## **Supporting Information**

## Stereocomplexation of Enantiomeric Star-Shaped Poly(lactide)s with a Chromophore Core

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10 °C/min.

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50 °C/min.

SSPLLA and SSPDLA were obtained by ring-opening polymerization of L-lactide and Dlactide, respectively, under identical conditions using dipyridamole as the macroinitiator and tin(II)ethylhexanoate (Sn(Oct)<sub>2</sub>) as the catalyst. The structure of SSPLLA and SSPDLA was confirmed by <sup>1</sup>H NMR (CDCl<sub>3</sub> solvent) using a Bruker NMR spectrometer operating at 500 MHz. The chemical shifts were recorded in units of parts per million (ppm).

<sup>1</sup>H NMR spectrum of the star-shaped PDLA and star-shaped PLLA with dipyridamole as core molecule are presented in Figure S1 and Figure S2, respectively.



Figure S1. <sup>1</sup>H-NMR spectrum of SSPDLA

(<sup>1</sup>H-NMR spectrum of SSPDLA: 1.57 (d, CH<sub>3</sub>), 1.7 (s, CH<sub>2</sub>), 5.2 (q, CH), 4.3 (q, CH<sub>2</sub>), 3.7 (s, CH<sub>2</sub>))



Figure S2. <sup>1</sup>H-NMR spectrum of SSPLLA

(<sup>1</sup>H-NMR spectrum of SSPLLA: 1.57 (d, CH<sub>3</sub>), 1.7 (s, CH<sub>2</sub>), 5.2 (q, CH), 4.3 (q, CH<sub>2</sub>), 3.7 (s, CH<sub>2</sub>))



Figure S3. <sup>1</sup>H-NMR spectrum of SSPDLA after cooling to room temperature from 240 °C at 10 °C/min.

(<sup>1</sup>H-NMR spectrum of SSPDLA: 1.57 (d, CH<sub>3</sub>), 1.7 (s, CH<sub>2</sub>), 5.2 (q, CH), 4.3 (q, CH<sub>2</sub>), 3.7 (s, CH<sub>2</sub>))



**Figure S4.** GPC traces of SSPDLA (a) as synthesized polymer, (b) heated to 240 °C and cooled to RT at 10 °C/min and (c) heated to 240 °C and cooled to RT at 50 °C/min.



Figure S5. CD spectra of melt-cooled SSPDLA from  $T_{\text{max}} = 240 \text{ °C}$  at (a) 10 °C/min and (b) 50 °C/min.