Supporting Information

Supramolecular chirality capture in solvent monomer-based co-assemblies *via* in situ photopolymerization

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1 Experimental Section

1.1. Characterizations.

The ^{1}H NMR spectra were recorded on a Bruker Avance III 400 HD spectrometer. Circular dichroism (CD) spectra were measured using JASCO J-810 CD spectrometer with a bandwidth of 1.0 nm, scanning speed of 500 nm min-1, and data integration time of 1 s. CPL spectra were obtained with JASCO CPL-300 spectrometer with the Ex and Em slit width of 3000 μm, scanning speed of 500 nm min-1, and data integration time of 1 s. Fluorescence spectra were performed using F-4500 fluorescence spectrophotometer using a xenon lamp as the excitation source. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 FE-SEM with an accelerating voltage of 5 kV. Mass spectral data were obtained by using a SolariX maldi-FTMS instrument. Infrared spectra were recorded using JASCO FTIR-660 spectrometer. UV-vis spectra were recorded on Hitachi U-3900 spectrophotometer. Fluorescence spectra were measured using F-4500 fluorescence spectrophotometer.

Materials. 4-aminopyridine and cholesteryl chloroformate were purchased from Shanghai Titan Scientific Co., Ltd. The organic solvents were purchased from Shanghai Titan Scientific Co., Ltd without further purification.

1.2. Synthetic procedure

Scheme S1 Synthesis of PCC.

