Supporting Information

Probing the Solvation of α-Helix with Extended Amide III Bands in Raman Optical Activity

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Contents

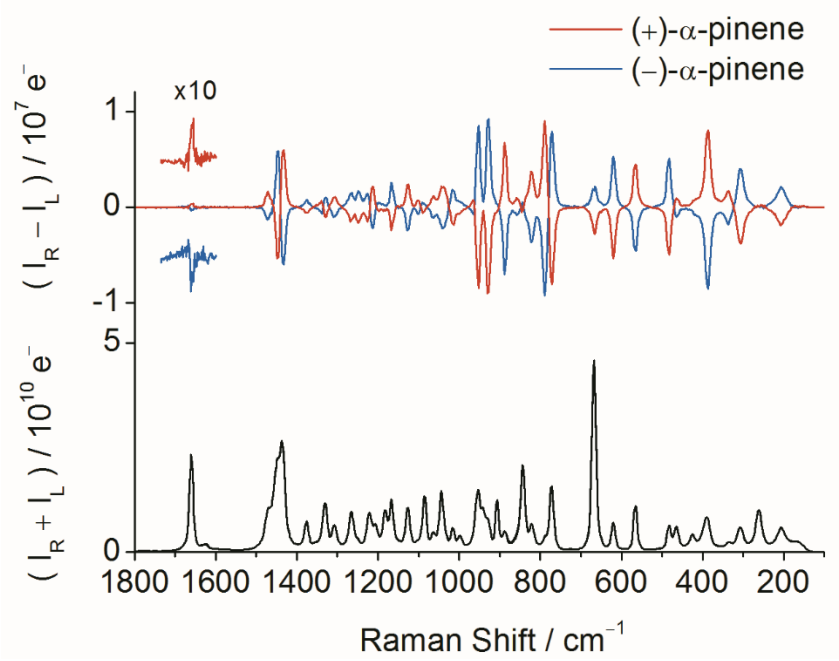

Fig. S1. ROA (top) and Raman (bottom) spectra of neat (+)- and (–)-α-pinene (both ≥ 99 %, e.e. 97 %, Sigma-Aldrich). Laser power at sample; 210 mW, exposure time; 89 min for each. Good mirror image is obtained for ROA spectra over the entire region, even for weak ROA bands at ~1670 cm^{-1} with $\Delta = (I_R - I_L)/(I_R + I_L)$ value of 2.0×10^{-5}. A small instrumental artifact appears for the highly polarized band at 680 cm^{-1}.

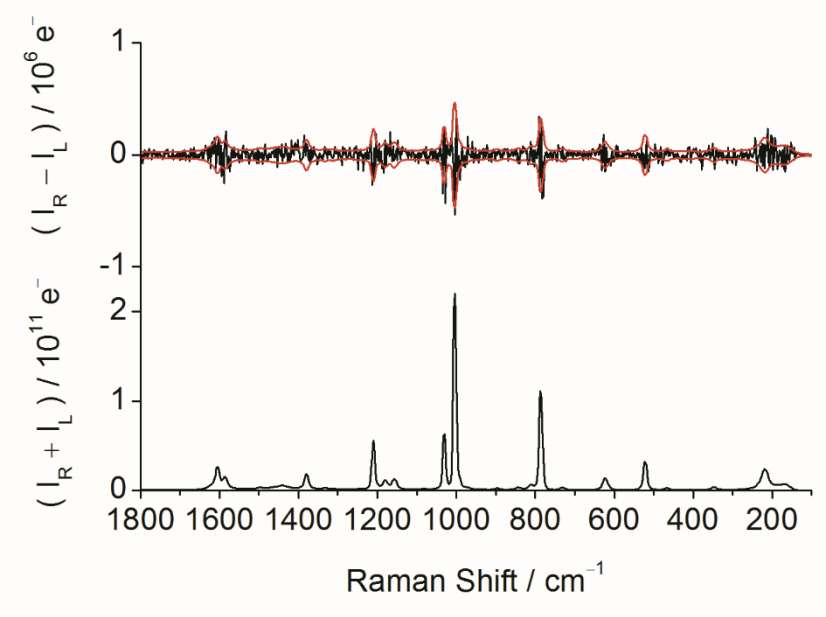

Fig. S2. Experimental ROA (top) and Raman (bottom) spectra of neat toluene (black lines) with photon-shot-noise (red lines) calculated from the Raman intensity. Laser power at sample; 47 mW, exposure time; 6.7 h. The obtained ROA signal is within the noise, indicating good suppression of instrumental artifact in the entire region.

