

Electronic Supplementary Information

Axial Chiral Aggregation-Induced Emission Luminogens with Aggregation-Annihilated Circular Dichroism Effect

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EXPERIMENTAL SECTION

Chemicals and materials.

Dioxane and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Potassium carbonate (K₂CO₃), acetone, dioxane, THF, *p*-toluene sulfonic acid, and toluene were purchased from Signopharm Chemical Reagent Co., Ltd. (*R*)-(-)-6,6'-Dibromo-1,1'-binaphthyl-2,2'-diol, (*S*)-(+)-6,6'-dibromo-1,1'-binaphthyl-2,2'-diol, (*R*)-(+)-3,3'-dibromo-1,1'-binaphthyl-2,2'-diol, (*R*)-(-)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate, *n*-butyllithium, tetrakis (triphenylphosphine) palladium and diiodomethane were obtained from J&K. Diphenylmethane, 4-bromobenzophenone, and bis(pinacolato) diboron were gotten from Energy Chemical. 1-Bromohexane and potassium Acetate came from Aladdin. 18-Crown-6 were obtained from Shanghai Chemical Reagent. Bis(triphenylphosphine) palladium dichloride was purchased from ABCR GmbH&Co.KG.

General information.

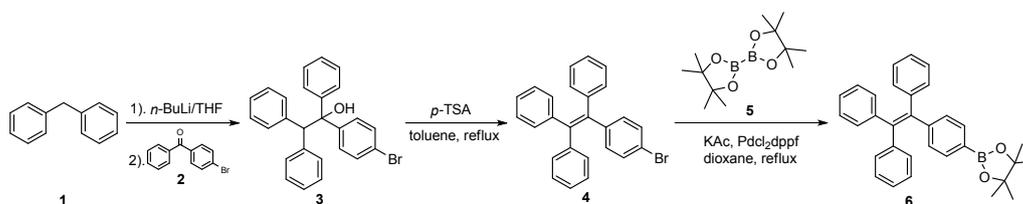
¹H and ¹³C NMR spectra were measured on Bruker DMX-500, Bruker AV 400 or Varian NMR 300 spectrometers in deuterated chloroform (CDCl₃) using tetramethylsilane (TMS; δ = 0) as internal reference. High-resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 Mass Spectrometer System operating in a MALDI-TOF mode. UV-Vis spectra were measured on a Varian CARY 100 Bio UV-visible spectrophotometer. Photoluminescence measurements were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer. Particle size was measured on

Brookhaven BI-90 Plus instrument. Thermogravimetric analysis (TGA) measurements were conducted on a TA-Q500 TGA under N₂ atmosphere at a heating rate of 10 °C/min. Circular Dichroism (CD) spectra were recorded on Bio-logic MOS-450 spectropolarimeter. Fluorescence quantum yields (Φ_F) were estimated using quinine sulfate in 0.1 N sulfuric acid ($\Phi_F = 54.6\%$) as standard.

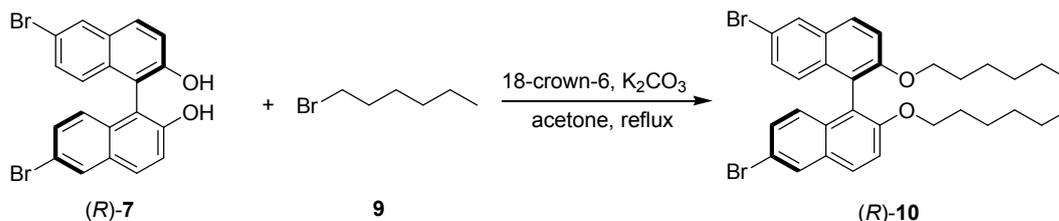
Synthesis

4,4,5,5-Tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (6):

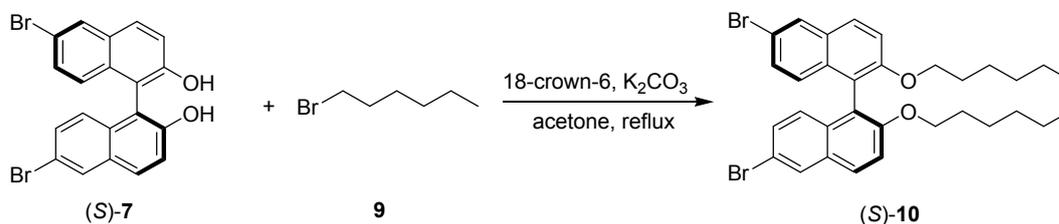
This compound was synthesized by our previous published procedures.^[1] A white powder was obtained in 85% yield. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.66 (d, 2H), 7.18–7.09 (m, 17H), 1.40 (s, 12H).



