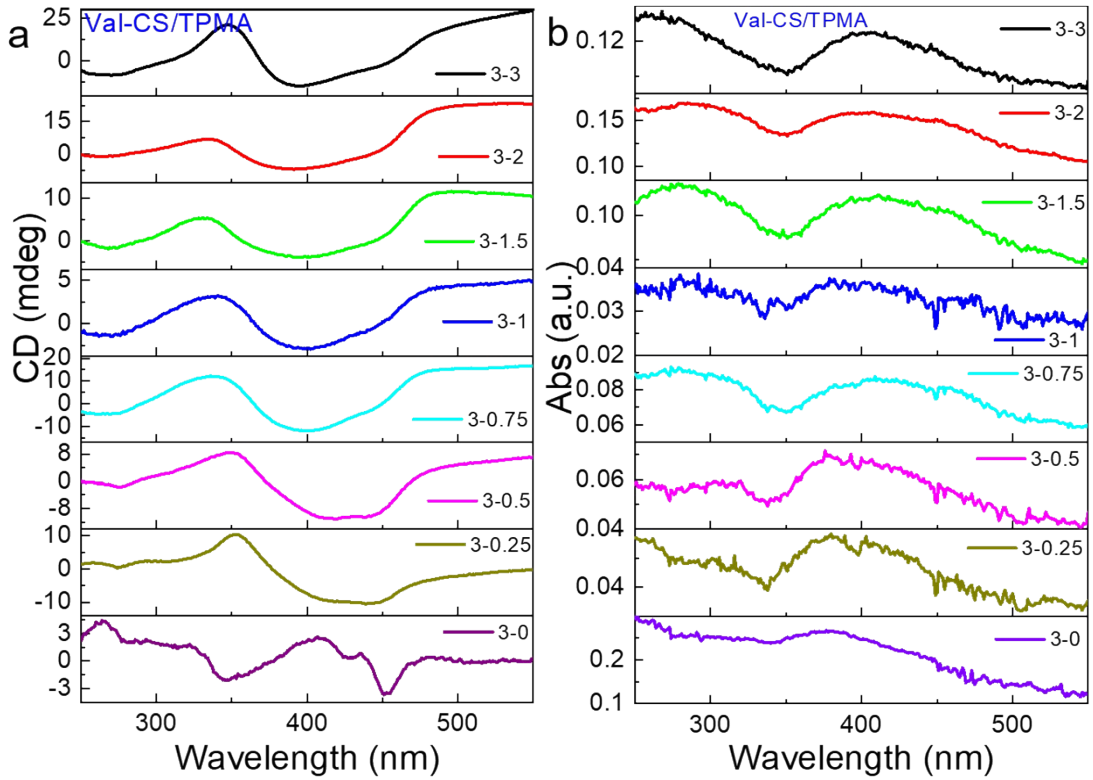


Figure S17. (a) CD spectra and (b) corresponding UV-Vis spectra of Val-CS (3 mM) with various concentration of TPMA.

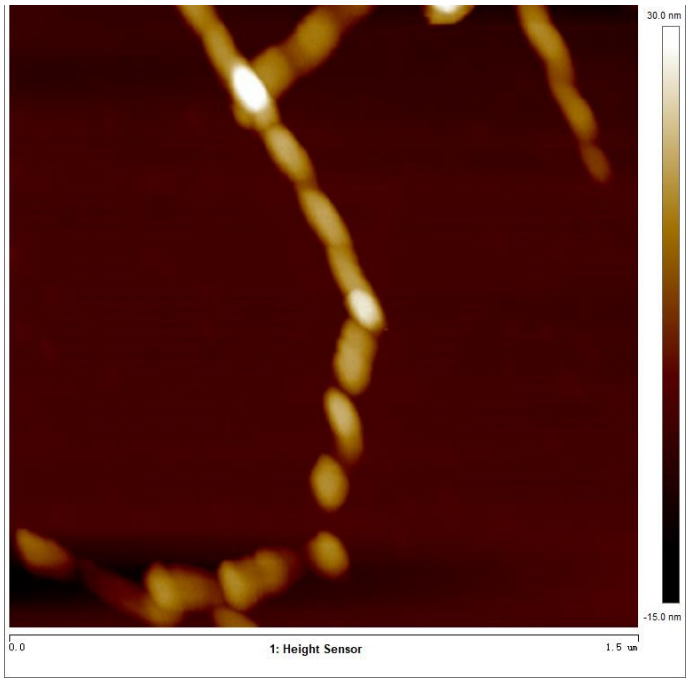


Figure S18. AFM image of Phe-CS/TPMA coassembly (3:9) in water.

