(Supporting Information)

Nonracemic Dopant-Mediated Hierarchical Amplification of Macromolecular Helicity in a Charged Polyacetylene Leading to a Cholesteric Liquid Crystal in Water

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Experimental Section

Materials. Deionized distilled water was used in all the experiments. (*S*)- and (*R*)-**2** were prepared by the reaction of (*S*)- and (*R*)-phenyl lactic acids (Aldrich) with aqueous NaOH. The stereoregular *cis-transoidal* poly-**1** was prepared by the polymerization of the corresponding monomer with a rhodium catalyst according to the previously reported method.[1,2] The resulting polymer was quantitatively converted to its HCl salt with aqueous HCl, followed by precipitation into acetone; its number average molecular weight was 3.4×10^5 ($M_w/M_n = 2.21$) as determined by size exclusion chromatography (SEC). The stereoregularity was confirmed to be *cis-transoidal* based on the ^{1}H NMR and Raman spectroscopies.[1,2]

Instruments. ^{1}H NMR spectra were taken using a Varian VXR-500S spectrometer operating at 500 MHz for [1]H. The Raman spectrum was taken on a Jasco RMP-CT200. An SEC measurement was performed with a Jasco PU-980 liquid chromatograph (Jasco) equipped with a RI (256 nm; Jasco RI-930) detector. A Tosoh TSK-GEL SUPER AWM-H column was connected and a water solution containing 9 mM tartaric acid and the 0.1 mM tartaric acid sodium salt was used as the eluent at a flow rate of 0.6 mL/min.

The molecular weight calibration curve was obtained with poly(ethylene oxide) and poly(ethylene glycol) standards.

Absorption and CD Measurements in Dilute Solution. All absorption (Jasco V-570, Hachioji, Japan) and CD (Jasco J-725) spectra were measured in water in a 1.0-mm quartz cell at ambient temperature (20—25 °C). The concentration of poly-**1**-HCl was calculated on the basis of the monomer units and was 1.0 mg/mL in dilute solution. The molar ratio of (*S*)- or (*R*)-**2** to the monomer units of poly-**1**-HCl was 0.5 (Figure. S-1) and 0.1 (Figure 2B, inset).   The CD titration experiments were carried out as follows. A stock solution of poly-**1**-HCl (2.0 mg/mL) in water was prepared in a 5-mL flask equipped with a stopcock. Stock solutions of (*S*)-**2** (7.94, 1.99, 0.40 and 0.20 mM) in water were also prepared in 5-, 25- and two 100-mL flasks, respectively. The 0.50 mL aliquots of the poly-**1**-HCl solution were transferred to thirteen 1-mL flasks equipped with stopcocks. Increasing amounts of the stock solution of the (*S*)-**2** were added to the flasks; the molar ratios of (*S*)-**2** to poly-**1**-HCl were 0.001, 0.002, 0.005 (0.20 mM (*S*)-**2** was used), 0.01, 0.02, 0.03 (0.40 mM (*S*)-**2**), 0.05 and 0.1 (1.99 mM (*S*)-**2**) and 0.2, 0.3, 0.5, 5.0, 10 (7.94 mM (*S*)-**2**), and the resulting solutions were diluted with water to maintain the poly-**1**-HCl concentrations at 1.0 mg/mL (4.0 mM). The absorption and CD spectra were then taken for each flask to determine the changes in the CD spectra (Figure 2A, inset). The association constant (K) was obtained according to the Hill equation, $\log(Y/(1-Y)) = n\log[G] + n\log K$, where Y, n, [G] and K represent the fractional saturation, the Hill coefficient, the concentration of the guest and the association constant, respectively.[3] The Hill plot gave a satisfactory linear fit (correlation coefficient > 0.99) with $K = 1.9 \times 10^4$ (M^{-1}) and $n = 1.20$.   The changes in

the ICD intensity of poly-**1**-HCl with respect to the ee of **2** (5% < ee < 100%, nonlinear effects) were investigated as follows.   The molar ratio of **2** to the monomer units of poly-**1**-HCl was held constant at 0.1. Stock solutions of the (*S*)- and (*R*)- **2** (0.93 mg/mL) in water were prepared in separate 25-mL flasks. The 0.50 mL aliquots of the poly-**1**-HCl solution (2.0 mg/mL) were transferred to seven 1-mL flasks equipped with stopcocks. Aliquots of the stock solutions of (*S*)- and (*R*)-**2** were then placed in the flasks so that the percent ee of the mixtures (*S*-rich) was 5, 10, 20, 40, 60, 80 and 100, and the solutions were finally diluted with water to maintain the poly-**1**-HCl concentration at 1 mg/mL. After mixing the solutions, the CD and absorption spectra were measured for each flask (Figure 2B, inset).

Preparation of Liquid Crystal Samples for Polarized Microscopy Studies. The concentrated poly-**1**-HCl (5 mg) solutions in water (10, 20, 30 and 40 wt. %; (weight of total polymer) / [(weight of total polymer) + (weight of water)]) were prepared in separate 2-mL test tubes, for the nematic LC poly-**1**-HCls. After the polymers were completely dissolved to give clear and homogeneous solutions, the solutions were transferred to a 1.0-mm (i.d.) glass capillary with a pipet and the ends were sealed. The cholesteric solutions were prepared in the same way using a 20 wt. % poly-**1**-HCl solution in water in the presence of appropriate amounts of (*S*)-**2** (from 0.0005 to 0.3 equiv.) or 0.1 equiv. nonracemic **2** (from 0.05 to 75 % ee). The samples were left at ambient temperature (20—25 °C) for an hour or days until stable fingerprint textures were obtained. The fingerprint textures showing the retardation lines for the cholesteric LCs were observed using a NIKON E600POL polarized microscope.   The fingerprint spacings, which are equal to half of the cholesteric helical pitch, were measured by

comparing it to a photograph of a standard microscopic ruler.

References

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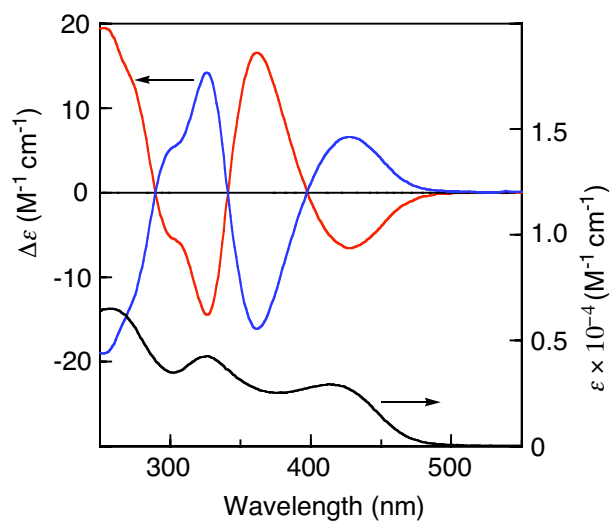3. Connors, K. A. *Binding Constants*; John Wiley: New York, 1987.

Figure S-1. One-handed helicity induction in poly-**1**-HCl in water. Shown are the CD spectra of poly-**1**-HCl with (*S*)- (blue line) and (*R*)-**2** (red line) and absorption spectrum of poly-**1**-HCl with (*S*)-**2** (black line) in water. Molar ratio of (*S*)- or (*R*)-**2** to the monomeric units of poly-**1**-HCl is 0.5.