Supporting Information

Edge-directed Rapid Chiral Assembly of Gold Nanorods by 2D Hexagonal Nanosheets of Helical Poly(phenylacetylene)s and the Synergistic Communication of Circular Polarized Luminescence

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1. Experimental Section

1.1 Materials

$HAuCl_4$ (98%, Innochem), cetyltrimethylammonium bromide (CTAB, 98%, Sigma-Aldrich), sodium borohydride ($NaBH_4$, 98%, Acros), silver nitrate ($AgNO_3$, 99%, Sigma-Aldrich), *L*-ascorbic acid (AA, 99%, Adamas), trisodium citrate (99%, Alfa Aesar), thiol PEG (E350: M_W = 350 g/mol, E1k: M_W = 1000 g/mol, E2k: M_W = 2000 g/mol, E5k: M_W = 5000 g/mol, Aladin), tetrahydrofuran (THF, HPLC, ThermoFisher), ethanol (EtOH, HPLC, Concord Technology (Tianjin) Co.)

1.2 The synthesis of gold nanorods (GNRs) and gold nanoparticles (GNPs)

GNRs were prepared by a seed-mediated growth approach.[1] A seed solution was firstly prepared. 250 μL of 10 mM $HAuCl_4$ was added to 7.5 mL of a 100 mM CTAB solution at 30 °C. After mixing, 600 μL of 10 mM $NaBH_4$ solution was added, followed by rapid stirring for 3 min. The Au seed solution was stored at 30 °C for 2 h. Secondly, a growth solution was prepared. 4 ml of 10 mM $HAuCl_4$, 10 mM $AgNO_3$, 480 μL of 100 mM AA and 96 uL of CTAB-capped gold seed solution were added into 80 ml of 100 mM CTAB solution. The solution was reacted for 24 h. GNRs were centrifuged three times (9000 rpm, 10 min) and redispersed in 1 mM CTAB solution. The amount of $AgNO_3$ for G1 is 240 μL, G2 is 320 μL, G3 is 400μL, G4 is 480 μL and G5 is 560 μL.[2]

GNPs were prepared by reduction of $HAuCl_4$ using trisodium citrate by previously reported approach.[3] 1.5 mL of 1 wt% trisodium citrate solution was quickly added to a boiling solution of 100 mL of 0.25 mM $HAuCl_4$. The solution was refluxed for 20 min. The reaction solution was subsequently cooled down to room temperature.

1.3 Surface modification of GNRs and GNPs

1 mL of 0.1 wt% PEG and 1mL of GNRs or GNPs were mixed and stirred overnight, and then centrifuged at 9000 rpm for 5 minutes. 1997 μL of the supernatant was discarded, and 1997 μL of H_2O was added. Repeat this process once, and retain 3 μL of the concentrated solution. G2-E5k-E1k was modified twice. 1 mL of 0.1 wt% E1k and 3 μL of G2-E5k were mixed and stirred 1 h. The next steps are the same as before.

1.4 The self-assembly of PPA

Synthesis of PPAs (P1, P2 and P3) and preparation of hexagonal assemblies were reported previously.[4] P1 assemblies: the solution of P1 in THF (0.40 mg/mL, 1 mL in 5 mL vial) was added with EtOH dropwise without stirring at 25°C. When the EtOH fraction reached 33% (500 μL). When the P1 assembly is placed for 1 hour, 24 h or 3 days, assemblies of different diameters can be obtained. P2 assemblies: the EtOH fraction reached 66% (1500 μL). P3 assemblies: the EtOH fraction reached 13% (150 μL).

Synthesis of P4 and preparation of fiber assemblies were also reported previously.[5] P4 assemblies: P4 was dissolved in THF (0.15 mg/mL, 1 mL in 5 mL vial) at 25°C.

1.5 Preparation of PPAs/GNRs (or GNPs) co-assemblies

The co-assemblies were obtained by blending the PPAs and GNRs (or GNPs) concentrated solution. Taking *R*-P1/G2-E1k (the concentration of *R*-P1 is 0.4 mg/mL) as an example. Add 3 μL H_2O to 3 μL G2-E1k, followed by adding 100 μL THF/EtOH (THF/EtOH = 2/1 (*V/V*)). The co-assembly can be obtained by adding the G2-E1k organic solution into the solution of *R*-P1 assemblies and stirring.

1.6 Computer simulations

1.6.1 Simulation of PPAs:

The molecular modeling and molecular mechanics calculations were conducted in the Material Studio10 software (version 5.0; Accerlys Software Inc.). The methods and parameters are consistent with those reported by our research group before.[4]

1.6.2 Simulation of GNRs:

To gain deeper insights into the mechanism of the chirality of the obtained CD signals, finite element method (FEM) simulations were carried out by using commercial software COMSOL Multiphysics software package. The CD signals were calculated as a difference in extinction of the left- and right-

circularly polarized light (*L*- and *R*-CPL). The assembled nanostructures were randomly dispersed in solution, and therefore we average the calculated values over the six directions of incident light. For simplicity, we used the GNRs-trimer as the model (illustrated in Fig. 3f). The GNRs were modeled with a diameter of 20 nm and the length of 60 nm. The refractive index was set as 1.40.

2. Characterization

2.1 Techniques

Circular dichroism (CD) spectra were obtained on a Jasco J-810 spectropolarimeter using THF as solvent at 25°C and analyzed by the associated J800 software. When the sample concentration was 0.4 mg/mL, using 0.5 mm cell (0.2 mg/mL: 1 mm cell, 0.1 mg/mL: 2 mm cell, 0.067 mg/mL: 3 mm cell, 0.04 mg/mL: 5 mm cell, 0.02 mg/mL: 10 mm cell). UV-Vis absorption measurements were carried out on a Varian Cary 1E UV-Vis spectrometer. Transmission electron microscope (TEM) images were obtained using Thermo Fisher Scientific (FEI) Tecnai T20 operating at 200 kV. The images were taken with Gatan Oneview IS camera. TEM samples were prepared by adding 10 μl solution to the thin pure carbon film coated Cu grids of 300 mesh and blotting away the excess solution with dust-free paper. Dynamic light scatter (DLS) was carried out on a commercialized spectrometer nano Omni from Brookhaven Instrument Corporation. Scanning electron microscope (SEM) images were obtained on a Zeiss Merlin Compact field-emission scanning electron microscope operated at 10 KV. The samples were prepared by dipping a drop of solution onto hydrophilic cleaning silica wafers kept at 25 °C and the solutions were absorbed by dust-free paper after 15 s. The wafers were stuck to the conductive adhesive. Atomic force microscope (AFM) images were performed on a Bruker BioScope Resolve under ScanAsyst mode in the air. The ScanAsyst-Air probe was used and has one silicon tip on the nitride lever with a reflective Al back side. Scan rate 1 Hz, Peak Force Amplitude 150 nm, Peak Force Frequency 2 kHz. The AFM samples were prepared on silica wafers, the method of which is similar to the SEM ones. Vibrational circular dichroism (VCD) spectra were obtained on a Jasco FVS-6000 in a 0.15 mm CaF_2 cell. All VCD spectra were collected for 10 h at a resolution of 4 cm^{-1}. Infrared spectra (IR) were performed on a Nicolet Fourier transform Magna-IR 750 spectrophotometer. Laser Raman spectra were recorded on a Thermo Scientific Nicolet NXR FT-Raman Spectrometer. Circularly polarized luminescence (CPL) spectra were carried out on a JASCO CPL-200 spectrofluoropolarimeter. An FLS980 Steady State & Time-resolved Fluorescence Spectrometer (Edinburgh Instruments Ltd.) was used to measure the photoluminescence intensity.

2.2 Supporting Figures

Table S1. Information of ***R*-P1**, **P2**, **P3** and **P4**.

Sample[a)]	[M]/[I]	M_n[b)](kDa)	$Đ$	DP	Yield[c)] (%)	T_d[d)](°C)
R-$P1_{44}$	120	69.8	1.09	44	61.1	341
S-$P1_{44}$	118	69.5	1.06	44	55.9	331
$P2_{34}$	120	54.3	1.16	34	66.3	337
$P3_{43}$	120	68.5	1.12	43	70.1	351
$P4_{451}$	500	1025	1.26	451	90.2	386

[a.a)] 30 °C, THF. [b)] Determined by SEC in THF using PS standards. [c)] Isolated yields after purification from MeOH while all the conversion of monomers are above 99% determined by ^{1}H NMR. [d)] 5% weight loss temperature under nitrogen at a heating rate of 10 °C/min.

