Investigation of the *cis-trans* structures and isomerization of oligoprolines by using Raman spectroscopy and density functional theory calculations: solute-solvent interactions and effects of terminal positively charged amino acid residues

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**Figure S10** Mode analysis results of PPI conformation of poly-L-proline. Panels A and B show mode analysis results on the amide-type motions and the collective type motions in which all atoms participate in the motions, respectively. In the amide-type motions, the number of each type (O, N, C, and H) atom is counted if the displacement is larger than 0.01 Å for each direction (a, b, and c-axis). In the collective type motions, we use the total displacement larger than 0.032 Å which is determined on the basis of the three acoustic phonon modes ($\omega=0$). In Panel A, * represents the motions due to the ring deformations.

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**Table S4** Vibrational mode of the PPI form of P12 and their assignments based on Gaussian 09 calculations.
1. Experimental and calculated Raman spectra of poly-L-proline

Figure S1. Experimental (top) and calculated (below) Raman spectra of poly-L-proline PPII crystals. The calculated curve is obtained by using Crystal 17 B3LYP-D3/6-31G(d). The assignments of vibrational modes are displayed.
2. Dipole moments and electrostatic potential surfaces of peptides calculated using Gaussian package

P12, PPI (gas)  

P12, PPI (prOH)  

RP11, PPI (prOH)  

P11R, PPI (prOH)  

KP11, PPI (prOH)  

P12, PPII (gas)  

P12, PPII (H₂O)  

RP11, PPII (H₂O)  

P11R, PPII (H₂O)  

KP11, PPII (H₂O)
Figure S2. Optimized geometry, dipoles, and electrostatic potential surfaces of P12, KP11, RP11, P11K, and P11R type PPI in propanol and PPII in H$_2$O using GAUSSIAN package. N terminal is NH and C is COOH in gas phase and NH$_2^+$ and COO$^-$ in water and 1-propanol for P12, P11K, and P11R and NH$_3^+$ and COO$^-$ for KP11 and RP11.

3. Raman spectra of poly-L-proline, P12, P11X, and XP11 in solid state and in solution

Figure S3. Raman curves of poly-L-proline II and I powder and the calculated spectra using CRYSTAL 17 at the B3LYP-D3/6-31G(d,p) level with the coupled-perturbed Kohn-Sham scheme.
Figure S4. Raman curves of P12 series (a) PPI in prOH and (b) PPII in aqueous solution. The intensity is normalized to the 365 and 310 cm$^{-1}$ band, respectively.
Figure S5. Raman spectra of powder P12 series PPII form.
Figure S6. Raman spectra of the PPII form of P12 series in aqueous solution.
Figure S7. Raman spectra of the PPI form of P12 series powder.
**Figure S8.** Plots of circular dichroism (CD) signals at 214 nm (PPI) versus the percentages of n-propanol in phosphate buffer for P12 series peptides.²⁷
4. Assignment of vibrational modes to the observed Raman shifts for peptides
Figure S9. Mode analysis results of PPII conformation of poly-L-proline. Panels A and B show mode analyses on the amide-type motions and the collective type motions where all atoms participate in the motions, respectively. In the amide-type motions, the number of each type (O, N, C, and H) atom is counted if the displacement is larger than 0.01 Å for each direction (a, b, and c-axis). In the collective type motions, we use the total displacement larger than 0.059 Å which is determined on the basis of the three acoustic phonon modes (ω=0). In Panel A, * represents the motions due to the ring deformations.
Figure S10. Mode analysis results of PPI conformation of poly-L-proline. Panels A and B show mode analysis results on the amide-type motions and the collective type motions in which all atoms participate in the motions, respectively. In the amide-type motions, the number of each type (O, N, C, and H) atom is counted if the displacement is larger than 0.01 Å for each direction (a, b, and c-axis). In the collective type motions, we use the total displacement larger than 0.032 Å which is determined on the basis of the three acoustic phonon modes (ω=0). In Panel A, * represents the motions due to the ring deformations.
3D crystal structure is quite different from 1D polymer structure as shown in Fig. S11. Both panels are views along the a-axis (1D) and c-axis (3D). Orange arrow in each panel shows the distance between two carbon atoms: 1D polymer (3.067 Å) and 3D crystal (3.120 Å). This difference can be due to the existence of inter-peptide hydrogen bonding in 3D crystal case. To see this, we should note that there are two types of hydrogen bonding in 3D crystal of the polyproline II (Figure S11(b)): one acts between oxygen atom and nearest H atom (~2.516 Å) in the same polypeptide (intra-polypeptide hydrogen bond) and the other interact with nearest H atom (~2.634 Å) of the different polypeptide (inter-polypeptide hydrogen bond). The bond distance suggests the intra-polypeptide hydrogen bonding may be stronger than hydrogen bonding acting on the different polypeptide. Polyproline I also have two types of hydrogen bonding one takes part in forming intra-polypeptide structure (2.383 Å ~ 2.561 Å) and the other one binds nearest neighboring polypeptide (~2.267 Å) (Figure S11(c)). The bond distance suggests the inter-polypeptide hydrogen bonding may be stronger than hydrogen bonding acting within the same polypeptide.
(a)

