Supporting Information

Induced blue, green, and red-colour circularly polarized luminescence from single dye-doped homochiral poly(lactic acid) microspheres

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Materials and Measurements

PLLA (M_n = 20 kg mol^{-1}), poly(vinyl alcohol) (PVA, M_w = 31–50 kg mol^{-1}), and solvents were purchased from Sigma-Aldrich Co. Ltd. BPEA was purchased from Tokyo Chemical Industry Co., Ltd. All reagents and solvents were used without purification. The spin-coated PLLA-BPEA films were fabricated by a Mikasa MS-A-100 spin-coater. Typically, a mixture of PLLA (10 mg) and BPEA (0.1–1.0 mg) was dissolved in 0.2 mL of dichloromethane (CH_2Cl_2). The solution was sonicated for 10 min, allowing a homogeneous solution. A 0.2 mL of the solution was dropped on a quartz substrate and spin-coated at 1000 rpm for 60 s with slopes of 10 s both before and after the spin-coating. The resulting films were air-dried before characterization. The surface morphologies of PLLA-BPEA microspheres and composite film were observed using scanning electron microscopy (SEM, Hitachi S-3700N). The sample was dispersed in ethanol, and the suspension was drop-cast onto a silicon substrate and air-dried. A thin gold layer (approximately 30 nm) was formed on the surface for the SEM observation. Powder X-ray diffraction (PXRD) of the PLLA-BPEA microspheres was conducted using a Rigaku MiniFlex600 diffractometer, operating at 40 kV and 15 mA with Cu *K*α radiation (λ = 1.5418 Å). The scan range was set from 5° to 30° at a scanning speed of 1° min^{-1}. The crystallite percentage (X_c) was determined by analysing the diffraction peak area of the PLLA-BPEA microspheres in relation to the total diffraction peak area of the amorphous phase. Optical (OM), fluorescence (FM), and polarized optical microscopy (POM) micrographs were measured by Olympus model BX53 upright microscope. Photoabsorption spectra were measured with JASCO V-630 spectrophotometer using quartz cuvette with a pathlength of 1 mm. Photoluminescence

spectra were measured with JASCO FP-8300 spectrofluorometer. The fluorescence intensity ratio was calculated by dividing the area under the curve at 510, 540, or 593 nm by the overall area. The PLQY of the PLLA-BPEA microspheres was measured using Hamamatsu model C9920-02 absolute PL quantum yield measurement system. The PL lifetime measurements were performed by using a time correlated single photon counting (TCSPC) system setup of Horiba Jobin Yvon Fluorocube (Model No. FL- 1057) with an excitation pulsed diode light source (NanoLED-405L, Peak WL 408 nm, pulse duration < 200ps). The PL decay signals were collected by Horiba picosecond photon detection module (PPD-850) at the emission wavelength of respective fluorophores and analyzed by Horiba DataStation software. CD measurement from the suspension of PLLA-BPEA microspheres was performed using a JASCO model J-800. The CPL from both the suspension of PLLA-BPEA microspheres and spin-coated films was measured using a JASCO model CPL-300. The CPL properties of the microsphere suspension were evaluated under a stirring at the speed of 600 rpm at 20 °C. The CPL signal for the film sample of the microsphere was obtained by measuring at four different angles (0°, 45°, 90°, and 135°) in both front and back side.

