## Supporting Information for

# Chirality Induction of Achiral Polydialkylfluorenes by Chiral Solvation: Odd-Even and Side-Chain-Length Dependence

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#### EXPERIMENTAL PROCEDURES

#### 2-Bromo-7-Iodo-9H-fluorene

2-bromofluorene (4.90 g, 20.0 mmol), I<sub>2</sub> (2.13 g, 8.4 mmol) and KIO<sub>3</sub> (1.02 g, 4.8 mmol) were added into a mixture of glacial acetic acid (85 mL) and H<sub>2</sub>O (4 mL). After being stirred at 90 °C for 2 h under a nitrogen atmosphere, the reaction mixture was cooled to room temperature and turned into a light-yellow precipitate. After filtration, the crude product was washed with acetic acid, water and methanol. The residue was then recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to afford a pale yellow crystalline solid. Yield 80 %; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 3.83 (*s*, 2H), 7.48-7.51 (*m*, 2H), 7.59 (*d*, 1H), 7.66-7.70 (*m*, 2H), 7.87 (*s*, 1H).

#### General synthetic procedure for 2-bromo-9,9-dialkyl-7-iodo-9H-fluorene

To a suspension of 2-bromo-7-iodo-9H-fluorene (5.00 g, 13.5 mmol) in DMSO (50 mL), 5 mL NaOH (50% aqueous solution) was dropwisely added by syringe under a nitrogen atmosphere. A bright orange solution was firstly formed, then darkened quickly to a maroon color. After being stirred vigorously for 10 min, 33.7 mmol bromoalkane (1-bromopentane (5.09 g),1-bromohexane (5.56 g), 1-bromoheptane (6.04 g), 1-bromooctane (6.51 g), 1-bromononane (6.98 g), 1-bromodecane (7.45 g), or 2-ethylhexylbromide (6.51 g)) was added and the solution turned purple immediately. After being stirred for 1 day at room temperature under inert atmosphere, the reaction mixture was poured into water (200 mL), extracted with hexane (100 mL), further washed with water  $(2 \times 100 \text{ mL})$ , brine (100 mL). Then, the organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to yield a viscous yellow oil. The oil was further purified by column chromatography. 2-Bromo-**7-iodo-9,9-dipentylfluorene**: yield, 74%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.49 - 0.66 (m, 4H), 0.66-0.80 (m, 6H), 0.96-1.16 (m, 8H), 1.79-2.01 (m, 4H), 7.37-7.48 (m, 3H), 7.52 (d, 1H), 7.61-7.68 (m, 2H). 2-Bromo-7-iodo-9,9-bis-n-hexylfluorene (M6): yield, 84%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.57 (dd, 4H), 0.78 (t, 6H), 0.95– 1.23 (m, 12H), 1.83–1.98 (m, 4H), 7.42 (ddd, 3H), 7.48–7.55 (m, 1H), and 7.61–7.68 (m, 2H). 2-Bromo-7-iodo-9,9-diheptylfluorene (M7): yield, 89%. <sup>1</sup>H NMR (300

MHz, CDCl<sub>3</sub>): δ (ppm) 0.70 – 0.47 (m, 4H), 0.81 (t, 6H), 1.34-0.93 (m, 16H), 2.02-1.78 (m, 4H), 7.48-7.36 (m, 3H), 7.52 (d, 1H), 7.69-7.61 (m, 2H). **2-Bromo-9,9-dioctyl-7-iodo-9H-fluorene (M8)**: yield, 88%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.59 (m, 4H), 0.85 (t, 6H), 1.05-1.26 (m, 20H), 1.88-1.92 (m, 4H), 7.40 (d, 1H), 7.44 (s, 1H), 7.46 (d, 1H), 7.52 (d, 1H), 7.65 (s, 1H), 7.66 (d, 1H). **2-Bromo-7-iodo-9,9-dinonylfluorene (M9)**: yield, 76%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 0.57 (td, 4H), 0.84 (t, 6H), 0.97-1.38 (m, 24H), 1.78- 2.05 (m, 4H), 7.36-7.47 (m, 3H), 7.52 (d, 1H), 7.65 (d, 2H). **2-Bromo-7-iodo-9,9-didecylfluorene (M10)**: yield, 80%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 0.47-0.70 (m, 4H), 0.86 (t, 6H), 0.96-1.35 (m, 28H), 1.79-2.02 (m, 4H), 7.36-7.47 (m, 3H), 7.52 (d, 1H), 7.65 (d, 2H). **2-Bromo-9,9-bis(2-ethylhexyl)-7-iodofluorene**: yield, 80%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 0.50 (m, 8H), 0.61 – 1.05 (m, 22H), 1.92 (dd, 4H), 7.36-7.56 (m, 4H), 7.61 – 7.73 (m, 2H).