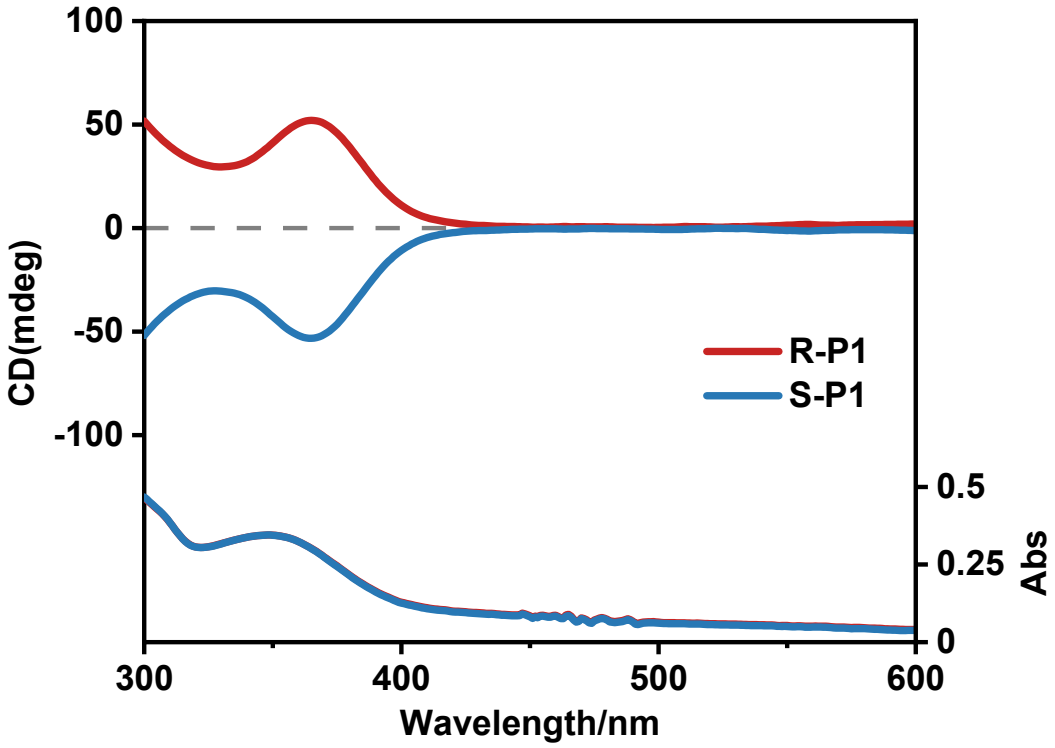
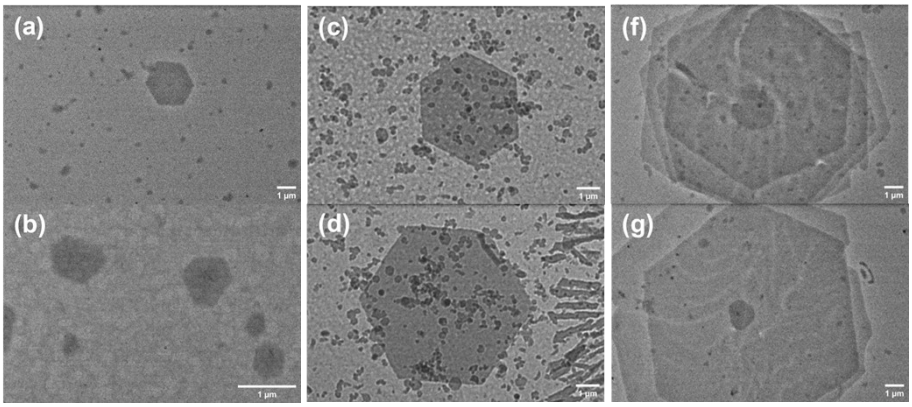


Figure S1. CD and UV-vis spectra of ***R*-P1** and ***S*-P1** in THF, c_0 = 0.20 mg/mL



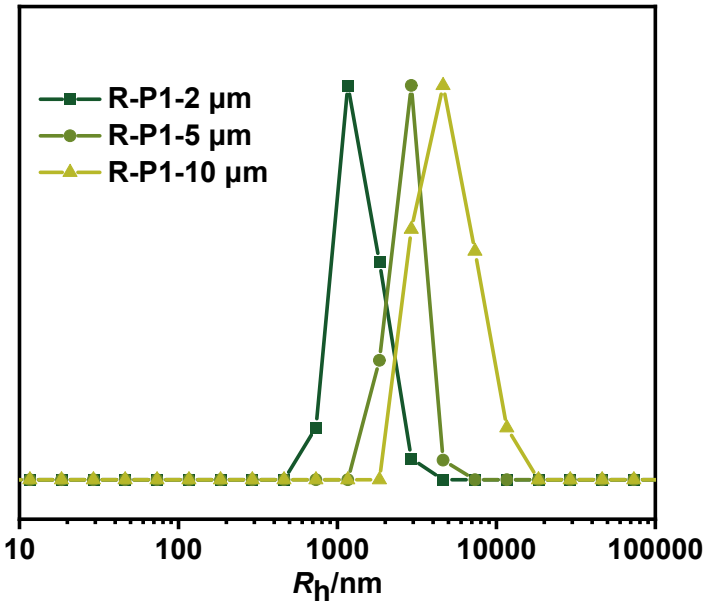


Figure S2. The TEM images of the ***R*-P1** in THF/EtOH solution (c_0 = 0.40 mg/mL) with an average diameter of (a-b) 2 μm; (c-d) 5 μm and (f-g) 10 μm. (h) The R_h distributions of **P1** assemblies in the THF/ EtOH solution.

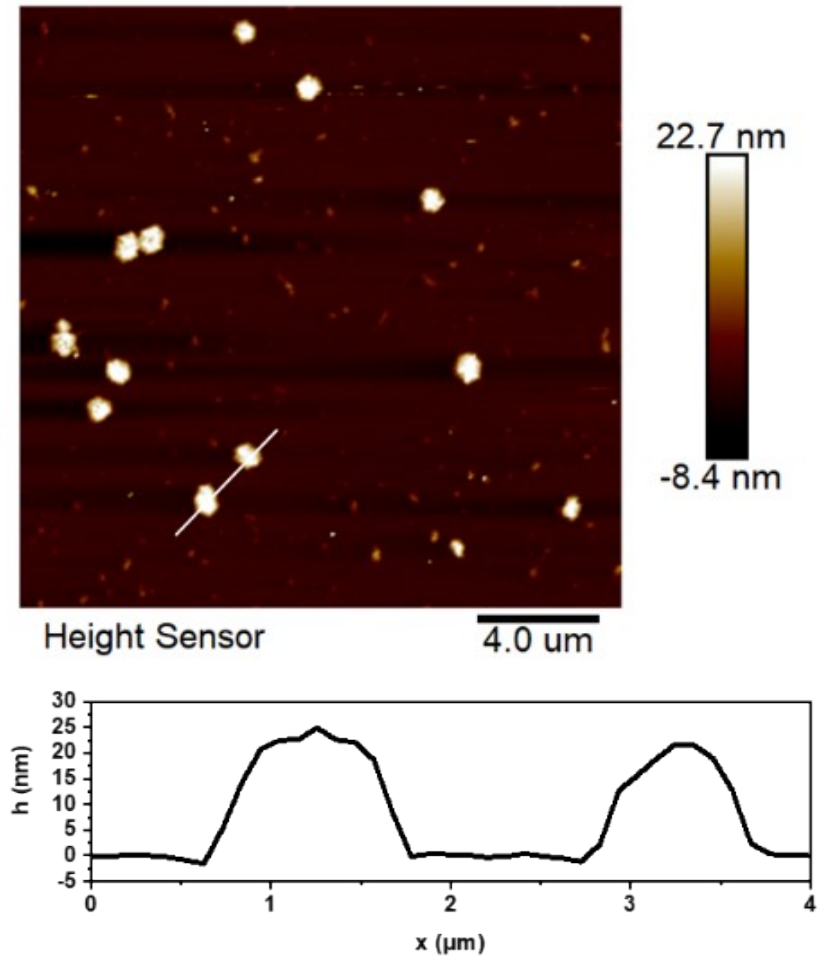


Figure S3. The AFM images as well as height analysis of **P1** assemblies.

Table S2. The mean sizes of discrete GNRs with different aspect ratios.

Sample	Wavelength of the Longitudinal LSPR Peak/nm	Length/nm	Width/nm
G1	620	40±5	20±5
G2	660	60±5	20±5
G3	700	45±5	15±5
G4	720	80±5	20±5
G5	750	56±5	15±5
G6	520	20±1	

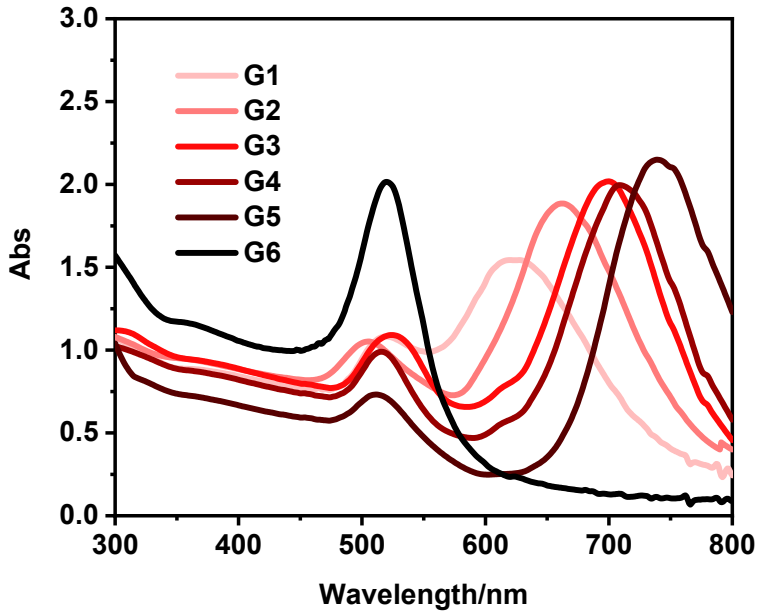


Figure S4. UV-Vis spectra of the GNRs.