To a dichloromethane (200 mL) solution of 4-aminopyridine (0.50 g, 5.3 mmol), triethylamine (3.0 mL, 22 mmol) was added under nitrogen and cooled in an ice bath. Into the solution, a dichloromethane solution (80 mL) of cholesteryl chloroformate (2.5 g, 5.6 mmol) was added dropwise over 1.5 h at 0 °C and the mixture was stirred for another day at room temperature. Chloroform was added to the reaction mixture and the solution was washed five times with HCl aq (0.1 M), twice with saturated $NaHCO_3$ aq, and twice with H_2O and the organic layer was dried over Na_2SO_4. Concentration followed by column chromatography (dichloromethane/methanol=10/1) afforded white solid (2.3 g, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 – 8.42 (m, 2H), 7.47 – 7.36 (m, 2H), 7.13 (s, 1H), 5.43 (d, *J* = 5.0 Hz, 1H), 4.65 (dt, *J* = 11.4, 6.1 Hz, 1H), 2.50 – 2.32 (m, 2H), 2.06 – 1.83 (m, 5H), 1.66 – 1.44 (m, 7H), 1.36 (d, *J* = 8.2 Hz, 2H), 1.28 (s, 2H), 1.25 – 1.09 (m, 7H), 1.04 (d, *J* = 8.6 Hz, 5H), 0.96 – 0.86 (m, 10H), 0.70 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.15 , 123.00 , 112.55 , 75.65 , 56.67 , 56.14 , 50.00 , 45.86 , 42.31 , 39.71 , 39.51 , 38.33 , 36.91 , 36.56 , 36.17 , 35.78 , 31.89 , 31.86 , 28.21 , 27.99 , 24.27 , 23.82 , 22.80 , 22.54 , 21.04 , 19.31 , 18.71 , 11.85 , 8.63 . HRMS (Maldi) calcd for $C_{33}H_{50}N_2O_2$ [M]: 506.3872, found: 506.3950.
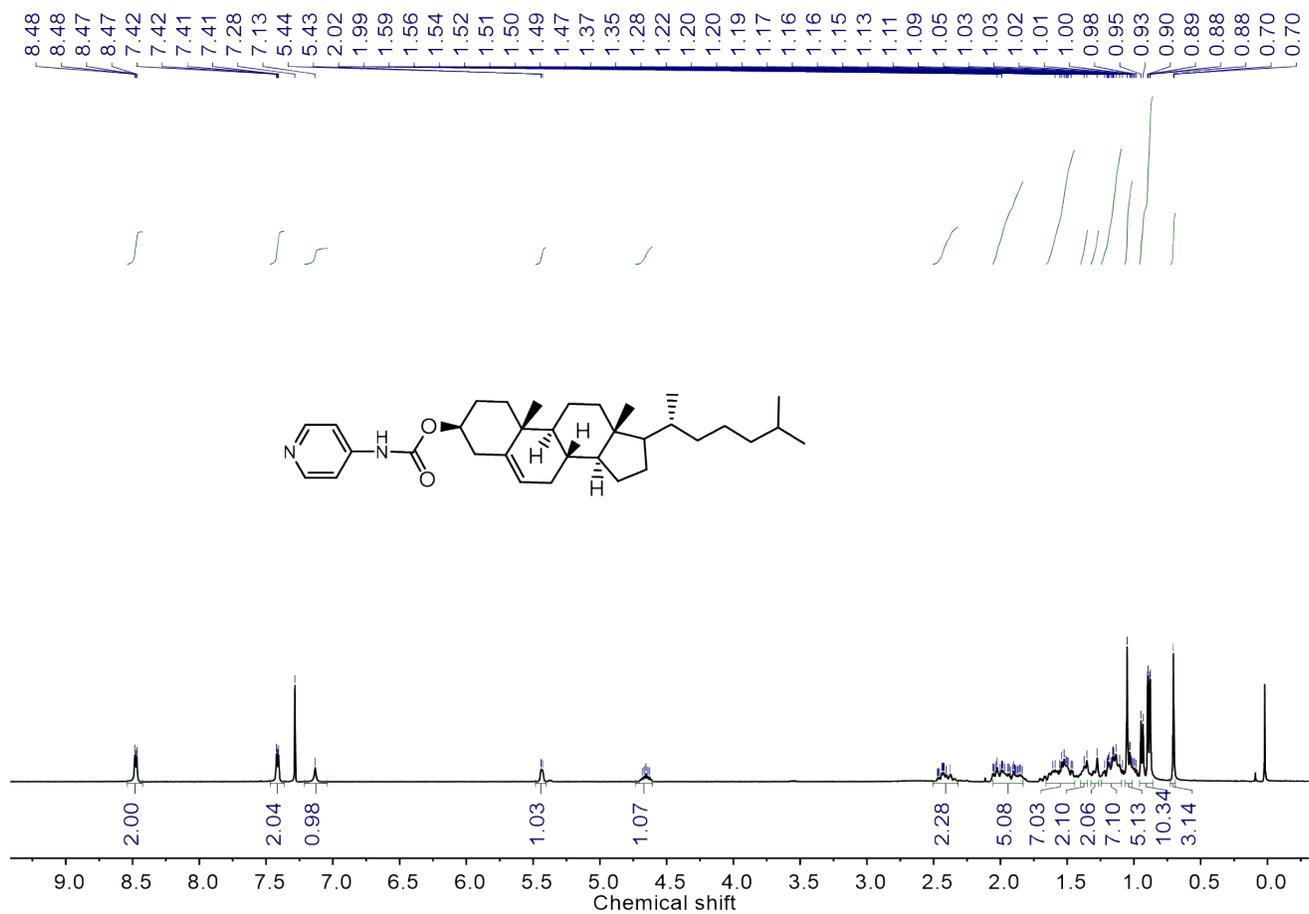
Fig. S1 ^{1}H NMR spectra of PCC.
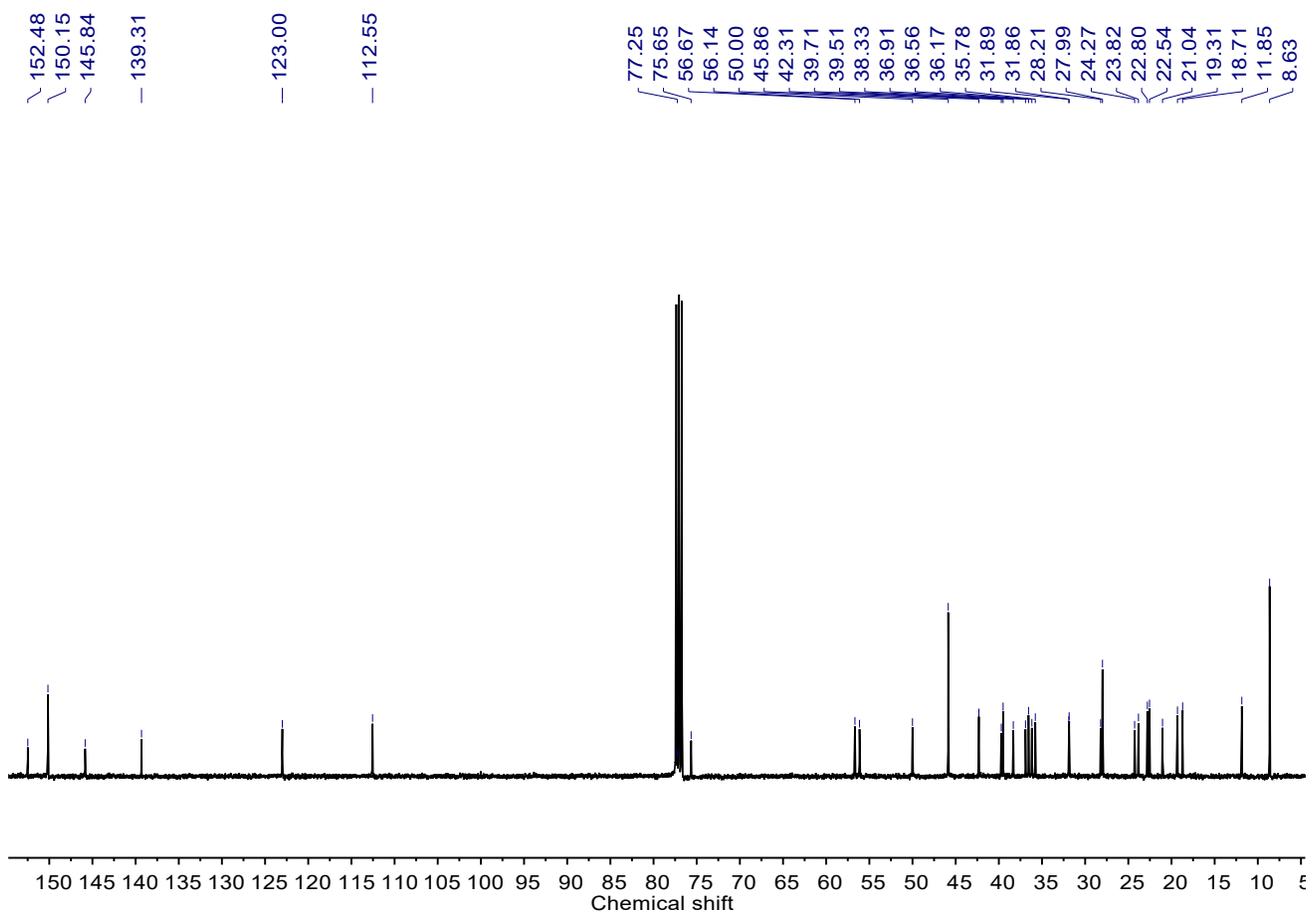
Fig. S2 ^{13}C NMR spectra of PCC.
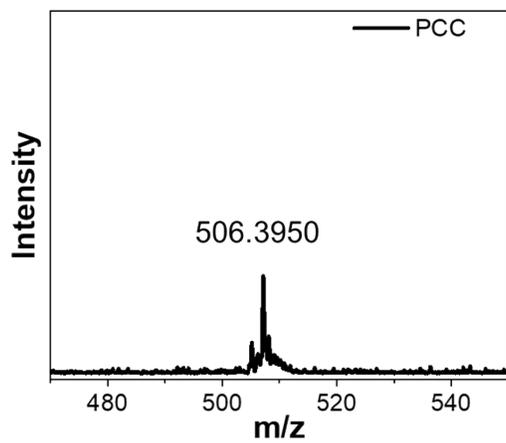
Fig. S3 MALDI-TOF-MS of PCC.