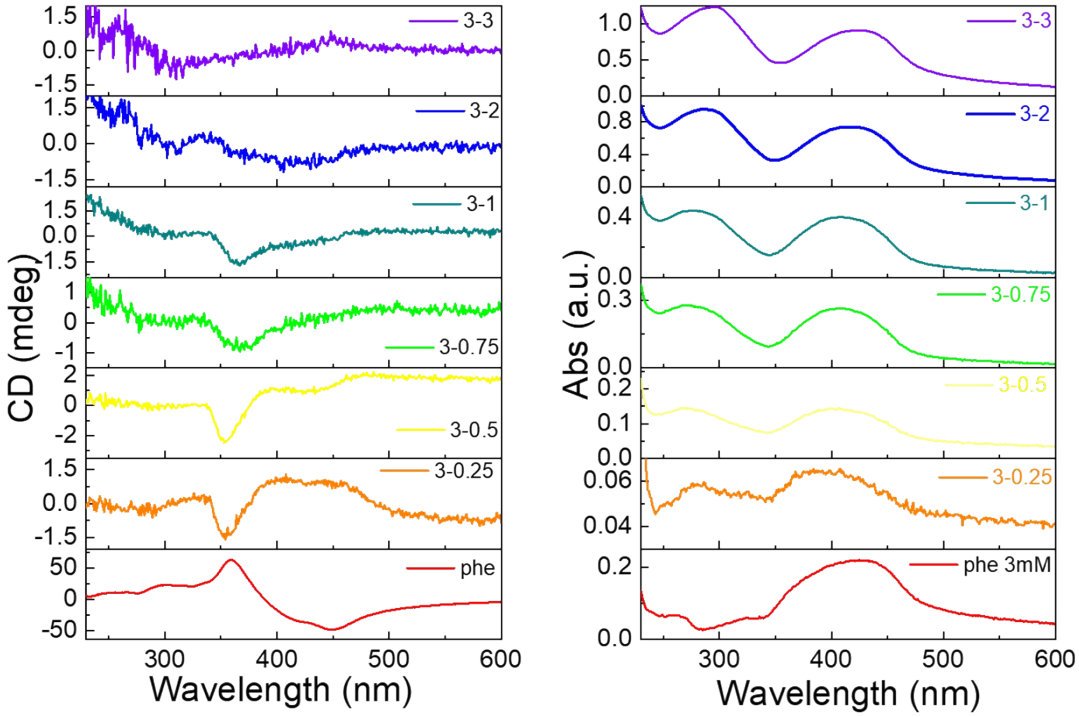


Figure S19. CD spectra and corresponding UV-Vis spectra of Phe-CS with various amount of TPMA in water.

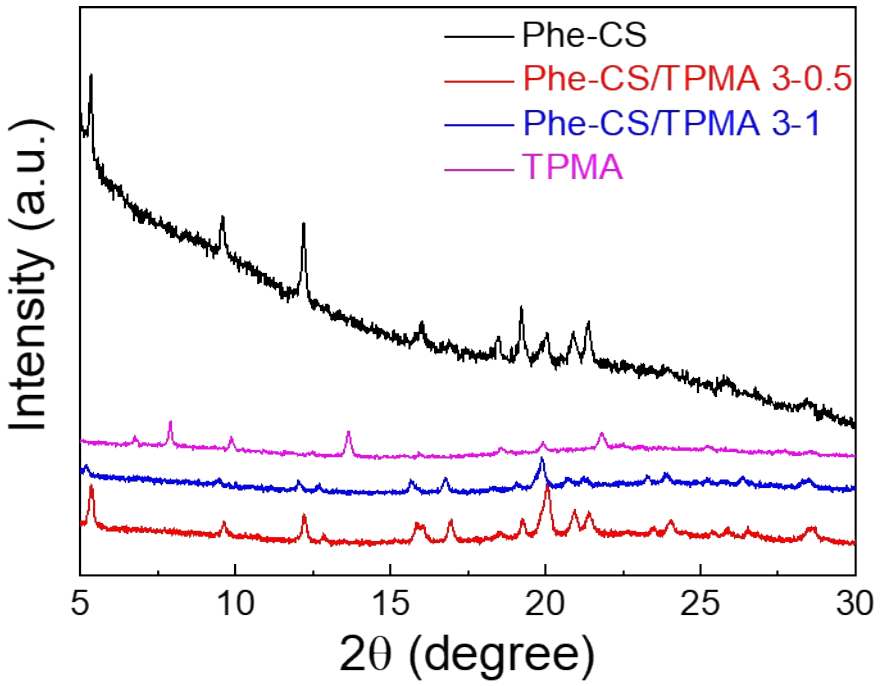


Figure S20. XRD patterns of different samples with variable Phe-CS molar ratios.

