

## Supporting Information

# Tuning the Emission and Lighting the Circularly Polarized Luminescence of Polyfluorene by Incorporating a Non-emissive Polycarbene

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## ***Measurements***

The  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 600 MHz spectrometer as denoted. Chemical shifts are reported in delta ( $\delta$ ) units and expressed in parts per million (ppm) downfield with tetramethylsilane or residual chloroform as an internal standard. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of two linear TSK gel GMHHR-H columns. The number-average molecular weight ( $M_n$ ) and its polydispersity ( $M_w/M_n$ ) data were reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. Fourier transform infrared (FT-IR) spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets at 25 °C. High performance liquid chromatography (HPLC) with UV-vis detector was carried out on SHIMADZU LC-20AT equipment using chiral columns. Circular dichroism (CD) spectra were obtained in a 1.0 cm quartz cell using a JASCO J1500 spectropolarimeter. The UV-vis absorption spectra were recorded on a UNICO 4802 UV/vis double beam spectrophotometer. Fluorescence spectra were recorded on Hitachi F-4600 fluorescence spectrophotometer using 1.0 cm quartz cell. The CPL spectra were measured using a JASCO CPL-300 spectrometer at room temperature. A 1.0 cm quartz cuvette was used. Atomic force microscope (AFM) was performed on a Cypher S microscope (Oxford Instruments, Asylum Research).

## ***Materials***

All solvents were purchased from Sinopharm Co. Ltd. and purified by the standard

procedures before use. All chemicals were purchased from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. The monomers **2s** and **2r** were prepared according to the procedures reported by our group previously.<sup>1,2</sup>

**Procedure for polymerization:** In a thoroughly dried 25 mL polymerization reaction flask, a mixture of 7-bromo-9,9-dihexyl-9H-fluoren-2-yl (269 mg 0.5 mmol), LiCl (21.2 mg, 0.5 mmol) and dry THF (10 mL) was added. The resulting solution was cooled to  $-20\text{ }^{\circ}\text{C}$ . Then a THF solution of *i*PrMgCl (0.3 mL, 0.54 mmol) was added via a micro syringe. The mixture was stirred at  $-20\text{ }^{\circ}\text{C}$  for 2 h to complete the monomer conversion. Then elevating the temperature to  $25\text{ }^{\circ}\text{C}$ , Ni(dppp)Cl<sub>2</sub> (dppp = 1,3-bis(diphenylphosphanyl)propane) (20.9 mg, 0.025 mmol) was added ( $[\mathbf{1}]_0/[\text{Ni}]_0 = 20$ ) under nitrogen atmosphere.<sup>3</sup> After the mixture was stirred at room temperature for 1 h, a small volume of the solution was withdrew by microsyringe and was quenched by methanol. The precipitate solid was separated by centrifugation and dried under vacuum to afford poly-**1**<sub>20</sub> as a green solid. SEC:  $M_n = 6.5\text{ kDa}$ ,  $M_w/M_n = 1.23$ . <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.85 (d, 2H), 7.66–7.69 (m, 4H), 2.12 (br, 4H), 1.12–1.23 (m, 20H), 0.78–0.85 (m, 6H).

To the resulting polymerization solution, a solution of **2s** (100 mg, 0.526 mmol) in dry THF (0.95 mL) was added via a syringe. After the mixture was stirred at room temperature for 12 h, the solution was poured into large amount of ether. The precipitate solid was collected via filtration and dry under vacuum to afford poly(**1**<sub>20</sub>-*b*-**2s**<sub>100</sub>) as a yellow solid (91% yield). As indicative of SEC analysis, the single

