Electronic Supplementary Information

Aggregation-induced Circularly Polarized Luminescence of (*R*)-Binaphthyl-based AIE-active Chiral Conjugated Polymer with Self-Assembly Helical Nanofibers

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ESI 1. Instrumentation and Materials.

Materials and Measurements

All solvents and reagents were commercially available and analytical reagent grade. THF was distilled from sodium in the presence of benzophenone. NMR spectra were obtained from Bruker Avance 300 spectrometer with 300 MHz for ¹H NMR and 75 MHz for ¹³C NMR and reported as parts per million (ppm) from the internal standard TMS. Mass spectrometry was performed on a SHIMADZU LCMS-2020 Instrument. FT-IR spectra were recorded on a Nexus 870 FT-IR spectrometer. Fluorescence spectra were obtained from an RF-5301PC spectrometer. Dynamic light scattering (DLS) measurements were conducted on a Brookheaven BI-200SM . Circular dichroism (CD) and UV-vis spectra were recorded on JASCO J-810 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were performed on a JASCO CPL-200 spectrofluoropolarimeter. Morphological studies were carried out with JEM-100S transmission electron microscopy and SPI 3800 atomic force microscopy. Elemental analysis was performed on an Elementar Vario MICRO analyzer. Thermogravimetric analyses (TGA) were obtained from a PerkinElmer Pyris-1 instrument under N_2 atmosphere. Molecular weight was determined by gel permeation chromatography (GPC) with a Waters 244 HPLC pump, and THF was used as solvent relative to polystyrene standards.

All optical measurements were investigated in THF and THF/water mixtures with a fixed concentration $(1.0 \times 10^{-5} \text{ mol/L} \text{ corresponding to TPE moiety})$. The magnitude of circular polarisation in the excited state is defined as $g_{\text{lum}} = 2 (I_{\text{L}} - I_{\text{R}})/(I_{\text{L}} + I_{\text{R}})$, where I_{L} and I_{R} indicate the output signals for left and right circularly polarized light, respectively. Experimentally, the value of g_{lum} is defined as $\Delta I/I = [\text{ellipticity}/(32980/\text{ln}10)] / (\text{unpolarized PL intensity})$ at the CPL extremum.

ESI 2. Synthesis procedures of the monomers and polymers.

The procedures for the synthesis of monomers, model **1** and polymers are outlined in **Scheme S1**, **S2** and **S3**. The monomers and **9** were synthesized according to our previously reported procedure.¹ Compound **12** were got from reported work.² **P-1** and **P-3** were synthesized from palladium-catalyzed Sonogashira coupling reaction, and **P-2** and **P-4** were prepared from palladium-catalyzed Suzuki coupling reaction.

Synthesis of the monomers



Scheme S1. Synthesis procedures of the monomers.

Synthesis of M-1

2 (1.00 g, 1.86 mmol), K₂CO₃ (0.77 g, 5.57 mmol) and 1-bromooctane (0.90 g, 4.65 mmol) were dissolved in 20 mL acetonitrile. After the reaction mixture was refluxed overnight, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1, v/v) to get **M-1** as a yellow oil (1.20 g, 84.5 %). ¹H NMR (300 MHz, CDCl₃): δ 8.53 (s, 2H), 7.80 (d, *J* = 6.0 Hz, 2H), 7.42(t, *J* = 6.0 Hz, 2H), 7.28 (d, *J* = 6.0 Hz, 2H), 7.15 (d, *J* = 6.0 Hz, 2H), 3.89-3.82 (m, 2H), 3.38-3.80 (m, 2H), 1.37-0.57 (m, 30H); ¹³C NMR (75 MHz, CDCl₃): δ 154.1 139.6 134.0, 132.1, 126.9, 125.9, 125.7, 125.5, 93.2, 73.6, 31.8, 29.7, 29.2, 29.0, 25.5, 22.8, 14.3; MS (ESI, m/z): 764.35 (M⁺⁺1); Anal. calcd for C₃₆H₄₄I₂O₂: C, 56.70; H, 5.82. Found: C, 56.68; H, 5.83.