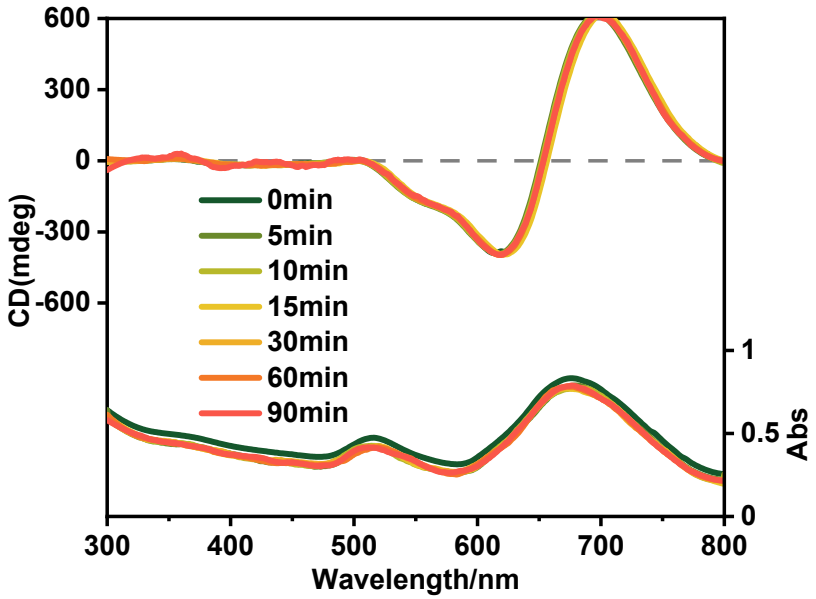


Figure S5. Time-dependent CD and UV-Vis spectra of ***R*-P1 /G2-E1k**.

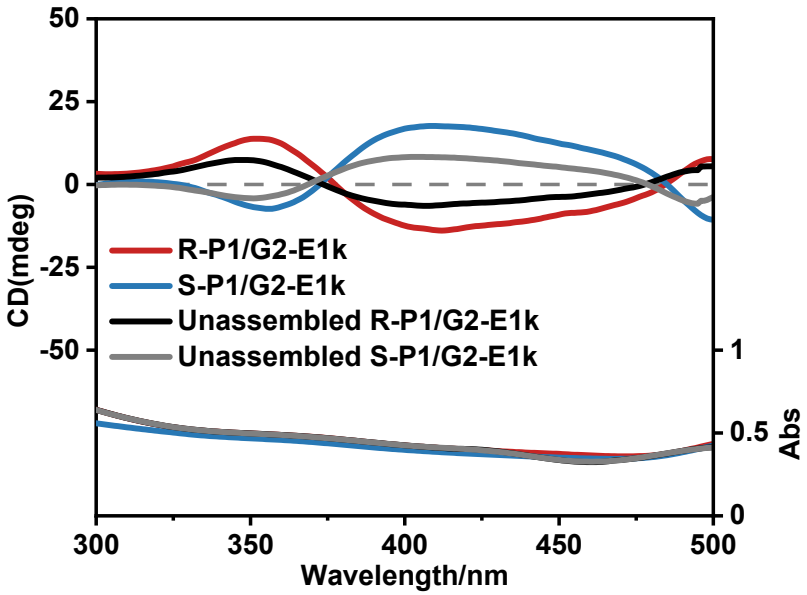


Figure S6. CD and UV-vis spectra of ***R*-P1 /G2-E1K** and ***S*-P1 /G2-E1K**. The CD and UV-vis of ***R*-P1** and ***S*-P1** are lower than those in ***Figure S1*** because the thickness of the fluorescence cell used here is 1 mm, while 10 mm in ***Figure S1***.

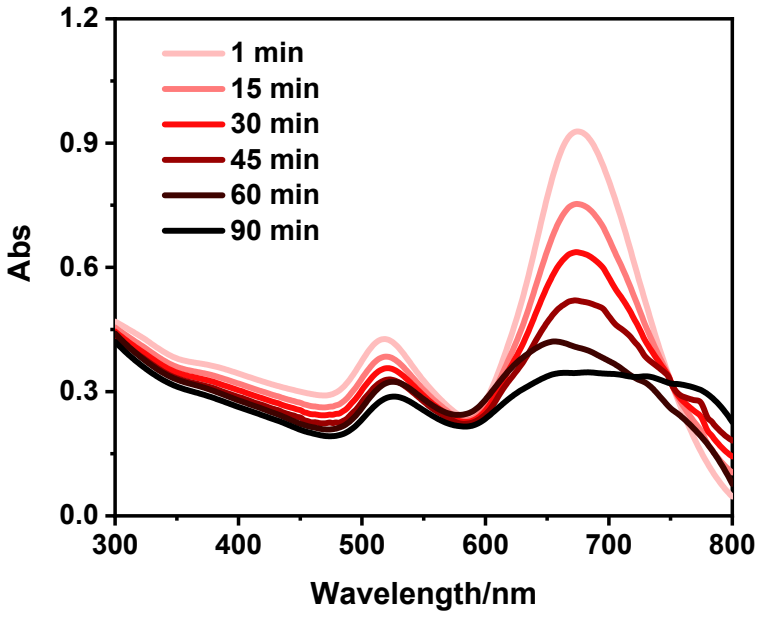


Figure S7. Time-dependent UV-Vis spectra of **G2-E1k** in THF.

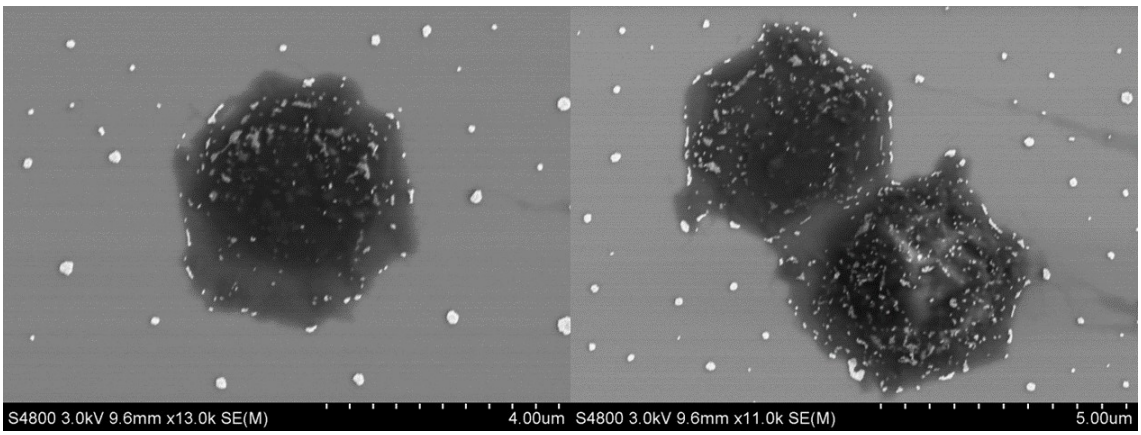


Figure S8. The SEM images of the ***R*-P1/G2-E1k** co-assemblies in THF/EtOH solution (c_0 = 0.40 mg/mL).

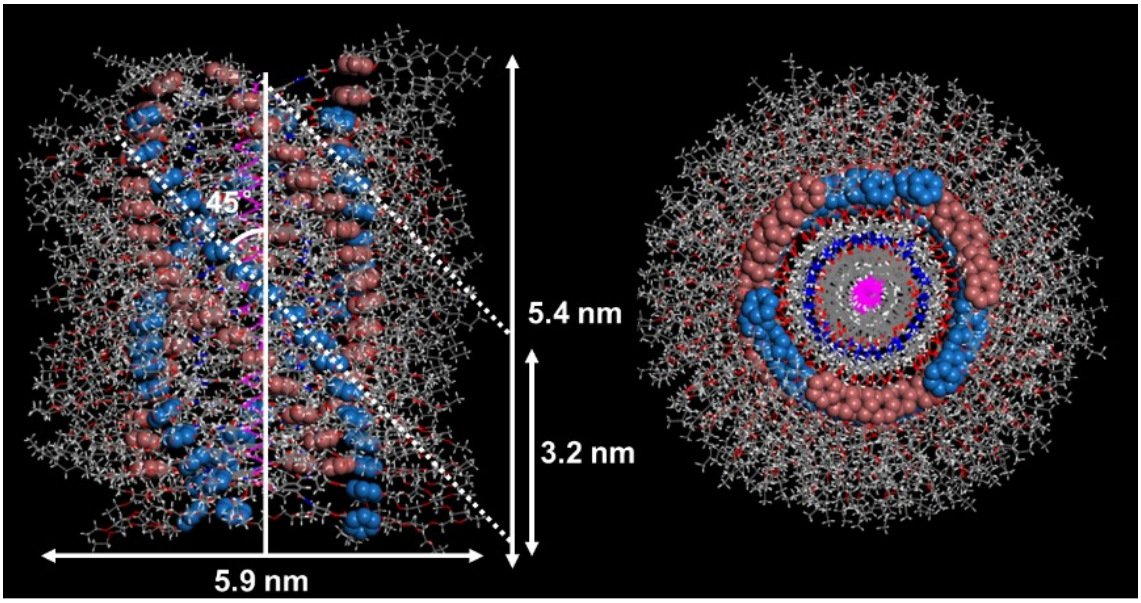


Figure S9. 3D models of *c-c* ***R*-P1** from the calculations at the dihedral angle $\varphi \approx 40°$.

$$R_F = N^{3/5}a \quad \text{eq (1)}$$

Equation S1. The equation was used to calculate R_F of PEG, where a is the characteristic monomer dimension and N is the degree of polymerization.