modal SEC trace of poly-**1**<sub>20</sub> was shifted to high- $M_n$  region after copolymerized with **2s**, while maintained single modal distribution. The  $M_n$  and  $M_w/M_n$  of the isolated poly(**1**<sub>20</sub>-*b*-**2s**<sub>100</sub>) was 10.7 kDa and 1.14, respectively. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  (ppm) 7.90–7.50 (brs, 1.0H, ArH of poly-**1**<sub>20</sub> segment), 7.81–6.44 (br, 5H, ArH of poly-**2s**<sub>100</sub> segment), 6.24–4.83 (br, 1H, CO<sub>2</sub>CH of poly-**2s**<sub>100</sub> segment), 4.39–2.49 (br, 1H, CH of poly-**2s**<sub>100</sub> main chain), 2.13 (br, 0.5H, CH<sub>2</sub> of poly-**1**<sub>20</sub>), 2.1–0.5 (brs, 39.7H, CH<sub>2</sub> of poly-**1**<sub>20</sub>), 1.15–0.50 (brs, 7.9H, CH<sub>3</sub> of poly-**1**<sub>20</sub>). 2.11–0.18 (br, 3H, CHCH<sub>3</sub>). FT-IR (KBr, cm<sup>-1</sup>): 3065 ( $\nu_{C-H}$ ), 3035 ( $\nu_{C-H}$ ), 2980 ( $\nu_{C-H}$ ), 2942 ( $\nu_{C-H}$ ), 2869 ( $\nu_{C-H}$ ), 1728 ( $\nu_{C=O}$ ), 809 ( $\nu_{C-H}$ ).

The poly-**2s**<sub>100</sub> and poly-**2r**<sub>100</sub> were prepared follow the procedure reported by our group previously.<sup>3</sup> SEC:  $M_n = 13.9$  kDa,  $M_w/M_n = 1.19$ . <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.85–6.44 (br, 5H, ArH), 6.23–4.84 (br, 1H, CO<sub>2</sub>CH), 4.39–2.51 (br, 1H, CH of main chain), 2.06–0.18 (br, 3H, CHCH<sub>3</sub>).

**Procedure for self-assembly:** A solution of poly(**1**<sub>20</sub>-*b*-**2s**<sub>100</sub>) or poly(**1**<sub>20</sub>-*b*-**2r**<sub>100</sub>) in THF (10.0 mg/mL in THF) was prepared in a small vial and the mixed THF/MeOH (v/v = 6/4) solvents were added dropwise (0.2 mg/mL). The clear yellow solution was turned orange. The solution was aged for 1 days, and then subjected to AFM, UV-vis, and CD analyses.

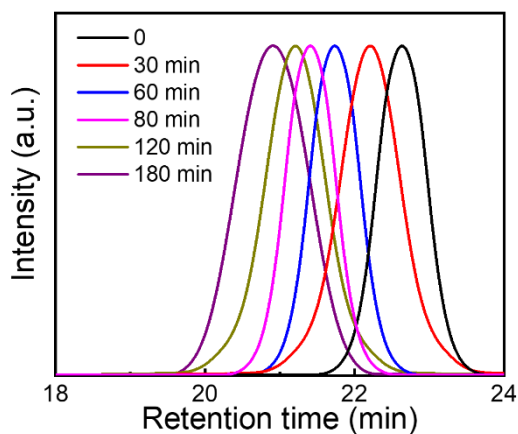
**AFM observation:** AFM were performed at room temperature in a dry state using Cypher S microscope (Oxford Instruments). Both topographic and phase images of assemblies of different nanostructures were obtained in Tapping Mode using rectangular silicon cantilever with a spring constant of 26 N m<sup>-1</sup>, a resonance frequency

lying in the 62-120 kHz range and a radius of curvature of less than 10 nm. A drop (20  $\mu$ L) of suspension was deposited onto clean silicon wafer and after 2 minutes the excess of solution was removed with blotting paper. Subsequently, the substrate was dried under nitrogen flow for several minutes. Measurements of the length and width of the nanofibers were taken using the section Particle Analysis tool provided with the AFM software (Asylum Research).