Synthesis of M-2

3 (1.50 g, 2.94 mmol) and N¹,N¹,N²,N²-tetramethylethane-1,2-diamine (1.02 g, 8.81 mmol) were dissolved in 30 mL anhydrous THF. Then n-BuLi ((4.11 mL, 2.5 M in hexanes, 10.3 mmol) was added by syringe injection at room temperature under N₂ atmosphere. After the reaction mixture was stirred for 1 h at room temperature, trimethyl borate (2.00 mL, 17.6 mmol) was added. The reaction mixture was stirred overnight, then quenched with 2N HCl (15 mL) at 0 °C and stirred for 3 h. After the solvent was removed under reduced pressure, the residue was dissolved in ethyl acetate and washed with water, brine, then dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 4:1 v/v) to afford **M-2** as a white solid (0.65 g, 36.9 %). ¹H NMR (300 MHz, *d*₆-Acetone): δ 8.60 (s, 2H), 8.07 (d, *J* = 6.0 Hz, 2H), 7.48(m, 2H), 7.36 (m, 6H), 7.16 (d, *J* = 6.0 Hz, 2H), 3.79-3.72 (m, 2H), 3.42-3.34 (m, 2H), 1.28-0.60 (m, 30H); ¹³C NMR (75 MHz, *d*₆-Acetone): δ 205.9, 159.7, 138.2, 135.6, 130.5, 128.8, 127.2, 127.0, 125.4, 124.7, 123.7, 74.3, 31.4, 28.9, 28.8, 28.6, 25.1, 22.3, 13.4; Anal. calcd for C₃₆H₄₈B₂O₆: C, 72.26; H, 8.09. Found: C, 72.24; H, 8.10.

Synthesis of M-3

4 (3.00 g, 6.75 mmol), K₂CO₃ (2.80 g, 20.3 mmol) and 1-bromooctane (3.26 g, 16.9 mmol) were dissolved in 60 mL acetonitrile. The reaction mixture was refluxed overnight. Then the solvent was removed. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1, v/v) to get **M-3** as a yellow oil (3.80 g, 84.1 %). ¹H NMR (300 MHz, CDCl₃): δ 8.03 (s, 2H), 7.85 (d, *J* = 9.0 Hz, 2H), 7.42(d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 4.03-3.89 (m, 4H), 1.48-0.88 (m, 30H); MS (ESI, m/z): 692.65 (M⁺+Na).

Synthesis of M-4

M-3 (3.00 g, 4.49 mmol) was dissolved in 80 mL anhydrous THF. Then n-BuLi ((5.38 mL, 2.5 M in hexanes, 13.5 mmol) was slowly added at -78 $^{\circ}$ C under N₂ atmosphere. After the mixture

was stirred 30 min at -78 °C, trimethyl borate (2.04 mL, 18.0 mmol) was added. The reaction mixture was gradually warmed to room temperature and stirred overnight, then quenched with 2N HCl (40 mL) at 0 °C and stirred for 3 h. After the solvent was removed under reduced pressure, the residue was dissolved in ethyl acetate and washed with water, brine, then dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 4:1 v/v) to afford **M**-4 as a white solid (1.42 g, 52.8 %). ¹H NMR (300 MHz, *d*₆-Acetone): δ 8.48 (s, 2H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.67(d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 4.09-3.96 (m, 4H), 1.44-0.83 (m, 30H).

Synthesis of M-5

TiCl₄ (1.83 mL, 16.7 mmol) was added to 40 mL anhydrous THF with zinc dust (2.17 g, 33.4 mmol) at ice bath under N₂ atmosphere. The mixture was refluxed for 2 h, then cooled to room temperature. **6** (3.10 g, 11.1 mmol) in 30 mL anhydrous THF was added. After the reaction mixture was refluxed for 4 h, the mixture was poured into 150 mL 10% aqueous K₂CO₃ solution. After filtration of the forming solid, the mixture was extracted with CH₂Cl₂, washed with brine, and dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the residue was dissolved in 60 mL THF, and K₂CO₃ (4.60 g, 33.3 mmol) was added. The reaction mixture was stirred for 3 h. Then the solvent was removed under reduced pressure, the residue was dissolved in ethyl acetate and washed with brine, dried over anhydrous Na₂SO₄. After the solvent was removed, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 60:1 v/v) to afford **M-5** as a little yellow solid (1.61 g, 76.3 %). ¹H NMR (300 MHz, CDCl₃): δ 7.32-7.27 (m, 4H), 7.19-7.14 (m, 6H), 7.07-7.02 (m, 8H), 3.08 (d, *J* = 6.0 Hz, 2H).