#### Synthetic procedure for 2,7-dibromo-9,9-dialkylfluorene

Under a nitrogen atmosphere, 5 mL NaOH (50 % aqueous solution) was dropwisely injected into a suspension of 2,7-dibromo-9*H*-fluorene (5.00 g, 15.4 mmol) in DMSO (50 mL). The solution firstly turned into bright orange, then darkened quickly to a maroon color. Stirred vigorously at room temperature for 10 min, then 1-bromopentane (6.99 g, 46.3 mmol) or 2-ethylhexylbromide (8.94 g, 46.3 mmol) was added. After continuously stirred for 1 day, the reaction mixture was poured into water (200 mL), extracted by hexane (100 mL), further washed with water (2×100 mL), brine (100 mL). The organic layer was concentrated under reduced pressure to yield a viscous pale oil. The oil was further purified by column chromatography. **2,7-Dibromo-9,9-bis(2-ethylhexyl)fluorene (M5)**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.47-0.83 (m, 10H), 1.06 (dtp, 8H), 1.79-2.00 (m, 4H), 7.39-7.56 (m, 6H). **2,7-Dibromo-9,9-bis(2-ethylhexyl)fluorene (M2/6)**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.37-0.60 (m, 8H), 0.61-1.04 (m, 22H), 1.92 (d, 4H), 7.36-7.55 (m, 4H), 7.65 (dd, 1H), 7.68-7.73 (m, 1H).

#### Synthetic procedure for Kumada catalyst transfer polycondensation (KCTP)

In a typical experiment (ligand = dppp, Ni(acac)2/dppp =1/1.02), 10 mL THF was

added into a mixture of Ni(acac)<sub>2</sub> (51.4 mg, 0.20 mmol) and dppp (84.1 mg, 0.204 mmol) in a 25 mL Schlenk tube flushed with argon. Then the Ni(acac)<sub>2</sub>/Ligand solution was stirred at 25 °C for 20 min and directly used for the polymerization.

In a thoroughly dried 50 mL Schlenk tube, a mixture of monomer M1 (1.00 mmol), LiCl (42.4mg, 1.00 mmol) and dry THF (20 mL) was added and the solution was cooled to -20 °C. Then a THF solution of 'PrMgCl (0.49 mL, 0.98 mmol) was added. The mixture was stirred at -20 °C for 2 h to complete the monomer conversion. Then elevating the temperature to 0 °C, 1.5 mL Ni(acac)<sub>2</sub>/dppp solution was added. After 2 h, the polymerization was quenched by addition of HCl aqueous solution (5 M, 5 mL). The mixture was extracted with toluene, and the organic extracts were washed with brine, and dried over anhydrous Na<sub>2</sub>SO4. After concentrated under reduced pressure, the polymer was further purified by the precipitation into methanol. The solid was filtered and dried to give polyfluorene as pale-yellow solids. Poly(9,9-dihexyl **fluorene) (PF6):** yield, 75%.  $M_n = 33200 \text{ g mol}^{-1}$ ,  $M_w = 39600 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.19$ ,  $n_{\text{(repeating unit)}} \approx 100$ . Poly(9,9-diheptylfluorene) (PF7): yield, 78%.  $M_{\text{n}} = 32300 \text{ g mol}^{-1}$ <sup>1</sup>,  $M_{\rm w} = 43000$  g mol<sup>-1</sup>,  $M_{\rm w}/M_{\rm n} = 1.33$ ,  $n_{\rm (repeating unit)} \approx 90$ . Poly(9,9-dioctylfluorene) (**PF8**): yield, 70%.  $M_{\rm n}$  = 42000 g mol<sup>-1</sup>,  $M_{\rm w}$  = 61400 g mol<sup>-1</sup>,  $M_{\rm w}/M_{\rm n}$  = 1.46,  $n_{\rm (repeating noise)}$ <sub>unit)</sub>  $\approx$  108. Poly(9,9-dinonylfluorene) (PF9): yield, 64%.  $M_{\rm n}$  = 50400 g mol<sup>-1</sup>,  $M_{\rm w}$  = 56100 g mol<sup>-1</sup>,  $M_w/M_n = 1.11$ ,  $n_{\text{(repeating unit)}} \approx 121$ . Poly(9,9-didecylfluorene) (PF10): yield, 60%.  $M_{\rm n} = 55600 \text{ g mol}^{-1}$ ,  $M_{\rm w} = 66500 \text{ g mol}^{-1}$ ,  $M_{\rm w}/M_{\rm n} = 1.20$ ,  $n_{\rm (repeating unit)} \approx 125$ .