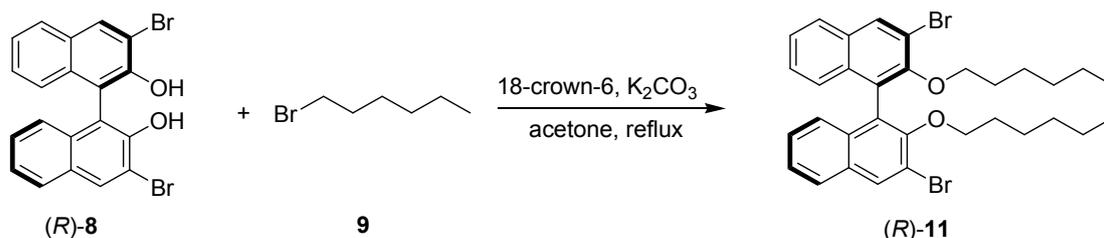
(R)-(-)-6,6'-dibromo-2,2'-bis(hexyloxy)-1,1'-binaphthyl [(R)-10]: 1-Bromohexane (0.76 ml, 5.40 mmol), *(R)-(-)-6,6'-dibromo-1,1'-binaphthyl-2,2'-diol* (0.40 g, 0.90 mmol), K₂CO₃ (0.05 mg, 3.62 mmol) and a catalytic amount of 18-crown-6 (0.05 mg, 0.19 mmol) were added into a 100 mL single-necked flask fitted with an allihn condenser, 50 mL acetone was injected into it to dissolve these materials. After stirring at 70 °C for 24 h, the mixture was extracted with dichloromethane (DCM). The organic layer was washed with deionized water and brine, and dried over anhydrous sodium sulfate. After filtration, the filtrate was evaporated under reduced pressure, and the crude product was purified through a silica gel column chromatograph using petroleum/dichloromethane (2/1, v/v) as eluent. A viscous liquid was obtained in 82% yield (0.45 g, 0.74 mmol). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.00 (s, 2H), 7.83 (d, 2H), 7.41 (d, 2H), 7.27 (d, 2H), 6.98 (d, 2H), 4.00–3.86 (m, 4H), 1.443–1.34 (m, 4H), 1.07–0.87 (m, 12H), 0.77–0.72 (m, 6H).



(S)-(+)-6,6'-Dibromo-2,2'-bis(hexyloxy)-1,1'-binaphthyl [(S)-10]: The synthetic procedures are similar with those of (R)-10. A viscous liquid was obtained in 84.4% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (TMS, ppm): 8.00 (s, 2H), 7.83 (d, 2H), 7.41 (d, 2H), 7.27 (d, 2H), 6.98 (d, 2H), 4.00-3.86 (m, 4H), 1.443-1.34 (m, 4H), 1.07-0.87 (m, 12H), 0.77-0.72 (m, 6H).

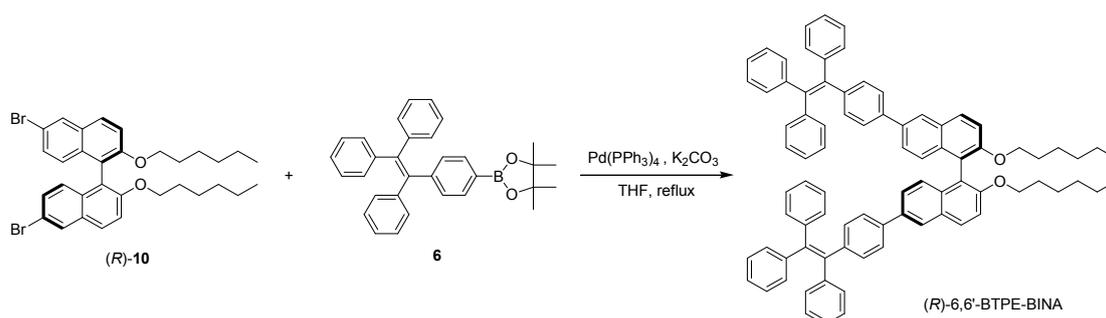


(R)-(+)-3,3'-Dibromo-2,2'-bis(hexyloxy)-1,1'-binaphthyl [(R)-11]: The synthetic procedures are similar with those of (R)-10. A white powder was obtained in 86% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (TMS, ppm): 8.24 (s, 2H), 7.80 (d, 2H), 7.43-7.38 (m, 2H), 7.29-7.24 (m, 2H), 7.12 (d, 2H), 3.93-3.86 (m, 2H), 3.49-3.42 (m, 2H), 1.28-1.22 (m, 4H), 1.08-0.99 (m, 4H), 0.90-0.62 (m, 14H).



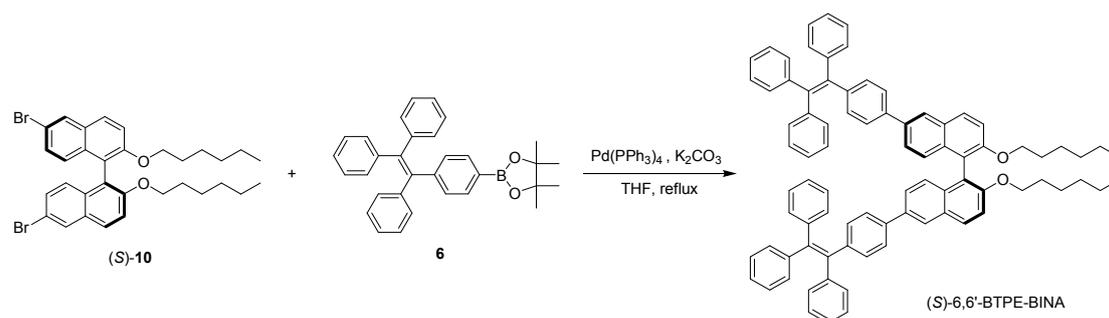
(R)-(-)-2,2'-bis(hexyloxy)-6,6'-bis(4-(1,2,2-triphenylvinyl)phenyl)-1,1'-binaphthyl [(R)-6,6'-BTPE-BINA]: (R)-10 (0.06 g, 0.10 mmol), **6** (0.09 g, 0.25 mmol) and a catalytic amount of tetrakis (triphenylphosphine) palladium were added into a two-necked flask fitted with an allihn condenser. The system was degassed and refilled with nitrogen for three times. Then, 50 mL distilled THF was injected, followed with potassium carbonate aqueous solution (100 mg, 15 mL). After stirring at 85 °C for 24 h., the