Supporting Figures

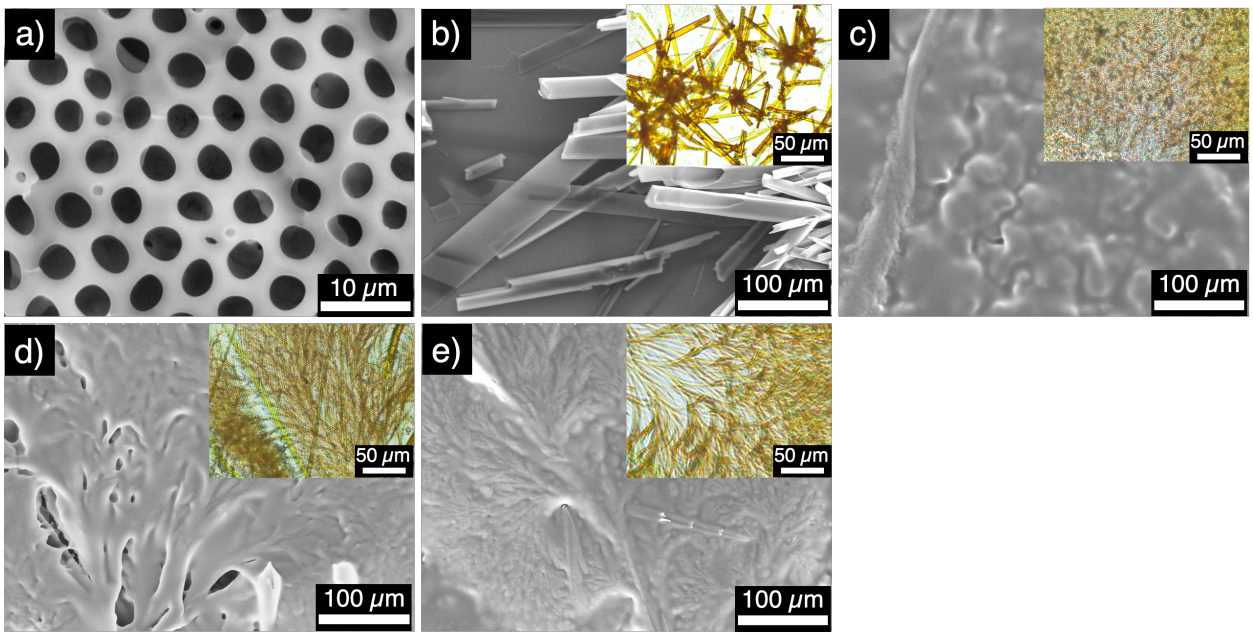

Figure S1. SEM micrographs of film samples of PLLA (a), BPEA (b), and PLLA-BPEA mixture with BPEA/PLLA ratio of 0.01 (c), 0.05 (d), and 0.1 (e) prepared by drop casting from CH_2Cl_2 solutions. Insets in (b)-(e) show OM images of the corresponding films.

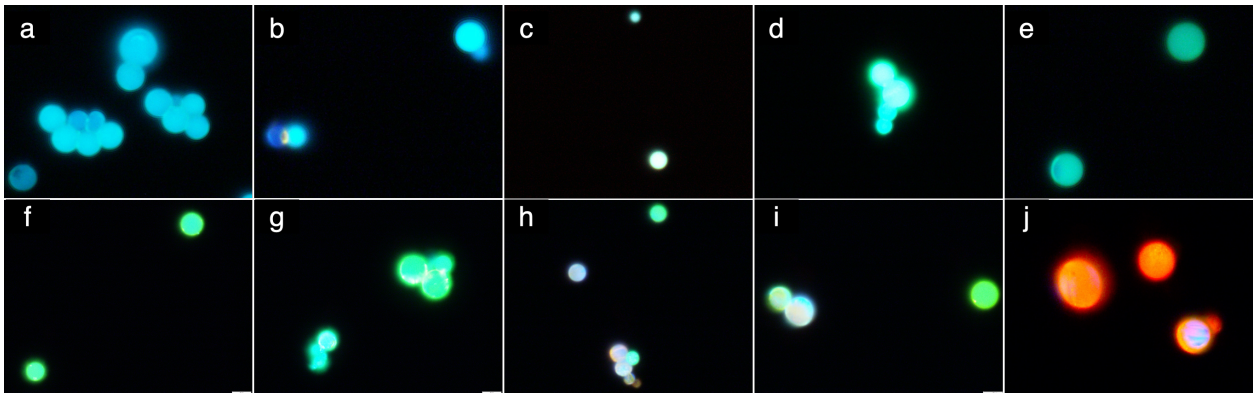

Figure S2. FM images (λ_{ex} = 450-480 nm) of self-assembled microspheres of PLLA-BPEA with different PLLA/BPEA ratio of 0.01 (a), 0.02 (b), 0.03 (c), 0.04 (d), 0.05 (e), 0.06 (f), 0.07 (g), 0.08 (h), 0.09 (i) and 0.1 (j).