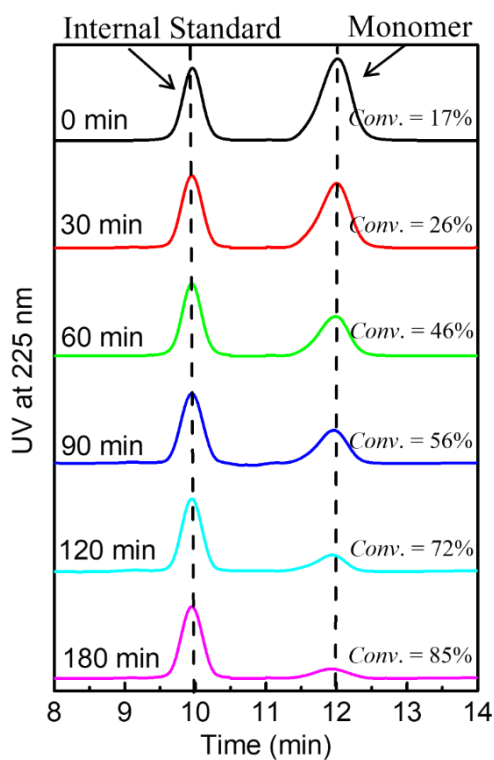
***Quantum yield measurements:*** The quantum yields were determined following the typical procedure described in literatures.<sup>4</sup> Rhodamine B was used as a standard for all samples. Taking the measurement of poly(**1<sub>20-b-2s</sub>100**) as an example. The UV-vis and fluorescent spectra were recorded for a series of dilute toluene solutions of poly(**1<sub>20-b-2s</sub>100**) in various concentrations. The optical density (OD) was kept lower than 0.1 for all quantum yield measurements to avoid the self-quenching. The OD value at the excitation wavelength was recorded and an emission spectrum of the diluted solution was then acquired. All the samples were excited at 360 nm. The entire set of measurements was repeated three or four times for each sample. The quantum yield was then determined by the following equation:

$$QY_X = QY_S \left( \frac{Grad_X}{Grad_S} \right) \left( \frac{n_S^2}{n_X^2} \right)$$

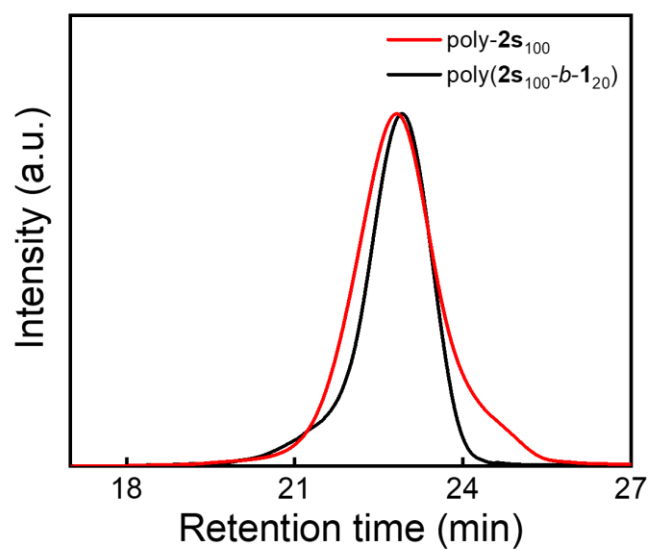
Where Grad<sub>X</sub> and Grad<sub>S</sub> are the slopes of absorption intensity vs. integrated fluorescent intensity for the block copolymers and standard, respectively. The n<sub>X</sub> and n<sub>S</sub> are the respective solvent indices of refraction, and QY<sub>X</sub> and QY<sub>S</sub> are the quantum yield values of the block copolymers and the standard, respectively.



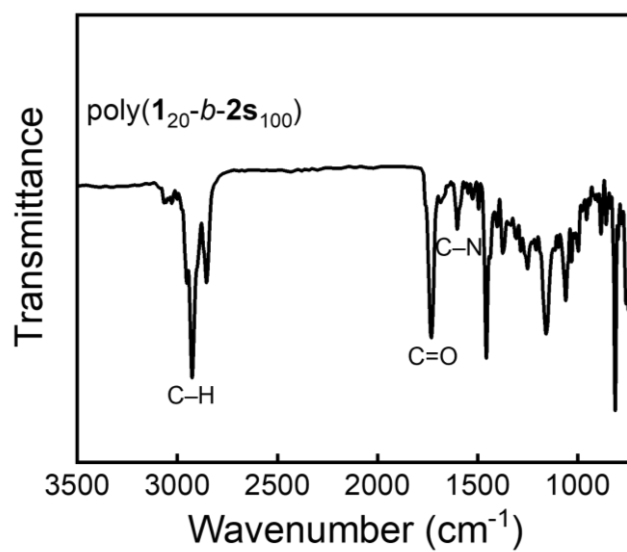
**Figure S1.** Time-dependent SEC for Ni(II)-terminated poly-**1**<sub>20</sub> initiated living polymerization of **2s** ( $[2s]_0/[Ni]_0 = 100$ , THF, 25 °C).