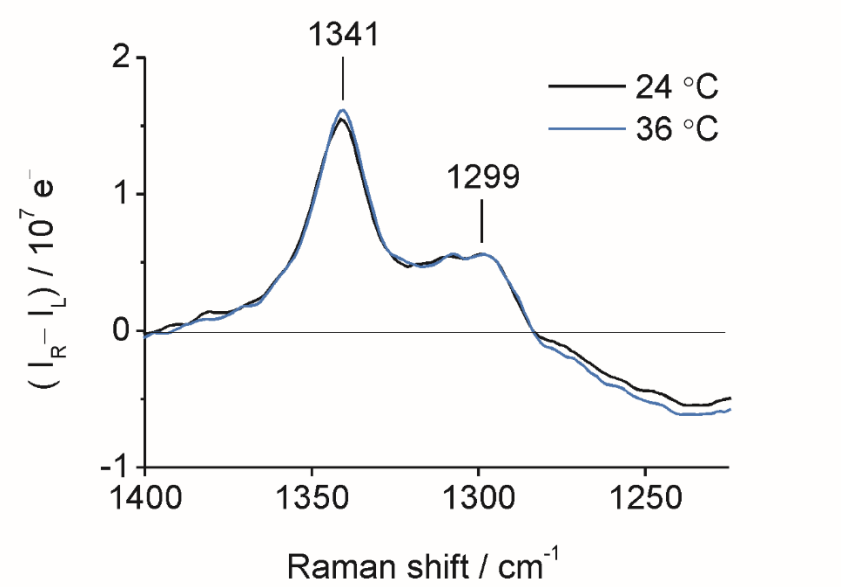

Fig. S3. Temperature dependence of ROA spectrum of HSA in pH 5.4 acetate buffer solution.

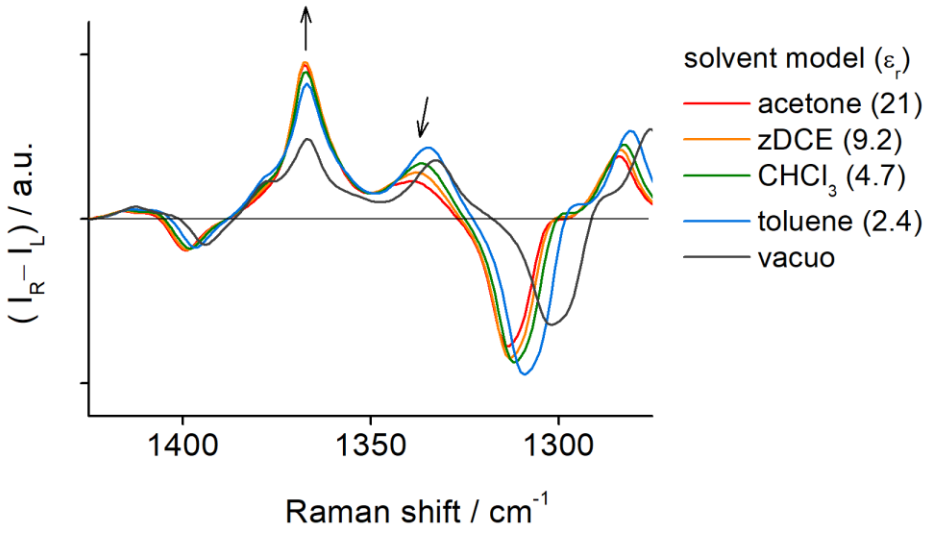

Fig. S4. Simulated ROA spectra of the explicit model of PLA with varying ε_r of the solvent model at B3LYP/6-31+G**/CPCM

