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Supporting Information

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Macroscopic origin of CD-effects by alignment of self-assembled fibers in solution

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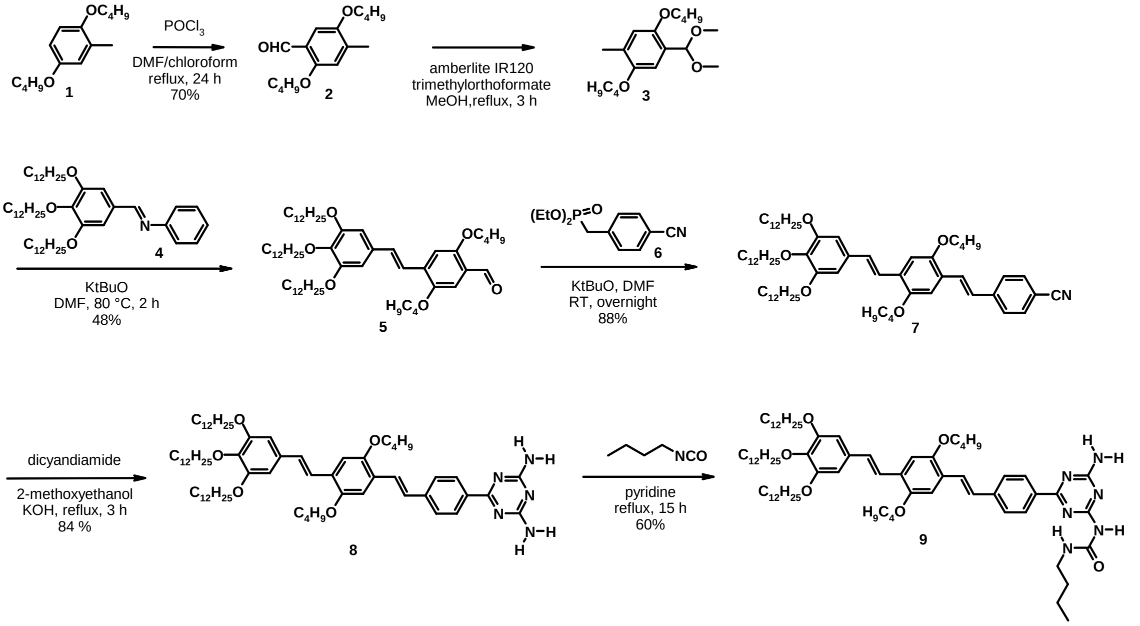
Materials and Methods

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25.0 °C on a Varian Mercury Vx (300 MHz or 400 MHz for ^{1}H and 75 MHz or 100 MHz for ^{13}C). All solvents were of AR quality and chemical were used as received. Chemical shifts are given in ppm (δ) relative to tetramethylsilane. Abbreviations used are s = singlet, d = doublet, t = triplet and br = broad. Infrared spectra were run on a Perkin Elmer Spectrum One UATR FT-IR spectrophotometer. MALDI-TOF MS spectra were measured on a Perspective DE Voyager spectrometer utilising an α-cyano-4-hydroxycinnamic acid matrix. Absorbance, LD and CD spectra were measured on a Jasco J-815 spectropolarimeter where the sensitivity, time constant and scan rate were chosen appropriately. Temperature dependent measurements were performed with a PFD-425S/15 Peltier-type temperature controller with a temperature range of 263-383 K and adjustable temperature slope. Atomic Force Microscopy images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the tapping mode regime. Microfabricated silicon cantilever tips (NS) with a resonance frequency of approximately 300 kHz and a spring constant of about 50 Nm^{-1} were used. Shaking of the cuvette was performed by placing the right index finger on the cap of the cuvette and the thumb on the bottom and shaking the cuvette in its vertical direction. The **A-OPV3** films were prepared by applying a couple of drops of a concentrated **A-OPV3** ($c = \sim 2$ mM) solution in heptane on a glass plate and let the solvent evaporate while the glass plate was held under an angle to induce flow.

Synthesis



Scheme S1

A-OPV3 was synthesized according to Scheme S1. The synthesis of (*E*)-N-Phenyl-3,4,5-tridodecyloxybenzaldehyde (**4**) and diethyl(4-cyanobenzyl) phosphonate (**6**) are published elsewhere.[1]