1.3. Sample Preparation

PCC assembly preparation in conventional solvents. To a 1.5 mL sample vital, 300 μL solvent and 3 mg PCC were added. The mixture was sonicated for tens of second, resulting in the formation of PCC assembly (m_{PCC} = 3 mg, [PCC] = 20 mM).

PCC assembly preparation in LMA (LMA@PCC). To a 1.5 mL sample vital, 300 μL LMA and 3 mg PCC were added. The mixture was heated to transparent at 150 ℃, followed by sonicating at room temperature for 3 min, resulting in the formation of LMA@PCC gel (m_{PCC} = 3 mg, [PCC] = 20 mM).

PCC assembly preparation in MA/AA. To a 1.5 mL sample vital, 300 μL of MA/AA mixed solvents with varying volume ratio of AA and 10 mg PCC were added. The mixtures were heated to transparent at 150 ℃, followed by sonicating at room temperature for 3 min, resulting in the formation of PCC assemblies (m_{PCC} = 10 mg, [PCC] = 67 mM). The gel formed at MA/AA (v/v, 9/1) was named as MA/AA@PCC co-assembly.

LMA@PCC polymer preparation. To a 1.5 mL sample vital, 300 μL LMA, 3 mg PCC, 1 mg Irgacure 2959, and 1mg trimethylolpropane triacrylate were added, the mixtures were heated to transparent at 150 ℃, followed by sonicating at room temperature for 3 min, resulting in the formation of assembly. Then the assembly was positioned into a 1cm × 1cm × 0.1cm mold and then irradiation under a 365 nm light (175 W) for 5 min, resulting in the formation of LMA@PCC polymer film.

MA/AA@PCC polymer preparation. To a 1.5 mL sample vital, 300 μL MA/AA (v/v, 9/1), 3 mg PCC, and 1 mg Irgacure 2959 were added, the mixtures were heated to transparent at 150 ℃, followed by sonicating at room temperature for 3 min, resulting in the formation of assembly. Then the assembly was positioned into a 1cm × 1cm × 0.1cm mold and then irradiation under a 365 nm light (175 W) for 5 min, resulting in the formation of MA/AA@PCC polymer film.

It should be noted that the methodology for fabricating the dye-doped PCC polymers were consistent with the sample preparation procedures outlined above. Specifically, the dye doping levels were set at 3 mol% relative to the PCC content.

2   Supplementary Figures
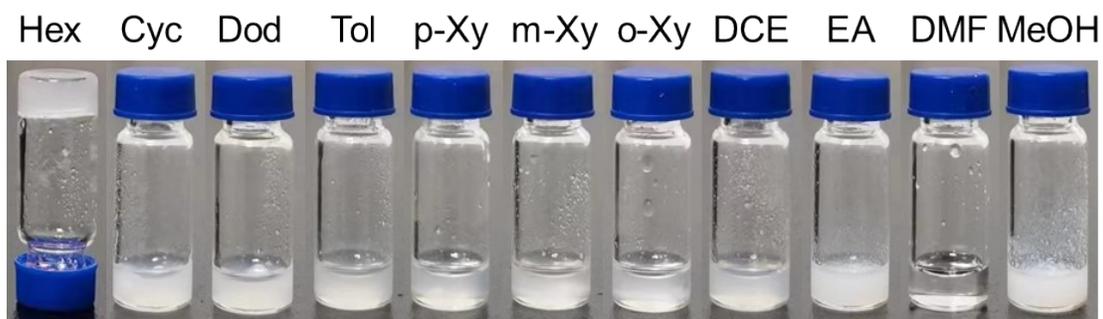
Fig. S4 Photographs of PCC assemblies obtained from different solvents (The concentrations of the PCC are 2×10^{-2} mol L^{-1}).
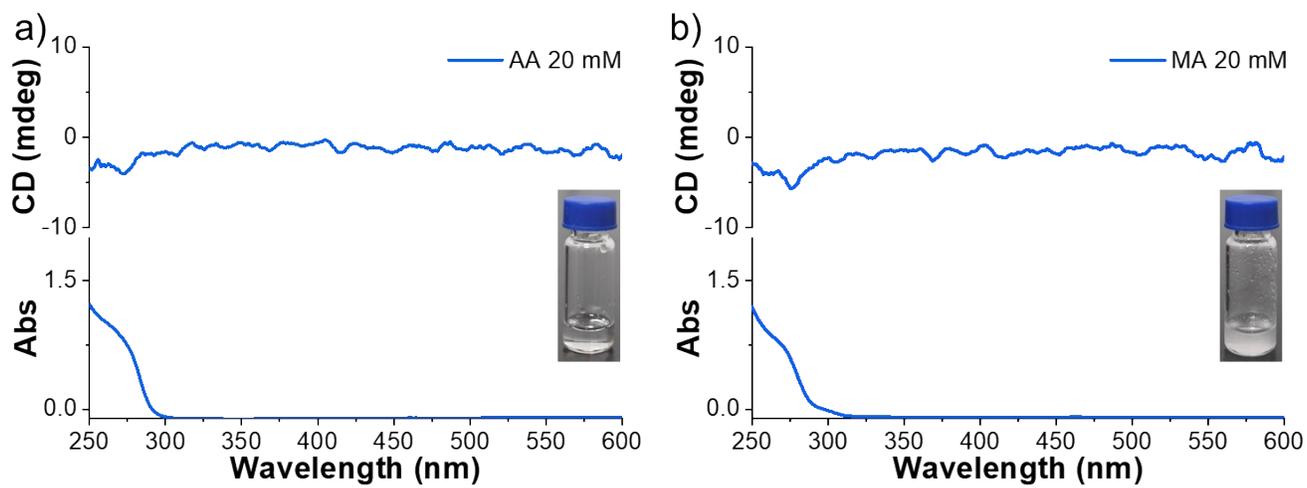
Fig. S5 CD spectra of PCC assemblies in a) AA and b) MA, respectively, at the concentration of 20 mM. The inserts were the pictures of PCC assemblies in AA and MA, respectively.

