Supplementary Information (SI) for Nanoscale.

Chiral Optically Active Photonic Crystals Exhibiting Enhanced Fluorescence and Circularly Polarized Luminescence

Qilin Guo, Xingye Huang, Huateng Li, Jia Guo and Changchun Wang*

Affiliations

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, China

* Corresponding author: C. C. Wang, E-mail: ccwang@fudan.edu.cn

Experimental Section

Materials

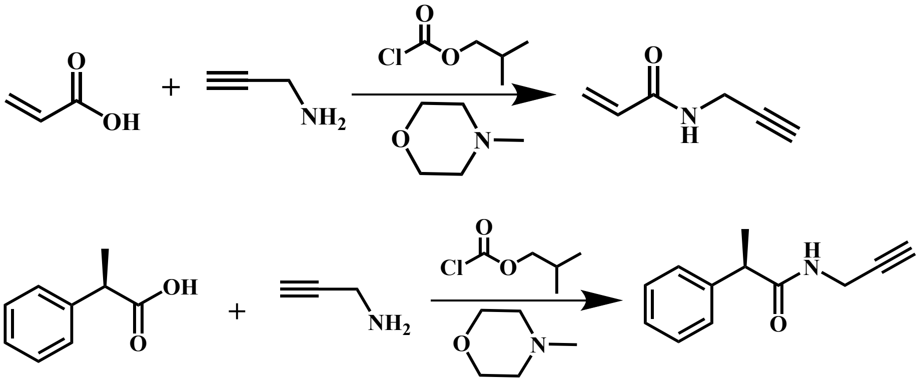
Styrene (St) and ethyl acrylate (EA) from Sinopharm Chemical Reagent Co., Ltd. was purified twice using alkaline alumina column to remove polymerization inhibitor before use. Sodium persulfate (SPS), sodium dodecylsulfate (SDS), acrylic acid (AA), potassium hydroxide (KOH), ethylene glycol dimethacrylate (EGDMA), 2-hydroxy-2-methylpropiophenone were purchased from Aladdin for using without further purification. Dowfax 2A1 and CO-436 surfactants were purchased from Dow Chemicals. Butanediol diacrylate (BDDA) was purchased from Tokyo Chemical Industry, Shanghai used for cross-linker. Deionized water was purified using a Millipore Milli-Q Synergy. (2-(4-vinylphenyl)ethene-1,1,2-triyl)tribenzene (TPEE, 98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. (S)-2-phenylpropanoic acid (Bide pharm), (R)-2-phenylpropanoic acid (Bide pharm), isobutyl chloroformate, 4-methylmorpholine and propargyl amine were used without further purification. (nbd)$Rh^+B^-(C_6H_5)_4$ was prepared as reported literature.[1]

Synthesis of PS@P(EA-co-AA) Core/ Shell Particles

The core/shell nanoparticles were synthesized by semi-continuous emulsion polymerization. Take the particles with 145 nm as an example, in a typical reaction process, 1.80 g styrene, 0.200 g BDDA, 0.120 g SDS and 140 g H_2O were added into a 500 mL flask and then the emulsion was heated to 85°C. Subsequently, 0.125 g SPS dissolved in 2.50 g water was added in the flask to initiate the emulsion polymerization for PS seeds. After 10 minutes, the emulsion containing 35.0 g St, 3.80 g BDDA, 45.0 g H_2O, 0.120 g SDS, 0.200 g KOH, 0110 g Dowfax2A1, 0.100 g SPS was added with a flow rate of 0.5mL/min to prepare PS cores. After 30 min of additional reaction, another emulsion consisting of 3.60 g AA, 32.4 g EA, 57.0 g H_2O, 0.29 g Dowfax2A1, 0.300 g KOH, 1.49 g CO436 and 0.250 g SPS were added with a flow rate of 0.7mL/min to prepare PS@P(EA-co-AA) core/shell particles. The obtained products were freeze-dried for 36 h in the freeze dryer (Ningbo Xinzhi Biotechnology Co., Ltd., SCIENTZ-10N) and ground for further use. Through changing the initial feeding of SDS with 0.110 g, 0.078 g and 0.070 g, various PS particles with 156, 182 and 204 nm can be obtained respectively.