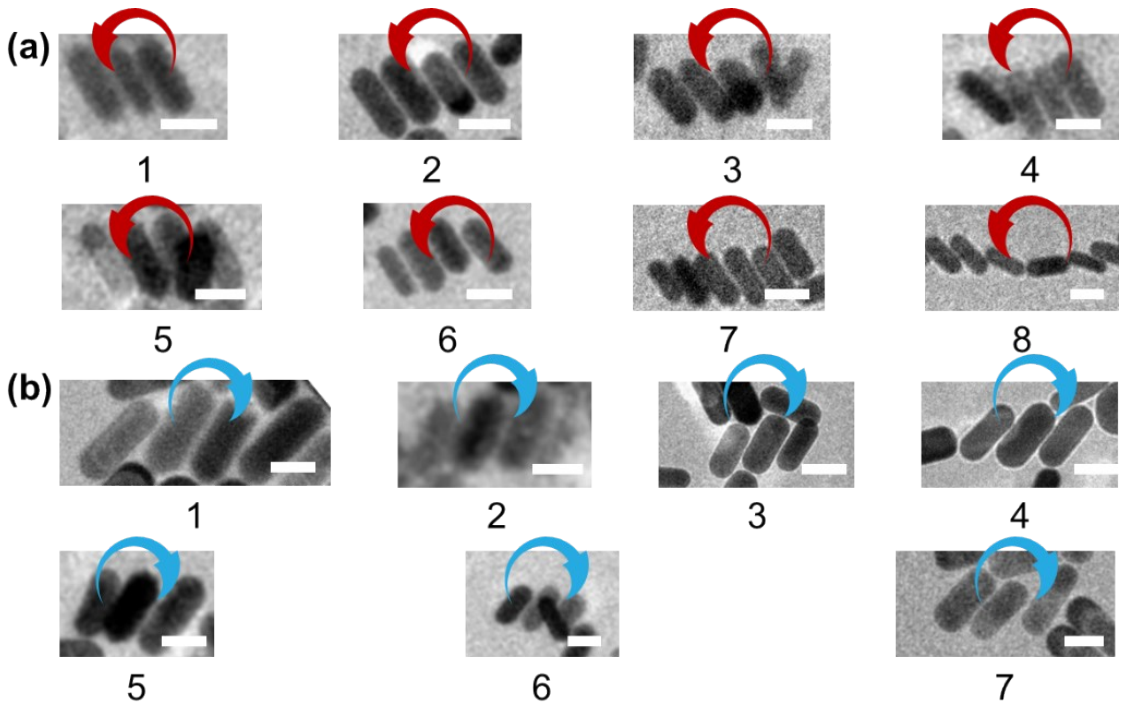


Figure S10a. The TEM images of ***R*-P1/G2-E1k** and ***S*-P1/G2-E1k** co-assemblies. (a) TYPE 1 of ***R*-P1/G2-E1k**. (b) TYPE1 of ***S*-P1/G2-E1k**. Scale bars: 50 nm for TEM images.

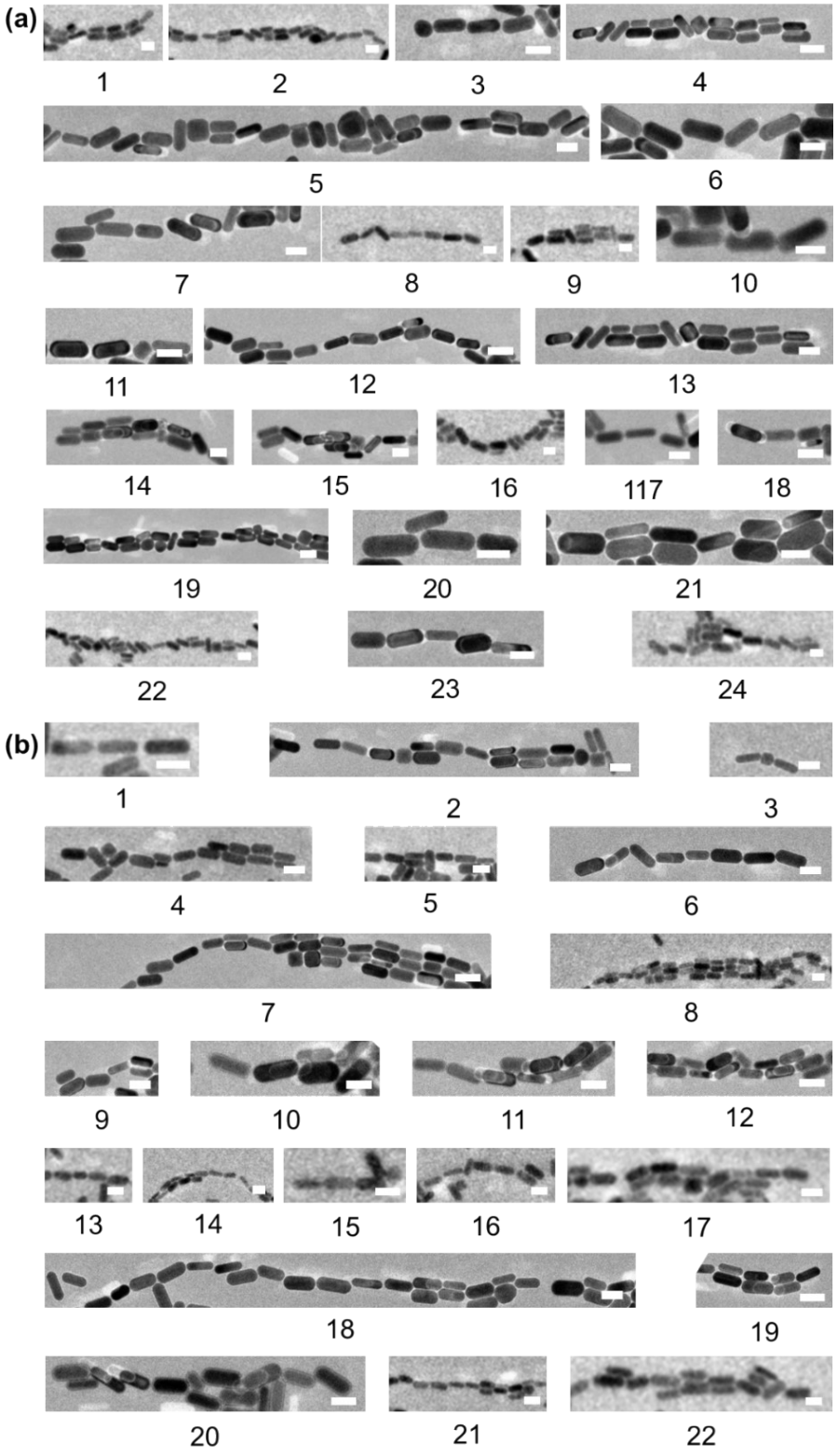


Figure S10b. The TEM images of ***R*-P1/G2-E1k** and ***S*-P1/G2-E1k** co-assemblies. (a) TYPE 2 of ***R*-P1/G2-E1k**. (b) TYPE2 of ***S*-P1/G2-E1k**. Scale bars: 50 nm for TEM images.

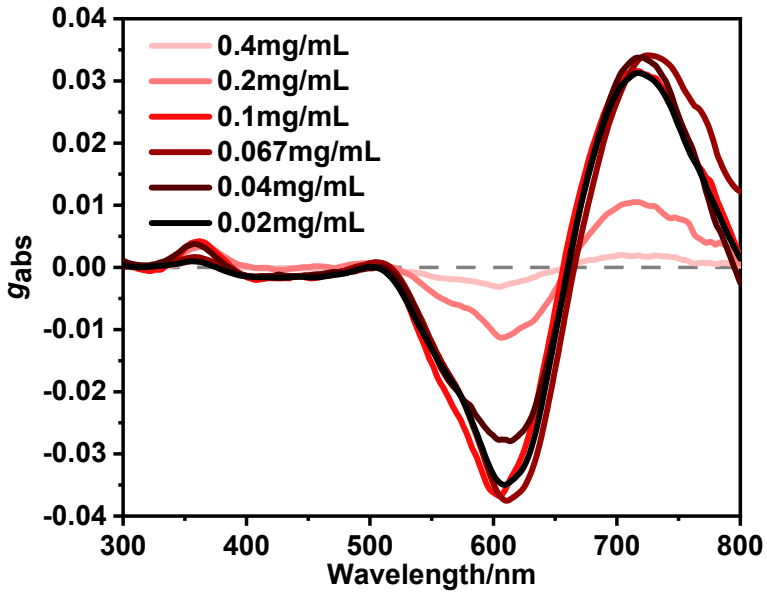


Figure S11. *g*-factor of ***R*-P1/G2-E1k** at different concentrations: 0.4-0.02 mg/mL.

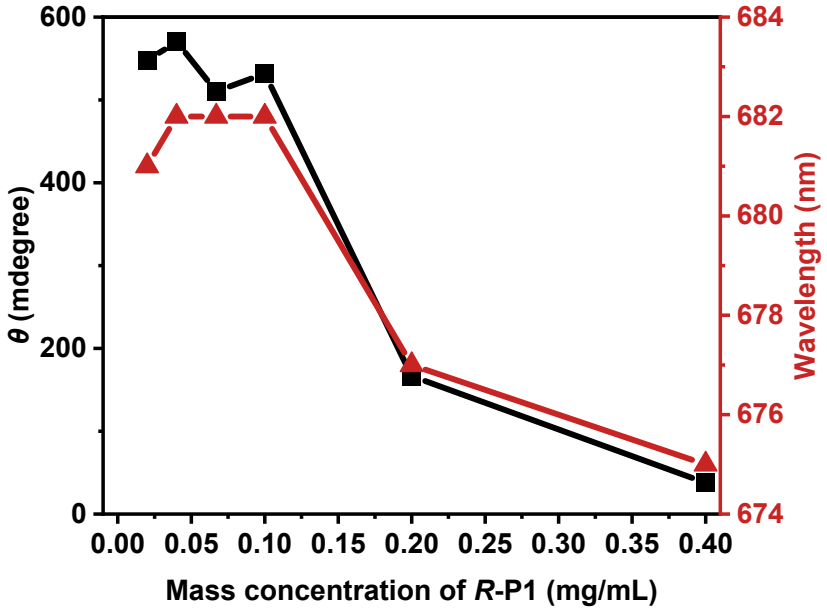


Figure S12. Peak value of PCD signal and long-axis absorption peak value at different concentrations.

