Supporting Information

Intense Chiral Signal from α-Helical Poly-L-Alanine Observed in Low-Frequency Raman Optical Activity

Shigeki Yamamoto,[1] Shota Ishiro,[1] Jiří Kessler,[2] and Petr Bouř[2*]*

[1] Department of Chemistry, Graduate School of Science, Osaka University, Osaka 560-0043, Japan. [2] Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo náměstí 2, 16610 Prague, Czech Republic.

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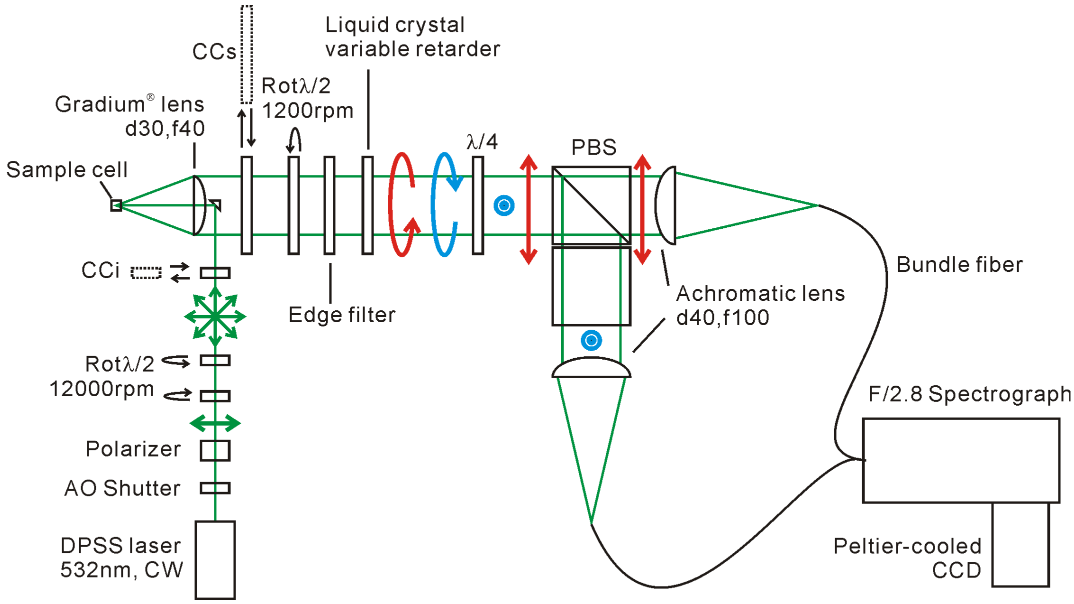

Figure S1. Scheme of the ROA instrument. Continuous DPSS laser at 532 nm (Ventus, Laser Quantum) was used for excitation; its polarization was temporally-unpolarized by passing through two counter-rotating half-wave plates at speed of 12000 rpm (Rotλ/2, home-made). The laser was reflected by two small mirrors (Silflex-Vis, Optics Balzers) and then focused on the sample by a lens (Gradium, f = 40 mm, D = 30 mm, Hikari Glass). Back-scattered light from the sample passed through correction optics and an edge filter (cut-off at ~60 cm^{-1}, US LPF, Iridian). Two half-wave plates (CC_i and CC_s) entered and left the light paths every ~20 seconds in the measurements to achieve the virtual enantiomer correction.[1] An electrically variable liquid crystal retarder (LRC-300, Meadowlark) and a rotating half-wave plate at 1200 rpm (Rotλ/2, home-made) were also adopted to suppress instrumental artifact. Right and left circularly polarized components of Raman light were separated by a quarter-wave plate and two polarized beam splitters, and then focused by achromatic lenses (f =100 mm, D =40 mm) to a custom-made branched bundled fiber (total 62 fibers, NA 0.22, core/clad =200/220 μm, Photonic Science Technology). At the input, each branch consisting of 31 fibers has a circular cross-section of ~1.4 mm diameter. At the output, 62 fibers are aligned in a curved line with a curvature of 108.5 mm to compensate for image-aberration of the spectrometer (home-made, F/2.8, transmitting grating). Two spectra are measured at the same time on a Peltier-cooled back-illuminated CCD (–70°C, PIXIS400B, Princeton Instruments). An acousto-optics modulator (rise time < 200 ns, 35085-3, NEOS) serves as a shutter and an intensity-modulator of the laser beam, which works as a master of CCD exposure time. All mechanics and electronics were controlled by the LabVIEW program.

