

## Supporting Information

### A Self-Assembled Helical Anthracene Nanofibre Whose *P*- and *M*-Isomers Show Unequal Linear Dichroism in a Vortex

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## 1. Materials

Unless otherwise noted, reagents and solvents were used as received from Kishida Chemical Co., Ltd. [ $\text{CHCl}_3$  (>99%) and hexane (>96%)] and Wako Pure Chemical Industries, Ltd. [*n*-octane (>98%)]. For column chromatography, Wakogel C-300HG (particle size 40–60 mm, silica), C-400HG (particle size 20–40 mm, silica) and standardized aluminum oxide 90 (Merck) was used. 3,4,5-[Tris-(*R*)-3,7-dimethyloctyloxy]benzoic acid (*R*)-**1**, 3,4,5-[tris-(*S*)-3,7-dimethyloctyloxy]benzoic acid (*S*)-**1** and 9,10-bis(aminomethyl)anthracene **2** were prepared by procedures analogous to those reported previously,<sup>1,2</sup> and unambiguously characterized by means of <sup>1</sup>H NMR, IR spectroscopy and fast atom bombardment (FAB) mass spectrometry.

## 2. Measurements

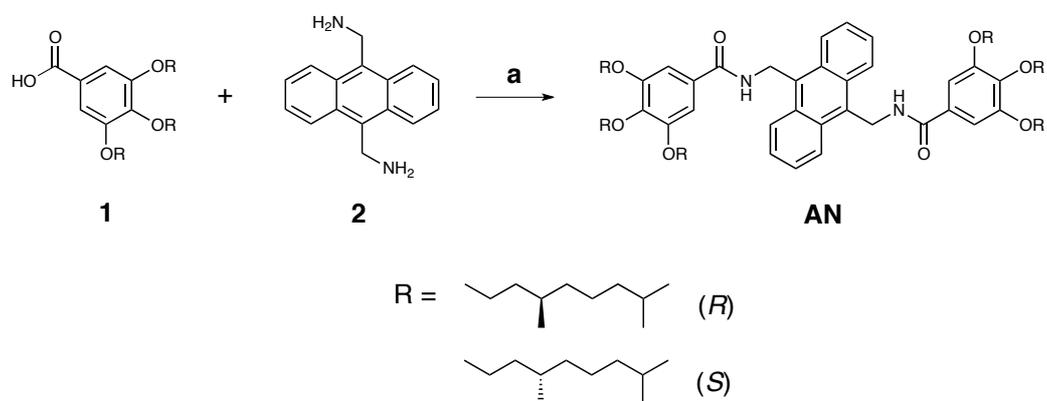
CD and LD spectra were recorded on a JASCO J-820 spectropolarimeter equipped with a JASCO PTC-423L temperature/stirring controller and a custom made CW/CCW-stirring system. The spectrometer is equipped with a 10 × 10 × 40 mm quartz optical cuvette, in which sample solutions (3 mL) are stirred mechanically using a  $\phi 2.0 \times 5.0$  mm Teflon-coated magnetic stirrer bar at the bottom of the cuvette, 14 mm below the centre of a  $\phi 8.0$  mm wide polarized light pass. LD intensity is defined as  $\Delta_{\text{LDA}} = A_{\parallel} - A_{\perp}$  ( $\Delta_{\text{LDA}}$  represents magnitude of LD, while  $A_{\parallel}$  and  $A_{\perp}$  denote horizontal and perpendicular absorbances, respectively). Prior to spectral measurements, sample *n*-hexane solutions ( $[\text{AN}] = 8.3 \times 10^{-5}$  M) were prepared by dilution of a  $\text{CHCl}_3$  solution of AN ( $[\text{AN}] = 5.0 \times 10^{-2}$  M), allowed to stand in the dark at 25 °C for 2 h, and then, stirred at 1350 rpm in both clockwise (CW) and counterclockwise (CCW) stirrings for 1 h. Photo-irradiation was performed on a USHIO Optical Modulex equipped with a 500 W Xenon short-arc lamp.

The frequency-modulation AFM (FM-AFM) apparatus used in this experiment was developed by a commercially available AFM (Shimadzu, SPM9600) modified with the low-noise optical deflection scheme after Fukuma et al.<sup>3</sup> The deflection noise was less than 40 fm  $\text{Hz}^{-1/2}$ . The resonance frequency and Q factor of the cantilever oscillation were typically 135 kHz. In FM-AFM,<sup>4</sup> a cantilever is used as a mechanical resonator in a self-oscillation

circuit such that the cantilever vibrates at its resonance frequency with a constant oscillation amplitude. The frequency shift ( $\Delta f$ ) of the cantilever resonance induced by the tip-sample interaction force is detected and used for the tip-sample distance regulation.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a VARIAN model INOVA 400 spectrometer, where chemical shifts ( $\delta$  in ppm) were determined with respect to tetramethylsilane as the internal standard. Infrared absorption spectra (IR) were recorded on a JASCO FT/IR-4200 fourier transform infrared spectrometer. FAB mass spectrometry was performed on a JEOL JMS-BU30 LC Mate spectrometer with 3-nitrobenzylalcohol as the matrix. Scanning electron microscopy (SEM) was performed using a JEOL JSM-7001FA FE-SEM operating at 15 kV. Dynamic light scattering (DLS) measurements were performed using an Otsuka model ELS-Z2 instrument.