Synthesis of N-propargyl acrylamide (M1) and N-propargyl-(R/S)-phenylpropanoamide (M2) monomers

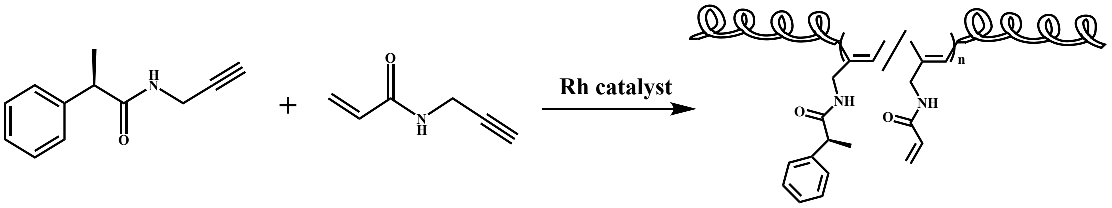
M1 and M2 (R and S) monomers were synthesized following the reported method.[2] Specifically, for M1 monomer, the acrylic acid (1.4 mL, 17.5 mmol), isobutyl chloroformate (2.3 mL, 17.5 mmol) and 4-methylmorpholine (2.2 mL, 17.5 mmol) were firstly added to tetrahydrofuran (THF) (100 mL) sequentially. After stirring for 10 min at room temperature, the propargyl amine (1.2 mL, 17.5 mmol) was added in the solution dropwise. Another 4 h later, the white precipitate formed in the reaction was filtered off. The solution was washed with 2 M HCl aqueous solution three times and then saturated aqueous $NaHCO_3$ to neutralize the solution. Finally, the solution was dried with anhydrous $MgSO_4$, filtered, and concentrated to give the target monomers. The crude M1 was further purified by column chromatography on silica gel (hexane/ethyl acetate=1/1). For M2 monomer, the main procedure was the same with M1 by simply changing acrylic acid to (S)-2-phenylpropanoic acid and (R)-2-phenylpropanoic acid, respectively. The synthetic route for M1 and M2 monomers are shown in Scheme S1.



Scheme S1 Synthetic route of the monomer M1 and M2 (R).

Synthesis of chiral helical copolymers (PM1-r-PM2)

Typically, 350 mg of M2 (R/S) and 50 mg M1 monomers were added to a Schlenk tube followed by an appropriate amount of anhydrous Trichloromethane. The concentration of the resulting solution was 0.1 M. The polymerization of M1 and M2 were initiated by adding a desired amount of $(nbd)Rh^+B^-(C_6H_5)_4$ catalyst (7 mg) in chloroform (TCM). When the copolymerization reaction was finished, the reaction mixture was poured into hexane to precipitate as-formed PM1-r-PM2 (R or S). The obtained copolymer was dried in a vacuum oven at 35 °C for 24 h to completely remove the residual solvent. The synthetic route for PM1-r-PM2 (R) copolymer is shown in Scheme S2.



Scheme S2 Synthetic route of the PM1-r-PM2 (R) copolymer.

Preparation of Optically Active Photonic Films

Appropriate amounts of nanoparticles (0.500 g) with TPEE (0.010 g) and chiral copolymer (0.020 g) were put in the vial, in which 0.220 g AA, 0.025 g EGDMA and 0.008 g 2-hydroxy-2-methylpropiophenone were added for well-mixed to form viscoelastic slurry. Then, 200 mg of slurry was pressed gently between two pieces of poly(ethylene terephthalate) (PET) films with a PET-slurry-PET sandwiched structure. After that, PET-slurry-PET was placed into the gap between the two rollers of the open mill to produce optically active photonic crystal films and photocrosslinked by ultraviolet light.

Preparation of Neat Photonic Films

Appropriate amounts of nanoparticles (0.500 g), 0.220 g AA, 0.025 g EGDMA and 0.008 g 2-hydroxy-2-methylpropiophenone were well-mixed to form viscoelastic slurry. Then, 200 mg of slurry was pressed gently between two pieces of PET films with a PET-slurry-PET sandwiched structure. After that, PET-slurry-PET was placed into the gap between the two rollers of the open mill to produce neat photonic crystal films.

Preparation of Neat AIE Films

0.010 g TPPE, 0.220 g AA, 0.025 g EGDMA and 0.008 g 2-hydroxy-2-methylpropiophenone were well-mixed, and then placed on the two PET films. Next, the composite films were exposed to ultraviolet light for 2 mins for cured.

Preparation of Composites Films without periodic colloids

0.010 g TPPE, 0.020 g chiral copolymers, 0.220 g AA, 0.025 g EGDMA and 0.008 g 2-hydroxy-2-methylpropiophenone were well-mixed, and then placed on the two PET films. Next, the composite films were exposed to ultraviolet light for 2 mins for cured.