mixture was extracted with DCM. The organic layer was washed with deionized water and brine, and dried over anhydrous sodium sulfate. After filtration, the filtrate was evaporated under reduced pressure, and the crude product was purified through a silica gel column chromatograph using petroleum/dichloromethane (5/1, v/v) as eluent. A cyan powder was obtained in 73.2% yield (0.08 g, 0.07 mmol). ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 8.01 (s, 2H), 7.93 (d, 2H), 7.43-7.39 (m, 8H), 7.18 (d, 2H), 7.10-7.03 (m, 34H), 3.95-3.91 (m, 4H), 1.40-1.39 (m, 4H), 1.01-0.92 (m, 12H), 0.71-0.68 (m, 6H). ¹³C NMR (125MHz, CDCl₃), δ (TMS, ppm): 154.07, 143.01, 143.76, 142.31, 140.97, 140.02, 138.01, 135.43, 133.37, 131.70, 131.42, 131.35, 129.41, 129.34, 127.72, 127.06, 127.00, 126.44, 126.37, 126.17, 125.96, 125.44, 125.40, 120.43, 116.14, 69.73, 31.33, 29.36, 25.33, 22.47, 13.93. HRMS (MALDI-TOF, *m/z*): [M⁺] Calcd for C₈₄H₇₄O₂: 1114.5689 (100.0%), 1115.5722 (90.9%), found: 1115.5770.

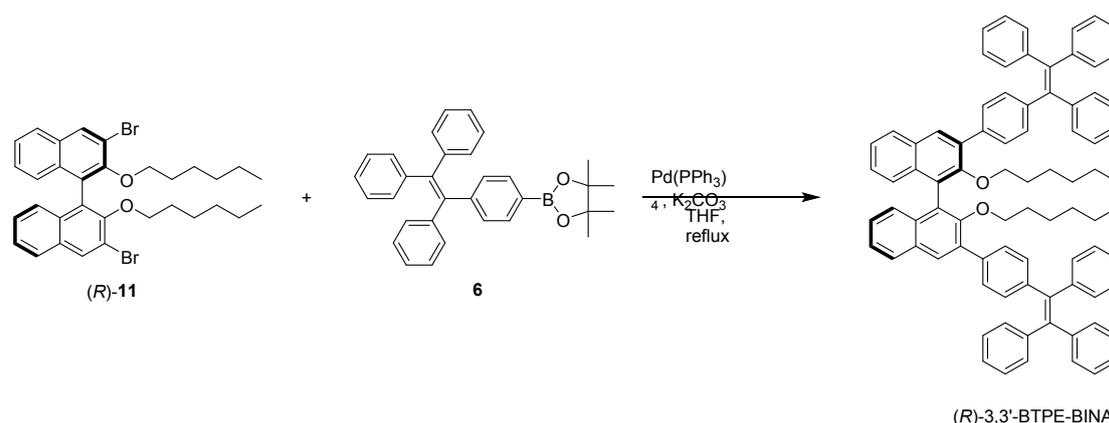


(S)-(+)-2,2'-Bis(hexyloxy)-6,6'-bis(4-(1,2,2-triphenylvinyl)phenyl)-1,1'-binaphthyl

[(S)-6,6'-BTPE-BINA]: The synthesis procedures are similar with those of *(R)*-6,6'-BTPE-BINA. A cyan powder was obtained in 76% yield. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 8.01 (s, 2H), 7.93 (d, 2H), 7.43-7.39 (m, 8H), 7.18 (d, 2H), 7.10-7.03 (m, 34H), 3.95-3.91 (m, 4H), 1.40-1.39 (m, 4H), 1.01-0.92 (m, 12H), 0.71-0.68 (m, 6H). ¹³C NMR (125MHz, CDCl₃), δ (TMS, ppm): 154.94, 144.08, 144.02, 142.66, 141.24, 140.89, 139.18, 135.70, 133.64, 132.03, 131.69, 131.62, 129.68, 129.61, 128.00, 127.92, 127.88, 126.70, 126.64, 126.44, 126.23, 125.71, 125.67, 120.70 116.41, 69.99, 31.60, 29.62, 25.60, 22.74, 14.19. HRMS (MALDI-TOF, *m/z*): [M⁺] Calcd for C₈₄H₇₄O₂: 1114.5689 (100.0%), 1115.5722 (90.9%), found: 1115.5688.

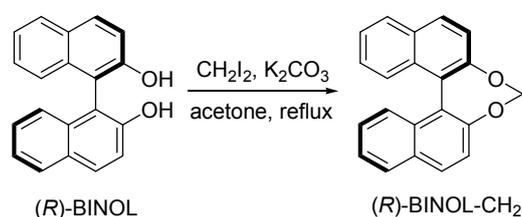


(R)-(+)-2,2'-Bis(hexyloxy)-3,3'-bis(4-(1,2,2-triphenylvinyl)phenyl)-1,1'-binaphthyl [(R)-3,3'-BTPE-BINA]: The synthesis procedures are similar with those of (R)-6,6'-BTPE-BINA. A white powder was obtained in 68% yield. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.88 (s, 2H), 7.84 (d, 2H), 7.50 (d, 4H), 7.35 (m, 2H), 7.20-7.17 (m, 4H), 7.12-7.05 (m, 34H), 3.33 (m, 2H), 3.06 (m, 2H), 0.95-0.88 (m, 8H), 0.75-0.64 (m, 12H), 0.48 (m, 2H). ^{13}C NMR (125MHz, CDCl_3), δ (TMS, ppm): 153.79, 144.11, 144.00, 143.95, 142.88, 141.28, 141.09, 137.45, 135.35, 133.94, 131.67, 131.62, 131.40, 130.92, 130.03, 128.90, 128.13, 127.90, 126.72, 126.68, 126.57, 126.19, 126.14, 124.88, 72.74, 31.48, 30.05, 25.35, 22.68, 14.22. HRMS (MALDI-TOF, m/z): $[\text{M}^+]$ Calcd for $\text{C}_{84}\text{H}_{74}\text{O}_2$: 1114.5689 (100.0%), 1115.5722 (90.9%), found: 1115.5660.