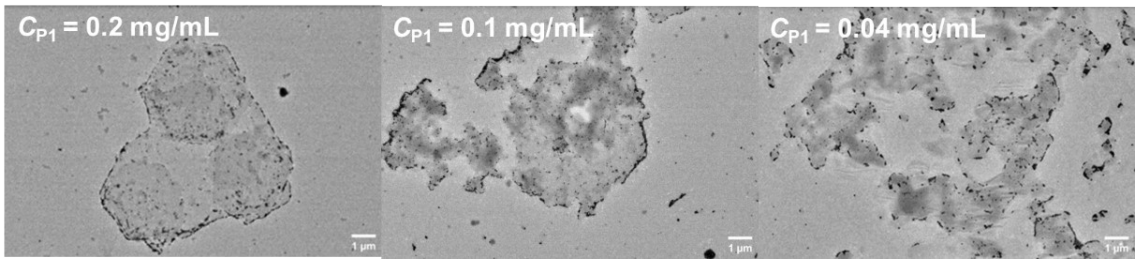


Figure S13. The TEM images of **P1/G2-E1k** at different concentrations.

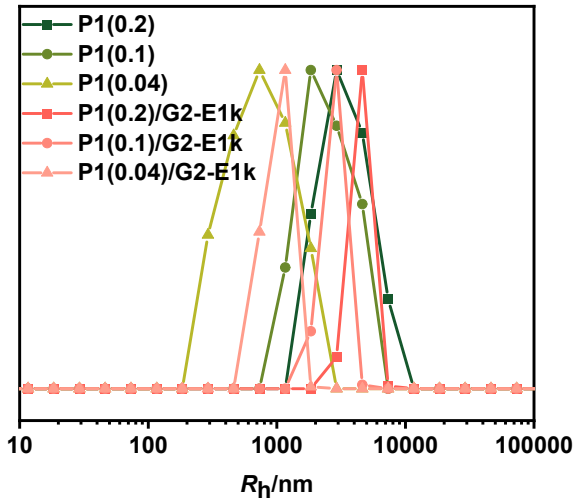


Figure S14. The R_h distributions of ***R*-P1/G2-E1k** at different concentration in THF/EtOH.

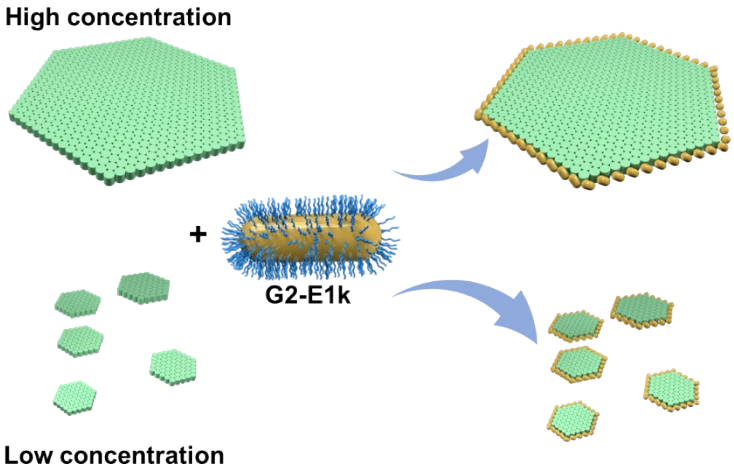


Figure S15. Schematic structure of ***R*-P1/G2-E1k** at different concentration of ***R*-P1**.

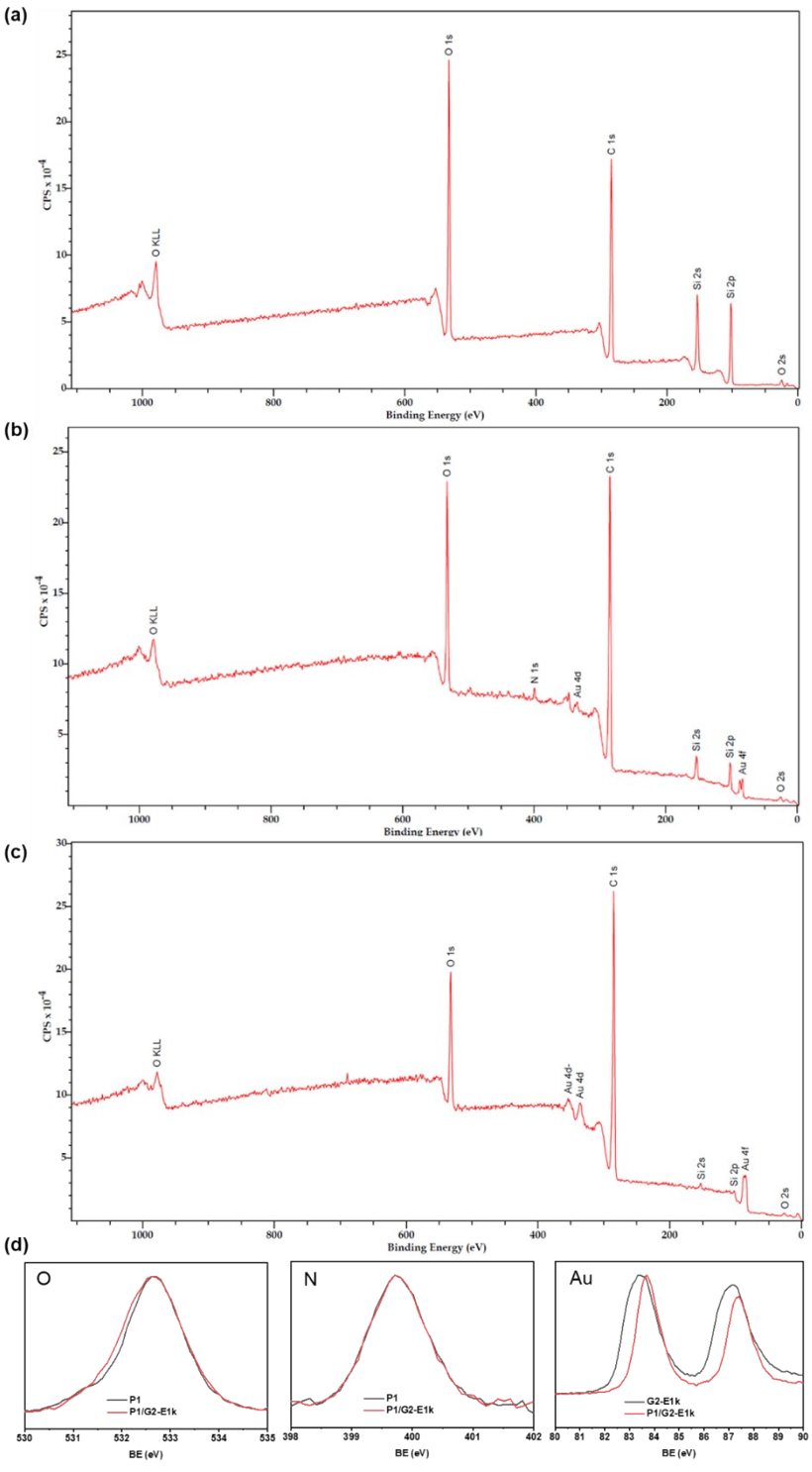


Figure S16. XPS spectra of ***R*-P1** (a), ***R*-P1/G2-E1k** (b) and **G2-E1k** (c). (d) Compare the XPS spectra before and after co-assembly.

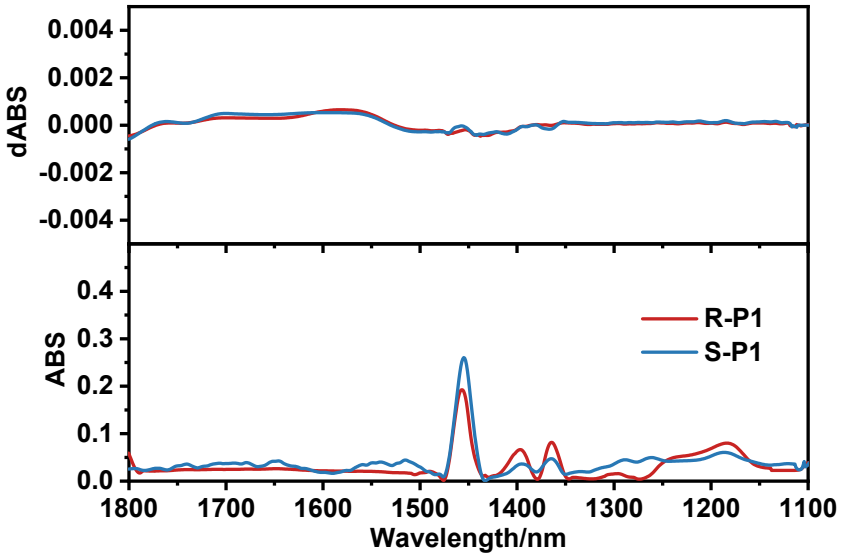


Figure S17. VCD spectra of ***R*-P1** and ***S*-P1** obtained from THF/EtOH.