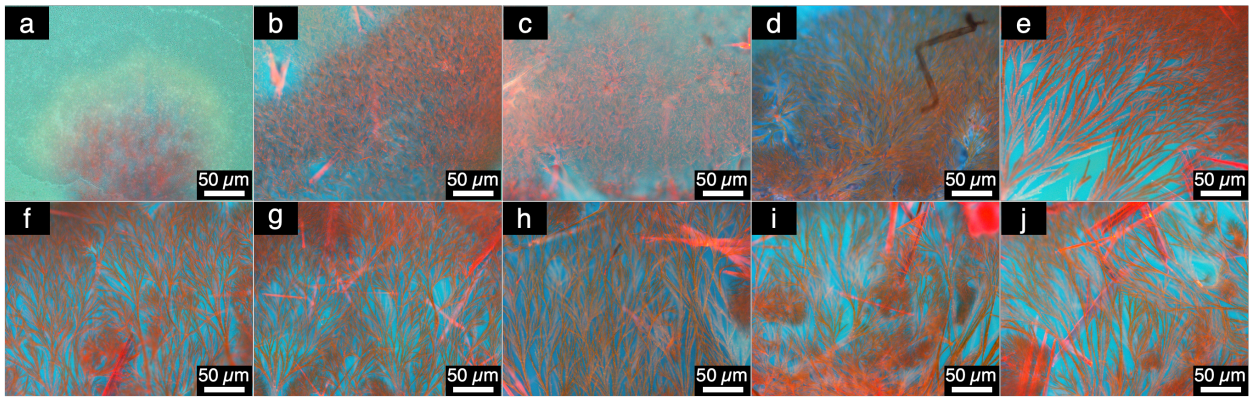

Figure S3. FM images (λ_{ex} = 450-480 nm) of cast films from CH_2Cl_2 solution of PLLA-BPEA with different PLLA/BPEA ratio of 0.01 (a), 0.02 (b), 0.03 (c), 0.04 (d), 0.05 (e), 0.06 (f), 0.07 (g), 0.08 (h), 0.09 (i) and 0.1 (j).

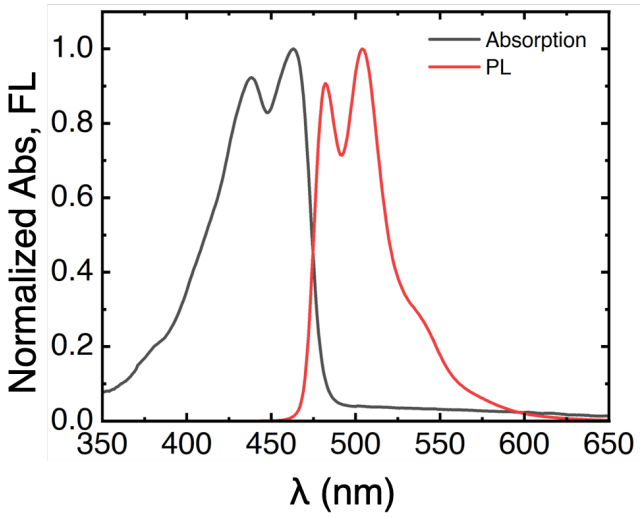

Figure S4. Photoabsorption and PL spectra (λ_{ex} = 380 nm) of a CH_2Cl_2 solution of BPEA.

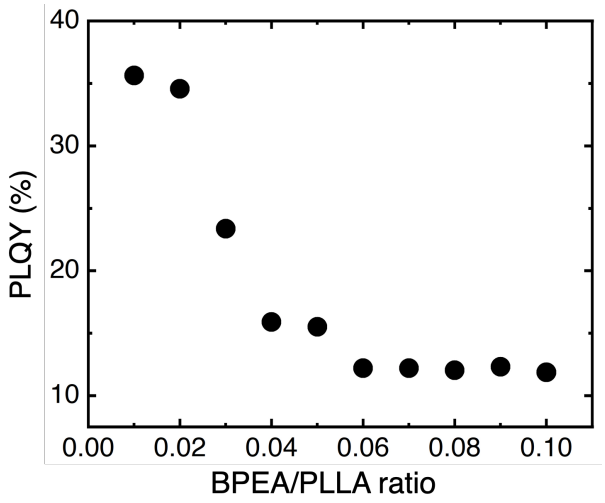

Figure S5. Plot of PLQY versus BPEA/PLLA mixing ratio (λ_{ex} = 380 nm).