Fig. S6 Photographs of assemblies obtained from MA/AA (v/v) mixed solvents (The concentrations of the PCC are 6.7×10^{-2} mol L^{-1}).
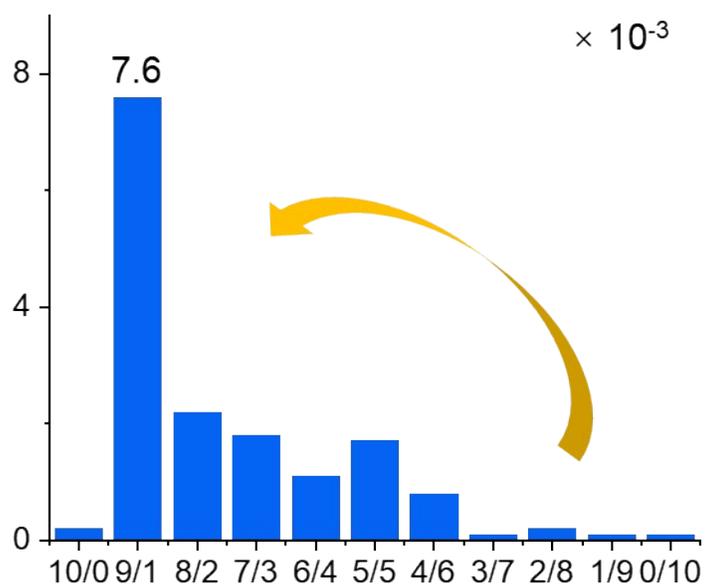
Fig. S7 g_{abs} spectra of PCC assemblies in MA/AA (v/v) mixed solvents with different AA fractions (The concentrations of the PCC are 6.7×10^{-2} mol L^{-1}).

a)

Irgacure 2959

b)
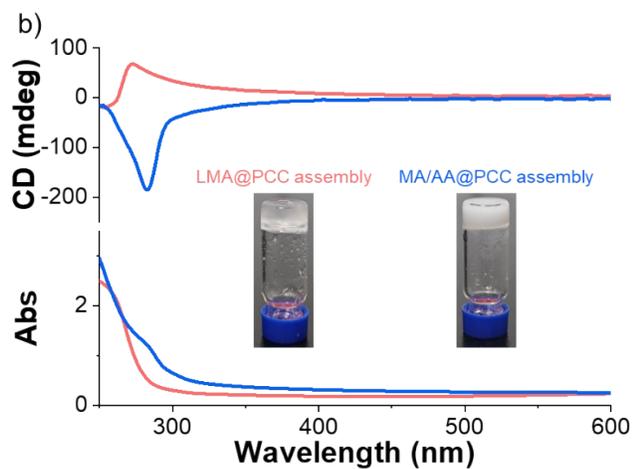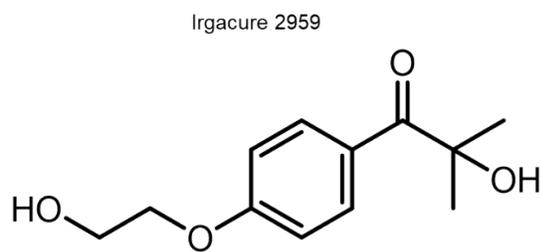
Fig. S8 a) The chemical structure of Irgacure 2959. b) CD spectra of PCC assemblies in LMA and MA/AA (v/v = 9/1) with 1 mg Igracure 2959. In LMA, the concentration of PCC is 2.0×10^{-2} mol L^{-1}; In MA/AA (v/v = 9/1), the PCC concentration is 6.7×10^{-2} mol L^{-1}.