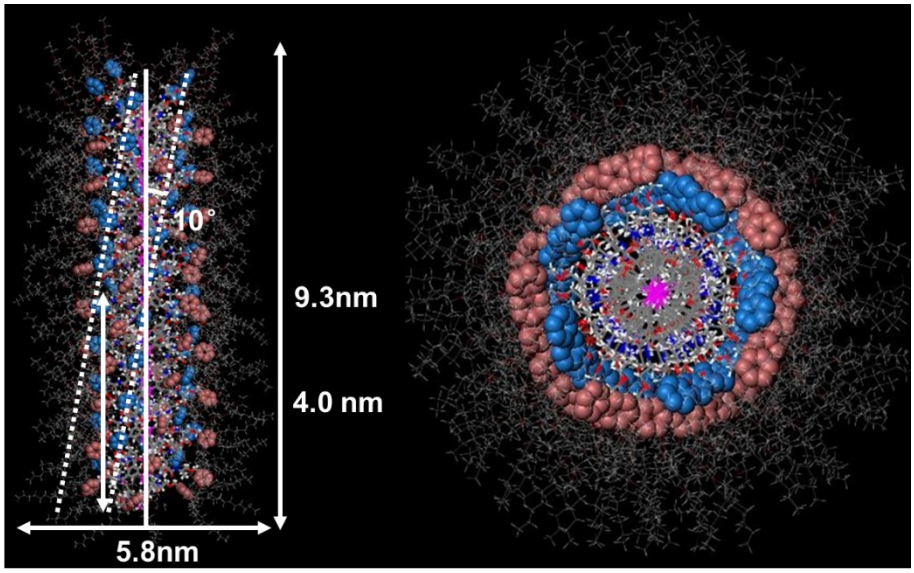


Figure S18. 3D models of *c-t* **P2** from the calculations at the dihedral angle $\varphi \approx -110°$.

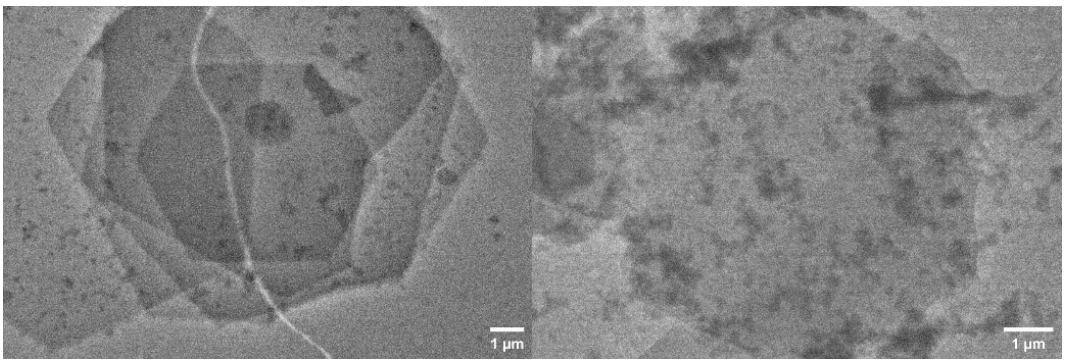


Figure S19. The TEM images of the **P2** in THF/EtOH solution (c_0 = 0.40 mg/mL).

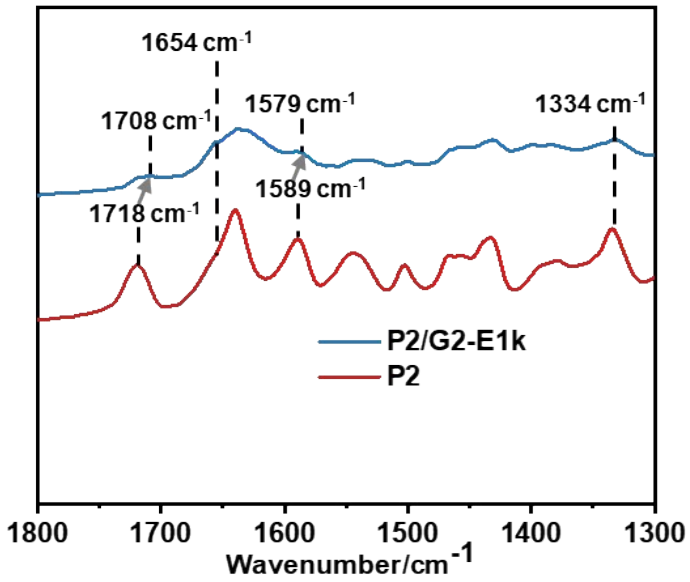


Figure S20. FT-IR spectra of **P2** and **P2/G2-E1k**.

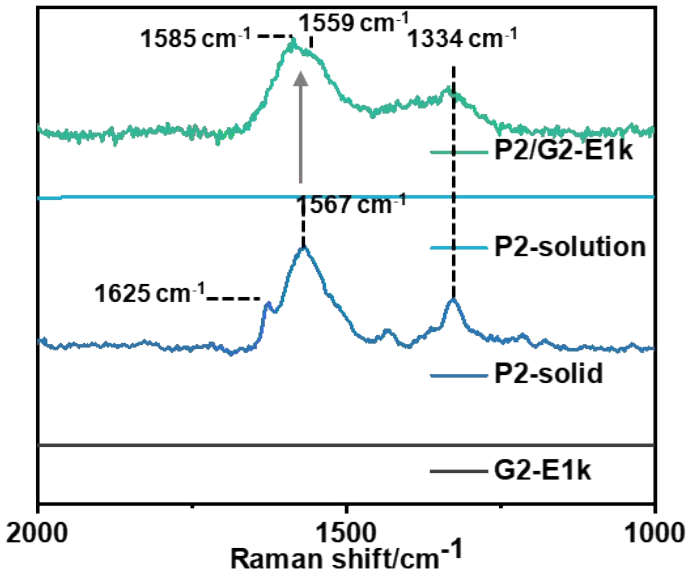


Figure S21. Raman spectra of **G2-E1k**, **P2** and **P2/G2-E1k** obtained from THF/EtOH.

In simulation of GNRs, the tilt angle θ (-90° ≤ *ϑ* ≤ 90°), is defined as the angle between the long axis of GNR and the Z-axis. The out-of-plane angel, α (-90° ≤ *α* ≤ 90°), is defined as the angle between the long axis of GNR and the Z-X plane. We first consider the range of *α*. When *α* approaches 90°, the GNRs are nearly parallel to the X-Y plane, resulting in a very small area of non-covalent interaction between the GNRs and the PPA nanosheets. Therefore, we thought that the sides of GNRs are close to edges of nanosheets, and*α* is small. The *α* values of the out-of-plane angles of adjacent GNRs are the same, but with the opposite signs (for example, alternating at 10° and -10°). *d* is the distance between adjacent GNRs. The tilt angels *ϑ* of *R*-P1/G2-E1k and P2/G2-E1k are set to -45° and 10°, which are in consisted with the tilt angle of the helix in the assembled P1 and P2.

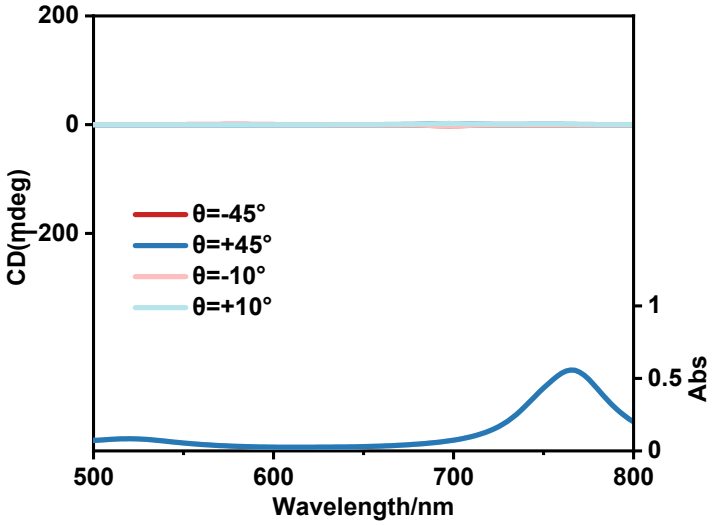


Figure S22. FDTD simulated CD and UV-Vis spectra. *d* = 15 nm, *α* = 0°, *ϑ* = -45° (***R*-P1/G2-E1k**), -10°, +10°(**P2/G2-E1k**) and +45° (***S*-P1/G2-E1k**).

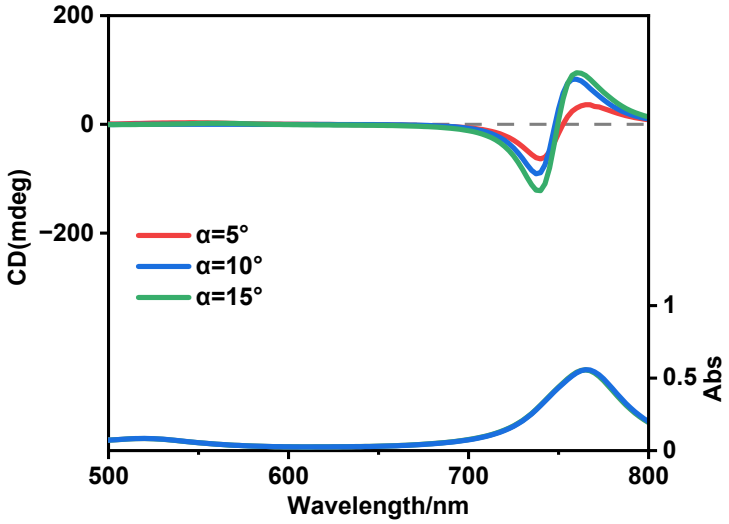


Figure S23. FDTD simulated CD and UV-Vis spectra. d = 15 nm, ϑ = -45° (***R*-P1/G2-E1k**), α = 5°, 10° and 15°.