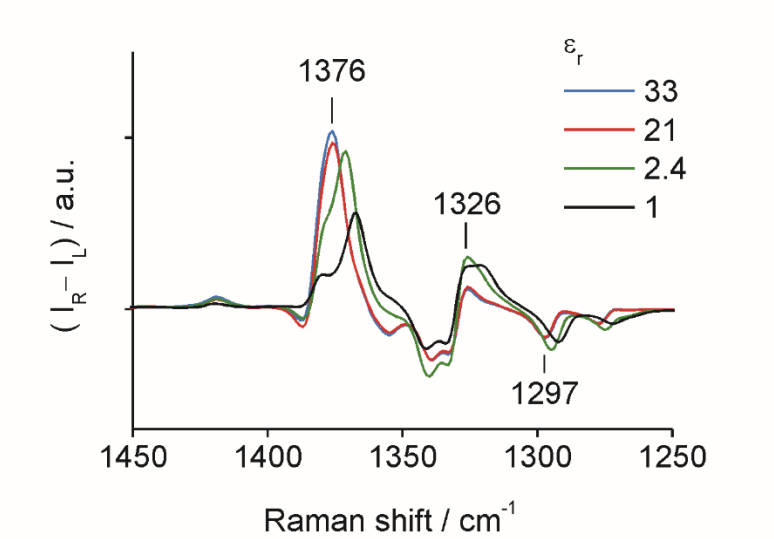

Fig. S5. Calculated ROA spectra of the α-helical PLL at the B3LYP/6-31+G**/CPCM with varying ε_r as vacuum (ε_r = 1), toluene (2.4), acetone (21), and methanol (33, peak positions indicated). The I_I/I_{II} increase gradually with increasing ε_r, accompanied by a higher-frequency shift of the *I* band.

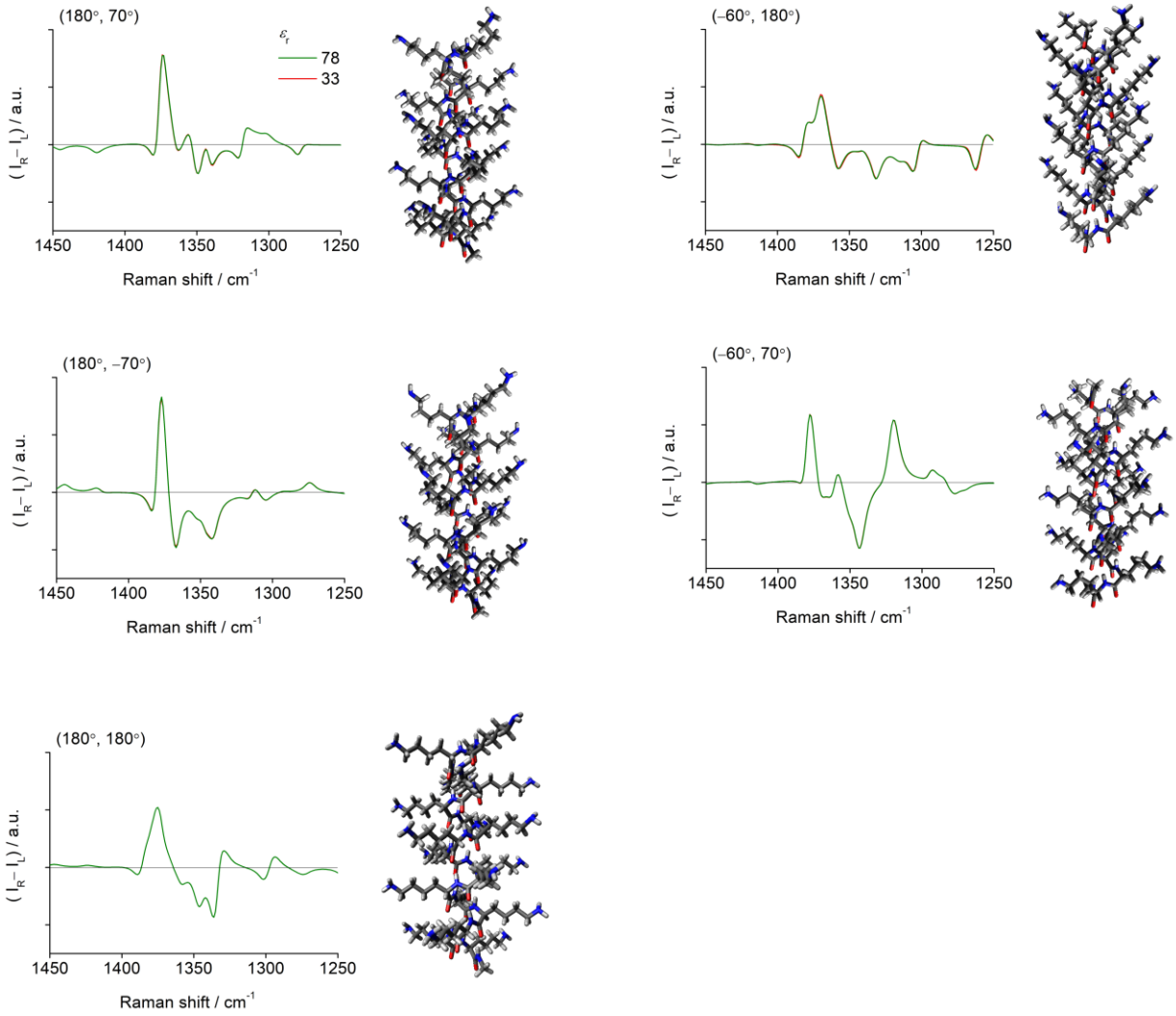

Fig. S6. Calculated ROA spectra of α-helical $(Lys)_{18}$ with CPCM water (green lines) and methanol (red lines, nearly identical to the water ones) for various side-chain conformations with regular torsional angles (χ_1, χ_3) = (180°, 70°), (180°, -70°), (180°, 180°), (-60°, 180°), (-60°, 70°) at the B3LYP/6-31G**/CPCM. χ_2 and χ_4 are set 180° in all models. Model structures are also indicated.