Characterization Methods

Dynamic light scattering instrument (DLS, Malvern Zetasizer Nano ZS90) was used to record the hydrodynamic particle size and distribution of PS@P(EA-co-AA) nanoparticles under a helium-neon laser light source. Transmission electron microscopy (TEM, Tecnai G2 20 TWIN, FEI) was used to characterized PS seeds, PS cores and PS@P(EA-co-AA) nanoparticles sizes at an operating voltage of 120 kV. Field emission scanning electron microscopy (FESEM) micrographs were collected with a Zeiss Ultra 55 operated at a 3 kV and a working distance of 5.0-8.0 mm. The well-prepared samples were coated with Au at 10 mA for 120 s using a spray coater before measurement. Portable fiber spectrometer (Ideaoptics PG2000-Pro) was used to carry out the reflective and transmission spectra, and the standard aluminum mirror (100% reflection) was used as a reference. Photographs were taken illuminated with a LED light source against a dark background using a smartphone. Ultrasmall angle X-ray scattering (USAXS) characteristic was carried out in the Shanghai Synchrotron Radiation Facility (SSRF), China and analyzed by FIT 2D (v12.077). Characterisation of chiral molecules and helical polymers were used by gel permeation chromatography (GPC) and nuclear magnetic resonance hydrogen spectroscopy (^{1}H NMR). Photoluminescence (PL) profiles were performed on Fluorescence Spectrophotometer Qm 40 (PTI, USA) with a 370 nm laser excitation source. The lifetimes of fluorescence spectra were examined by FLS1000 (EdinburghInstruments, UK) equipped with a 420 nm laser as the excitation source and employing Time Correlated Single Photon Counting (TCSPC) technique. Circular dichroism spectra were carried out at room temperature using a Chirascan (Applied Photophysics Ltd,UK). Circularly polarized luminescence (CPL) measurements were performed with a JASCO CPL-300 spectrometer.

Figures:

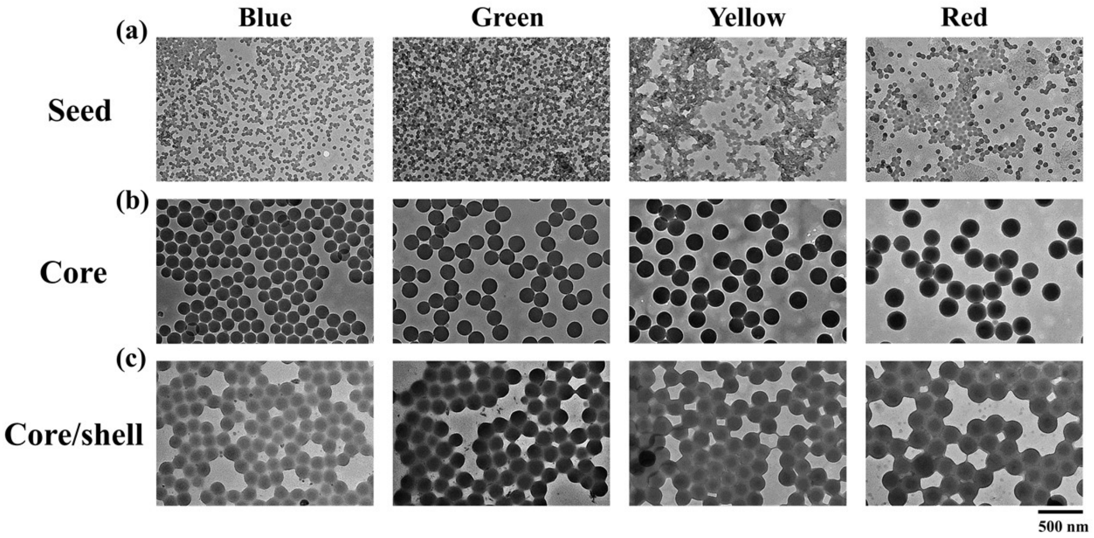


Figure S1 TEM images of (a) PS seed, (b) PS core and (c) PS@P(EA-co-AA) core/shell nanoparticles of blue, green, yellow and red, respectively

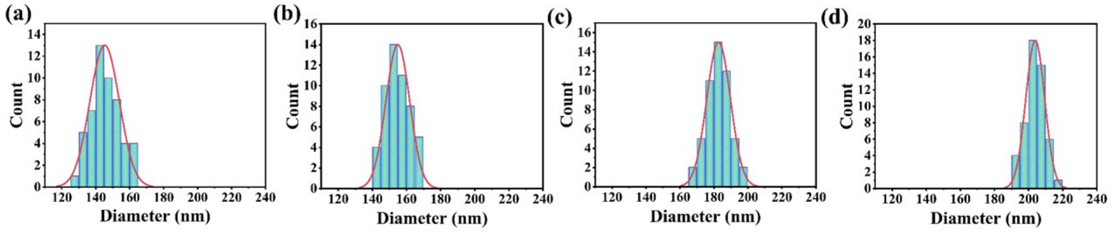


Figure S2 The diameter distribution histograms of PS core with (a) 145 nm, (b) 156 nm, (c) 182 nm and (d) 204 nm, respectively.