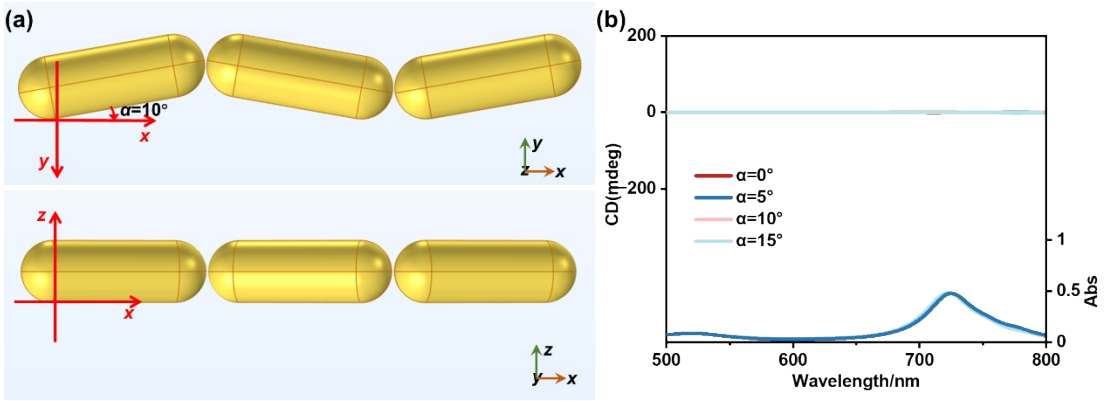


Figure S24 (a) Schematic structures of EE arrangement, ϑ = 90°; (b) FDTD simulated CD and UV-Vis spectra. d = 60 nm, ϑ = 90° (***R*-P1/G2-E1k**), α = 0°, 5°, 10° and 15°.

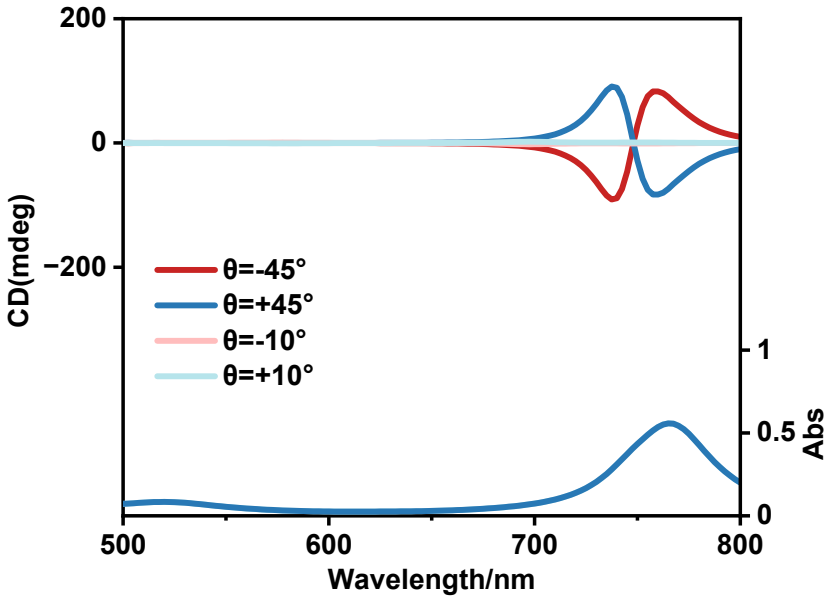


Figure S25. FDTD simulated CD and UV-Vis spectra. d = 5 nm, α = 10°, ϑ = -45° (***R*-P1/G2-E1k**), -10°, +10°(**P2/G2-E1k**) and +45° (***S*-P1/G2-E1k**).

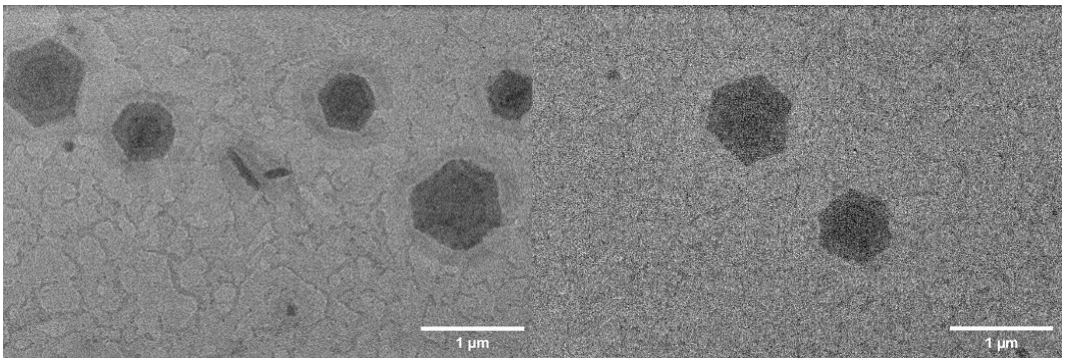


Figure S26. The TEM images of the **P3** in THF/EtOH solution (c_0 = 0.40 mg/mL).

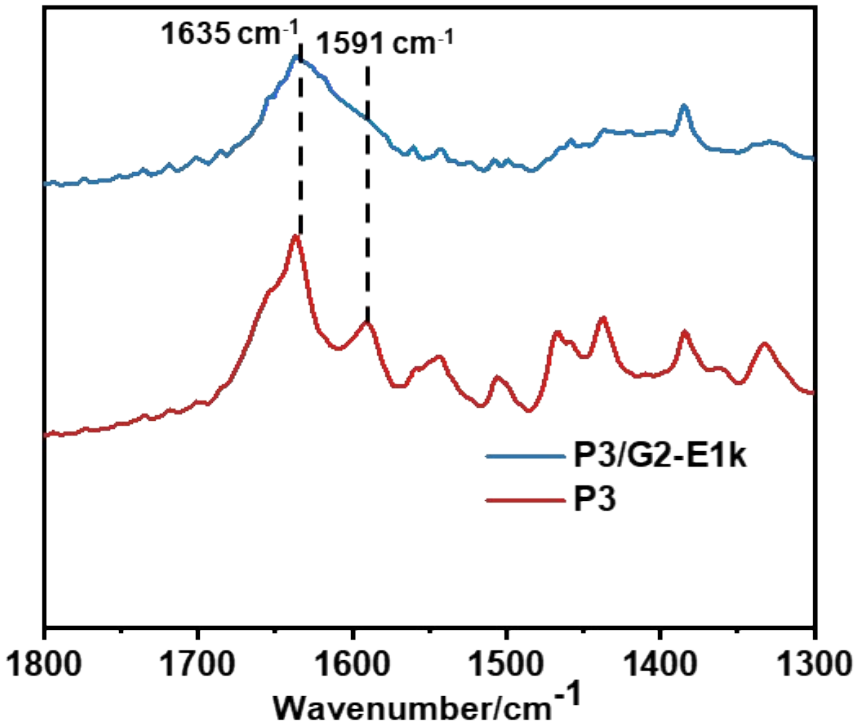


Figure S27. FT-IR spectra of **P3** and **P3/G2-E1k**.

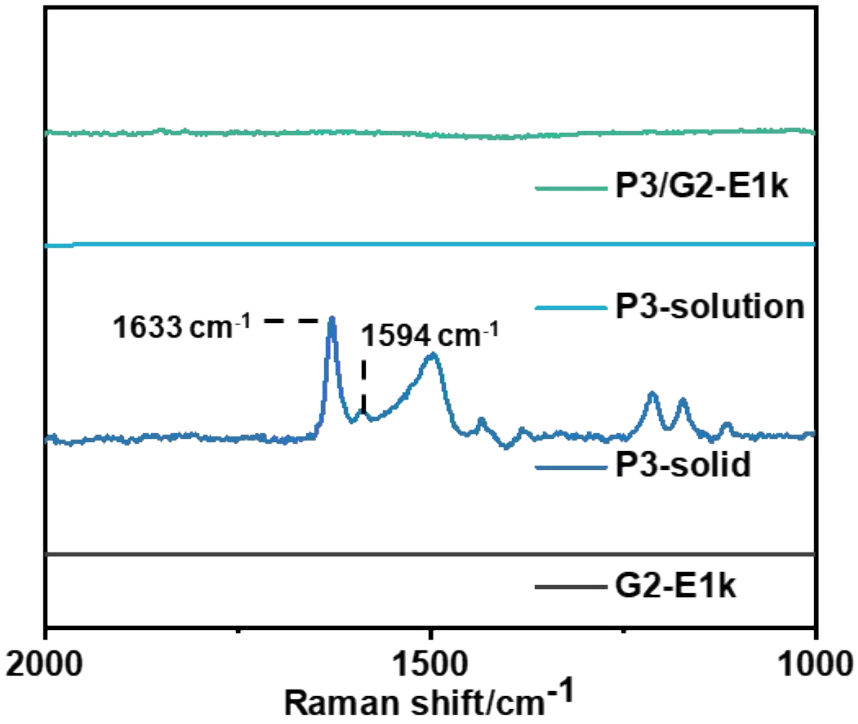


Figure S28. Raman spectra of **G2-E1k**, **P3** and **P3/G2-E1k** obtained from THF/EtOH.