2,5-Bisbutoxy-4-methylbenzaldehyde (2). POCl$_3$ (7.8 mL, 85 mmol) was added to a mixture of dry DMF (5.5 mL) and dry CHCl$_3$ (10 mL) under an atmosphere of dry argon. After the mixture was stirred for 1 h, **1** (4.5 g, 19 mmol) was added and the reaction mixture was stirred for 24 h at reflux temperature. After the mixture was cooled to room temperature, the mixture was poured on ice water (150 mL), stirred for 45 minutes, and extracted with diethyl ether (100 mL). The organic phase was washed with 1 M HCl (2 x 100 mL), water (3 x 200 mL), and a saturated NaHCO$_3$ solution (150 mL). After the organic phase was dried over Na$_2$SO$_4$ and the solvent was evaporated in vacuo, the crude product was purified by column chromatography (silica gel, hexane/CH$_2$Cl$_2$ 1:4*)*. Recrystallization from methanol yielded 3.5 g (70 %) of **2** as white crystals. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.97-1.00 (t, 6H, CH$_3$), 1.46-1.55 (m, 4H, CH$_2$), 1.74-1.82 (4H, m, CH$_2$), 2.27 (s, 3H, ArCH$_3$), 3.94-4.05 (m, 4H, OCH$_2$), 6.79 (s, 1H, ArH), 7.22 (s, 1H, ArH), 10.42 (s, 1H, -CHO); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 14.14, 14.18, 17.59, 19.61, 19.65, 31.63, 31.67, 68.51, 69.2, 108.63, 116.0, 123.38, 137.12, 151.72, 156.51, 189.74; GCMS (MW = 264.3): *m*/z = 264.3 [M]$^+$.

4-Methyl-2,5-bisbutoxybenzaldehyde dimethylacetal (3). 2,5-Bisbutoxy-4-methylbenzaldehyde **(2)** (0.5 g, 1.89 mmol), Amberlite IR-120 (1.1 g) and trimethylorthoformate (9 mL) were added to methanol (65 mL) and the mixture was refluxed for 3h. After cooling to room temperature, Na$_2$CO$_3$ (3.0 g) was added and the solution was stirred for 10 min. After filtration, the solvent was removed in *vacuo,* affording **3** as a colorless oil, which was used without further purification. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.94-1.00 (t, 6H, CH$_3$), 1.45-1.56 (m, 4H, CH$_2$), 1.72-1.77 (4H, m, CH$_2$), 2.21 (s, 3H, ArCH$_3$), 3.38 (s, 6H, OCH$_3$), 3.91-3.96 (m, 4H, OCH$_2$), 5.60 (s, 1H, CH(OCH$_3$)$_2$), 6.70 (s, 1H, ArH), 6.98 (s, 1H, ArH); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 14.21, 14.24, 16.71, 19.66, 19.70, 31.92, 31.95, 54.48, 68.81, 69.41, 100.08, 110.50, 115.82, 124.87, 128.43, 150.64, 151.55; GCMS (MW = 310.4): *m*/z = 310.3 [M]$^+$.

(*E*)-4-[3,4,5-tris-{dodecyloxy}styryl]-2,5-bisbutoxybenzaldehyde (5). (*E*)-*N*-Phenyl-3,4,5-tris-{dodecyloxy}benzaldimine (**4**) (1.08 g, 1.47 mmol) and **3** (0.48 g, 1.55 mmol) were dissolved in anhydrous DMF (5 mL). Under an argon atmosphere, *t*BuOK (0.63 g, 5.62 mmol) was added and the solution was stirred for 2 h at 80 °C. After cooling to room temperature, the solution was poured onto a mixture of crushed ice and 3N HCl (30 mL). The mixture was extracted with dichloromethane (3 x 100 mL) and the combined organic fractions were washed with water (100 mL). After an additional extraction with diisopropyl ether, the combined organic fractions were dried over Na_2SO_4. After evaporation of the solvent in *vacu*o, column chromatography (silica gel, pentane/CH_2Cl_2 4:6), size exclusion chromatography (Bio Beads S-X1, THF) and precipitation from CH_2Cl_2 with methanol, the product was obtained in 48% (0.67 g) yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.86-0.90 (t, 9H, CH_3), 0.98-1.03 (t, 6H, CH_3), 1.12-1.87 (m, 68H, CH_2), 3.96-4.14 (m, 10H, OCH_2), 6.74 (s, 2H, ArH), 7.13 (d, J = 16.5 Hz, 1H, ArCH=CHAr), 7.15(s, 1H, ArH), 7.32 (s, 1H, ArH), 7.34 (d, J = 16.2 Hz, 1H, ArCH=CHAr), 10.44 (s, 1H, CHO); MALDI-TOF MS (MW = 905.45): m/z = 904.94 $[M]^+$, 927.94 $[M+Na]^+$.