### 3. Synthetic scheme

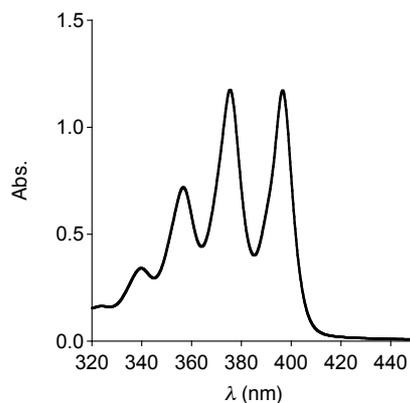


**Scheme S1.** Reagents and conditions: **a**, (1)  $\text{SOCl}_2$ , reflux; (2) *N,N*-dimethyl-4-aminopyridine, dry  $\text{CH}_2\text{Cl}_2$ , reflux.

#### 4. Synthesis

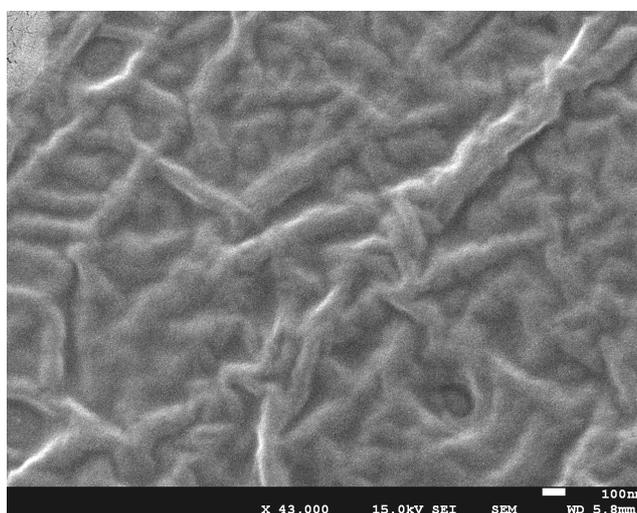
**(R)- and (S)-AN:** 3,4,5-[Tris-(*R*)-3,7-dimethyloctyloxy]benzoic acid (*R*)-**1** or 3,4,5-[tris-(*S*)-3,7-dimethyloctyloxy]benzoic acid (*S*)-**1** (0.17 g, 0.29 mmol) was dissolved in thionyl chloride (5 mL), and the reaction mixture refluxed under Ar for 4 h and then evaporated to dryness. The residue was mixed with 9,10-bis(aminomethyl)anthracene **2** (0.02 g, 0.08 mmol) and *N, N'*-dimethyl-4-aminopyridine (0.07 g, 0.57 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and the solution refluxed under Ar for 24 h and then evaporated to dryness. The residue was then dissolved into CHCl<sub>3</sub> and washed with aqueous solutions of 1 N HCl, saturated NaHCO<sub>3</sub> and saturated NaCl. The organic layer was then extracted, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was washed with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH to leave AN as orange oil [34% for (*R*)-AN, 69% for (*S*)-AN]. FAB-MS *m/z* calcd for M<sup>+</sup> (C<sub>90</sub>H<sub>144</sub>N<sub>2</sub>O<sub>8</sub>) 1382, found 1383 (M + H<sup>+</sup>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ 8.48–8.46 (dd, 4H, *J* = 3.2 Hz, 7.0 Hz, anthracene), 7.66–7.64 (dd, 4H, *J* = 3.2 Hz, 7.0 Hz, anthracene), 6.91 (s, 4H, phenyl), 6.22–6.19 (t, 2H, *J* = 4.7 Hz, amide), 5.67–5.66 (d, 4H, *J* = 4.6 Hz, methylene), 3.98–3.95 (m, 12H, -OCH<sub>2</sub>-), 1.87–1.11 (m, 60H, alkyl), 0.89–0.84 (m, 54H, methyl); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ 167.1, 153.2, 141.4, 130.4, 130.1, 128.9, 126.7, 124.8, 105.8, 71.7, 67.7, 39.3, 37.4, 36.3, 29.7, 28.0, 24.7, 22.6, 19.5; IR (KBr): 3304, 2956, 2925, 2852, 1630, 1580, 1544, 1498, 1466, 1426, 1382, 1334, 1261, 1114 cm<sup>-1</sup>; UV-Vis (CHCl<sub>3</sub>, 25 °C): λ<sub>max</sub> 262, 340, 357, 376, 397 nm.