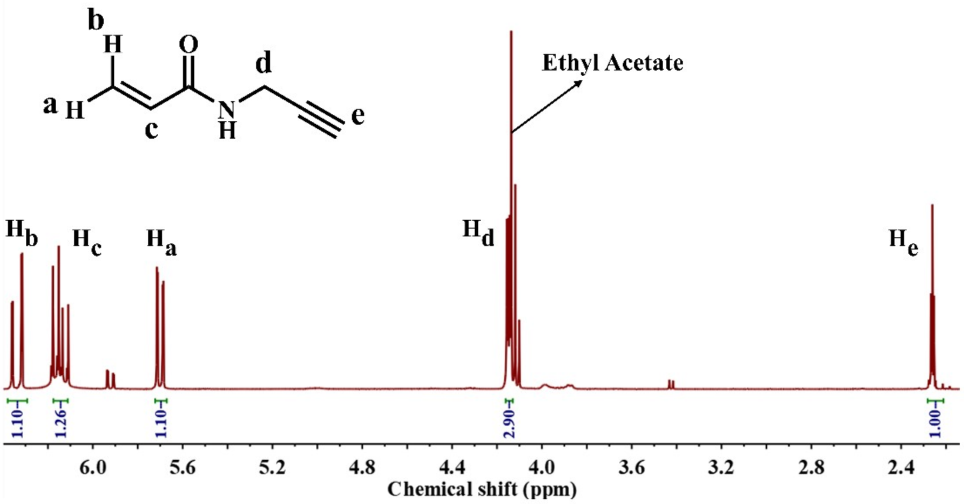


Figure S3 ^{1}H NMR spectra of as-synthesized M1 monomer.

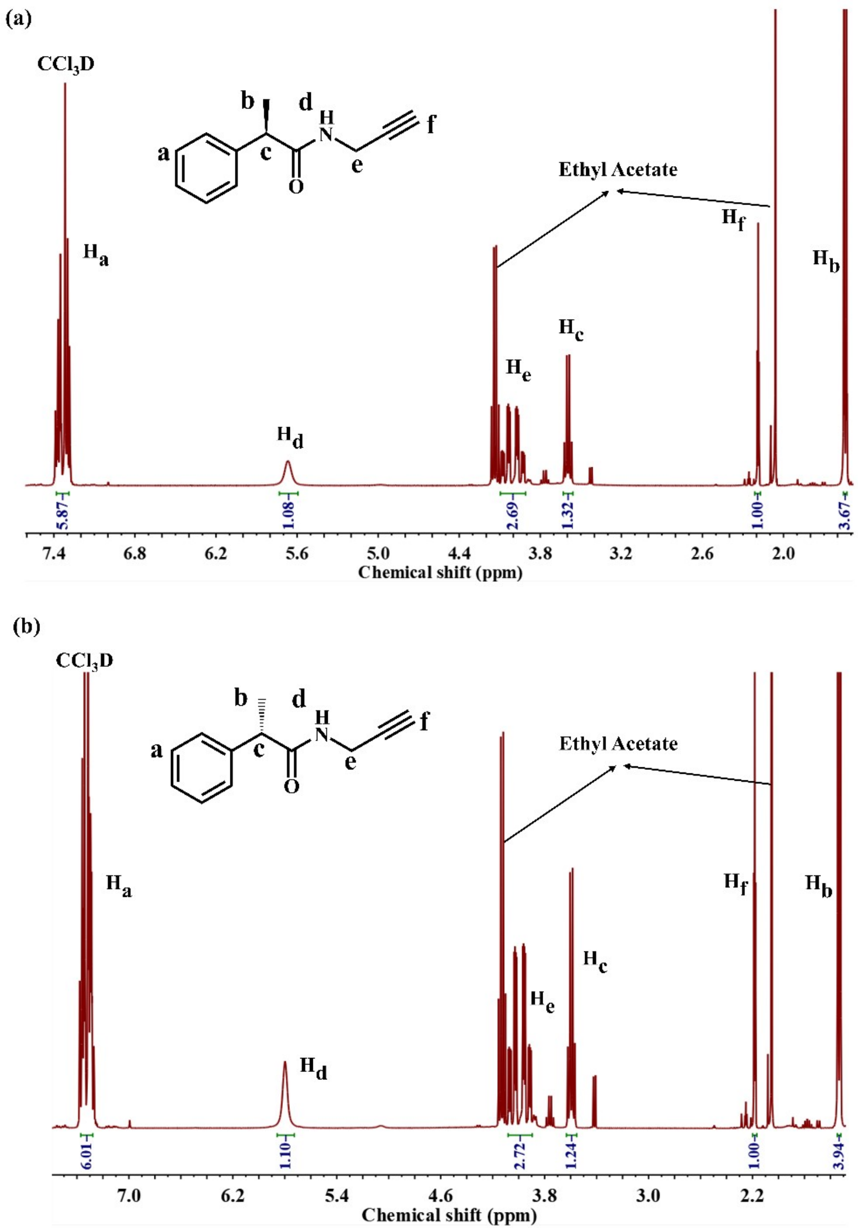


Figure S4 ^{1}H NMR spectra of as-synthesized (a) M2 (R) and (b) M2 (S).