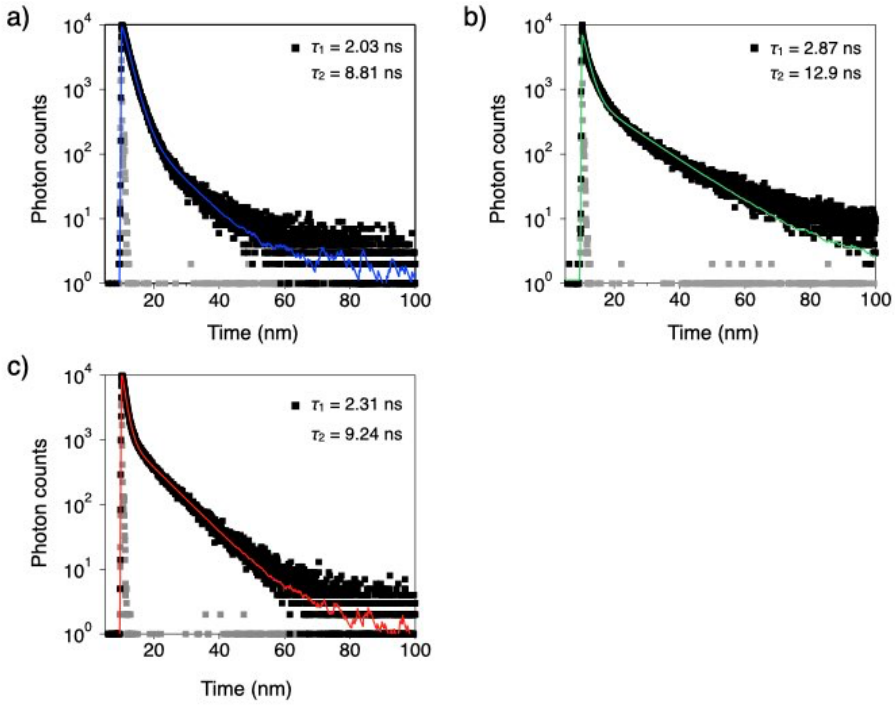

Figure S6. PL lifetime decay of PLLA-BPEA microspheres of BPEA/PLLA ratio of 0.01 (λ_{em} = 482 nm) (a), 0.05 (λ_{em} = 540 nm) (b) and 0.1 (λ_{em} = 593 nm) (c) with the LED excitation at 405 nm.

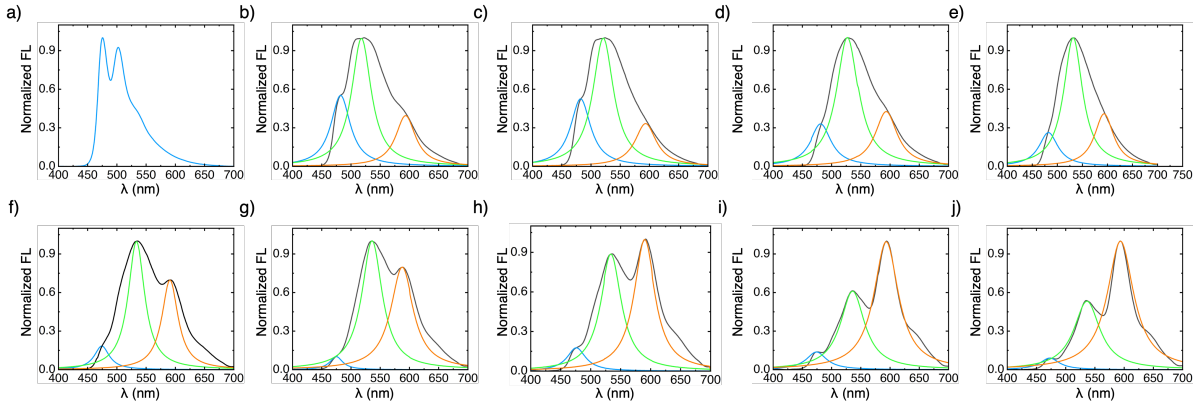

Figure S7. Deconvolution of PL spectra (λ_{ex} = 380 nm) of an aqueous suspension of PLLA-BPEA microspheres with different BPEA/PLLA ratio of 0.01 (a), 0.02 (b), 0.03, (c), 0.04 (d), 0.05 (e), 0.06 (f), 0.07 (g), 0.08 (h), 0.09 (i), and 0.1 (j).

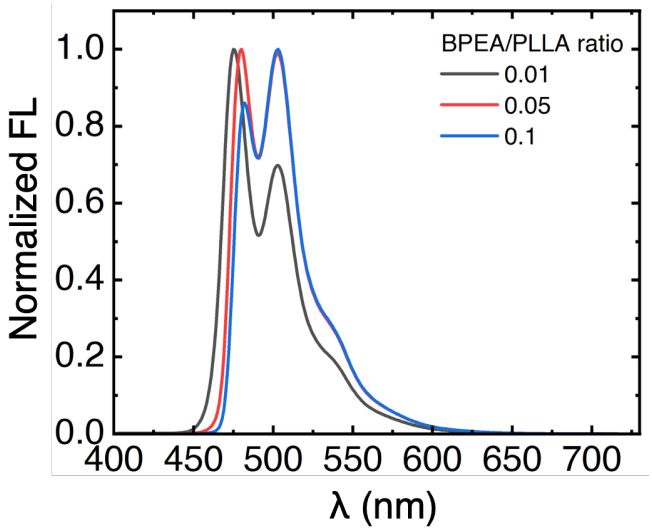

Figure S8. PL spectra (λ_{ex} = 380 nm) of CH_2Cl_2 solutions of a mixture of PLLA and BPEA with PLLA/BPEA ratios of 0.01 (black), 0.05 (red) and 0.1 (blue).