**Figure S2.** Time-dependent HPLC curves for the polymerization of monomer **2s** with the presence of 1,4-dimethoxybenzene as internal standard. HPLC conditions: column: AD-H; eluent: *n*-hexane/isopropanol = 9/1 (v/v); eluent rate: 0.50 mL/min.

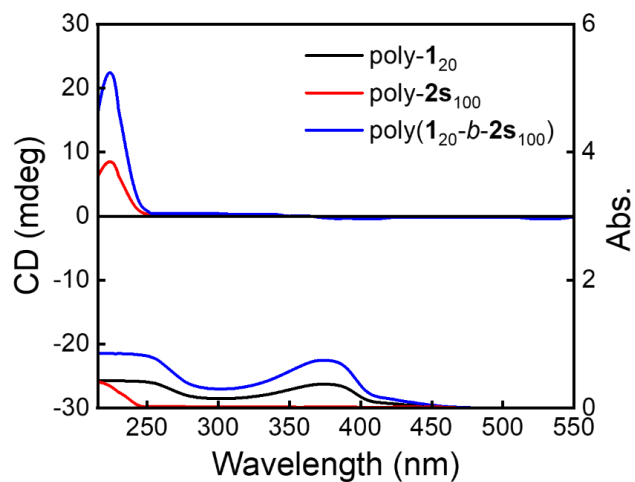


**Figure S3.** SEC for poly-2s<sub>100</sub> and poly(2s<sub>100</sub>-b-1<sub>20</sub>)

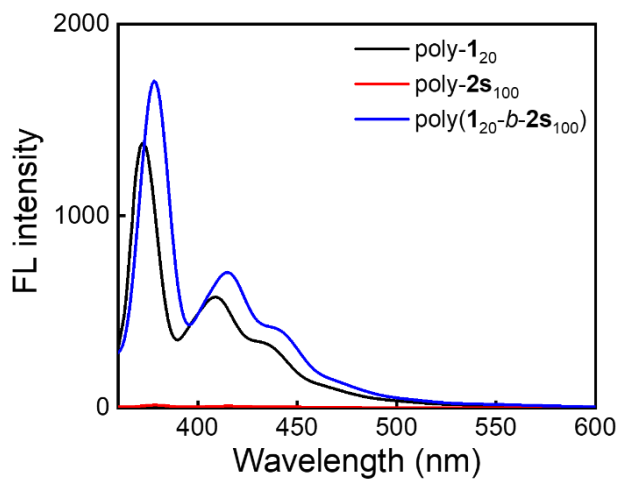


**Figure S4.** FT-IR spectra of poly(1<sub>20</sub>-b-2s<sub>100</sub>) measured at 25 °C using KBr pellets.

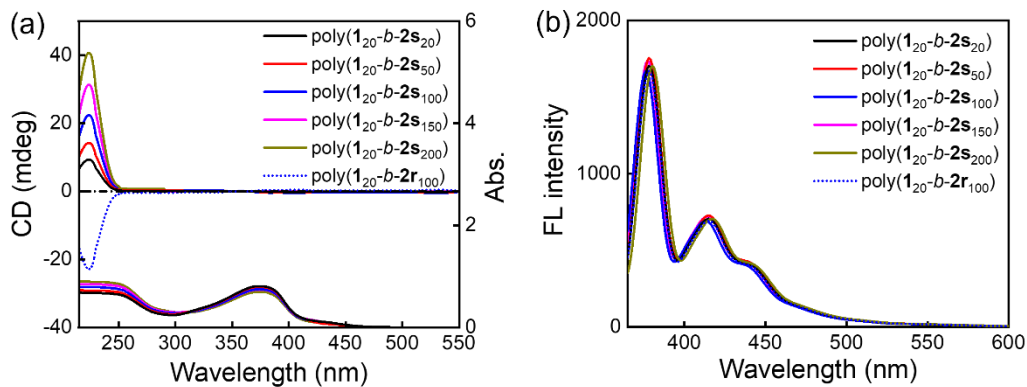