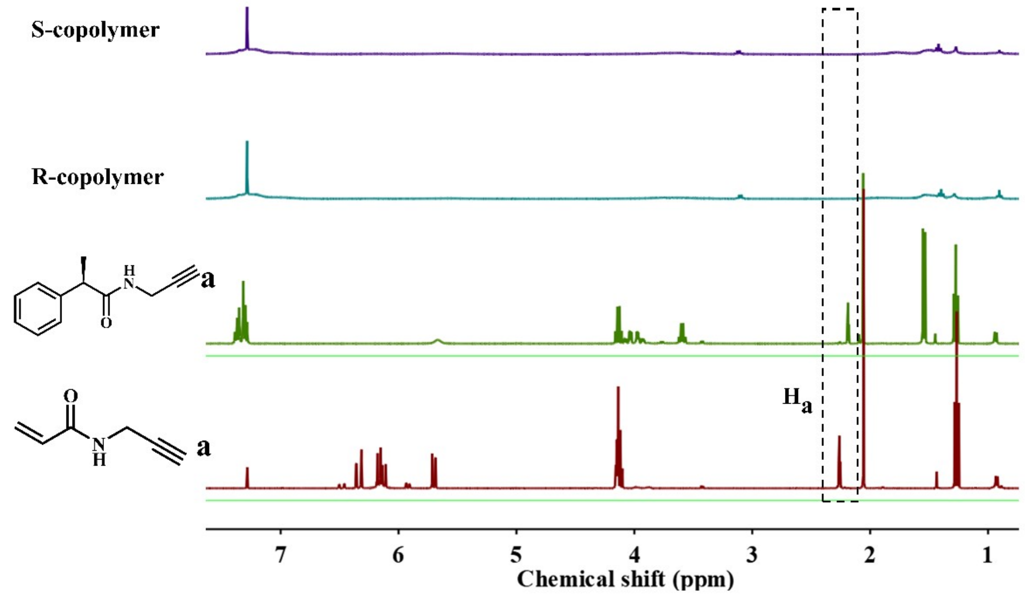


Figure S5 ^{1}H NMR spectra of M1, M2 monomer, and PM1-r-PM2 (R/S) chiral helical copolymers.

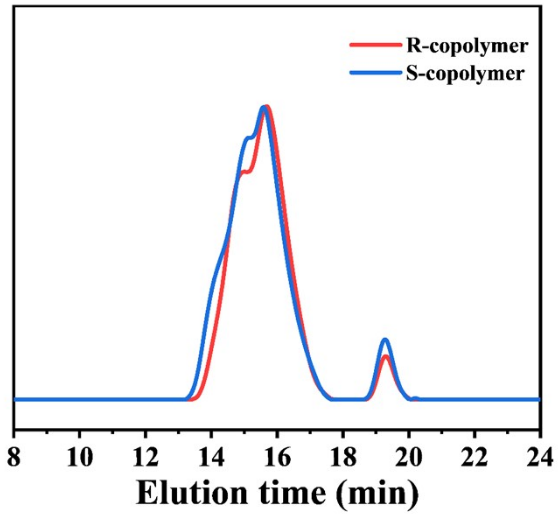


Figure S6 GPC curves of R-copolymer and S-copolymer. The obtained M_n of R-copolymer and S-copolymer is 8.2 kDa and 8.5 kDa, respectively.