(R)-(-)-1,1'-Binaphthyl-2,2'-methylenedioxy [(R)-BINOL-CH₂]: (R)-(-)-Binaphthol (0.20 g, 0.70 mmol), CH_2I_2 (0.56 mg, 2.10 mmol), K_2CO_3 (0.58 mg, 4.19 mmol), acetone (50 ml) were added into a single-necked flask, then refluxed overnight. Afterward, the mixture was cooled down to room temperature and extracted with

DCM and water for three times. The organic layer was dried with anhydrous NaSO_4 , and condensed by a rotatory evaporation under reduced pressure. The crude product was purified through a silica gel column chromatograph using petroleum/dichloromethane (10/1, v/v) as eluent. A white powder was obtained in 71.4% yield (0.15 g, 0.50 mmol). ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.96 (d, 2H), 7.92 (d, 2H), 7.51 (d, 2H), 7.47 (d, 2H), 7.43 (m, 2H), 7.28 (m, 2H), 5.68 (m, 2H). ^{13}C NMR (125MHz, CDCl_3), δ (TMS, ppm): 151.23, 132.17, 131.76, 130.28, 128.38, 126.87, 126.07, 124.97, 120.88, 103.13. HRMS (MALDI-TOF, m/z): $[\text{M}^+]$ Calcd for $\text{C}_{21}\text{H}_{14}\text{O}_2$: 298.0994, found: 298.0963.



Structural characterization.

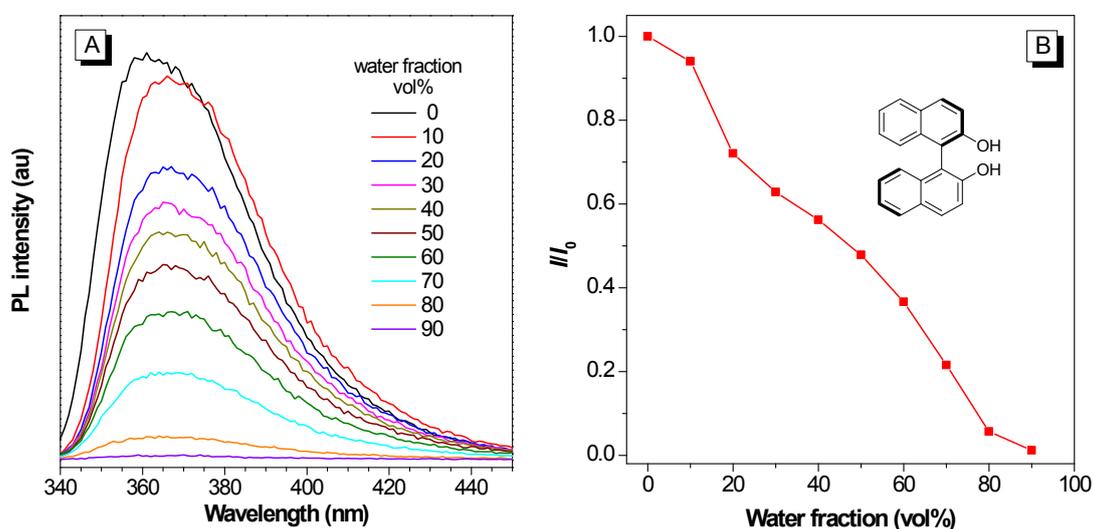


Figure S1. (A) PL spectra of (R)-BINOL in THF/water mixtures with different water fractions (f_w). Concentration: 10^{-5} M. (B) Plot of I/I_0 versus water fraction, I : maximum PL intensity, I_0 : maximum PL intensity at $f_w = 0\%$, $\lambda_{\text{ex}} = 300$ nm.

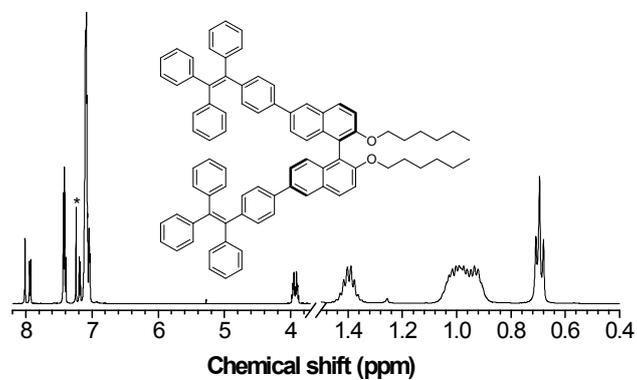


Figure S2. ^1H NMR spectrum of (*R*)-6,6'-BTPE-BINA in CDCl_3 . The solvent peak is marked with asterisk.

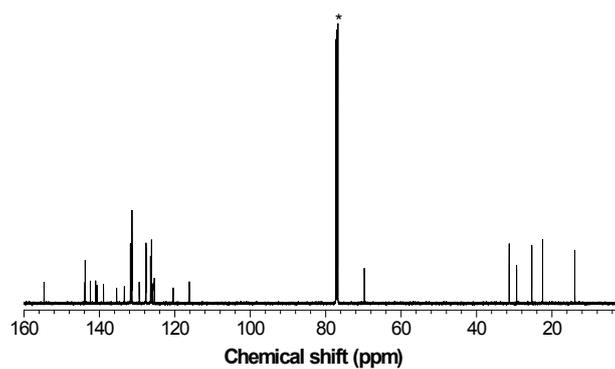


Figure S3. ^{13}C NMR spectrum of (*R*)-6,6'-BTPE-BINA in CDCl_3 . The solvent peak is marked with asterisk.