Synthesis of M-6

TiCl₄ (1.88 mL, 17.3 mmol) was added to 40 mL anhydrous THF with zinc dust (2.25 g, 34.5 mmol) at ice bath under N₂ atmosphere. The mixture was refluxed for 2 h, then cooled to room temperature. **6** (3.00 g, 11.5 mmol) in 30 mL anhydrous THF was added. After the reaction mixture was refluxed for 4 h, the mixture was poured into 150 mL 10% aqueous K₂CO₃ solution. After filtration of the forming solid, the mixture was extracted with CH₂Cl₂, washed with brine, and dried over anhydrous Na₂SO₄. Then the solvent was removed, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 80:1 v/v) to afford **M-6** as a white solid (1.96 g, 69.5 %). ¹H NMR (300 MHz, CDCl₃): δ 7.32-7.24 (m, 4H), 7.20-7.14 (m, 6H), 7.09-7.03 (m, 4H), 6.97-6.91 (m, 4H).

Synthesis of the model compound 1



Scheme S2. Synthesis procedures of model compound 1.

A mixture of **9** (0.60 mg, 0.94 mmol), **12** (0.34 mg, 0.94 mmol), Pd(PPh₃)₂Cl₂ (33.1 mg, 5% mmol), CuI (26.9 mg, 15% mmol) were added to 10 mL Et₃N under N₂ atmosphere. The reaction was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was filtrated through a short silica gel column. After remove the solvent to afford crude product. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 50:1 v/v) to afford the desired product as a yellow solid (0.62 g, 76.0 %). ¹H NMR (300 MHz, CDCl₃): δ 8.15(s, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.86 (t, *J* = 6.0 Hz, 2H), 7.44-7.02 (m, 26H), 4.08-3.77 (m, 4H), 1.46-0.71 (m, 30H); ¹³C NMR (75 MHz, CDCl₃): δ 154.9, 154.5, 143.8, 143.5, 143.4, 143.3, 141.6, 140.3, 134.1, 134.0, 133.3, 131.3, 130.8, 130.2, 129.4, 129.0, 127.8, 127.7, 127.6, 126.6, 126.5, 126.4, 125.9, 125.8, 125.4, 124.8, 123.4, 121.4, 119.6, 117.7, 114.9, 93.2, 87.3, 73.5, 69.3, 31.6, 30.0, 29.3, 29.0, 25.6, 25.4, 22.6, 14.1; MS (ESI, m/z): 865.52 (M⁺⁺1); Anal. calcd for C₆₄H₆₄O₆: C, 88.85; H, 7.46. Found: C, 88.81; H, 7.48.

Synthesis of the polymers



Scheme S3. Synthesis procedures of the polymers.

Synthesis of P-1

A mixture of **M-1** (226.0 mg, 0.30 mmol), **M-5** (112.8 mg, 0.30 mmol), $Pd(PPh_3)_4$ (17.1 mg, 5% mmol), CuI (5.64 mg, 10% mmol) were added to 8 mL DMF and 4 mL Et₃N under N₂ atmosphere. The reaction was stirred at 60 °C for 40 h. After cooling to room temperature, the reaction mixture was filtrated through a short silica gel column. Then the polymer was precipitated in methanol. The polymer was filtrated and washed with methanol several times. Further purification could be conducted by dissolving the polymer in CH_2Cl_2 to precipitate in

methanol again. The polymer was dried in vacuum to afford **P-1** as a yellow solid (190 mg, 70.1 %). GPC: $M_w = 15680$, $M_n = 9650$, PDI =1.62; ¹H NMR (300 MHz, CDCl₃): δ 8.15 (s), 7.85 (m), 7.40-7.01 (m), 4.10-3.76 (m), 1.40-0.66 (m); FT-IR(KBr, cm⁻¹): 3054, 2924, 2853, 1594, 1506, 1492, 1430, 1377, 1261, 1219, 1017, 748, 699.

Synthesis of P-2

A mixture of M-2 (108.0 mg, 0.18 mmol), M-6 (88.5 mg, 0.18 mmol), Pd(PPh₃)₄ (20.9 mg, 10 % mmol), Na₂CO₃ (0.38 g, 3.61 mmol) were added to a mixture solvent of 8 mL toluene, 4 mL ethanol and 2 mL water under N₂ atmosphere. The resulting mixture was refluxed for 48 h. After cooling to room temperature, the mixture was poured into water and extracted with CH₂Cl₂. The organic layer was filtrated through a short silica gel column, then concentrated under reduced pressure. Then the polymer was precipitated in methanol. Further purification could be conducted by dissolving the polymer in CH₂Cl₂ to precipitate in methanol again. The polymer was dried in vacuum to afford **P-2** as a yellow solid (85.5 mg, 54.5 %). GPC: M_w =24450, M_n =16450, PDI =1.49; ¹H NMR (300 MHz, CDCl₃): δ 7.92-7.82 (m), 7.56-7.51 (m), 7.41-7.36 (m), 7.23-7.10 (m), 3.35-3.08 (m), 4.10-3.76 (m), 1.22-0.49 (m); FT-IR(KBr, cm⁻¹): 3054, 2924, 2853, 1595, 1506, 1492, 1429, 1378, 1246, 1194, 1021, 749, 699.

