#### **Experimental section**

# Materials

All chemicals were purchased from Guoyao Chemical Reagent Co. Ltd, Shanghai, which were used without further purification. PG and NG was synthesized according to the previous report <sup>S1</sup>. TBIB was synthesized according to our previous report.<sup>s2</sup>

#### Characterization

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were measured on a Bruker AM-400 spectrometer at room temperature with tetramethylsilane (TMS) as the reference. Scanning electron microscope (SEM) images were attained by a Zeiss scanning electron microscope. The samples for SEM detection were dropped in the silicon pellet, dried and then sprayed by the gold. Transmission electron microscope (TEM) were measured on a JEM-100CX II electron microscope. The samples for TEM detection were dropped in the copper grid and air-dried. X-ray diffraction (XRD) patterns were collected on a German Bruker/D8 Advanced diffractometer with Cu Ka radiation ( $\lambda$ = 0.15406 nm, voltage 40 KV, current 40 mA). The samples were casted onto cover glasses (18 mm  $\times$  18 mm) and dried to form thin film. AFM testing was conducted with a Veeco Nanoscope Multimode III SPM and operated in tapping contact mode at ambient temperature. The AFM sample was dropped on the mica wafer and dried. Rheological properties were measured by a Thermo Haake RS6000 rheometer with cone and plate geometry (35 mm diameter, 0.105 mm cone gap). The frequency spectra were conducted in the linear viscoelastic regime of the samples determined from dynamic strain sweep measurements at 25 °C. CD and CPL were collected with an Applied Photophysics ChirascanV100 model. FT-IR was characterized on a Bruker ALPHA model, and KBr was used as the disperse media.

# **Sample preparation**

PG, NG and TBIB were respectively dissolved in DMSO as concentrated stock solutions (100 mM). In order to trigger the coassembly, a certain amount of stock solutions was mixed together, followed by the addition of DI water. Taking the preparation of PG/TBIB coassembly as an example. PG and TBIB were dissolved in DMSO(1 mL) separately to obtain the stock solutions (100 mM). Then, PG stock

solution (30  $\mu$ L) and TBIB stock solution (10  $\mu$ L) were taken out by pipettes into a 1 mL vial, followed by gentle shaking to mix homogeneously. DI water (960  $\mu$ L) was added by a pipette into the stock solution mixture. The vial was sealed by a cap and parafilm, and slightly shaken to make a homogenous phase(PG: TBIB = 3mM:1mM). An aging period at least for 8 h at room temperature was applied. Dried samples for FT-IR tests were prepared by centrifuging assemblies (5000 rpm, 10 mins), followed by air-drying. XRD samples were obtained by drying centrifuged samples on glass slides.

# **Computational Methods**

## **Structural Parameterization for EGCG**

The geometric structure of NG, PG and TBIB were built from the GaussView06 program. [S3] The configuration optimization of three molecules were performed by Hartree-Fork method [S4, S5] at the B3LYP/6-31G\*(d) basis by employing Gaussian16 program. [S6] Then the electrostatic potential (ESP) was can be obtained at the same parameters correspondingly. To acquire the topology files, the Antechamber program in the Amber-Tools package was used to fit the restrained electrostatic potential (RESP) charge [S7, S8], and then the Generalized Amber Force Field (GAFF) was adopted to parameterized for bonded interaction of EGCG molecule for subsequent MD simulations.

#### **Design of system model**

To elaborate the effect of self-assembly mechanism, two systematic models of NG-TBIB and PG-TBIB were set up for the study with various molar ratios of NG/PG to TBIB, which were 3:1. As shown in **Scheme S1**, for the initial coordinate of each system, the pre-assembled 15TBIB-45NG and 15TBIB-45PG were respectively immersed in the centre of suitable simulation box filled with TIP3P water, of which the minimal distance from the solute to the box wall was 1.2 nm. The simulation box sizes were  $5.35 \times 5.43 \times 8.85$  nm<sup>3</sup> and  $5.23 \times 5.87 \times 8.83$  nm<sup>3</sup>, with a total of 25650 and 27453 atoms in the respective systems.



Scheme S1. The initial structure of pre-assembled NG-TBIB and PG-TBIB systems.

# 1.3 MD Simulation methods for pre-assembled system.

We performed all MD simulations using GROMACS 5.1.2 [S9] and adopted the AMBER03 force field to parameterize the fibrillar  $A\beta_{17-42}$  pentamer [S10]. The solvent used was the TIP3P water model [S11] and each system was neutralized by five counterions (Na<sup>+</sup>). The temperature at 310 K was controlled by the V-rescale temperature coupling. [S12] The barostat with constant pressure of 1 atm was described by the Berendsen pressure coupling method. [S13] The LINCS algorithm was utilized to restrain the atomic bonds of the organic molecules. [S14] The cut-off distance for non-bonded interactions was set at 1 nm. The electrostatic interactions were treated with particle mesh Ewald (PME) method with a cut-off of 1 nm. [S15] Periodic boundary conditions were conducted in all three directions. Energy minimization was carried out using the steepest descent algorithm prior to performing dynamic simulations. MD simulations for the systems were carried out for 1000 ns with a time step of 0.002 ps per integration step.



Fig. S1 FT-IR spectra of PG/TBIB coassembled system.



Figure S2. FT-IR spectra of NG/TBIB coassembled system.



Figure S3. Small and wide angle XRD patterns of PG-TBIB coassembled system.



Figure S4. XRD pattern of PG/NG/TBIB (3:3:1) coassembly.



Fig. S5 TEM images of different self-assembly modalities.



Fig. S6 Enlarged SEM image of NG/TBIB coassembly (3:1).



Fig. S7 Enlarged SEM image of PG/TBIB coassembly (3:1).





Fig. S8 Enlarged SEM image of PG/NG/TBIB coassembly (3:3:2).

Figure S9. CPL and fluorescent spectra of PG/TBIB coassembly. Ex = 350 nm



Figure S10. CPL and fluorescent spectra of PG/NG/TBIB coassembly. **Results and Discussion rergarding MD simulations** 

# The Hydrogen Bond evolution



**Figure S11**. (a) The average root-mean-square deviations (RMSD) of NG-TBIB system during MD simulation. The hydrogen bond number of TBIB-SOL (b), NG-SOL (c), NG-TBIB (d). (e) The representative snapshots of the equilibrium configuration. NG and TBIB are shown in light pink and green, respectively, and the hydrogen bond were highlighted in blue.



**Figure S12.** (a) The average root-mean-square deviations (RMSD) of PG-TBIB system during MD simulation. The hydrogen bond number of PG-SOL (b), TBIB-SOL (c), PG-TBIB (d). (e) The representative snapshots of the equilibrium configuration. PG and TBIB are shown in light purple and green, respectively, and the hydrogen bond were highlighted in blue.

# The energy evolution



**Figure S13**. The Coulomb energy of (a1) NG, (b1) TBIB, (c1) NG-SOL, (d1) TBIB-SOL and (e) NG-TBIB; The van der Waals (vDW) energy of (a2) NG, (b2) TBIB, (c2) NG-SOL, (d2) TBIB-SOL and (f) NG-TBIB.



**Figure S14**. The Coulomb energy of (a1) PG, (b1) TBIB, (c1) PG-SOL, (d1) TBIB-SOL and (e) OG-TBIB; The van der Waals (vDW) energy of (a2) PG, (b2) TBIB, (c2) PG-SOL, (d2) TBIB-SOL and (f) PG-TBIB.

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