(*E,E*)-4-[-4-(3,4,5-tris-{dodecyloxy}styryl)-2,5-bisbutoxystyryl]-phenylnitrile (7). Diethyl(4-cyanobenzyl) phosphonate (**6**) (200 mg, 0.79 mmol) was dissolved in 3 mL anhydrous DMF under an argon atmosphere and *t*BuOK (130 mg, 1.15 mmol) was added to the solution. After 15 min a solution of **5** (400 mg, 0.44 mmol) in 25 mL DMF/THF (1:2) was added drop wise to the reaction mixture. The solution was stirred for 15 h and subsequently poured onto crushed ice. 40 mL of 3N HCl was added and the aqueous phase was extracted three times with diisopropyl ether. The collected organic fractions were washed with water and dried over Na_2SO_4. After evaporation of the solvent in *vacu*o, the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 4:6) to afford 390 mg of **7** (88% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.86-0.91 (t, 9H, CH_3), 1.01-1.06 (t, 6H, CH_3), 1.27-1.89 (m, 68 H, CH_2), 3.96-4.10 (m, 10H, OCH_2), 6.74 (s, 2H, ArH), 7.05 (d, J = 16.5 Hz, 1H, ArCH=CHAr), 7.11 (s, 2H, ArH), 7.12 (d, J = 16.8 Hz, 1H, ArCH=CHAr), 7.35 (d, J = 16.8 Hz, 1H, ArCH=CHAr), 7.58 (d, J = 16.5 Hz, 1H, ArCH=CHAr), 7.59 (dd, J=8.4 Hz, 2H, ArH), 7.63 (dd, J=8.4 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.26, 14.32, 14.43, 19.78, 19.89, 23.01, 26.47, 29.71, 29.78, 29.99, 30.03, 30.08, 30.62, 30.68, 31.84, 31.92, 32.26, 69.31, 69.45, 69.68, 73.86, 105. 60, 110.43, 111.42, 119.47, 122.59, 125.63, 125.81, 126.87, 127.06, 127.59, 128.59, 129.89, 132.73, 133.29, 138.71, 142.90, 151.91, 151.86, 153.60; MALDI-TOF MS (MW=1004.59): m/z = 1003.80 $[M]^+$.

2,4-diamino-6-[(*E,E*)-4-[-4-(3,4,5-tris-{dodecyloxy}styryl)-2,5-bisbutoxystyryl]phenyl]-s-triazine (8). 320 mg (0.32 mmol) **7** and 40 mg (0.48 mmol) dicyandiamide were dissolved in 5 mL 2-methoxyethanol, under an argon atmosphere. Then, 60 mg (1.07 mmol) KOH was added and the solution was refluxed for 3 h. After cooling the reaction mixture to room temperature, 50 mL of brine was added and the aqueous phase was extracted three times with dichloromethane. The collected organic fractions were dried over Na_2SO_4, and after evaporation of the solvent, the crude product was purified with column chromatography (silica gel, THF/CH_2Cl_2 2:8; silica gel, EtOH/CH_2Cl_2 5:95). After precipitation from chloroform in cold methanol, pure OPV3 triazine derivative **8** (291 mg, 84%) was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.86-0.90 (t, 9H, CH_3), 1.01-1.06 (t, 6H, CH_3), 1.27-1.90 (m, 68H, CH_2), 3.96-4.09 (m, 10H, OCH_2), 5.24 (br, 4H, NH), 6.74 (s, 2H, ArH), 7.04 (d, J = 16.2 Hz, 1H, ArCH=CHAr), 7.11 (s, 1H, ArH), 7.14 (s, 1H, ArH), 7.18 (d, J = 16.5 Hz, 1H, ArCH=CHAr), 7.35 (d, J = 16.5 Hz, 1H, ArCH=CHAr), 7.58 (d, J = 16.8 Hz, 1H, ArCH=CHAr), 7.60 (d, 2H, J= 8.4 Hz, ArH), 8.31 (d, 2H, J = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.31, 14.36, 14.46, 19.83, 19.91, 23.04, 26.49, 29.72, 29.74, 29.79, 30.02, 30.06, 30.09, 30.11, 30.70, 31.92, 31.97, 32.28, 69.49, 69.54, 69.69, 73.91, 105.58, 110.72, 111. 28, 122.83, 125.46, 126.69, 126.74, 127.83, 128.42, 129.07, 129.48, 133.48, 135.52, 138.61, 141.69, 151.31, 151.59, 151.70, 153.61, 167.99, 172.35; IR (UATR): ν (cm^{-1}) = 694, 721, 810, 854, 906, 962, 1028, 1068, 1117, 1202, 1243, 1340, 1395, 1424, 1467, 1504, 1540, 1578, 1601, 1638, 2853, 2922, 2955, 3061, 3197, 3325, 3476; MALDI-TOF MS (MW=1088.67): m/z =1087.75 $[M]^+$.