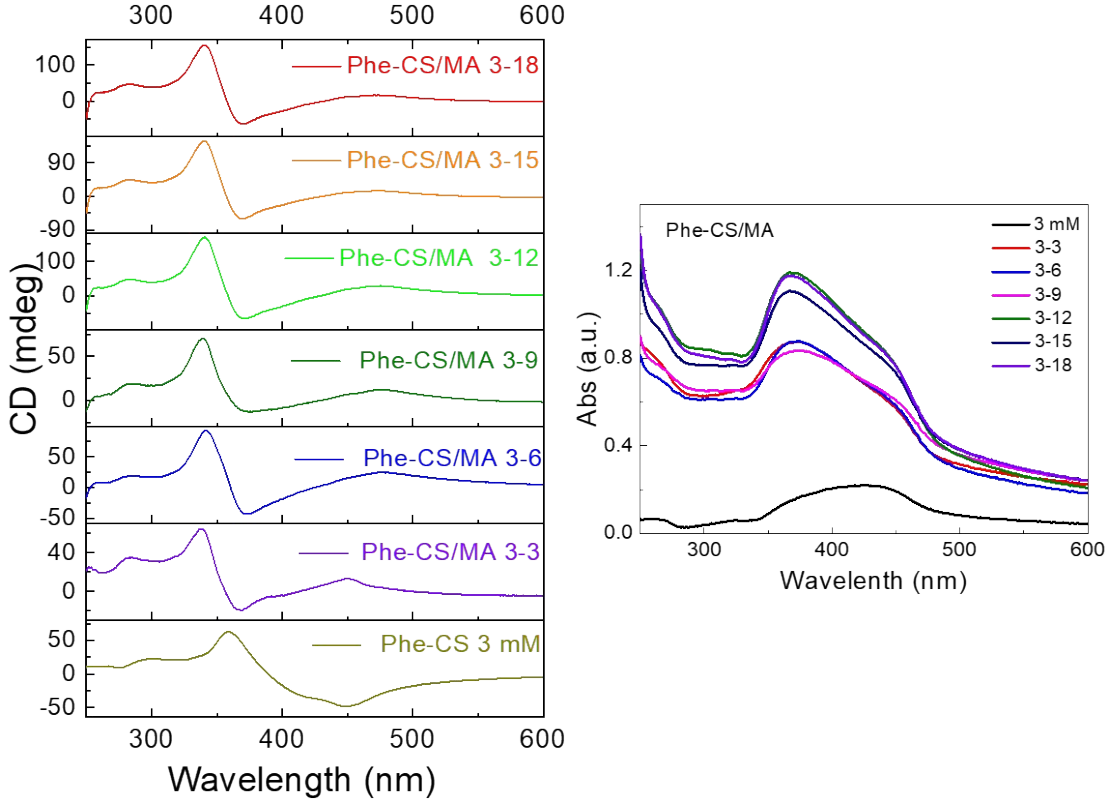


Figure S21. CD spectra and corresponding UV-Vis spectra of Phe-CS with various amount of MA in water.

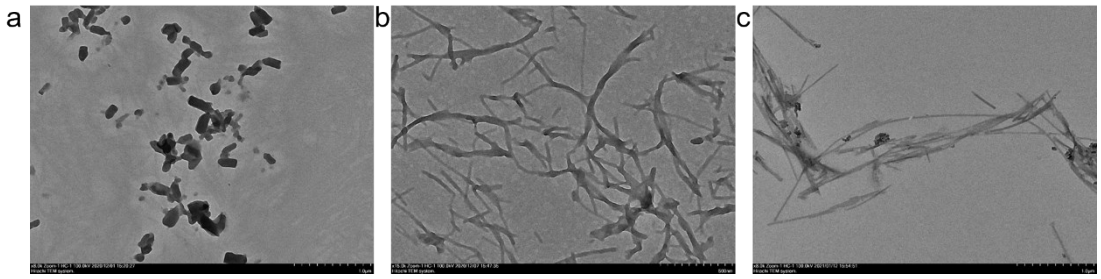


Figure S22.TEM images upon blue light irradiation of (a) Ala-CS self-assembly (0.3 mM in water), (b) Ala-CS/MA (3:9) and (c) Ala-CS/TPMA (3:3) (445 nm, 1.5 h).