### 5. Absorption spectrum of (*R*)-AN in CHCl<sub>3</sub>



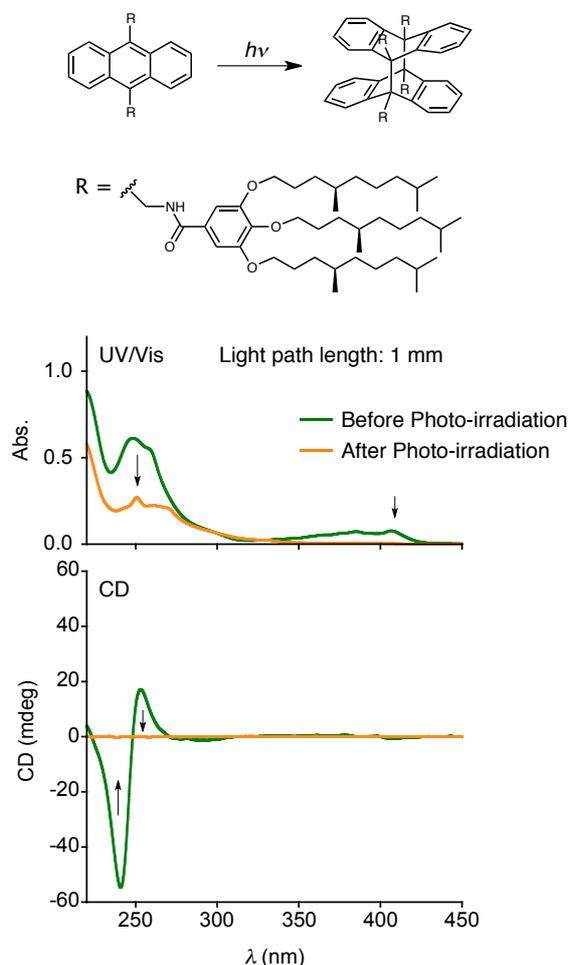
**Fig. S1.** Absorption spectrum of a CHCl<sub>3</sub> solution of (*R*)-AN at 25 °C. [(*R*)-AN] =  $8.3 \times 10^{-5}$  M.

### 6. SEM micrograph of self-assembled nanofibres formed from (*R*)-AN



**Fig. S2.** SEM micrograph of an air-dried sample of self-assembled (*R*)-AN in *n*-hexane solution ( $8.3 \times 10^{-5}$  M) deposited on a silicon substrate at room temperature.

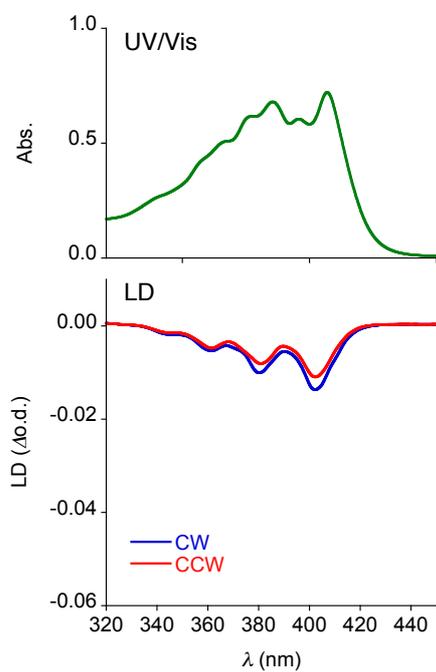
## 7. Photo-dimerization of (*R*)-AN in hexane



**Fig. S3.** Changes in absorption (top) and CD (bottom) spectra at 25 °C upon photo-irradiation for 20 min of hexane solutions of self-assembled (*R*)-AN in a Pyrex glass tube with a 500 W Xenon lamp. The spectral measurements were demonstrated with a quartz optical cuvettes having light path length of 1 mm.  $[(R)\text{-AN}] = 8.3 \times 10^{-5}$  M.