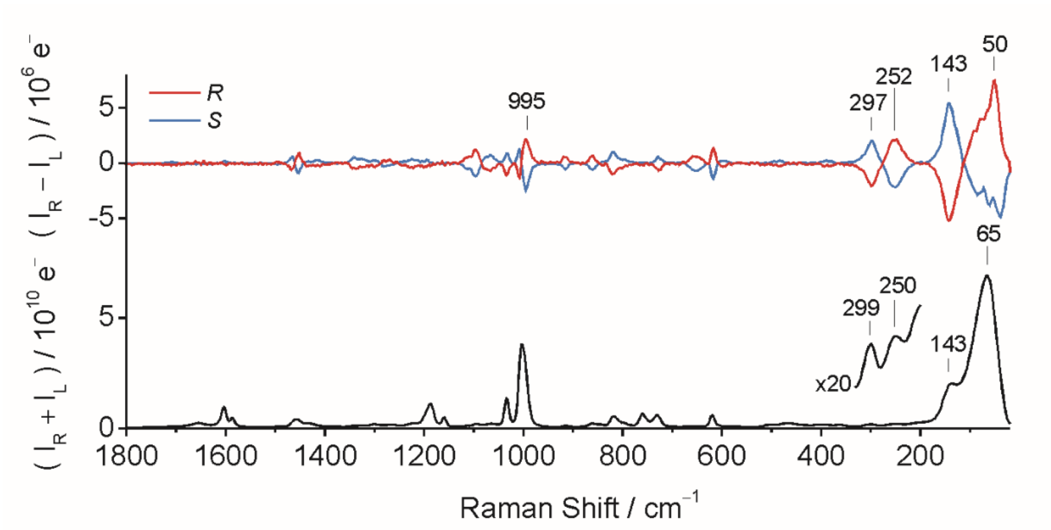

Figure S2. Instrumental test: Experimental ROA (top) and Raman (bottom) spectra of neat (*R*)- and (*S*)-2-phenylpropionic acid. Relative intensities were not corrected. The ROA spectra show a good "mirror image" for two enantiomers in the entire region but slightly distorted close to the filter-cut-off ~65 cm^{-1}. At 65 cm^{-1}, the ROA intensity of the *R* enantiomer is 123 % of that of the *S*-enantiomer, at 143 cm^{-1} the ratio is 96 %, etc.

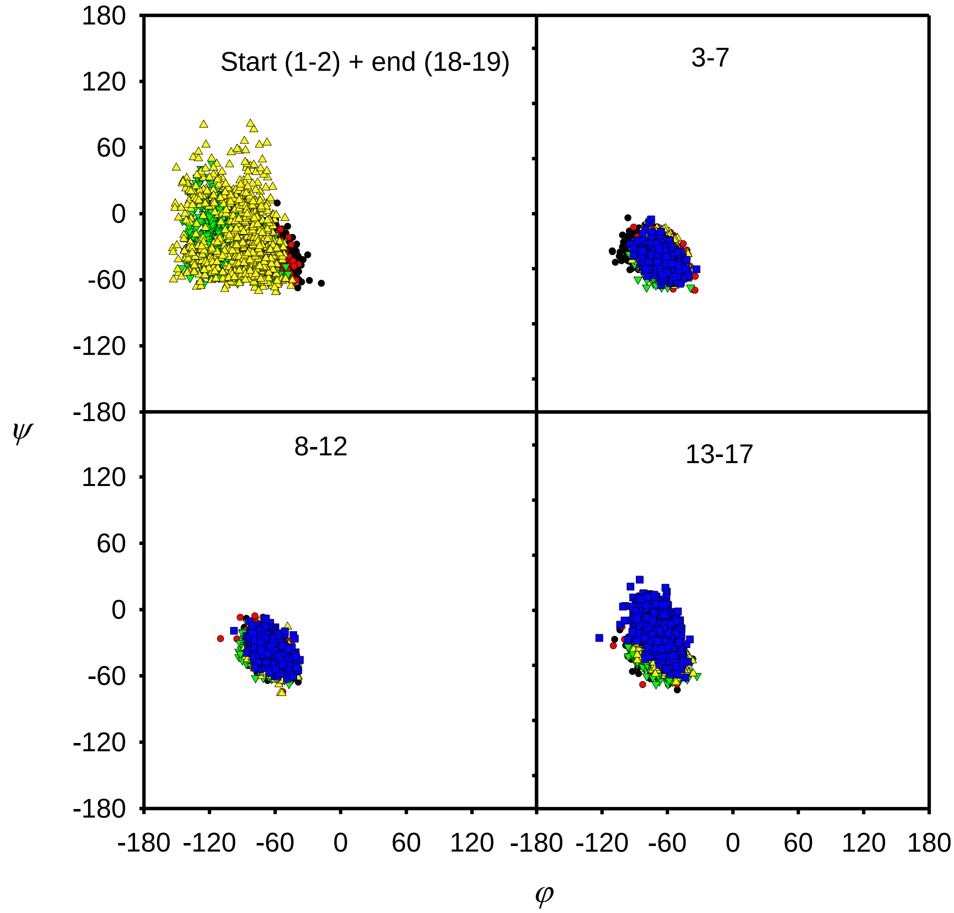

Figure S3. Backbone torsions of (φ, ψ) in the Ala_{19} helix sampled during the 10 ns MD run, for different parts of the molecules (numbers of amino acid residues).