2-amino-4-butylureido-6-[(*E*,*E*)-4-{4-(3,4,5-Tridodecyloxystyryl)-2,5-bisbutoxystyryl}]phenyl-s-triazine (9, A-OPV3): Under an argon atmosphere, 140 mg (0.13 mmol) of **8** was dissolved in 15 mL dry pyridine and heated to reflux. The reaction flask was evacuated every 15 minutes to remove the water, for one hour. *n*-Butylisocyanate (53 mg, 0.53 mmol) was added and the reaction mixture was refluxed for 15 h. After cooling, the solvent was removed under reduced pressure, and the residue purified by column chromatography (silica gel, EtOH/CH$_2$Cl$_2$ 1:99). After precipitation from chloroform in methanol, 91 mg (60%) **A-OPV3** (**9**) was obtained. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.88-1.01 (t, 9H, CH$_3$), 1.02-1.22 (m, 9H, CH$_3$), 1.24-2.27 (m, 72H, CH$_3$), 3.44-3.47 (q, 2H, NHCONHC*H*$_2$), 3.96-4.01 (m, 10H), 5.46 (br, 1H, ArN*H*H), 6.74 (s, 2H, ArH), 7.04 (d, J = 16.8 Hz, 1H, ArCH=CHAr), 7.11 (s, 1H, ArH), 7.14 (s, 1H, ArH), 7.19 (d, J = 15.3 Hz, 1H, ArCH=CHAr), 7.35 (d, J = 16.8 Hz, 1H, ArCH=CHAr), 7.61 (d, J = 15.9 Hz, 1H, ArCH=CHAr), 7.62 (d, 2H, J= 8.4 Hz, ArH), 8.21 (d, 2H, J = 8.4 Hz, ArH), 9.31 (br, 1H, ArNHCON*H*), 9.89 (br, 1H, ArN*H*CONH), 10.25 (br, 1H, ArNH*H*); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 14.20, 14.32, 14.37, 14.47, 19.86, 19.93, 20.67, 23.05, 26.50, 29.73, 29.76, 29.81, 30.03, 30.07, 30.12, 30.67, 31.94, 31.98, 32.10, 32.29, 34.58, 40.34,69.50, 69.74, 73.92, 105.60, 110.66, 111.25, 122.75, 125.87, 126.04, 126.40, 126.80, 127.94, 128.09, 128.60, 129.04, 129.62, 133.43, 134.61, 136.12, 138.67, 142.43, 151.32, 151.78, 153.63, 156.30, 164.24, 167.80, 170.66; IR (UATR): υ (cm^{-1}) = 668, 699, 721, 749, 808, 853, 962, 1027, 1068, 1117, 1168, 1203, 1244, 1359, 1415, 1467, 1505, 1523, 1573, 1594, 1641, 1687, 2854, 2928, 2955, 3051, 3134, 3202, 3405, 3496; MALDI-TOF MS (MW=1187.80): m/z = 1186.80 [M]$^+$.

Figures

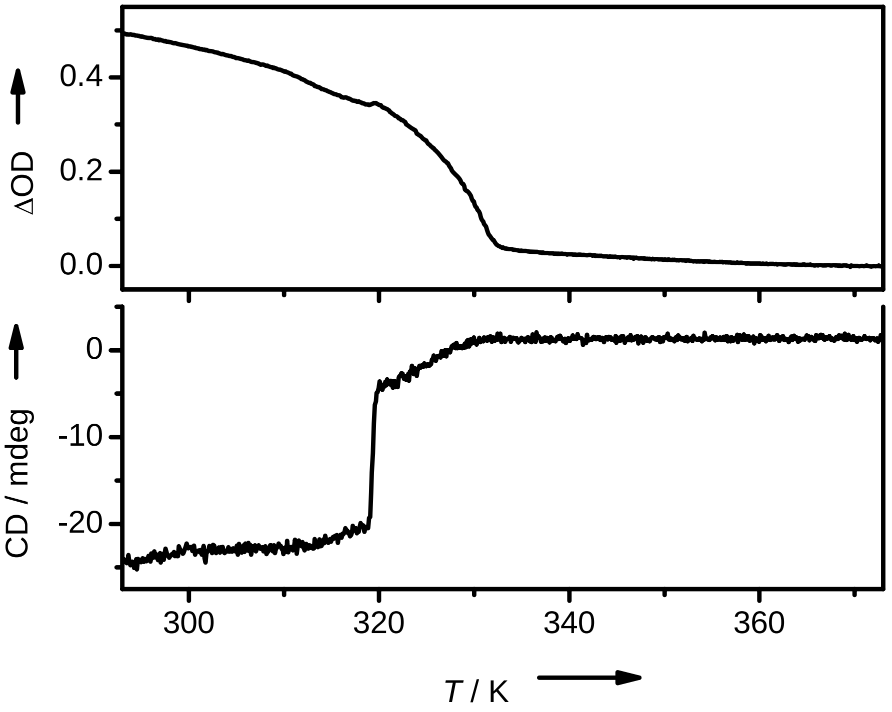


Figure S1: Temperature induced changes in Absorbance (upper graph) and CD (lower graph) cooling curve of **A-OPV3** in a dodecane solution (c = 5 x 10^{-5} M, ΔT = 60 K/hr, λ = 475 nm).