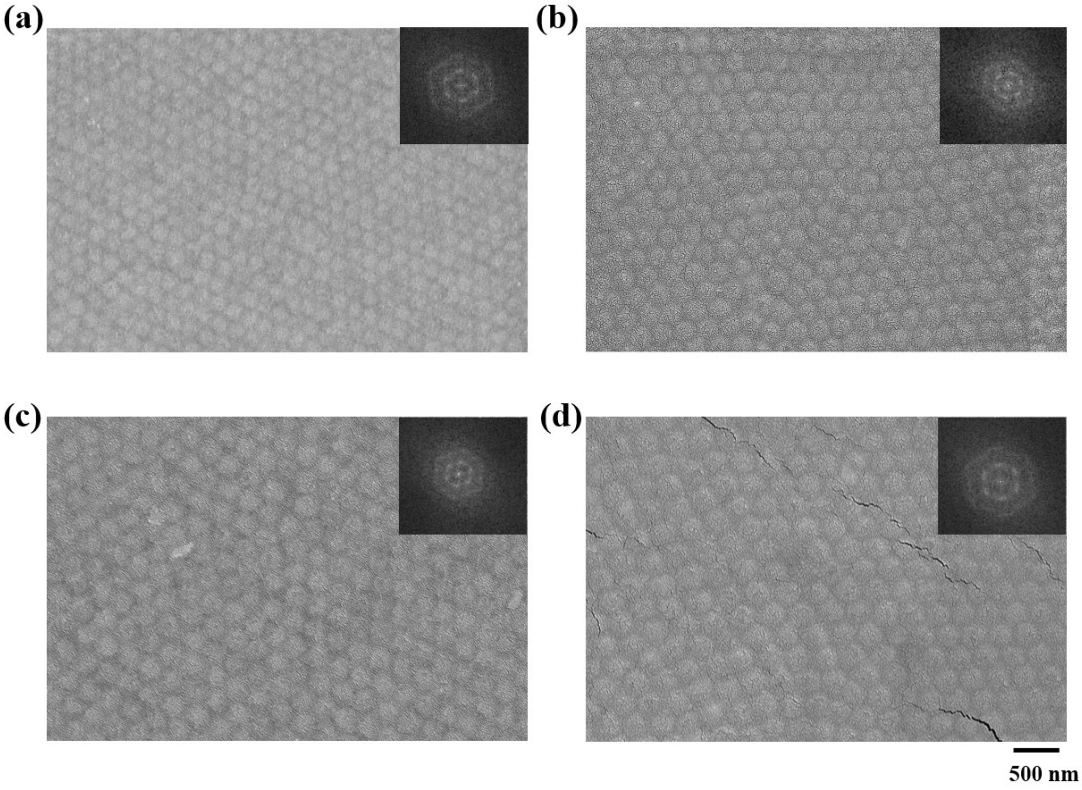


Figure S7 SEM images of photonic crystal films composed with colloidal nanoparticles with (a) 145 nm, (b) 156 nm, (c) 182 nm and (d) 204 nm. Inset shows the corresponding 2D fast Fourier transform (FFT) diagrams.

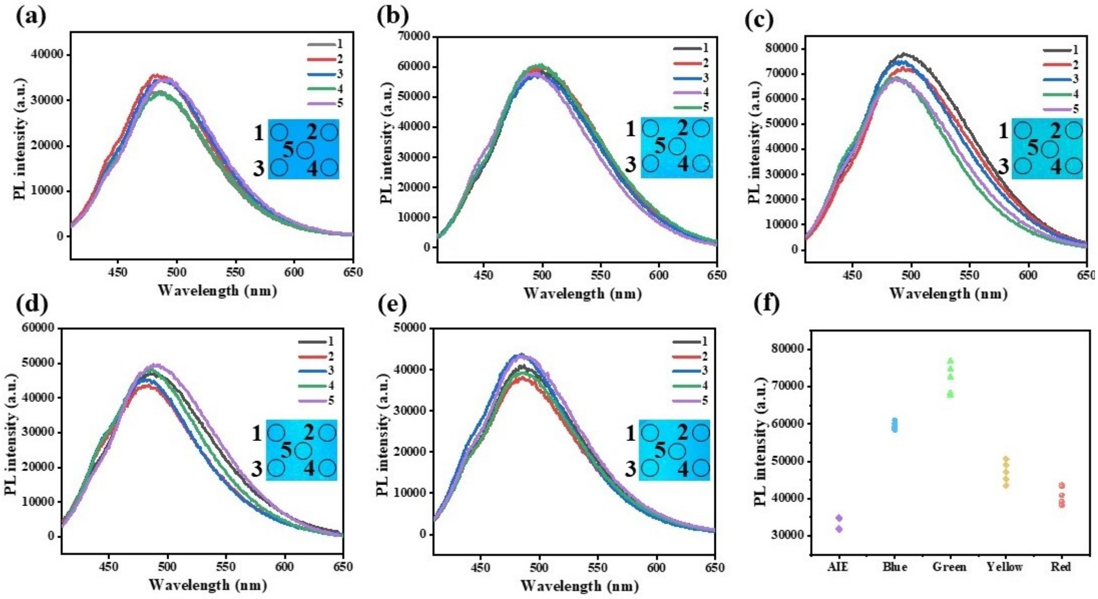


Figure S8 PL spectra of (a) neat AIE film, (b) blue, (c) green, (d) yellow and (e) red composite photonic films with five random points. The inset is the corresponding photographs under UV. (f) The summarized PL intensity of various films.