Synthesis of P-3

A mixture of **M-3** (238.0 mg, 0.36 mmol), **M-5** (135.5 mg, 0.36 mmol), Pd(PPh₃)₄ (20.6 mg, 5% mmol), CuI (6.78 mg, 10% mmol) were added to 8 mL DMF and 4 mL Et₃N under N₂ atmosphere. The reaction was stirred at 60 °C for 40 h. After cooling to room temperature, the reaction mixture was filtrated through a short silica gel column. Then the polymer was precipitated in methanol. The polymer was filtrated and washed with methanol several times. Further purification could be conducted by dissolving the polymer in CH₂Cl₂ to precipitate in methanol again. The polymer was dried in vacuum to afford **P-3** as a little brown solid (225 mg, 68.9 %). GPC: $M_w = 11760$, $M_n = 8910$, PDI =1.32; ¹H NMR (300 MHz, CDCl₃): δ 8.04-8.02 (m, 2H), 7.92-7.84 (m, 2H), 7.44-7.41 (m, 2H), 7.34-7.25 (m, 6H), 7.15-7.01 (m, 16H), 4.00-3.91 (m, 4H), 1.42-0.84 (m, 30H); FT-IR (KBr, cm⁻¹): 3054, 2921, 2851, 1586, 1491, 1463, 1341, 1265, 1089, 698.

Synthesis of P-4

A mixture of **M-4** (200.0 mg, 0.33 mmol), **M-6** (163.9 mg, 0.33 mmol), Pd(PPh₃)₄ (38.6 mg, 10 % mmol), Na₂CO₃ (0.71 g, 6.68 mmol) were added to a mixture solvent of 8 mL toluene, 4 mL ethanol and 2 mL water under N₂ atmosphere. The resulting mixture was refluxed for 48 h. After cooling to room temperature, the mixture was poured into water and extracted with CH₂Cl₂. The organic layer was filtrated through a short silica gel column, then concentrated under reduced pressure. Then the polymer was precipitated in methanol. Further purification could be conducted by dissolving the polymer in CH₂Cl₂ to precipitate in methanol again. The polymer was dried in vacuum to afford **P-4** as a brown solid (121.0 mg, 41.6 %). GPC: M_w =27120, M_n =15410, PDI =1.76; ¹H NMR (300 MHz, CDCl₃): δ 8.04-7.95 (m, 4H), 7.49-7.42 (m, 8H), 7.24-7.05 (m, 16H), 4.03-3.92 (m, 4H), 1.42-0.78 (m, 30H); FT-IR (KBr, cm⁻¹): 3054,

2923, 2853, 1593, 1492, 1464, 1341, 1245, 1018, 699.

Reference:

- (a) X. W. Zou, S. W. Zhang, Y. X. Cheng, Y. Liu, H. Huang, C. Y. Wang, *J. Appl. Polym. Sci.* 2007, 104, 821-827; (b) X. W. Zou, L. F. zheng, L. L. Wu, L. L. Zong, Y. X. Cheng, *Chin. J. Chem.* 2008, 26, 373-378; (c) X. H. Liu, J. M. Jiao, X. X. Jiang, J. F. Li, Y. X. Cheng, C. J. Zhu, *J. Mater. Chem. C* 2013, 1, 4713-4719.
- 2. W. Z. Yuan, F. Mahtab, Y. Y. Gong, Z. Q. Yu, P. Lu, Y. H. Tang, J. W. Y. Lam, C. Z. Zhu, B. Z. Tang, *J. Mater. Chem.* **2012**, 22, 10472-10479.

	Yield	M_w	M_n	PDI	T_d
	[%]	$[g mol^{-1}]$	[g mol ⁻¹]	$[M_w/M_n]$	[°C]
P-1	70.1	15680	9650	1.62	260
P-2	54.5	24450	16450	1.49	350
P-3	68.9	11760	8910	1.32	380
P-4	41.6	27120	15410	1.76	420

Table S1. Yields, GPC data and thermal properties of polymers.