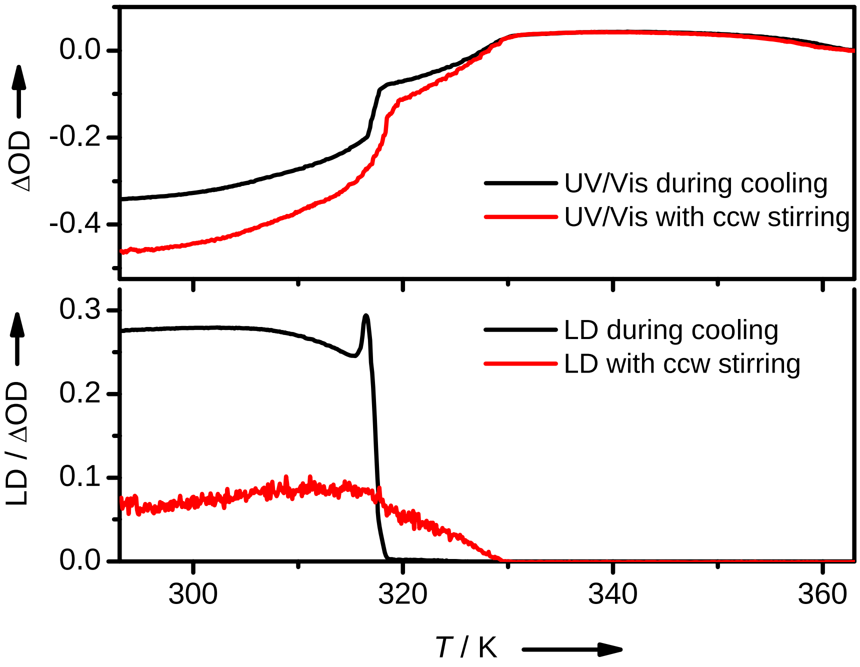


Figure S2: Temperature induced changes in Absorbance (upper graph) and LD (lower graph) cooling curve of **A-OPV3** in a dodecane solution (***1 cm cuvet***, c = 5 x 10^{-5} M, ΔT = 60 K/hr, λ = 400 nm).

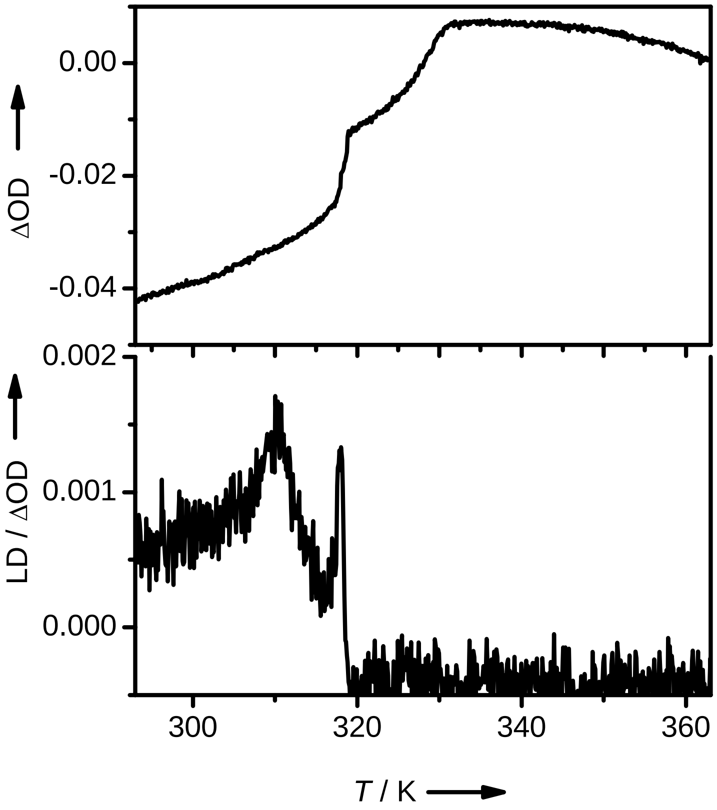


Figure S3: Temperature induced changes in Absorbance (upper graph) and LD (lower graph) cooling curve of **A-OPV3** in a dodecane solution (***1 mm cuvet***, c = 5 x 10^{-5} M, ΔT = 60 K/hr, λ = 400 nm).