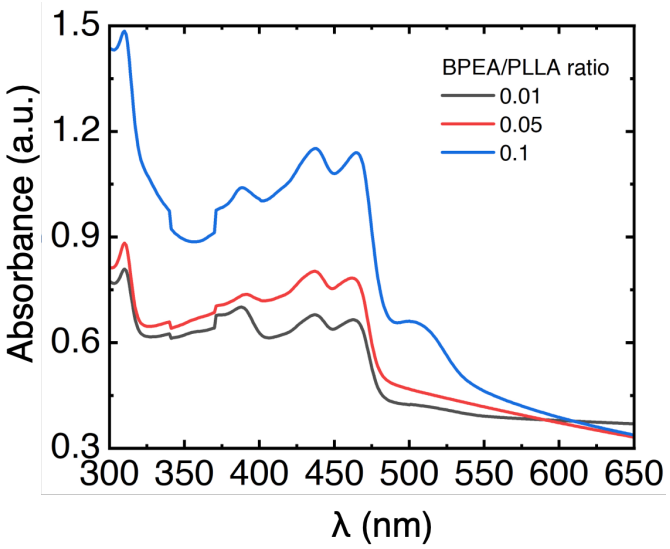

Figure S9. Photoabsorption spectra of PLLA-BPEA microsphere in an aqueous suspension.

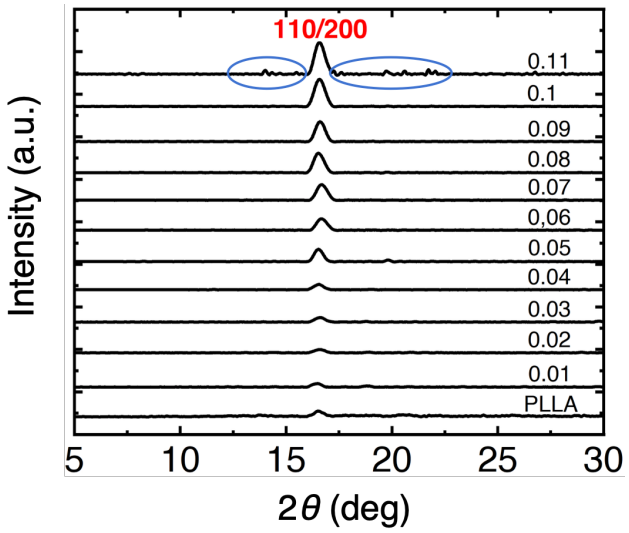

Figure S10. Powder X-ray diffraction (PXRD) patterns of PLLA-BPEA microsphere with different BPEA/PLLA ratio.

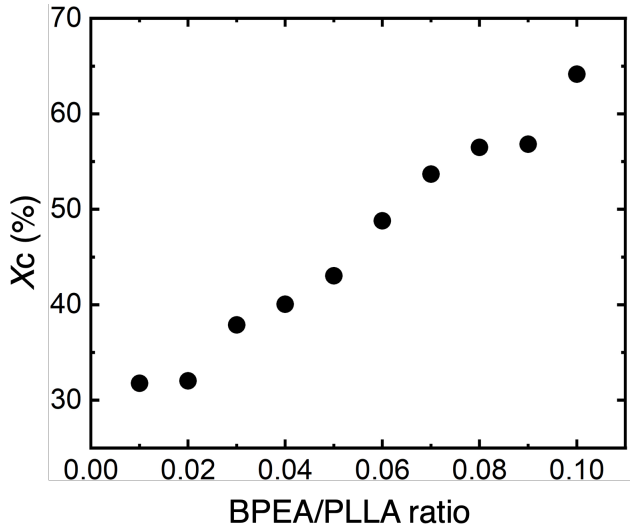

Figure S11. The degree of crystallinity of L20-BPEA microsphere by the increase of BPEA concentration.