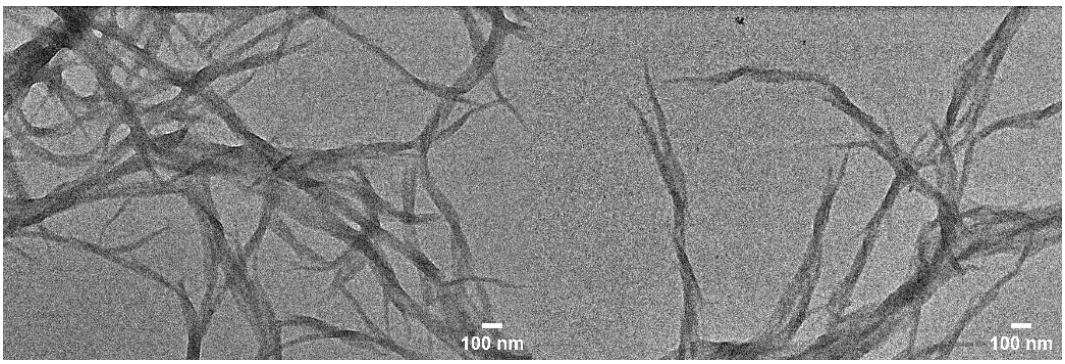


Figure S29. The TEM images of the **P4** in THF/EtOH solution (c_0 = 0.15 mg/mL).

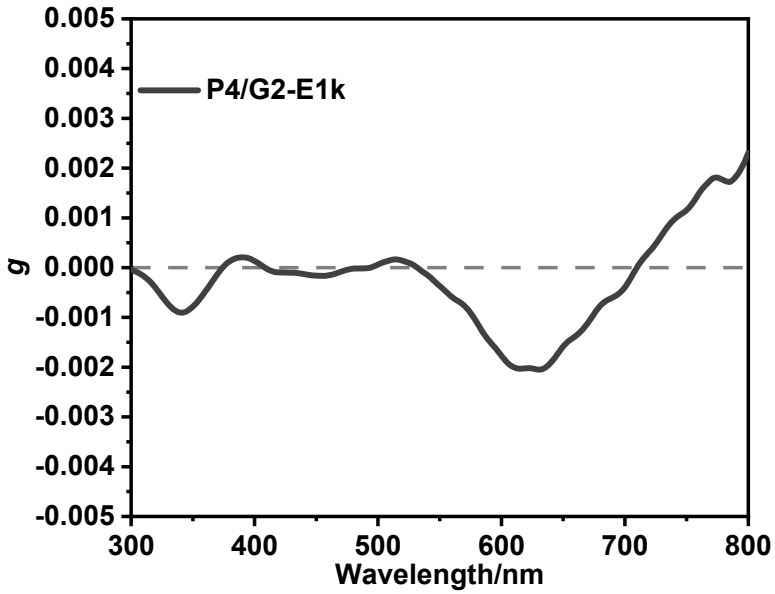


Figure S30. g-factor of P4/G2-E1k.

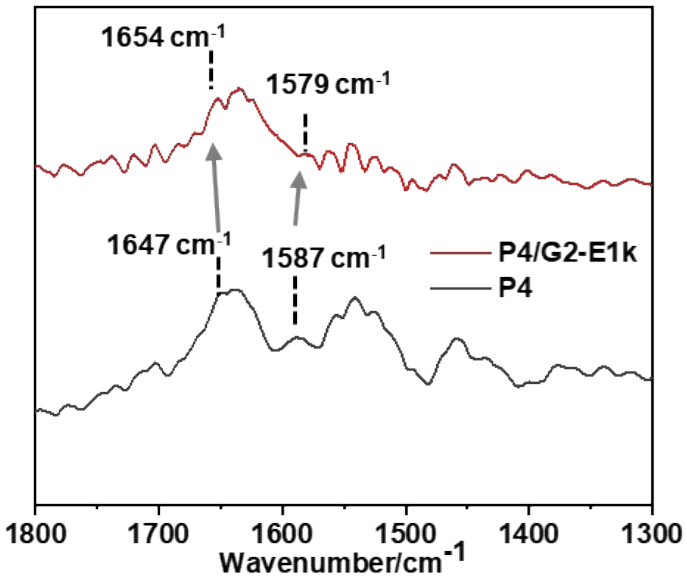


Figure S31. FT-IR spectra of **P4** and **P4/G2-E1k**.

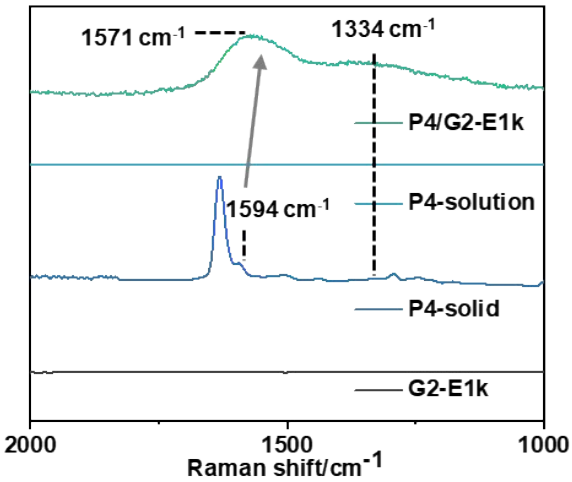


Figure S32. Raman spectra of **G2-E1k**, **P4** and **P4/G2-E1k** obtained from THF/EtOH.

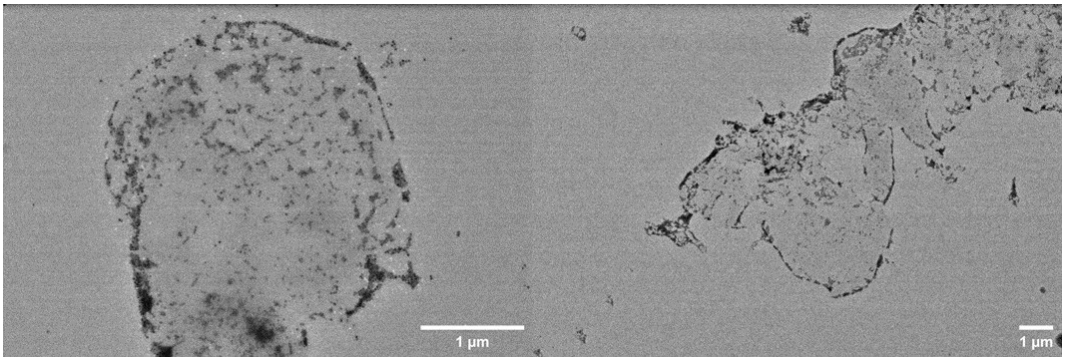


Figure S33. The TEM images of ***R*-P1/G6-E1k** co-assemblies.

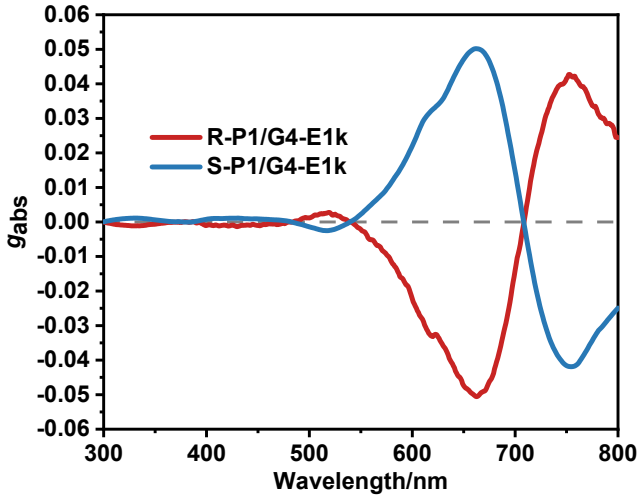


Figure S34. The *g*-Value of ***R*-P1/G4-E1k** and ***S*-P1/G4-E1k**.

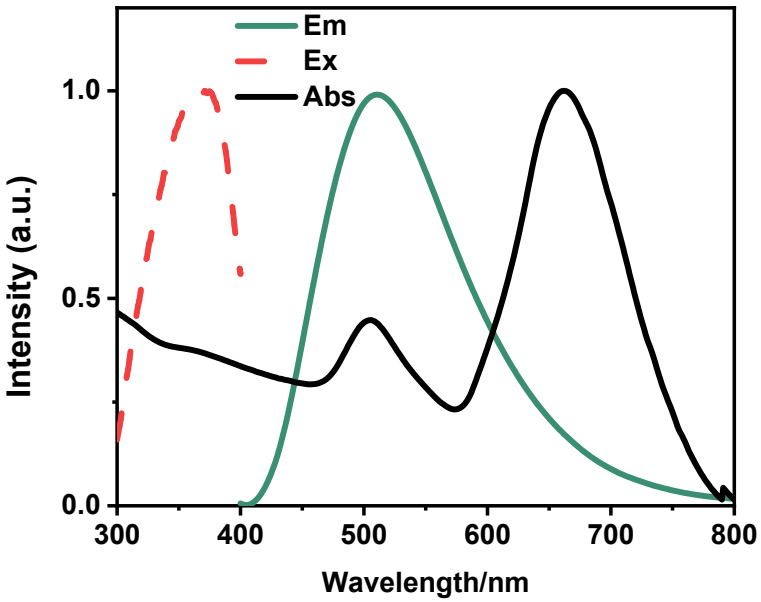


Figure S35. The fluorescence spectra of ***R*-P1** assemblies in THF/EtOH solution (c_0 = 0.4 mg/mL) and UV-Vis spectra of **G2-E1k**.

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