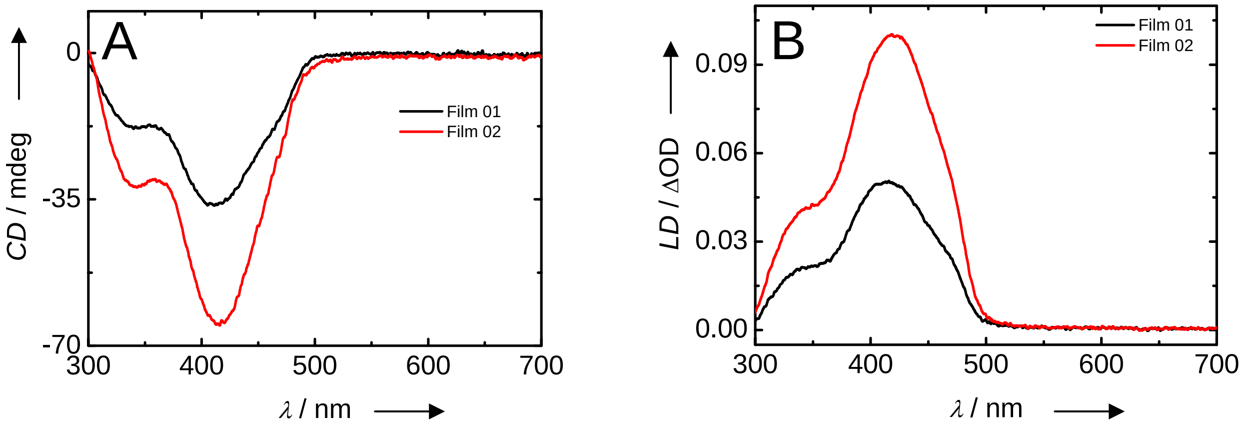


Figure S4: CD (A) and LD (B) measurements on the **A-OPV3** film 01 (black) and film 02 (red).

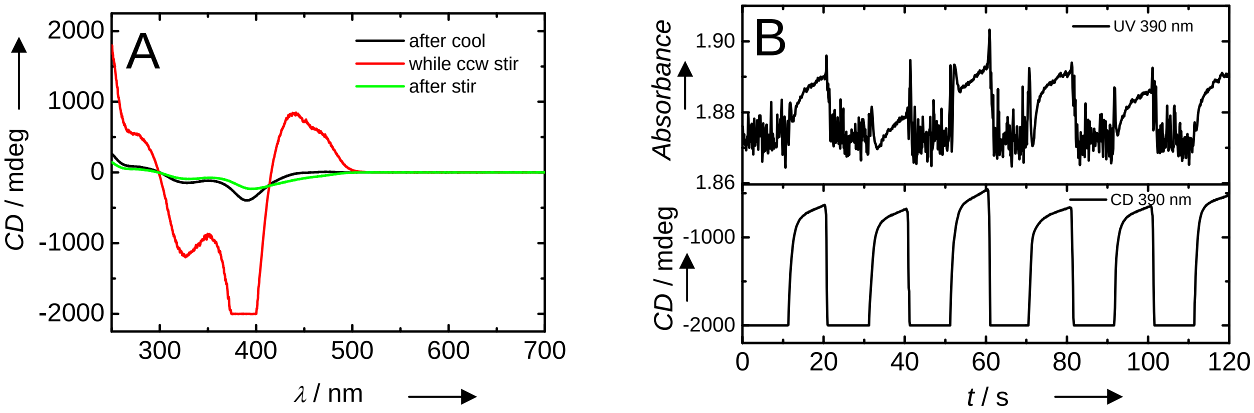


Figure S5: A) CD measurements of an **A-OPV3** solution in dodecane after cooling (black), while stirring (red) and after stirring (green) (c = 5 x 10^{-5} M, T = 293 K) B) CD intensity at 390 nm in time while stirring was stopped and started each 10 seconds (c = 5 x 10^{-5} M, T = 293 K).

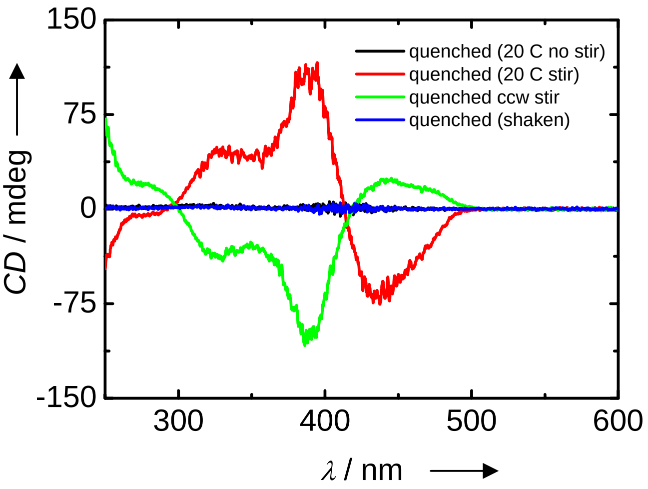


Figure S6: CD measurements of a quenched **A-OPV3** solution in dodecane after cooling (black), shaking (blue) and with clockwise (red) and counter-clockwise (green) stirring (c = 5 x 10^{-5} M, T = 293 K).