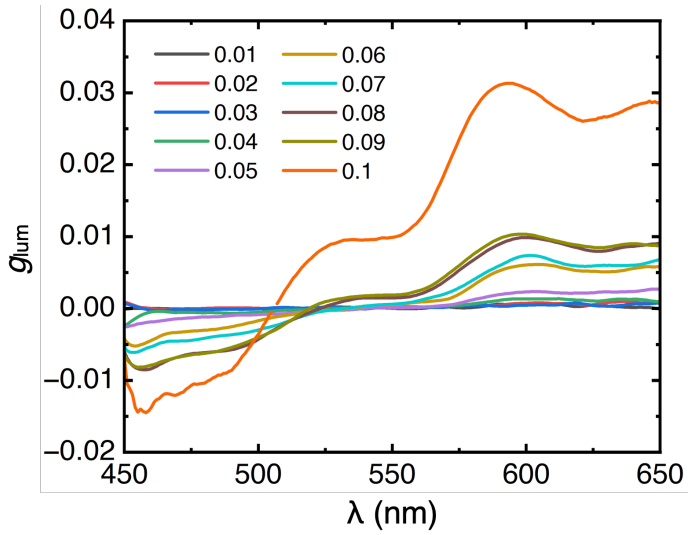

Figure S12. g_{lum} spectra of PLLA-BPEA microsphere with different BPEA/PLLA ratio.

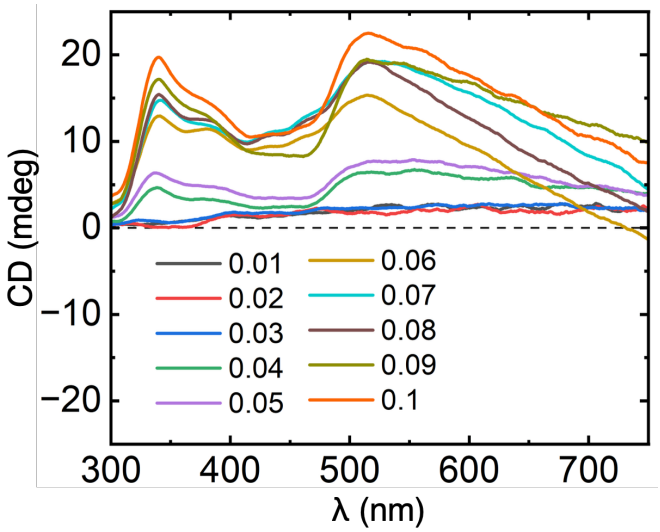

Figure S13. CD spectra of aqueous suspensions of PLLA-BPEA microspheres with different BPEA/PLLA ratio.