Fig. S9 Photograph of LMA@PCC co-assembly after photo-curing under UV-365 light (175 W) for 5 min without trimethylolpropane triacrylate (The concentration of the PCC is 2.0×10^{-2} mol L^{-1}).
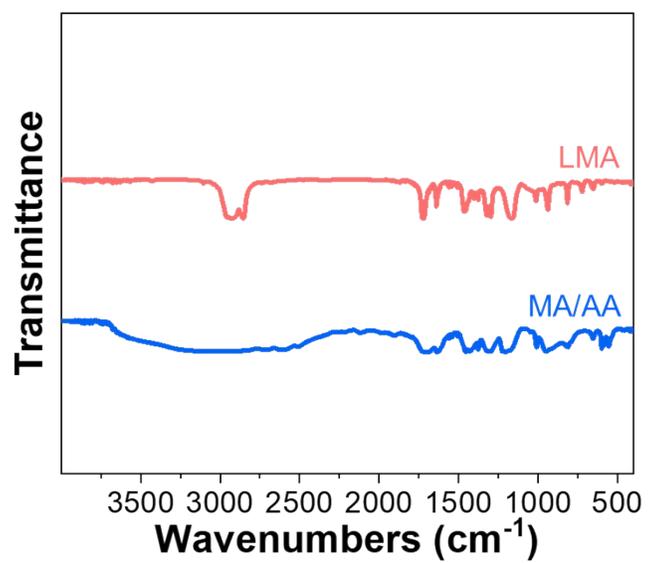
Fig. S10 FTIR spectra of LMA and MA/AA (v/v, 9/1), respectively.
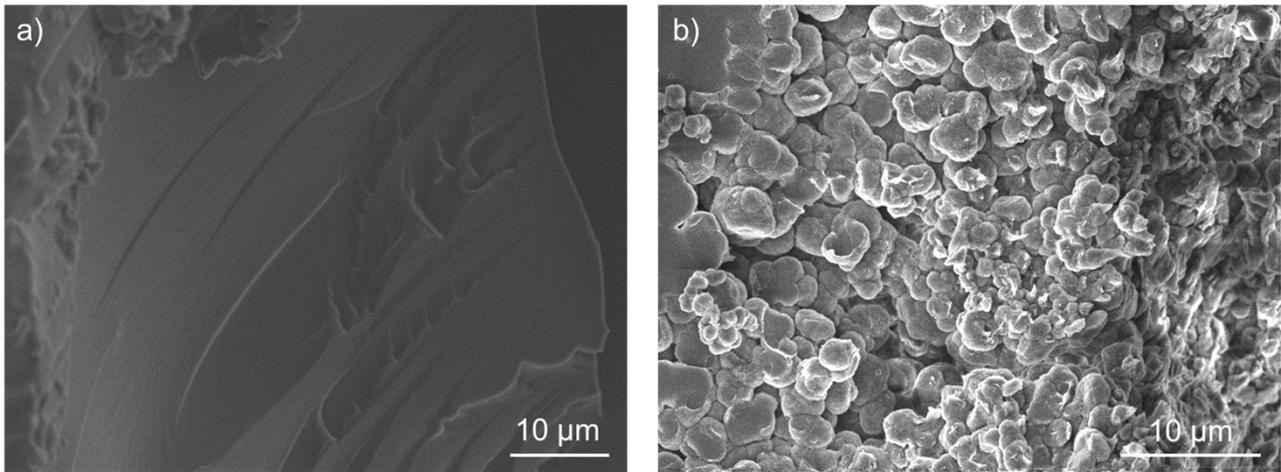
Fig. S11 SEM images of the cross-section of the a) LMA and b) MA/AA (v/v, 9/1) polymerization films without PCC.
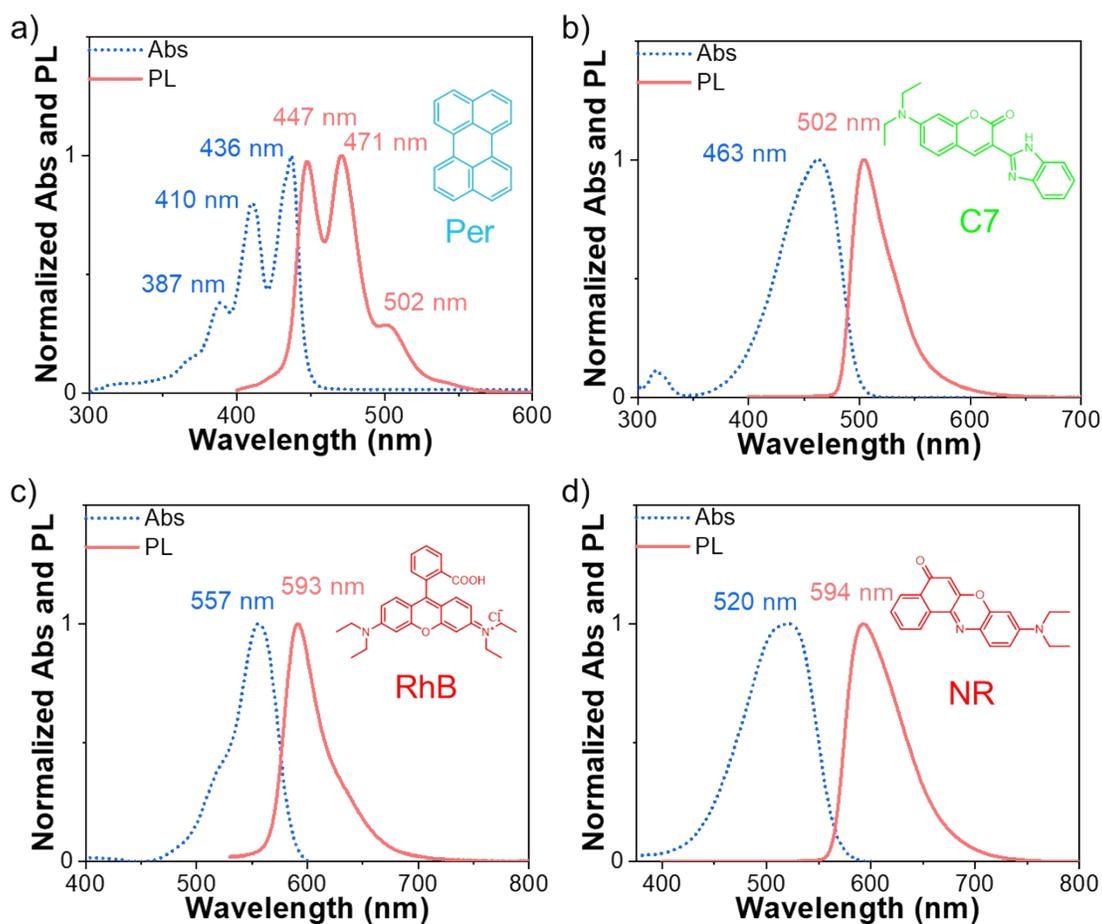
Fig. S12 Normalized emission spectra of a) Per, b) C7, c) RhB in MA/AA (v/v, 9/1) mixed solvent. d) Normalized emission spectra of NR in LMA. The concentrations of these dyes are 3.0×10^{-5} mol L^{-1}.
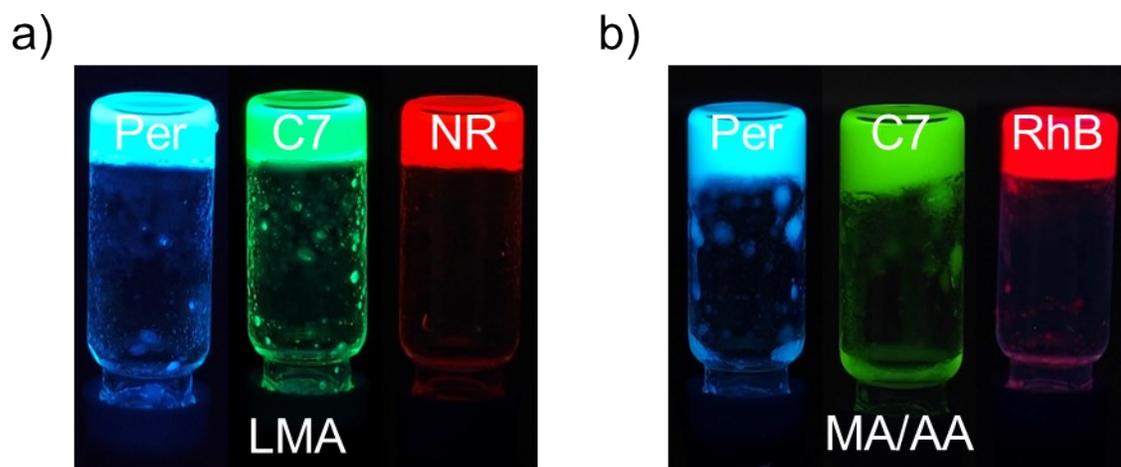
Fig. S13 The photographs of the achiral fluorescence dye co-assembly with PCC in a) LMA and b) MA/AA (v/v, 9/1), respectively, under 365 nm irradiation. In LMA, the concentrations of PCC are 2.0×10^{-2} mol L^{-1}, $n_{PCC}/n_{dyes} = 100/3$. In MA/AA (v/v, 9/1), the concentrations of PCC are 6.7×10^{-2} mol L^{-1}, $n_{PCC}/n_{dyes} = 100/3$.