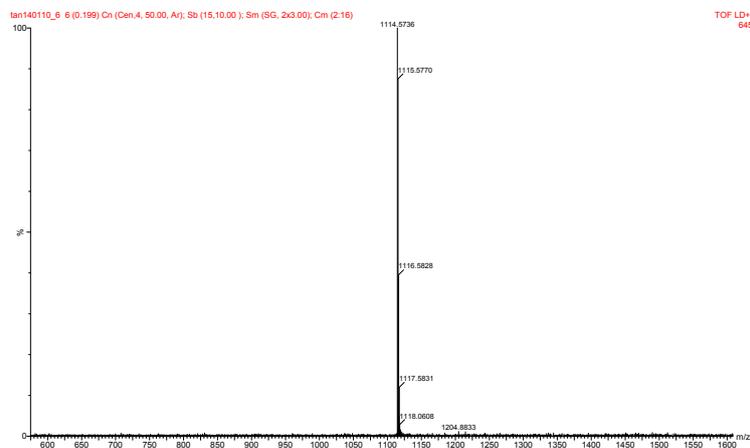


Figure S4. HRMS spectrum of (*R*)-6,6'-BTPE-BINA.

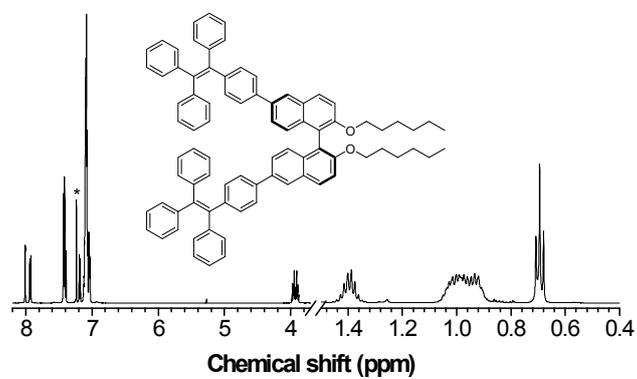


Figure S5. ^1H NMR spectrum of (*S*)-6,6'-BTPE-BINA in CDCl_3 . The solvent peak is marked with asterisk.

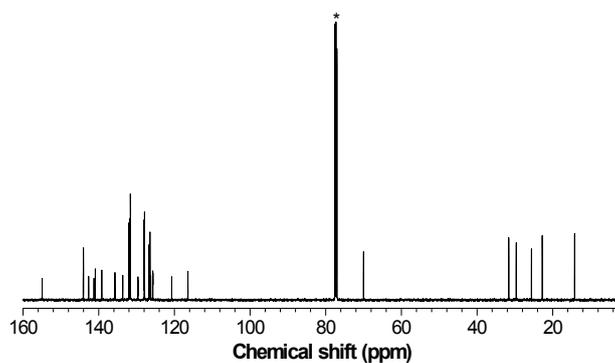


Figure S6. ^{13}C NMR spectrum of (*S*)-6,6'-BTPE-BINA in CDCl_3 . The solvent peak is marked with asterisk.

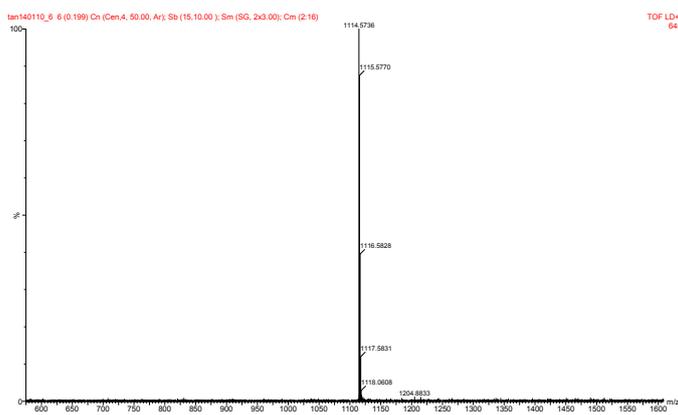


Figure S7. HRMS spectrum of (*S*)-6,6'-BTPE-BINA.

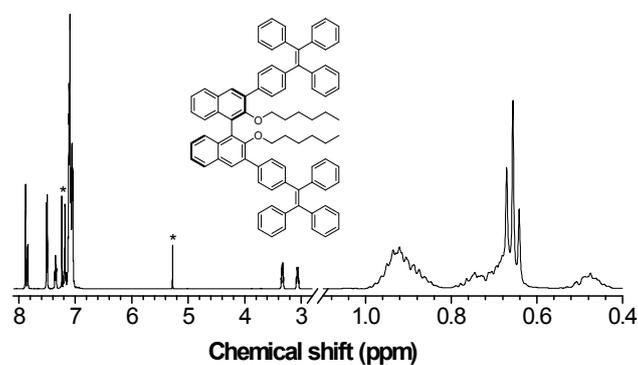


Figure S8. ^1H NMR spectrum of (*R*)-3,3'-BTPE-BINA in CDCl_3 . The solvent peaks are marked with asterisks.

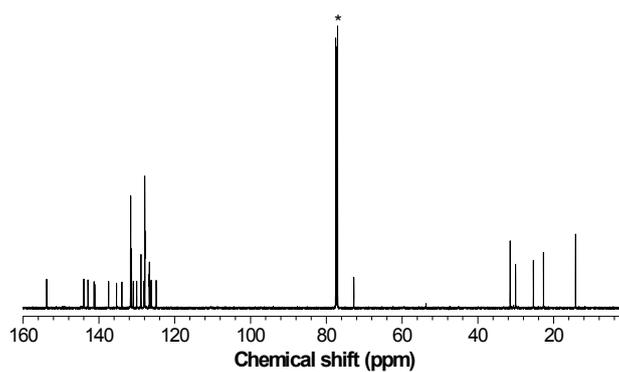


Figure S9. ^{13}C NMR spectrum of (*R*)-3,3'-BTPE-BINA in CDCl_3 . The solvent peak is marked with asterisk.