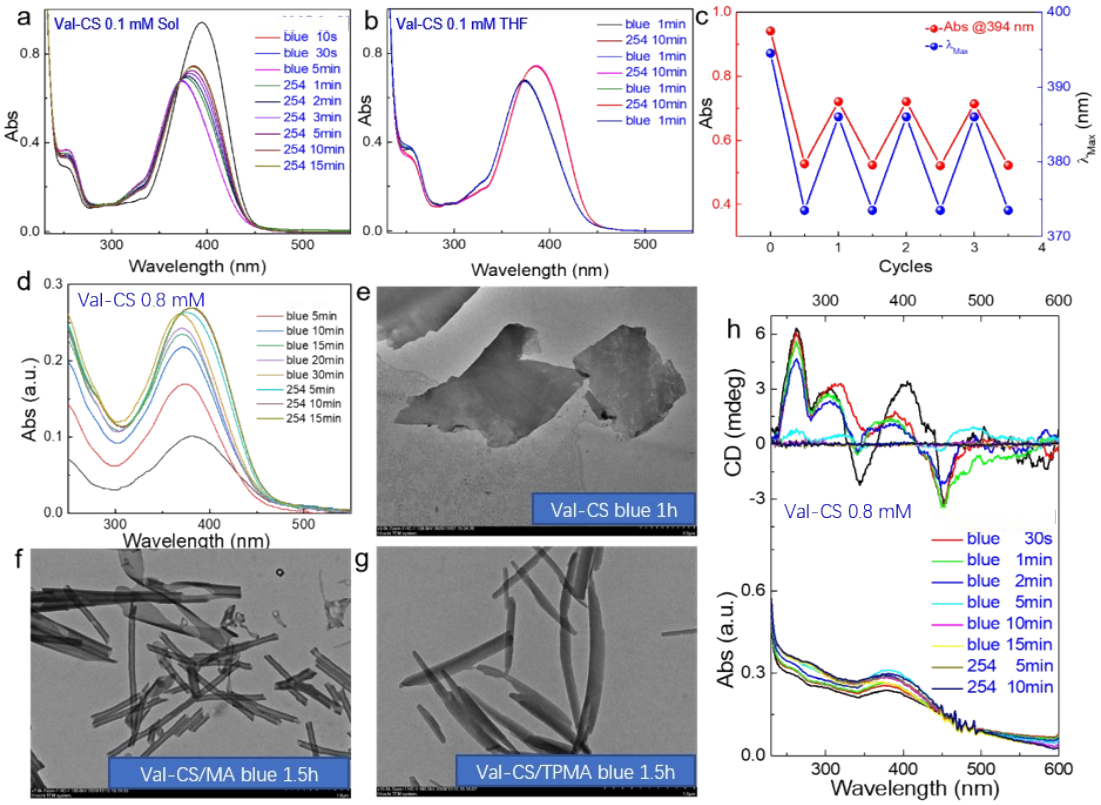


Figure S23. (a-c) Absorption spectra changes upon different light irradiation of Val-CS (0.1 mM in THF). (d) Absorpation spectra changes upon different light irradiation of Val-CS aggregations in water (3 mM). TEM images upon blue light irradiation of (e) Val-CS self-assembly (0.3 mM in water), (f) Val-CS/MA (3:9) and Val-CS/TPMA (3:1) in water (445 nm, 1.5 h). (h) CD spectra variations upon different light irradiation of Val-CS self-assembly (0.3 mM in water).

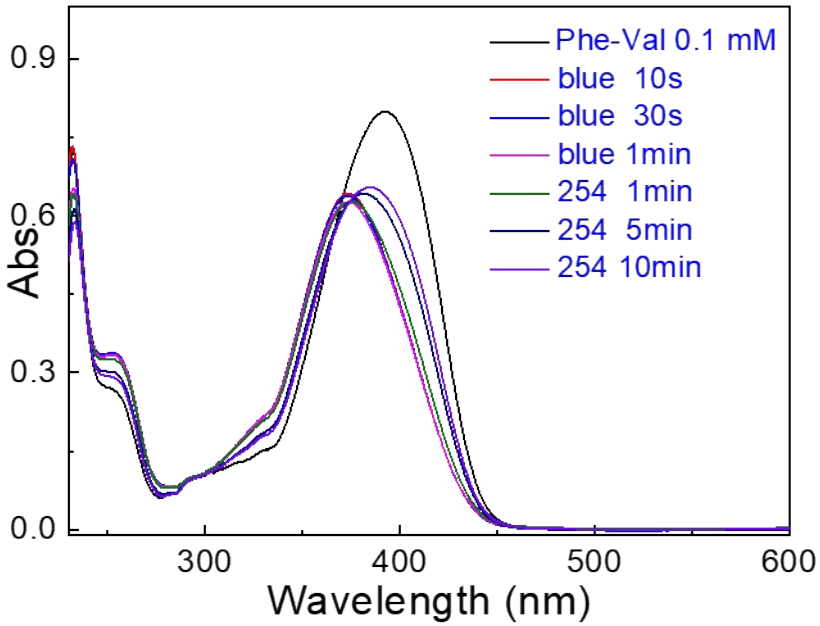


Figure S24. Absorption spectra changes upon different light irradiation of Phe-Val (0.1 mM in THF)

References

S1. Palakollu, V., Vasu, A. K.; Thiruvenkatam, V.; Kanvah, S. A Sensitive AIEE Probe for Amphiphilic Compounds. *New J. Chem.*, **2016**, 40, 4588.