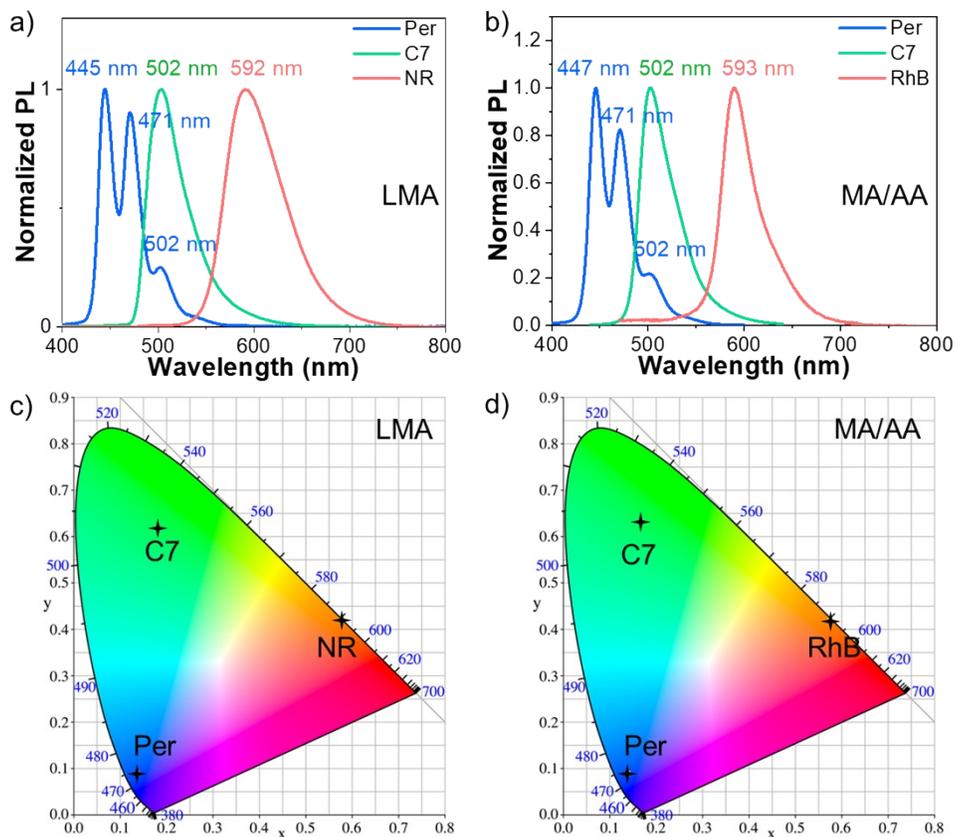
Fig. S14 a) The normalized emission spectra and c) the corresponding CIE coordinates diagram of LMA@PCC co-assemblies doped with the achiral fluorescence dyes (The concentrations of PCC are 2.0×10^{-2} mol L^{-1}, n_{PCC}/n_{dyes} = 100/3). b) The normalized emission spectra and d) the corresponding CIE coordinates diagram of MA/AA@PCC co-assemblies doped with the achiral fluorescence dyes (The concentrations of PCC are 6.7×10^{-2} mol L^{-1}, n_{PCC}/n_{dyes} = 100/3).
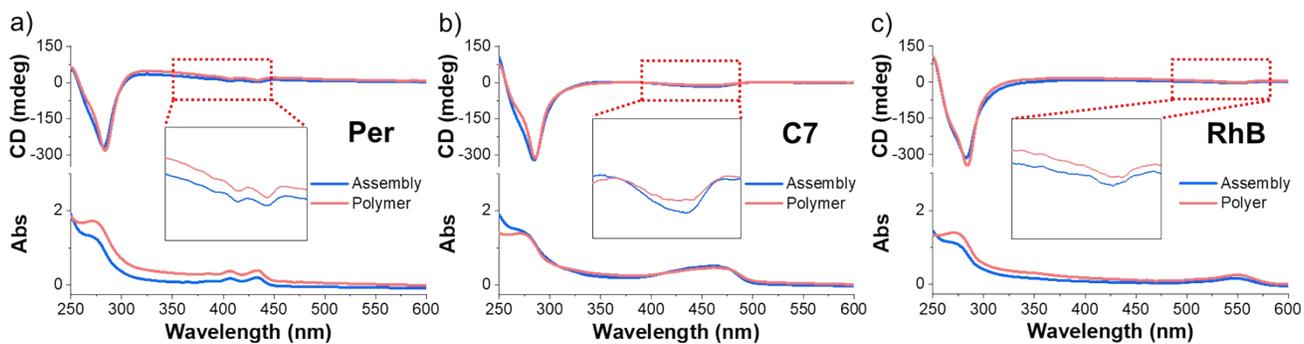
Fig. S15 CD and UV-Vis spectra of MA/AA@PCC co-assemblies and polymers doped with a) Per, b) C7, and c) RhB (The concentrations of PCC are 6.7×10^{-2} mol L^{-1}, $n_{PCC}/n_{dyes} = 100/3$). The inserts were the CD signals corresponding to the UV-Vis absorption of the achiral dyes which zoomed in from the red box.