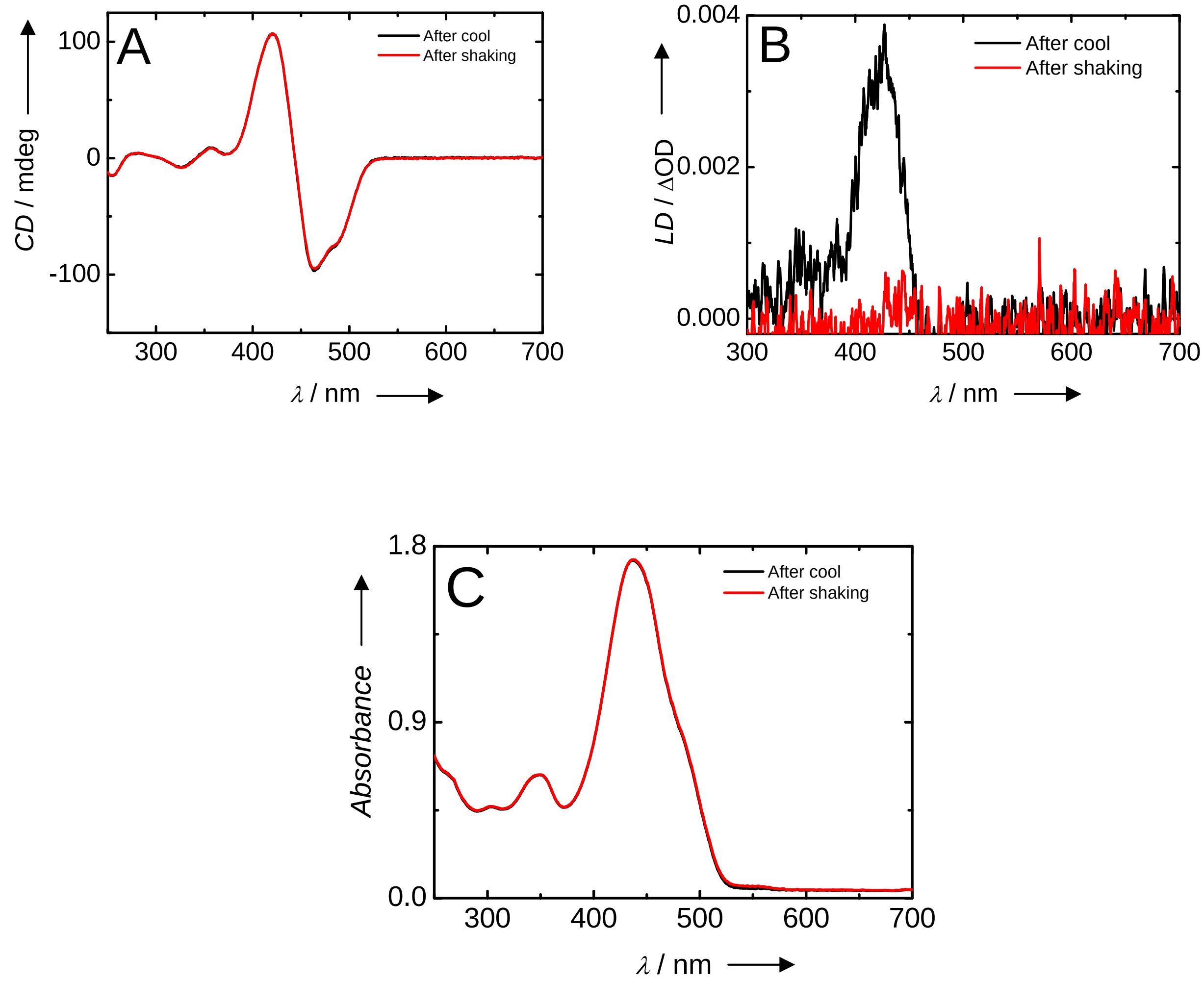


Figure S7: CD (A) LD (B) and absorbance (C) spectra of an **S-OPV4** solution in dodecane before (black) and after (red) shaking (2.4 x 10^{-5} M, T = 293 K).