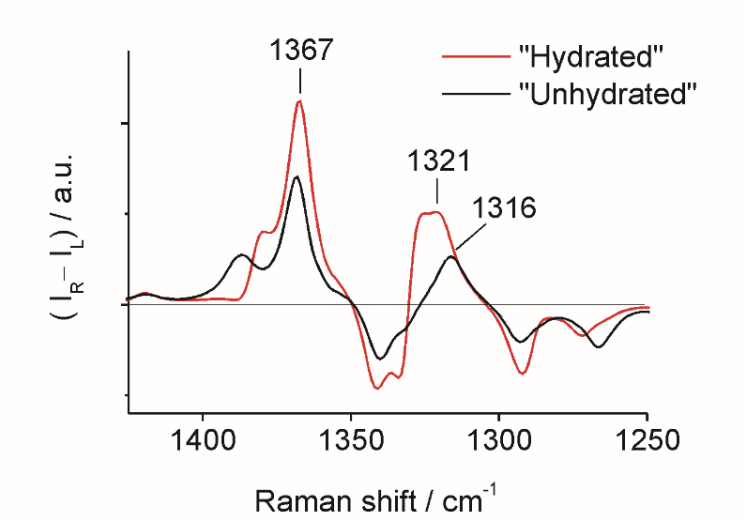

Fig. S7. Calculated ROA spectra for the "hydrated" (red line) and "unhydrated" (black line) structures of α-helical PLL using the B3LYP/6-31+G** theory.

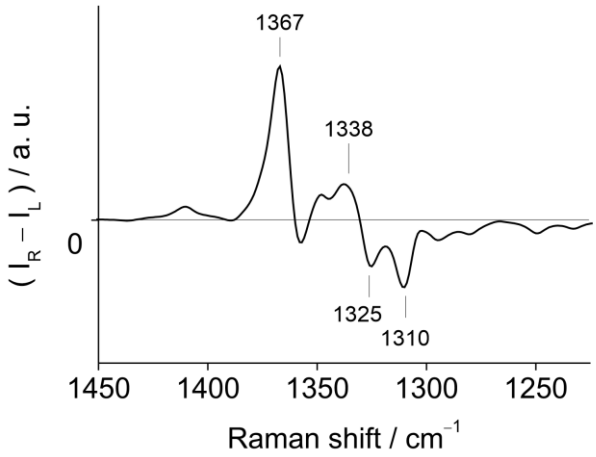

Fig. S8. Calculated ROA spectrum for α-helical AK21 at B3LYP/6-31+G**/CPCM(water).

Table S1. Assignments of ROA bands of PLL and PLG in cm^{-1}.

PLL[a]			PLG[b]		
Exp.	Calc.	Atomic motions[c]	Exp.	Calc.	Atomic motions
893	894	δ(OCN) ip			
942	958	ν(CN)			
~1030	1044	ν(NC_α)			
1060	1076	δ($C_\alpha H$), δ(NH) ip			
~1083	1104	〃	1094	1076	ν($C_\alpha C_\beta$), δ(NH) ip
1133	1158	ν($C_\alpha C_\beta$), δ(NH) ip	1125	1122	ν(NC_α), side chain
1249	1292	δ(NH) ip, *Amide III*		1300	δ(NH) ip, δ($C_\alpha H$), side chain, *Amide III*
1296	1321	δ($C_\alpha H$), δ(NH) ip, *Ext-Amide III*	~1300	1328	δ($C_\alpha H$), side chain, δ(NH) ip, *Ext-amide III*
1320	1342	δ(NH) ip			
1341	1367	δ($C_\alpha H$), δ(NH) ip, *Ext-Amide III*	1339	1373	〃
1450	1495	Side chain			
1636	1752	ν(C=O), δ(NH) ip,	1630	1695	ν(C=O), δ(NH) ip,
1664	1767	δ($C_\alpha H$), *Amide I*	1668	1702	δ($C_\alpha H$), *Amide I*

Based on (a) Fig. 7 and (b) Fig. 8 in the main text. c; $C_\alpha H$ and Lys side chain contribute to all bands below 1400 cm^{-1}. ip; in-plane of amide, oop; out-of-plane of amide.