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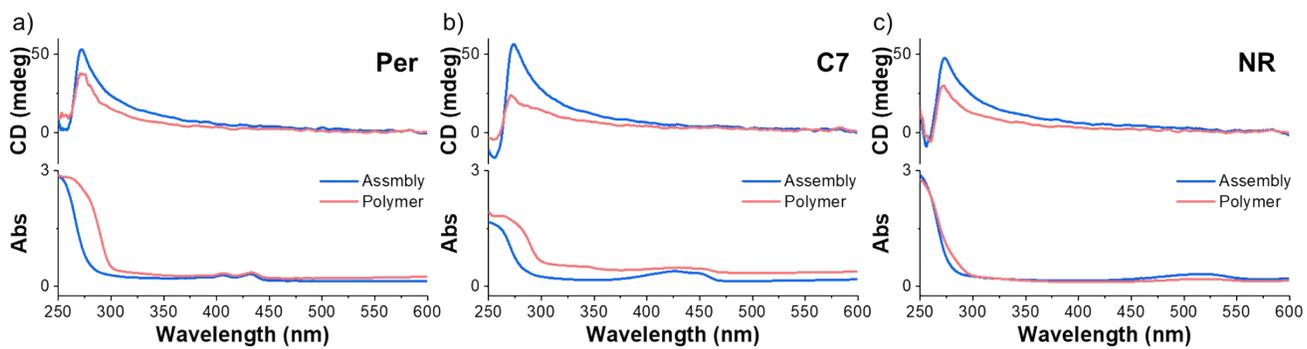
Fig. 16 CD and UV-Vis spectra of LMA@PCC co-assemblies and polymers doped with a) Per, b) C7, and c) NR (The concentrations of PCC are 2.0×10^{-2} mol L^{-1}, $n_{PCC}/n_{dyes} = 100/3$).
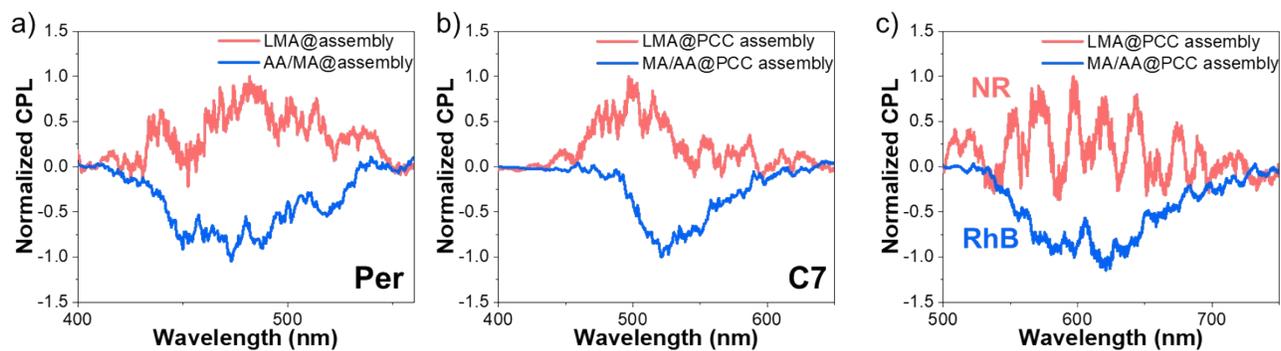
Fig. S17 a) Normalized CPL spectra of LMA@PCC co-assembly and MA/AA@PCC co-assembly doped with Per. b) Normalized CPL spectra of LMA@PCC co-assembly and MA/AA@PCC co-assembly doped with C7. c) Normalized CPL spectra of LMA@PCC co-assembly (Rose red line) and MA/AA@PCC co-assembly (blue line) doped with NR and RhB, respectively.
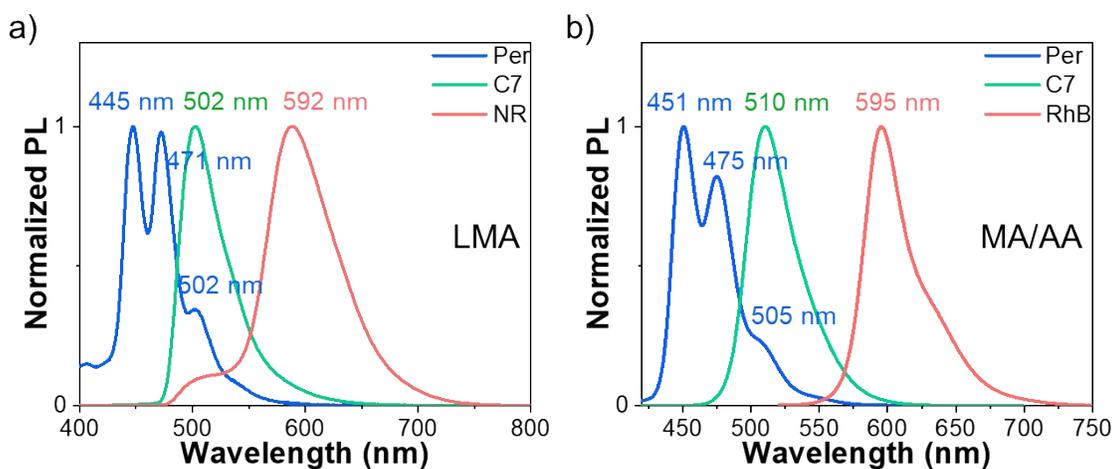
Fig. S18 a) The normalized emission spectra of LMA@PCC polymers doped with the achiral fluorescence dyes (The concentrations of PCC are 2.0×10^{-2} mol L^{-1}, $n_{PCC}/n_{dyes} = 100/3$). b) The normalized emission spectra of MA/AA@PCC polymers doped with the achiral fluorescence dyes (The concentrations of PCC are 6.7×10^{-2} mol L^{-1}, $n_{PCC}/n_{dyes} = 100/3$).
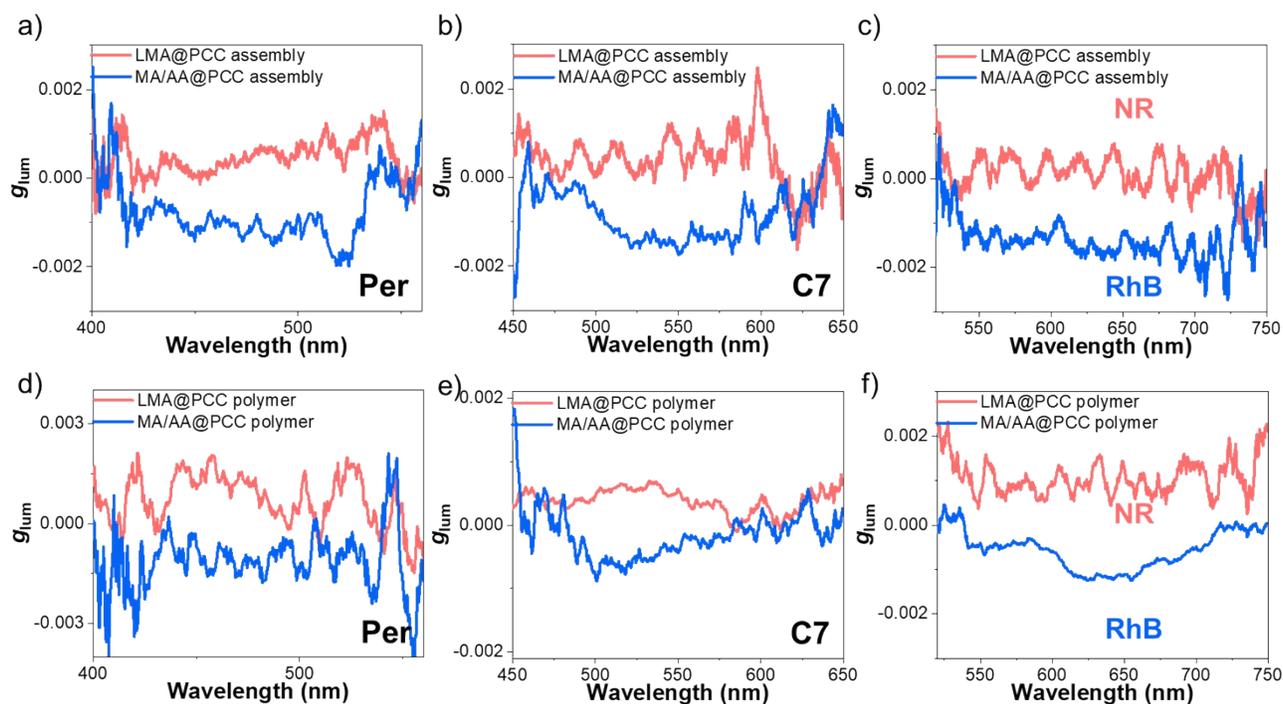
Fig. S19 a) g_{lum} spectra of LMA@PCC co-assembly and MA/AA@PCC co-assembly doped with Per. b) g_{lum} spectra of LMA@PCC co-assembly and MA/AA@PCC co-assembly doped with C7. c) g_{lum} spectra of LMA@PCC co-assembly (Rose red line) and MA/AA@PCC co-assembly (blue line) doped with NR and RhB, respectively. d) g_{lum} spectra of LMA@PCC polymer and MA/AA@PCC polymer doped with Per. e) g_{lum} spectra of LMA@PCC polymer and MA/AA@PCC polymer doped with C7. f) g_{lum} spectra of LMA@PCC polymer (Rose red line) and MA/AA@PCC polymer (blue line) doped with NR and RhB, respectively.