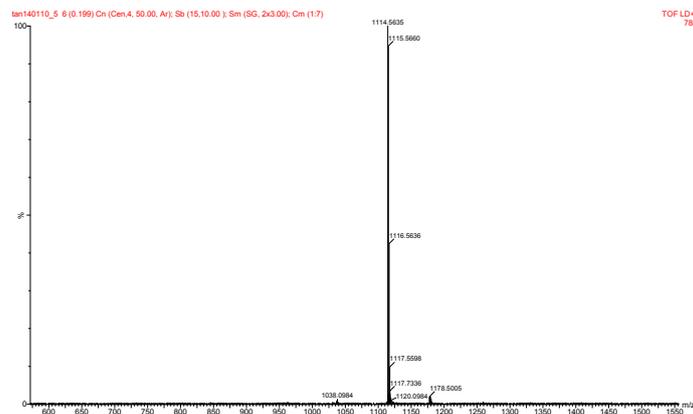


Figure S10. HRMS spectrum of (*R*)-3,3'-BTPE-BINA.

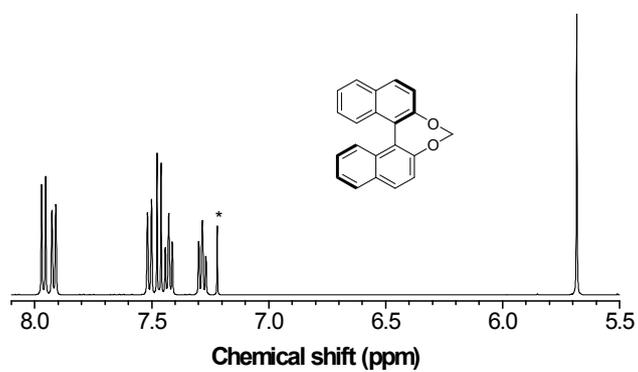


Figure S11. ^1H NMR spectrum of (*R*)-BINOL- CH_2 in CDCl_3 . The solvent peak is marked with asterisk.

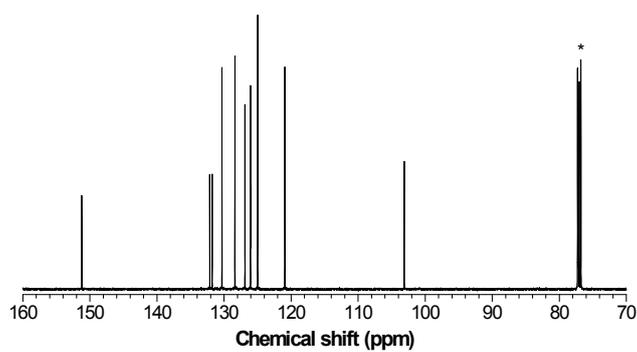


Figure S12. ^{13}C NMR spectrum of (*R*)-BINOL- CH_2 in CDCl_3 . The solvent peak is marked with asterisk.

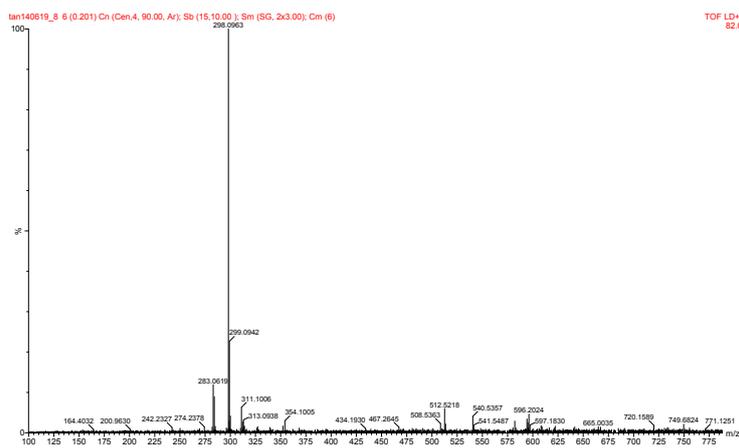


Figure S13. HRMS spectrum of (*R*)-BINOL- CH_2 .

Results

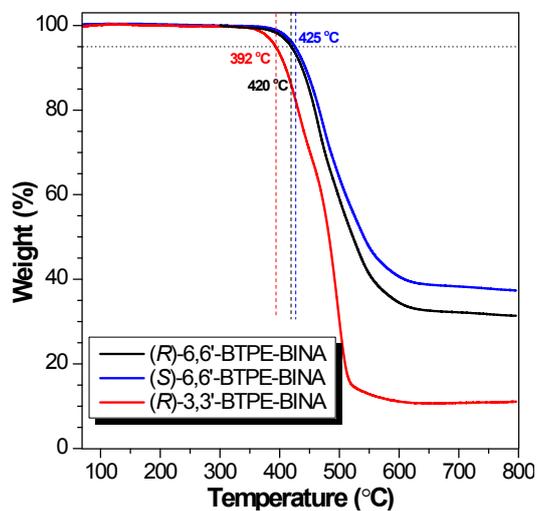


Figure S14. TGA thermograms of (*R*)-6,6'-BTPE-BINA, (*S*)-6,6'-BTPE-BINA and (*R*)-3,3'-BTPE-BINA recorded under N₂ at a heating rate of 10 °C/min.