### Synthetic procedure for Yamamoto-type coupling reaction

To a thoroughly dried 50 mL Schlenk flask containing a magnetic stir bar was added bis(pinacolato)diboron (0.225 g, 0.912 mmol), **monomer M2** (2,7-dibromo-9,9-dipentylfluorene (0.423 g, 0.912 mmol) or 2,7-dibromo-9,9-di(2-ethylhexyl)fluorene (0.500 g, 0.912 mmol)). Then the flask was transferred into a glove box.  $Pd_2(dba)_3$  (19.9 mg, 0.018 mmol), tricyclohexylphosphonium tetrafluoroborate (18.9 mg, 0.054 mmol), and cesium fluoride (0.94 g, 6.20 mmol) were added under anaerobic, anhydrous conditions. The degassed toluene (35 mL) was transferred to the mixture. The mixture was immediately immersed in an oil bath at 80 °C. After being stirred at 80 °C for 24

h, tetrabutylammonium bromide (58.8 mg, 0.184 mmol) dissolved in degassed toluene (5 mL) was added to the reaction via a syringe, and the reaction was continuously stirred for an additional 24 h. After the reaction, the solvent was removed under vacuum, and crude product was dissolved in a minimal amount of hot THF (~5 mL) and precipitated into methanol (100 mL). After filtration, the product was isolated as a gray solid. **Poly(9,9-dipentyl fluorene) (PF5):** yield, 77%.  $M_n = 24800$  g mol<sup>-1</sup>,  $M_w = 32800$  g mol<sup>-1</sup>,  $M_w/M_n = 1.32$ ,  $n_{(repeating unit)} \approx 82$ . **Poly(9,9-bis(2-ethylhexyl)fluorene) (PF2/6):** yield, 68%.  $M_n = 30800$  g mol<sup>-1</sup>,  $M_w = 57500$  g mol<sup>-1</sup>,  $M_w/M_n = 1.86$ ,  $n_{(repeating unit)} \approx 80$ .



Figure S1. <sup>1</sup>H NMR spectra for monomers (F5, F6, F7, F8, F2/6, F9, and F10).



Figure S2. <sup>1</sup>H NMR spectra for polymers (PF5, PF6, PF7, PF8, PF2/6, PF9, and PF10).

**Table S1.** Comparisons of Cotton CD sign,  $\lambda_{max}$  (nm), and  $\lambda_{ex}$  (nm) values of PFs aggregates induced by limonene.

	$\lambda_{\rm max}$ (nm)	$\lambda_{\rm ex}$ (nm)				CD signs induced by 1R			
		1st cotton	2nd cotton	3rd cotton	4th cotton	1st cotton	2nd cotton	3rd cotton	4th cotton
		band	band	band	band	band	band	band	band
PF5	383.5 (R and	429.0, 431.0	410.0, 417.0	348.5, 342.5		-	-	+	
	S)								
PF6	387.5	428.0, 425.5	412.0, 400.0	365.5		-	+	-	
PF7	390.5	435.5, 435.0	410.5	373.0		-	-	+	
PF8	386.0	445.5	434.5	404.0	351.0	+	-	-	+
PF9	386.0	436.5, 436.0	412.0, 409.5	347.0		-	-	+	
PF10	390.0	439.0, 441.0	428.5, 429.5	405.0, 408.0	352.5	+	-	-	+



**Figure S3.** DSC thermograms for polydialkylfluorenes. a) PF6, b) PF7, c) PF8, d) PF9, e) PF10.



**Figure S4.** UV-vis absorption and fluorescence spectra of PF5 (black line), PF6 (red line), PF7 (blue line), PF8 (magenta line), PF9 (olive line) and PF9 (wine line) in limonene after complete dissolving at 150 °C. The concentrations were  $5.0 \times 10^{-4}$  mol/L. The curves are already offset for clarity.



**Figure S5.**  $\beta$  phase contents with changing alkyl side chain length for PFs/1*R* or PFs/1*S* aggregates formed by cooling the solutions at -25 °C For four days.



**Figure S6.** Calculated  $g_{CD}$  values at the first Cotton band monitored the stability of PFs aggregates formed at -25 °C in pure 1*R* or 1*S* at 20 °C for one month. CD signals of PF10/1*R* or PF10/1*S* aggregates could not be kept stable at 20 °C, but disappeared quickly.



**Figure S7.** The  $g_{CD}$  values at the first cotton band employed to monitor the disassembly process of PFs/limonene mixtures during heating treatments.