1D  3D

(b)

Inter-polypeptide H-bond

Intra-polypeptide H-bond
Figure S11. (a) 1D and 3D crystal structure of poly proline peptide, (b) H-bond in polyproline II, and (c) H-bond in polyproline I.
Table S1. Experimental and simulated crystal lattice of PPI and PPII conformations of poly-L-proline by using Crystal 17 at the B3LYP-D3/6-31G(d,p) level with the coupled-perturbed Kohn-Sham scheme.

|       | PPI |      | PPII |      |
|-------|-----|------|------|------|
|       | Expt. | Calc. | Expt. | Calc. |
| a (Å) | 9.15 | 9.12 | 6.64 | 6.65 |
| b (Å) | 18.93 | 18.87 | 6.64 | 6.65 |
| c (Å) | 9.20 | 9.25 | 9.60 | 9.54 |
| β (deg) | 59.28 | 59.84 | 90 | 90 |
| V (Å³) | 1369.98 | 1376.73 | 366.97 | 365.01 |
|       | (+0.49%) |     | (-0.53%) |     |

a Ref. 11.
**Table S2-1.** Vibrational modes of poly-L-proline II and assignments based on CRYSTAL 17 calculations. Assignments are deduced from Fig. S9.

| $\omega_{\text{expt.}}$ | mode #  | $\omega_{\text{calc.}}$ | Assignment                                      |
|-------------------------|---------|--------------------------|-------------------------------------------------|
| 56                      | 4       | 56                       | Libration around c-axis                         |
| 74                      | 6,7     | * 74                     | spring-type motion involving pyrrolidine rings  |
| 106                     | 8, 9    | * 104                    | twist of carbonyl groups, twist of pyrrolidine rings |
| 129                     | 10,11   | * 129                    | twist of pyrrolidine rings, twist of carbonyl groups |
| 165                     | 13,14   | * 165                    | CH$_2$ rocking                                  |
| 259                     | 20,21   | * 261                    | CH$_2$ rocking                                  |
| 313                     | 22      | 315                      | CH$_2$ rocking, NC in-plane bending (plane: pyrrolidine ring plane) |
| 334                     | 23,24   | * 343                    | CH$_2$ rocking, NC out-of-plane bending         |
| 362                     | 25      | 372                      | CH$_2$ rocking, NC out-of-plane bending, CO in-plane bending |
| 404                     | 26,27   | * 416                    | NC out-of-plane bending                         |
| 497                     | 28      | 502                      | NC in-plane bending                             |
| 536                     | 29,30   | * 548                    | NC bending, CO bending                          |
| 737                     | 37      | 753                      | CO out-of-plane bending                         |
| 838                     | 40      | 847                      | ring twist                                      |
| 875                     | 45      | 875                      | ring twist                                      |
| 898                     | 46,47   | * 913                    | ring twist                                      |
| 920                     | 49      | 931                      | ring deformation, C$_3$-C$_4$-C$_5$ stretching |
| 1050                    | 59,60   | * 1066                   | ring deformation, C$_3$-C$_4$ stretching        |
| 1176                    | 65,66   | * 1191                   | ring deformation, CH$_2$ twisting, C$_2$-C$_3$ stretching |