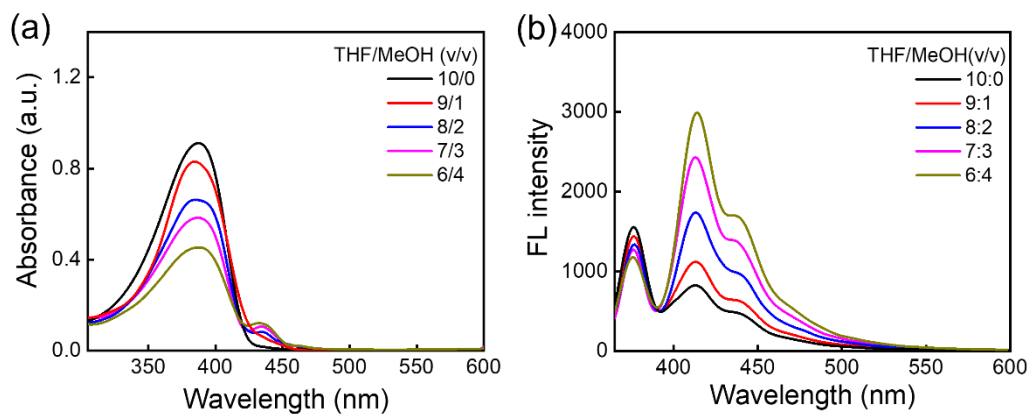
**Figure S5.** CD and UV-vis spectra of poly-**1**<sub>20</sub>, poly-**2s**<sub>100</sub>, and poly(**1**<sub>20</sub>-*b*-**2s**<sub>100</sub>) recorded in THF at room temperature ( $c = 0.2$  mg/mL).



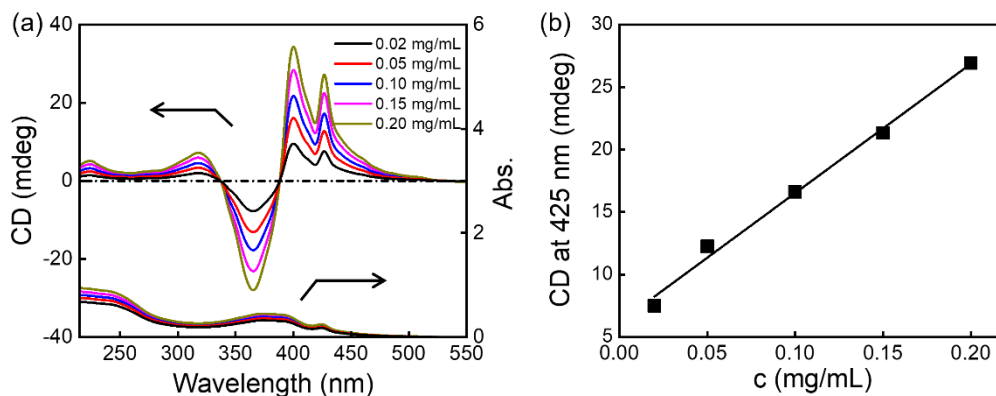
**Figure S6.** Photoluminescence (PL) spectra of poly-**1**<sub>20</sub>, poly-**2s**<sub>100</sub>, and poly(**1**<sub>20</sub>-*b*-**2s**<sub>100</sub>) recorded in THF at 25 °C ( $c = 0.2$  mg/mL).