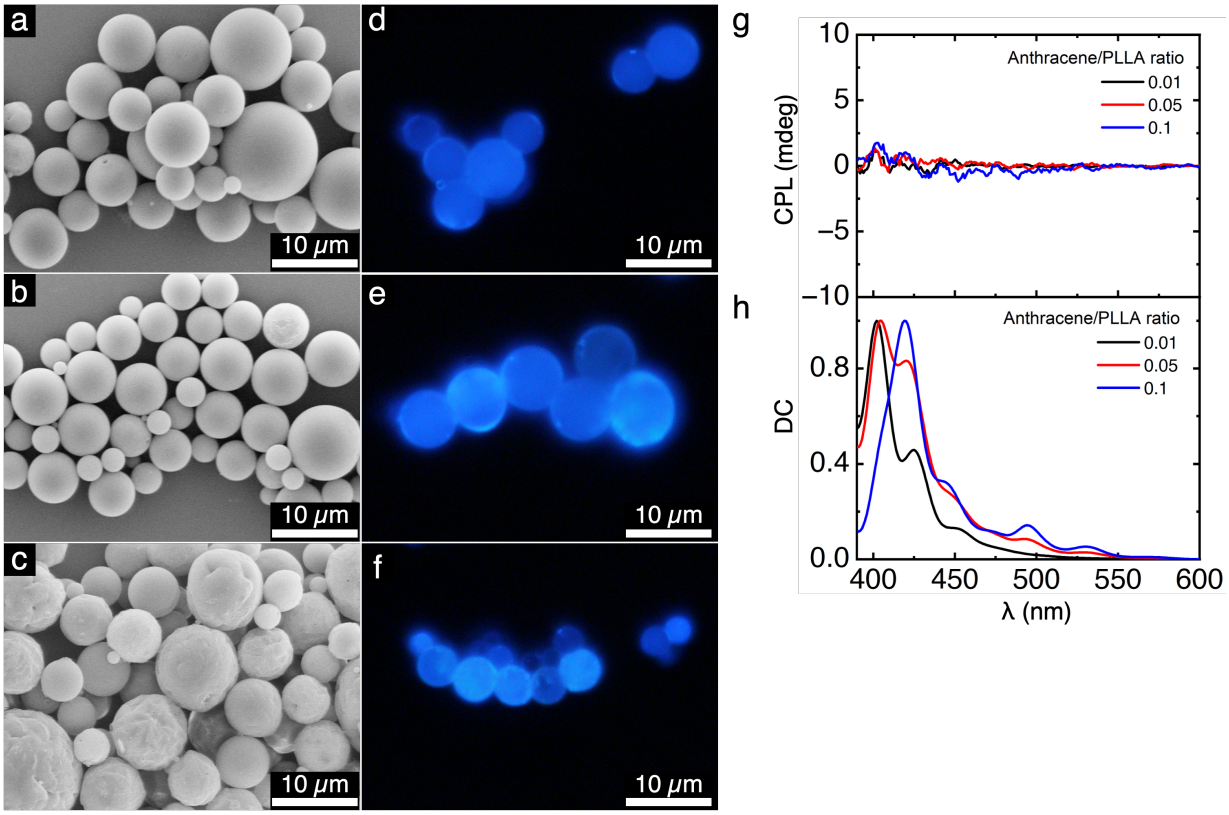

Figure S14. SEM (a-c) and FM images (d-f) of PLLA-AN microspheres with AN/PLLA ratio of 0.01 (a,d), 0.05 (b,e) and 0.1 (c,f). CPL spectra (c) and its DC spectra (d) of the suspensions of PLLA-AN microspheres with AN/PLLA ratio of 0.01, 0.05 and 0.1.

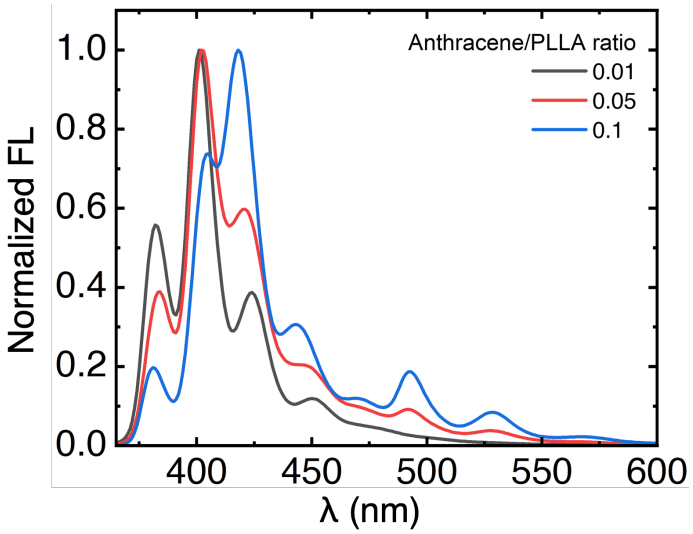

Figure S15. PL spectra (λ_{ex} = 350 nm) of an aqueous suspension of PLLA-AN microspheres with different AN/PLLA ratio of 0.01, 0.05 and 0.1

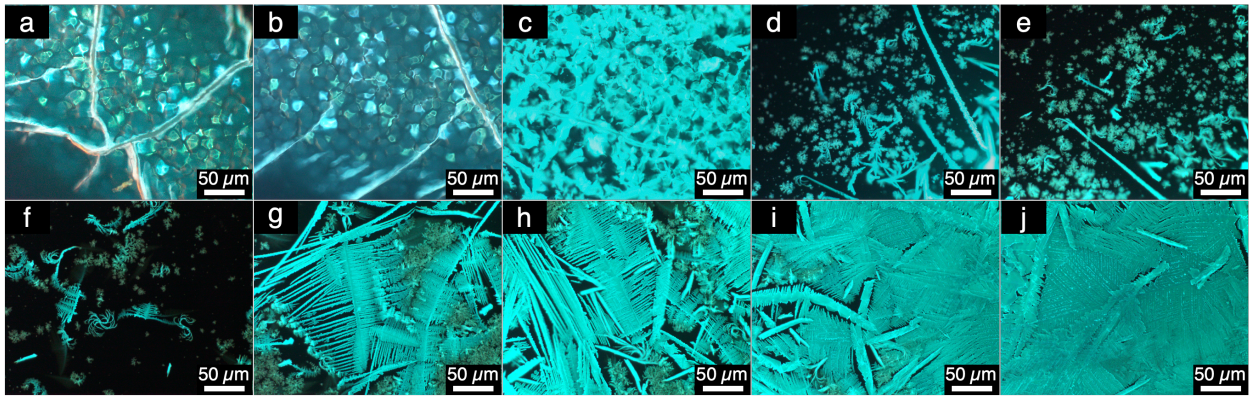

Figure S16. FM images (λ_{ex} = 450-480 nm) of cast films from CH_2Cl_2 solution of PLLA-AN with different AN/PLLA ratio of 0.01 (a), 0.02 (b), 0.03 (c), 0.04 (d), 0.05 (e), 0.06 (f), 0.07 (g), 0.08 (h), 0.09 (i) and 0.1 (j).