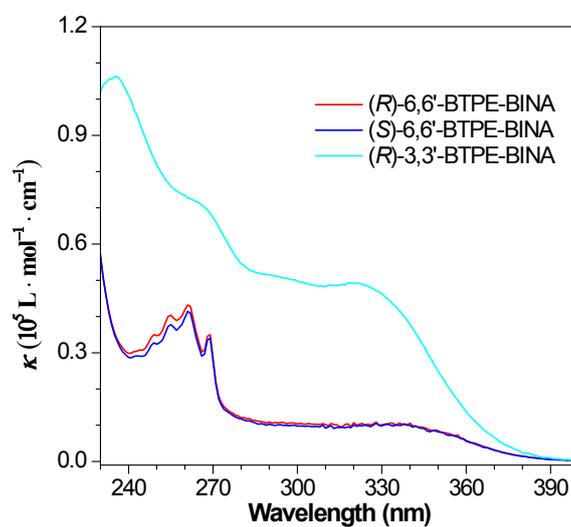


Figure S15. Absorption spectra of (*R*)-6,6'-BTPE-BINA, (*S*)-6,6'-BTPE-BINA and (*R*)-3,3'-BTPE-BINA in THF. Concentration = 10⁻⁵ M.

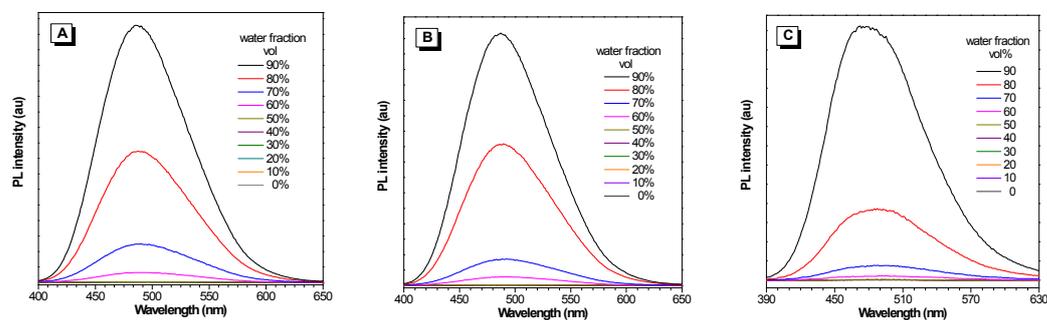


Figure S16. PL spectra of (A) (*R*)-6,6'-BTPE-BINA, (B) (*S*)-6,6'-BTPE-BINA and (C) (*R*)-3,3'-BTPE-BINA in THF/water mixtures with different f_w . Concentration: 10^{-5} M; $\lambda_{ex} = 330$ nm.

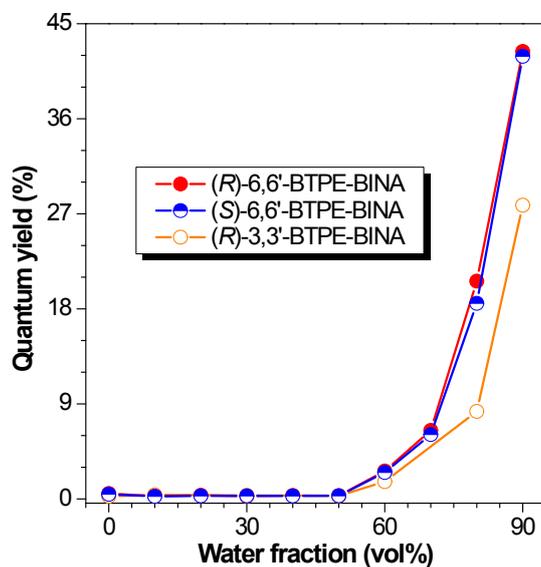


Figure S17. The plots of quantum yield to (*R*)-6,6'-BTPE-BINA, (*S*)-6,6'-BTPE-BINA and (*R*)-3,3'-BTPE-BINA versus water fraction in the THF/water mixtures. (Reference: Quinine sulfate in 0.1 N sulfuric acid, $\Phi_F = 56$ %).

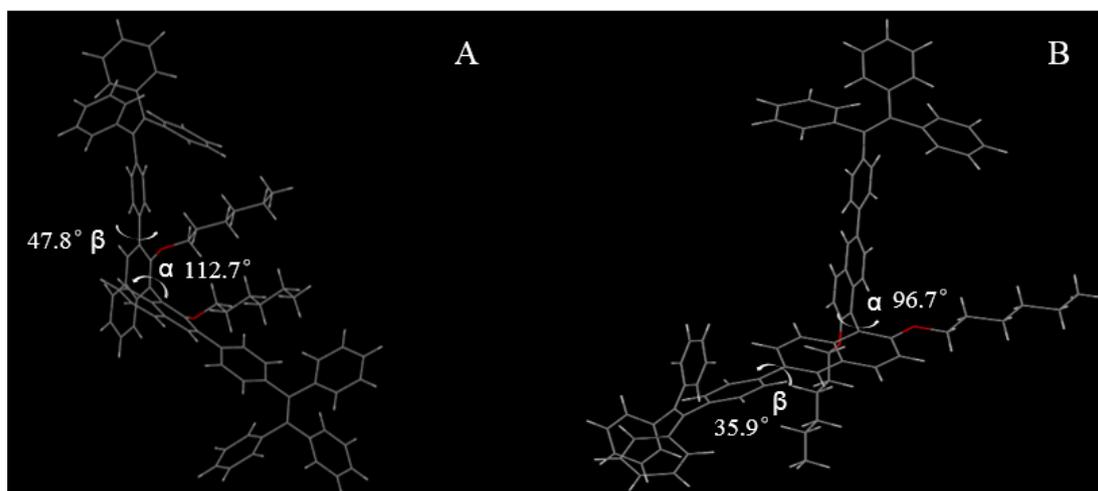


Figure S18. Optimized molecular structures of (A) (*R*)-3,3'-BTPE-BINA and B) (*S*)-6,6'-BTPE-BINA. (The ground-state geometries were optimized through density functional theory (DFT) with a B3LYP hybrid functional at the basis set level of 6-31G (d,p). All the calculations were performed using the Gaussian 03 package.)