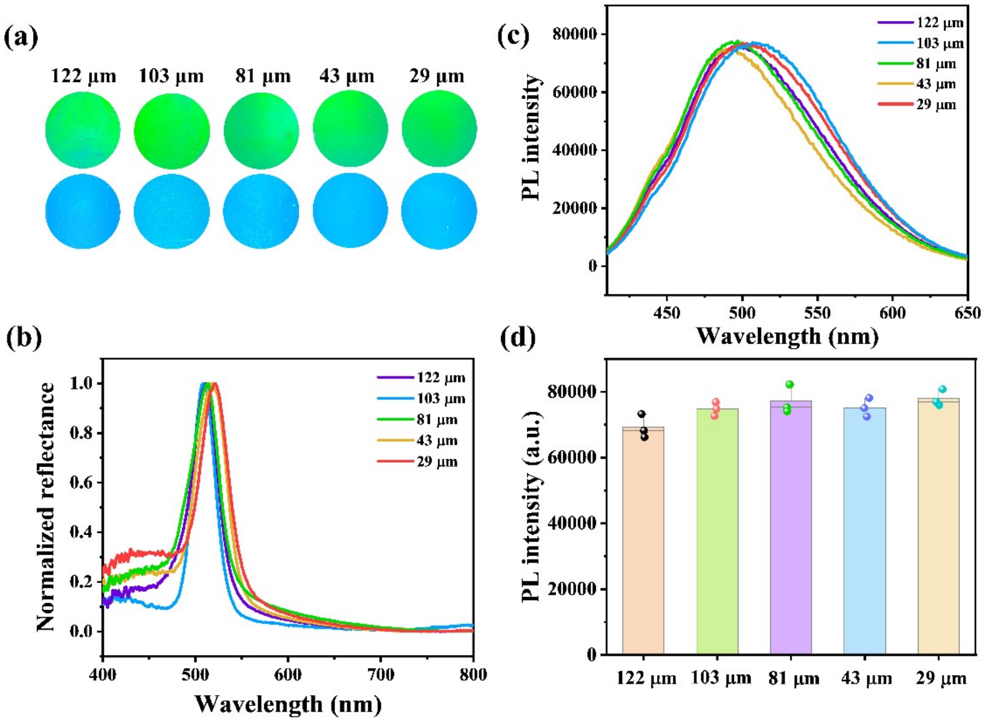


Figure S9 (a) Photographs, (b) reflection spectra, (c) PL spectra and (d) summarized PL intensity of green photonic crystal films with different thickness.

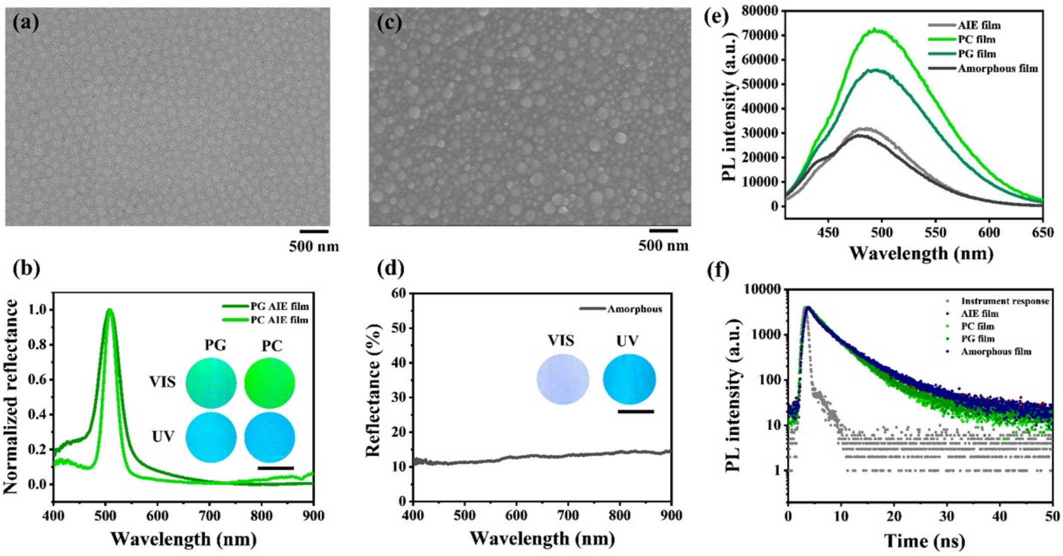


Figure S10 (a) SEM images and (b) reflection spectra of green photonic glass film. (c) SEM images and (d) reflection spectra of amorphous film. The scale bar is 1 cm. (e) PL spectra and (f) the time-resolved single-photon counting measurement of neat and composite AIE films. The scale bar is 1 cm.