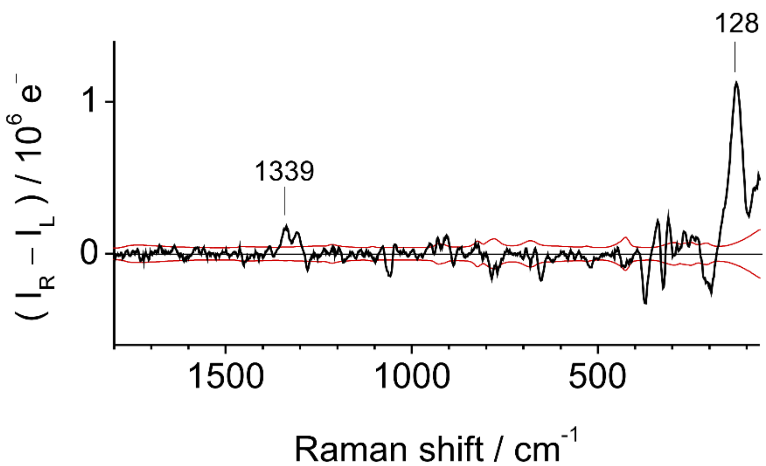

Figure S4. Experimental ROA spectrum of PLA dissolved in solvent DCA as accumulated for 1.1 h without intensity correction. The red lines are photon-shot-noise calculated from the parent Raman spectrum.

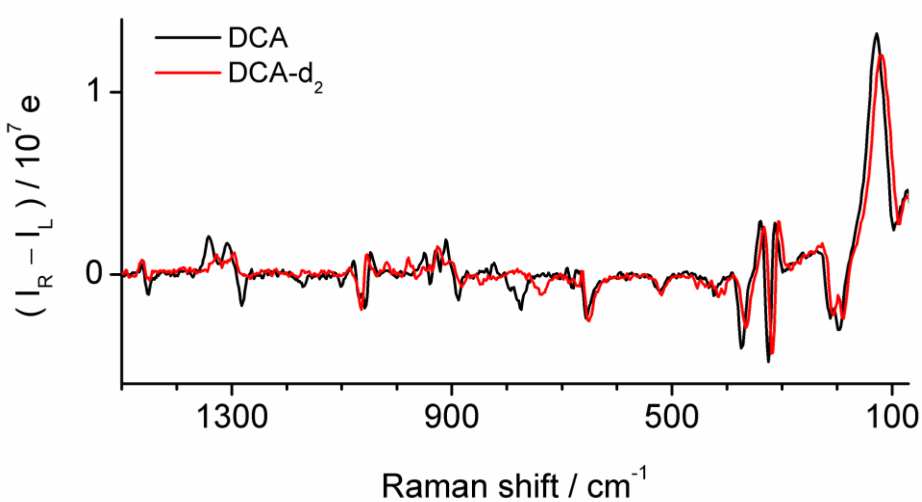

Figure S5. Comparison of experimental ROA spectrum of PLA dissolved in DCA (black line) and DCA-d_2 (red line).