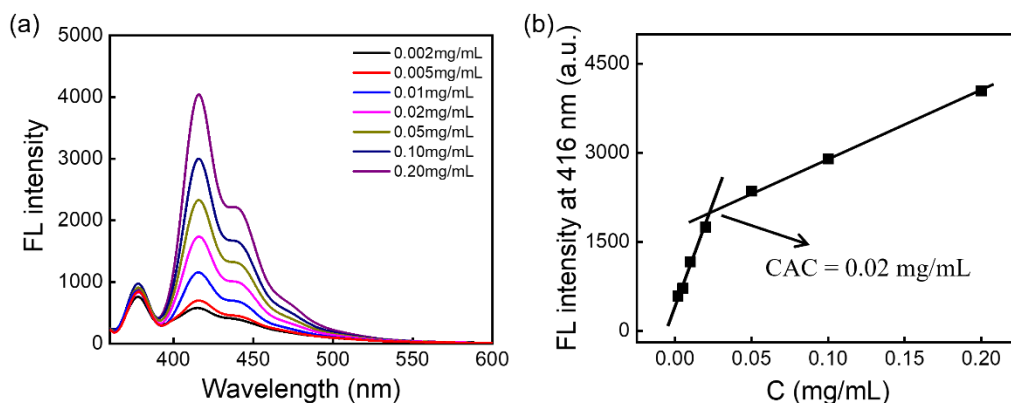
**Figure S7.** (a) CD and UV-vis, and (b) FL spectra of poly(1<sub>20</sub>-b-2s<sub>n</sub>) (n = 20, 50, 100, 150, and 200) (solid lines) and poly(1<sub>20</sub>-b-2r<sub>100</sub>) (short dash line) recorded in THF at 25 °C (*c* = 0.2 mg/mL).



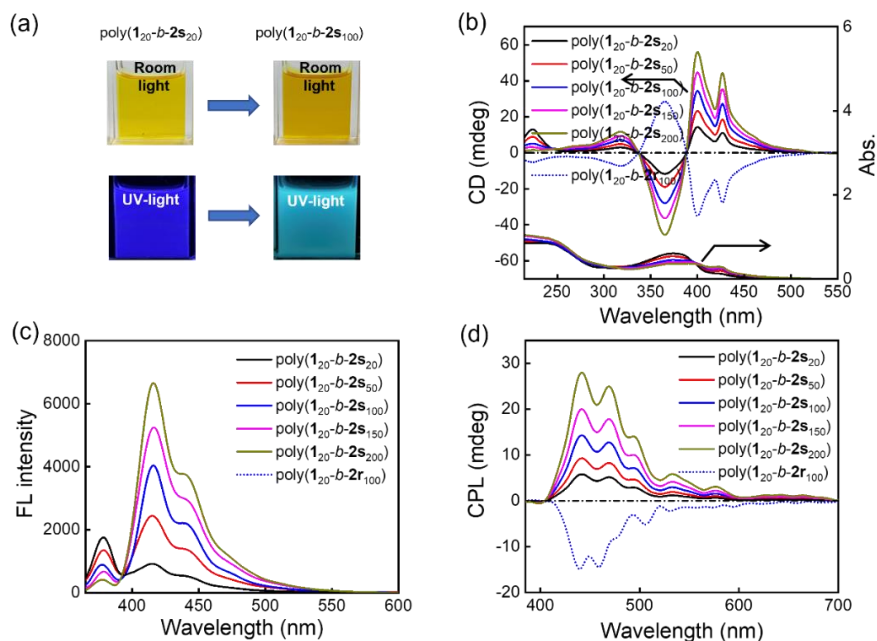
**Figure S8.** UV-vis and PL spectra of poly-1<sub>20</sub> recorded in THF/MeOH (v/v = 6/4, *c* = 0.2 mg/mL).