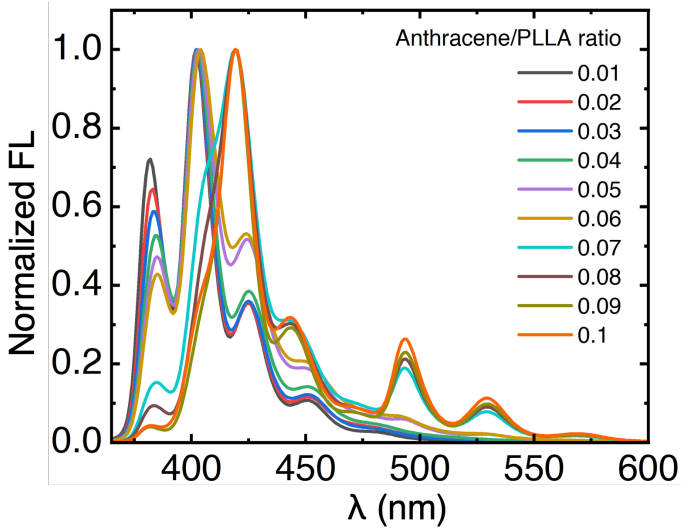

Figure S17. PL spectra (λ_{ex} = 350 nm) of cast films from CH_2Cl_2 solution of PLLA-AN with different AN/PLLA ratio.

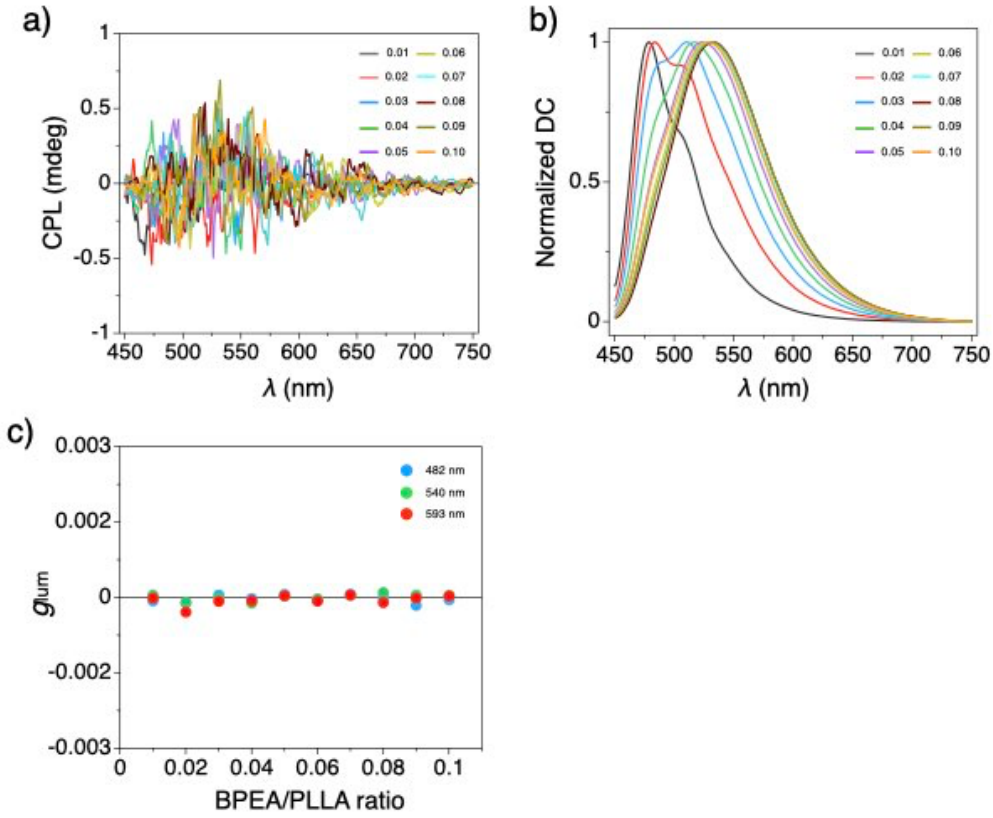

Figure S18. CPL spectra (λ_{ex} = 380 nm) (a) and its DC spectra (b) of PLLA-BPEA spin-coated films. (c) Plots of g_{lum} of the PLLA-BPEA spin-coated films with BPEA/PLLA ratio of 0.01–0.1 at 482 (blue), 540 (green), and 593 nm (red).