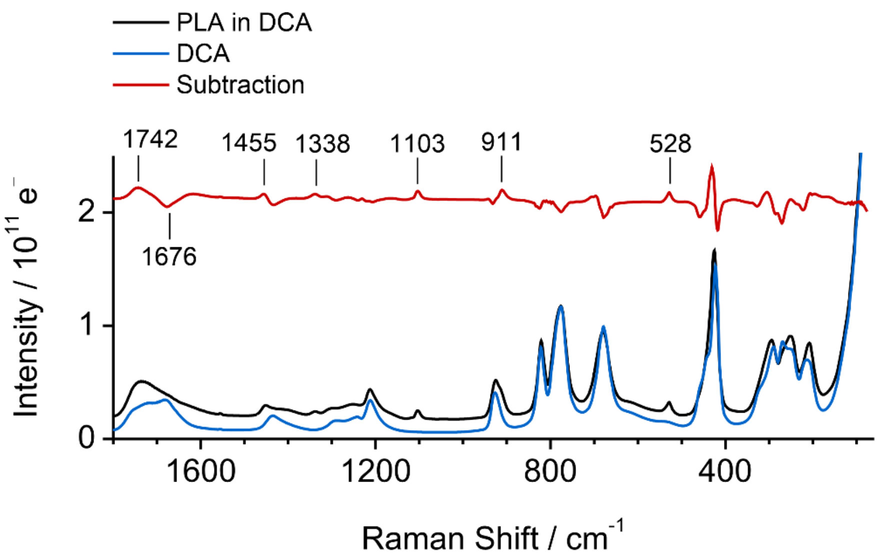

Figure S6. Experimental Raman spectra of PLA in solvent DCA (black), neat DCA (blue), and subtraction of the two (red, baseline was shifted for clarity). Peak frequencies indicated are those from PLA except for a decreased DCA peak at 1676 cm^{-1}. Due to the solvation, the peak of DCA at 1676 cm^{-1} decreased its intensity by 0.70 times compared to the neat DCA. The concentration of PLA 75 g/L corresponds to about 11 DCA molecules per one alanine residue.

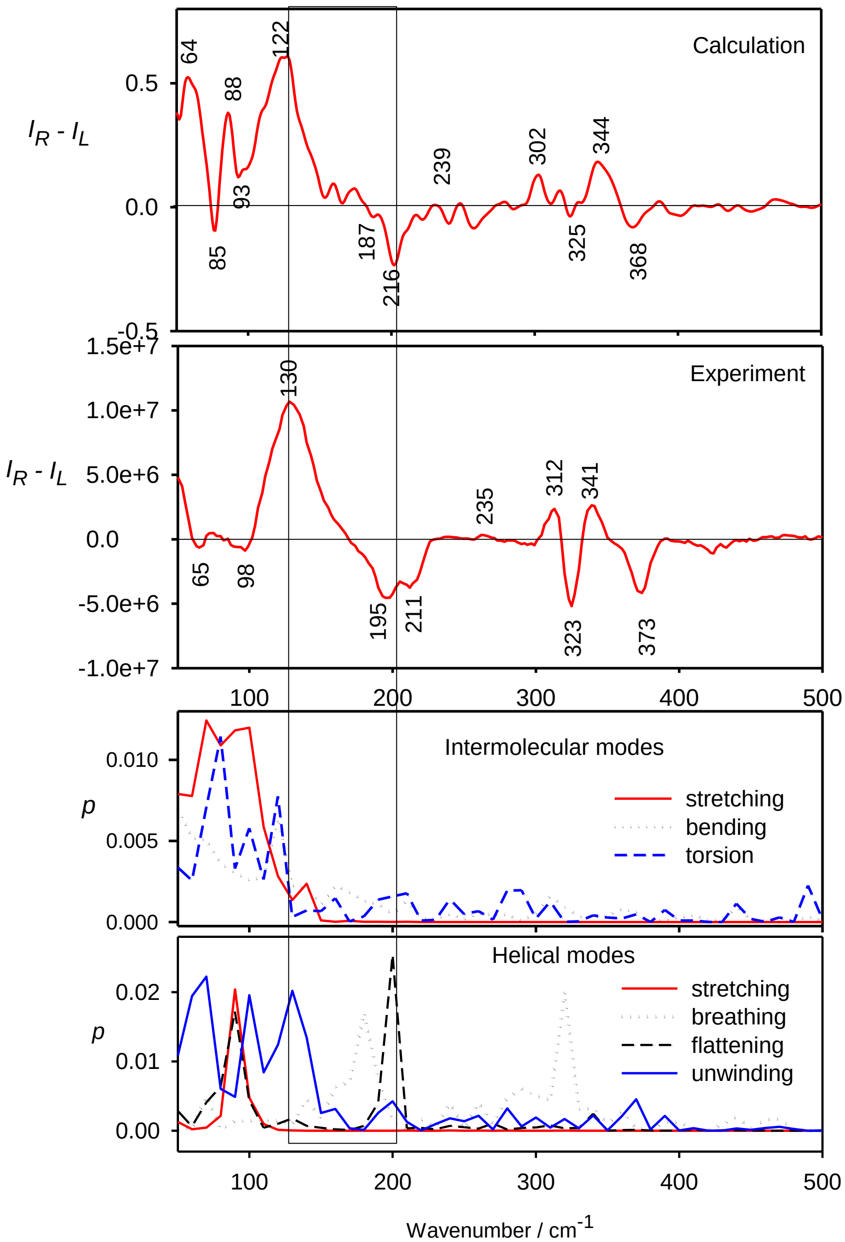

Figure S7. PLA ROA spectra, and calculated relative potential energy distributions for selected internal coordinates.

Reference

(1) Hug, W. Virtual Enantiomers as the Solution of Optical Activity's Deterministic Offset Problem. *Appl. Spectrosc.* **2003**, *57* (1), 1–13.