ESI 3. Thermogravimetric analyses



Figure S1. TGA curve of the chiral polymer



ESI 4. 4. Aggregation-induced emission of the polymers and model compound 1

Figure S2. (a) Emission spectra of **P-1** in THF/water mixtures. (b) Plot of (I/I_0) values versus the compositions of the aqueous mixtures. (Excitation wavelength: 360 nm). Inset: Photographs of **P-1** in THF/water mixtures taken under UV illumination (365 nm). Solution concentration: 1.0×10^{-5} mol/L.





Figure S3. (a) Emission spectra of **P-2** in THF/water mixtures. (b) Plot of (I/I_0) values versus the compositions of the aqueous mixtures. (Excitation wavelength: 350 nm). Inset: Photographs of **P-2** in THF/water mixtures taken under UV illumination (365 nm). Solution concentration: 1.0×10^{-5} mol/L.





Figure S4. Emission spectra of **P-3** in THF/water mixtures. (b) Plot of (I/I_0) values versus the compositions of the aqueous mixtures. (Excitation wavelength: 360 nm). Inset: Photographs of **P-3** in THF/water mixtures taken under UV illumination (365 nm). Solution concentration: 1.0×10^{-5} mol/L.





Figure S5. Emission spectra of **P-4** in THF/water mixtures. (b) Plot of (I/I_0) values versus the compositions of the aqueous mixtures. (Excitation wavelength: 350 nm). Inset: Photographs of **P-4** in THF/water mixtures taken under UV illumination (365 nm). Solution concentration: 1.0×10^{-5} mol/L.





Figure S6. Emission spectra of **model compound1** in THF/water mixtures. (b) Plot of (I/I_0) values versus the compositions of the aqueous mixtures. (Excitation wavelength: 340 nm). Inset: Photographs of **model compound 1** in THF/water mixtures taken under UV illumination (365 nm). Solution concentration: 1.0×10^{-5} mol/L.





Figure S7. Particle size distribution of **P-1** in THF/water mixtures (a) 80/20 v/v; (b) 60/40 v/v; (c) 40/60 v/v; (d) 20/80 v/v and (e) 5/95 v/v, where d_m is the mean diameter. Solution Concentration: $1.0 \times 10^{-5} \text{ mol/L}$



ESI 5. CD and UV-vis spectra of polymers and model compound 1

Figure S8. CD and UV-vis spectra of P-1 in THF/water mixtures. Solution concentration: 1.0×10^{-5} mol/L.



Figure S9. CD and UV-vis spectra of P-2 in THF/water mixtures. Solution concentration: 1.0×10^{-5} mol/L.



Figure S10. CD and UV-vis spectra of P-3 in THF/water mixtures. Solution concentration: 1.0×10^{-5} mol/L.



Figure S11. CD and UV-vis spectra of P-4 in THF/water mixtures. Solution concentration: 1.0×10^{-5} mol/L.



Figure S12. CD and UV-vis spectra of model 1 in THF/water mixtures. Solution concentration: 1.0×10^{-5} mol/L.

ESI 6. CPL and PL spectra of polymers and model compound 1



Figure S13. CPL and PL spectra of polymers and model compound 1 in THF. Solution concentration: 1.0×10^{-5} mol/L.



Figure S14. CPL and PL spectra of polymers and model compound 1 in THF/water (5/95, v/v). Solution concentration: 1.0×10^{-5} mol/L.



Figure S15. CPL and PL spectra of P-1 in THF/water mixtures. Solution concentration: 1.0×10^{-5} mol/L.



Figure S16. CPL and PL spectra of P-1 in THF/water (v/v, 20/80). Solution concentration: 1.0×10^{-5} mol/L.

ESI 7. TEM and AFM images of polymers



Figure S17. TEM images of polymers in THF/water (40/60, v/v) obtained from (a) P-1; (b) P-2; (c) P-3; (d) P-4. Solution concentration: 1.0×10^{-5} mol/L.



Figure S18. TEM images of **P-1** obtained from (a) THF/water (60/40, v/v); (b) THF/water (40/60, v/v); (c) THF/water (20/80, v/v) and (d) THF/water (5/95, v/v). Solution concentration: 1.0×10^{-5} mol/L.



Figure S19. AFM images of **P-1** obtained from (a,b) THF/water (60/40, v/v) and (c,d) THF/water (40/60, v/v). Solution concentration: 0.01 mg/mL.

ESI 8. NMR spectra







Figure S22. ¹H NMR of **M-2** in d_6 -Acetone.

























Figure S28. ¹H NMR of model 1 in CDCl₃.



Figure S30. ¹H NMR of P-1 in CDCl₃.



Figure S31 ¹H NMR of P-2 in CDCl₃.





Figure S32. ¹H NMR of P-3 in CDCl₃.