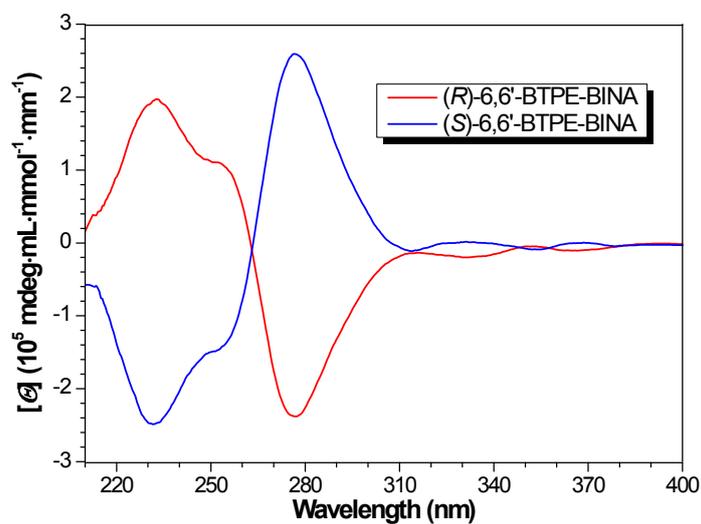


Figure S19. CD spectra of (*R*)-6,6'-BTPE-BINA and (*S*)-6,6'-BTPE-BINA in THF. Concentration: 10^{-4} M.

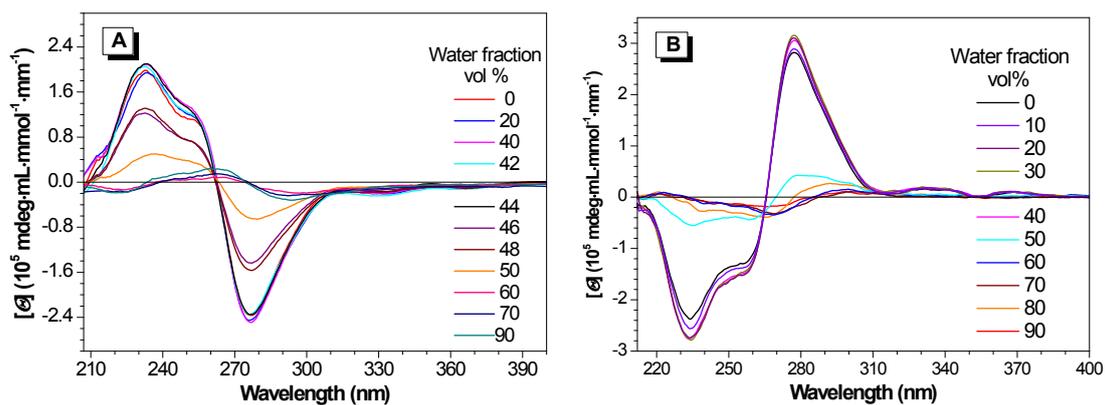


Figure S20. CD spectra of (A) (*R*)-6,6'-BTPE-BINA and (B) (*S*)-6,6'-BTPE-BINA in THF/water mixtures with different f_w . Concentration: 10^{-4} M .

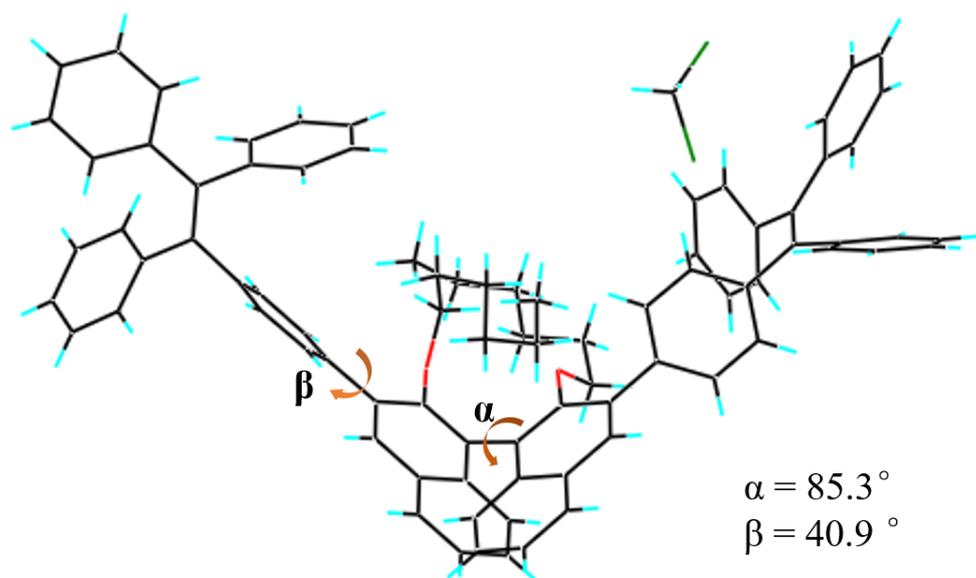


Figure S21. Single crystal structure and torsion angles of (*R*)-3,3'-BTPE-BINA.

Reference

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