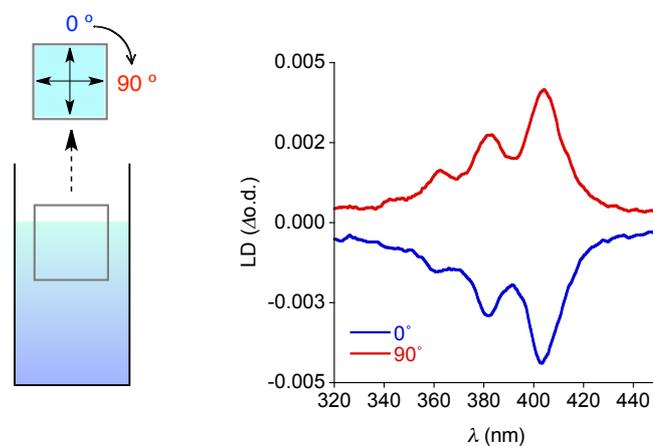
→ Since dynamic light scattering (DLS) response of the hexane solution of (*R*)-AN was also disappeared upon photo-irradiation, these spectral changes indicate dissociation of the self-assembled nanofibres of (*R*)-AN due to photo-dimerization of the anthracene components.

## 8. Absorption and LD spectroscopy of self-assembled (*R*)-AN in octane



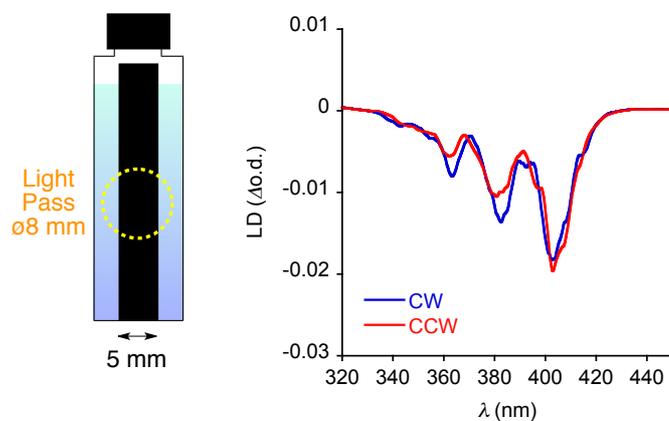
**Fig. S4.** Absorption (top) and LD (bottom) spectra of an octane solution (3.0 mL) of self-assembled (*R*)-AN ( $8.3 \times 10^{-5}$  M) upon CW (—) or CCW (—) rotary stirring at 1350 rpm using a  $\phi 2.0 \times 5.0$  mm Teflon-coated magnetic stir bar at 25 °C.

### 9. LD spectroscopy of a thin film of aligned nanofibres of (*R*)-AN formed by dip coating



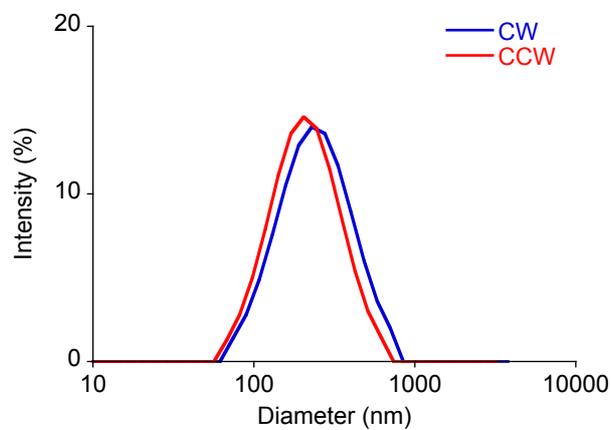
**Fig. S5.** Linear dichroism (LD) spectroscopy of an oriented thin film of the nanofibres of (*R*)-AN. The films were positioned in such a way that their oriented directions were angled by 0° (blue curve) and 90° (red curve) relative to the vertical axis of a linearly polarized incident light for the spectroscopy. The films were prepared by dip-coating of a *n*-hexane solution of (*R*)-AN ( $8.3 \times 10^{-5}$  M) at 25 °C on a 0.12–0.17 mm thick glass plates.

## 10. Pointwise LD spectroscopy for a stirred *n*-hexane solution of (*R*)-AN



**Fig. S6.** LD spectroscopy of a *n*-hexane solution (3.0 mL) of the nanofibres of (*R*)-AN ( $8.3 \times 10^{-5}$  M), upon lower-side rotary stirring at 1350 rpm in CW (blue curve) or CCW (red curve) direction using a  $\phi 2.0 \times 5.0$  mm Teflon-coated magnetic stir bar at 25 °C in a  $10 \times 10 \times 40$  mm quartz optical cell masked at a vertical centre with a 5 mm wide black tape.

### 11. DLS measurements of self-assembled (*R*)-AN in hexane after CW and CCW stirring



**Fig. S7.** DLS histogram profiles of nanofibres of (*R*)-AN in hexane ( $[(R)\text{-AN}] = 16.6 \times 10^{-5}$  M) at 25 °C after CW (—) or CCW (—) stirring for 30 min.

## 12. References

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