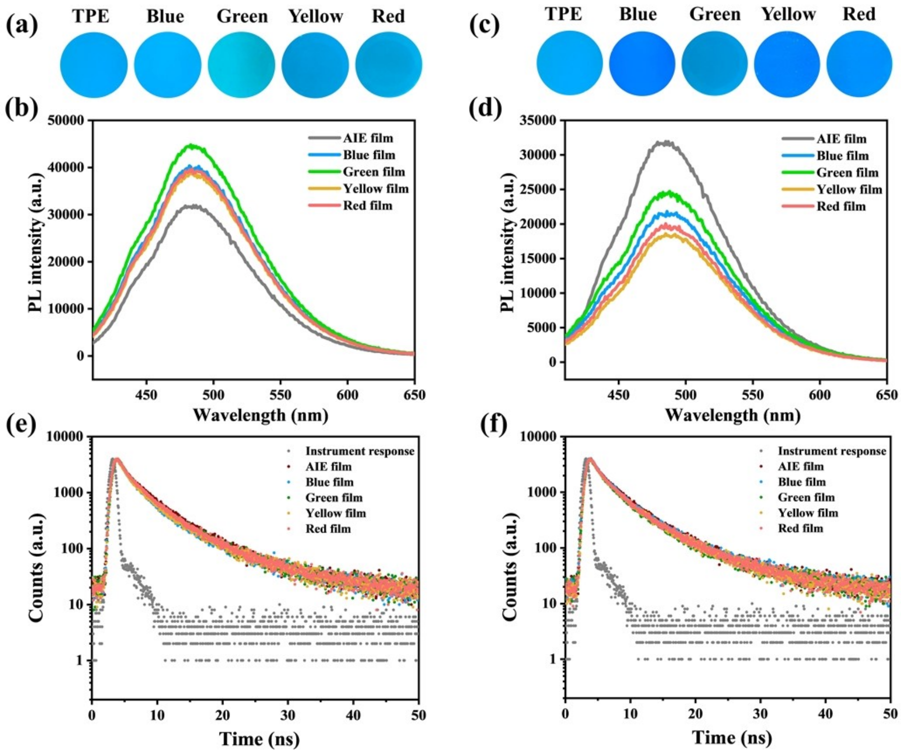


Figure S11 (a) Photographs, (b) PL spectra and (e) the time-resolved single-photon counting measurement of neat AIE films above the photonic films. (c) Photographs, (d) PL spectra and (f) the time-resolved single-photon counting measurement of neat AIE films beneath the photonic films.

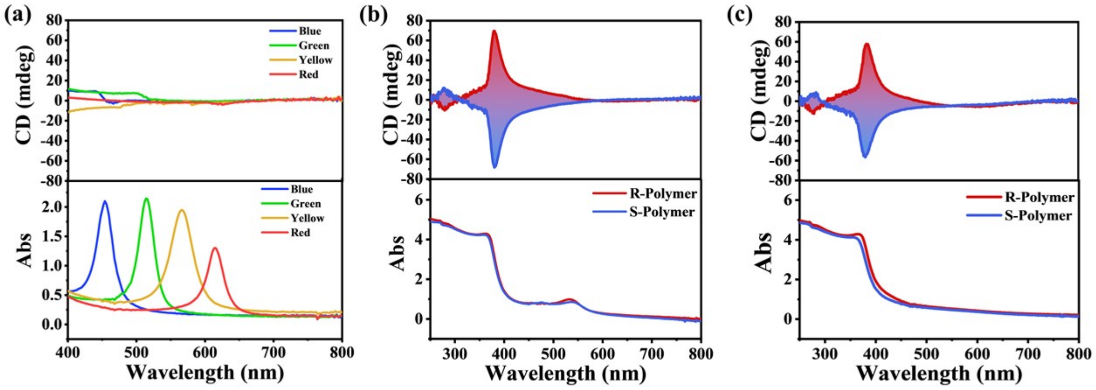


Figure S12 CD spectra and UV–vis spectra of (a) neat photonic crystal films, (b) composite photonic glass films and (c) the composite amorphous films.

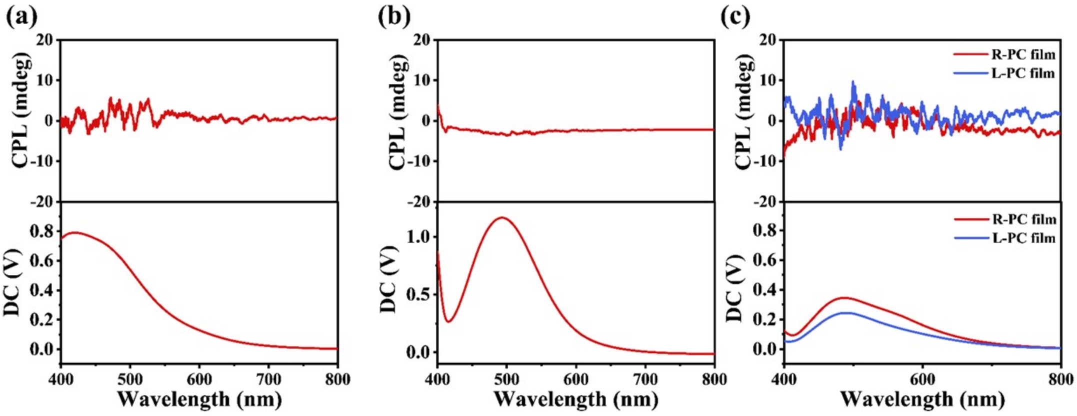


Figure S13 CPL spectra of neat (a) PC films, (b) AIE films and (c) chiral photonic crystal films.

References:

[1] R. R. Schrock, J. A. Osborn, *Inorg. Chem.* **1970**, *9,* 2339-2343.

[2] X. Du, J. Liu, J. Deng, W. Yang, *Polym. Chem.* **2010**, *1*, 1030-1038.