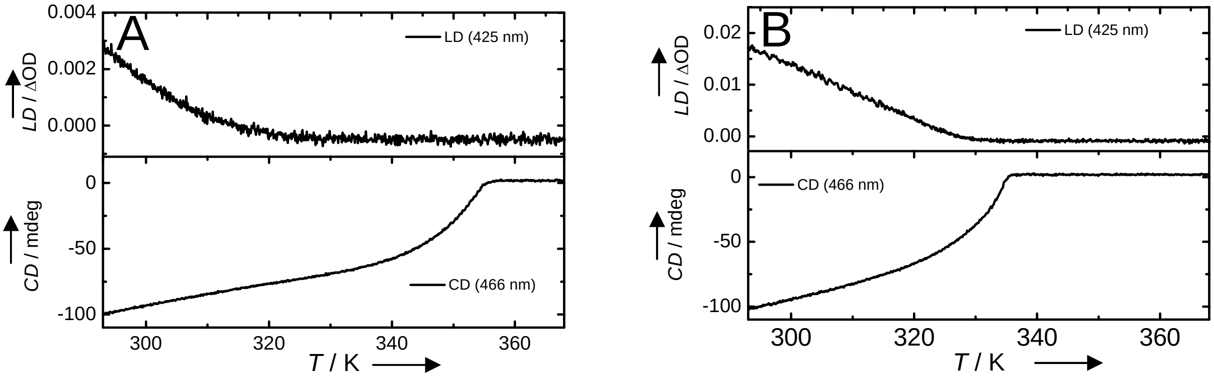


Figure S8: Temperature dependent LD (top, 425 nm) and CD (bottom, 466 nm) spectra of chiral **S-OPV4** in dodecane, A) ***1 mm cuvet*** (c = 2.4 x 10^{-4} M, ΔT = 60 K/hr) B) ***1 cm cuvet*** (c = 2.4 x 10^{-5} M, ΔT = 60 K/hr).

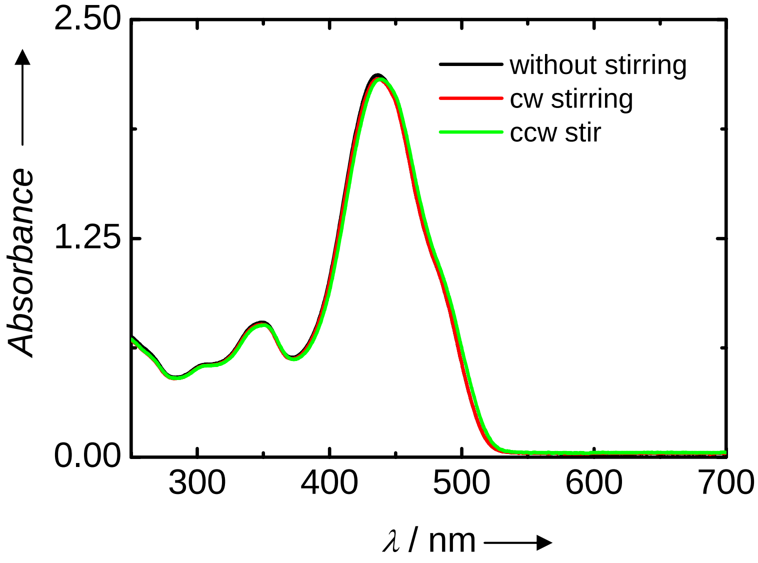


Figure S9: Absorbance measurement on **S-OPV4** without stirring (black) and with clockwise (red) and counter-clockwise stirring (green).

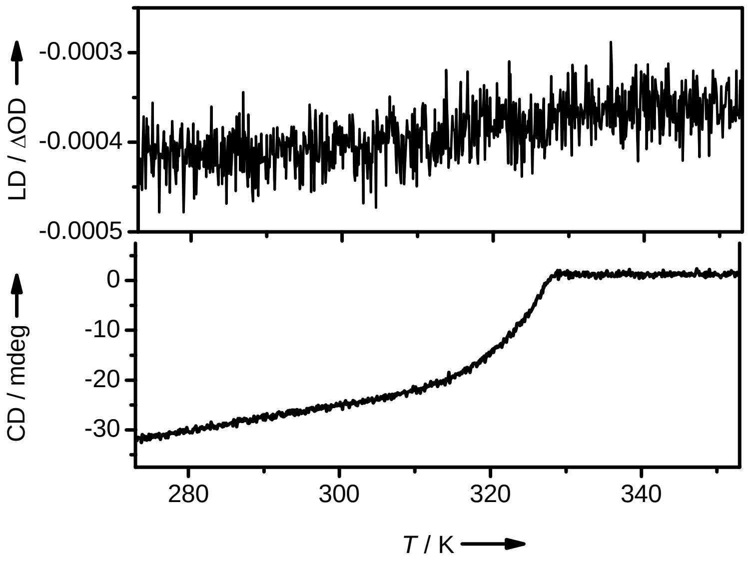


Figure S10: Temperature dependent LD (top, 428 nm) and CD (bottom, 428 nm) spectra of chiral **S-OPV3** (chiral analogue of **A-OPV3** containing *S*-methylbutyloxy sidechains) in dodecane (c = 2.4 x 10^{-4} M, l = 1 mm, ΔT = 60 K/hr).

References

[1] A. P. H. J. Schenning, P. Jonkheijm, E. Peeters, E. W. Meijer, *J. Am. Chem. Soc.* **2001**, *123*, 409.