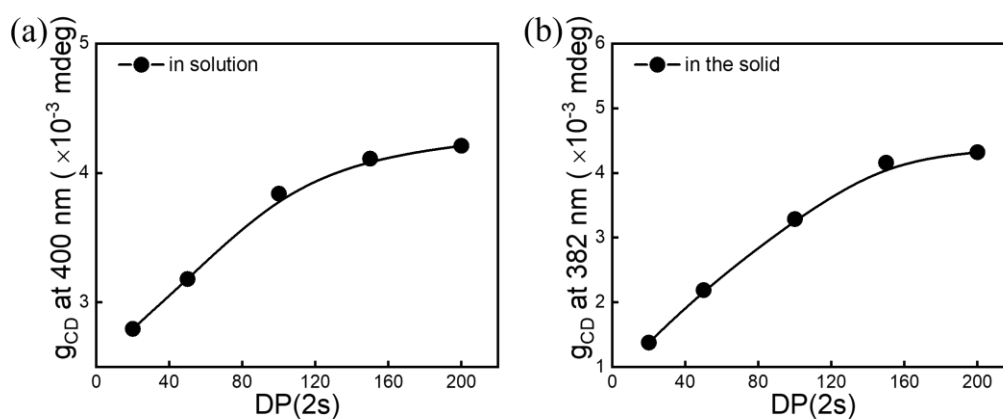
**Figure S9.** (a) Concentration-dependent CD and UV-vis spectra of poly( $1_{20}$ - $b$ - $2s_{100}$ ) in THF/MeOH ( $v/v = 6/4$ ,  $c = 0.2$  mg/mL) at room temperature. (b) Plots of the CD intensity at 425 nm vs. the concentration ( $c$ , mg/mL).



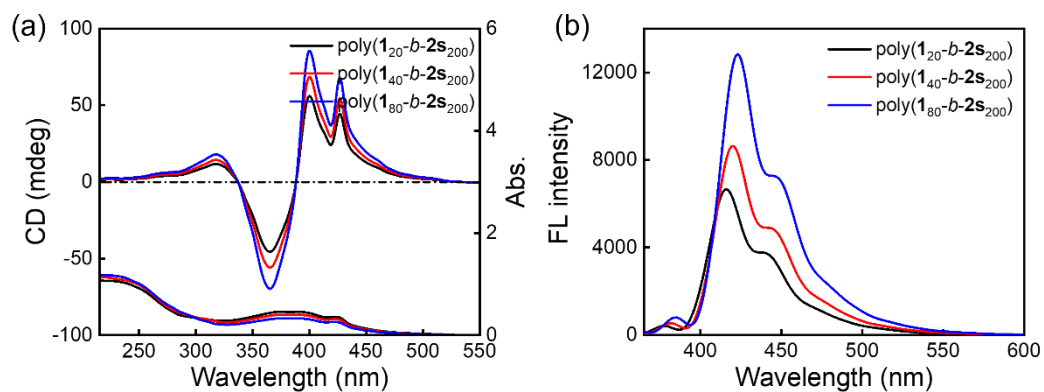
**Figure S10.** (a) FL spectra of poly( $1_{20}$ - $b$ - $2s_{100}$ ) with different concentration excited at 360 nm in THF at 25 °C. (b) Plots of the ratio of fluorescence intensity at 416 nm vs. concentration.



**Figure S11.** (a) Photographs of poly(1<sub>20</sub>-b-2s<sub>20</sub>) and poly(1<sub>20</sub>-b-2s<sub>200</sub>) in the mixture of THF/MeOH (v/v = 6/4) under room light and UV-365 nm light. (b) CD and UV-vis, and (c) FL and (d) CPL spectra of poly(1<sub>20</sub>-b-2s<sub>n</sub>) (n = 20, 50, 100, 150, and 200) (solid lines) and poly(1<sub>20</sub>-b-2r<sub>100</sub>) (short dash line) recorded in THF/MeOH (v/v = 6/4, c = 0.2 mg/mL, λ<sub>exc</sub> = 360 nm).



**Figure S12.** Plots of g<sub>CD</sub> vs. DP of the iminomethylene segment of poly(1<sub>20</sub>-b-2s<sub>n</sub>s) in solution (a) and in the solid state (b).



**Figure S13.** (a) CD and UV-vis, (c) FL spectra of poly( $1_m$ -b- $2s_{200}$ ) ( $m = 20, 40$  and  $80$ )

recorded in THF/MeOH ( $v/v = 6/4$ ,  $c = 0.2$  mg/mL,  $\lambda_{exc} = 360$  nm).

## References

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