| 1202                    | 71,72   | * 1236                   | ring deformation, NC stretching (two C atoms each side of the N atom on the ring) |
| 1242                    | 73,74   | * 1270                   | CH$_2$ twisting                                 |
| 1266                    | 76      | 1292                     | ring deformation                               |
| 1325                    | 81      | 1346                     | CH$_2$ wagging                                  |
| 1343                    | 88,89   | * 1378                   | CH$_2$ wagging, ring deformation                |
| 1424                    | 91      | 1451                     | $^a$amide II                                    |
| 1450                    | 94,95   | * 1496                   | $^a$CH$_2$ scissoring                           |
| 1475                    | 101,102 | * 1537                   | $^a$CH$_2$ scissoring                           |
| 1650                    | 105     | 1717                     | $^a$amide I                                    |

* represents doubly degenerated state; $^a$ represents characteristic frequencies of the band (see Table S2-2)
Table S2-2. Characteristic bands of poly-l-proline II

| Band            | Mode #s            | Simulated frequencies / cm\(^{-1}\) |
|-----------------|--------------------|--------------------------------------|
| CH\(_2\) wagging| 87-90              |                                      |
| \(^a\)Amid II   | \(^*\)91(A), \(^**\)92(E), \(^**\)93(E) | 1451.3(A), 1466.0(E)                |
| CH\(_2\) scissoring | 94-102            | 1495.7-1537.1                       |
| Amide I         | \(^**\)103(E), \(^**\)104(E), \(^*\)105 (A) | 1702.8(E), 1716.8(A)                |

\(^a\)mixing of wagging and Amid II

\(^*\) and \(^**\) represent the largest and the second largest Raman intensities in the band, respectively.

A and E represent symmetry: E is a doubly degenerated state

Note collective motions in the lower frequency region (< 500 cm\(^{-1}\)) may need more detailed analysis (see Fig. S9).
Table S3-1. Vibrational mode of poly-L-proline I and their assignments based on CRYSTAL 17 calculations. Assignments are deduced from Fig. S10.

| $\omega$expt. | Mode # | $\omega$calc. | Assignment |
|---------------|-------|---------------|------------|
| 68            | 15    | 64            | twist of pyrrolidine ring pair |
| 75            | 18    | 76            | twist of pyrrolidine ring pair, CO wagging+ spring-type motion |
| 99            | 25    | 101           | scissoring of carbonyl groups |
| 130           | 31    | 122           | CO bending from $||$ to $\perp$ helix axis, rocking of pyrrolidine rings |
| 315           | 63    | 287           | ring twist |
| 365           | 72    | 320           | ring-CO scissoring out of helix axial |
| 410           | 81    | 374           | pyrrolidine ring twist |
| 499           | 95    | 524           | NC-CO scissoring |
| 543           | 100   | 569           | NC bending, CO bending |
| 663           | 111   | 663           | ring deformation |
| 740           | 122   | 740           | CO out-of-plane bending |
| 840           | 131   | 853           | ring deformation, C1-C2 stretching |
| 900           | 154   | 902           | ring twist, CH$_2$ twisting |
| 920           | 164   | 923           | ring deformation, C$_3$-C$_4$-C$_5$ stretching |
| 960           | 179   | 980           | ring deformation |
| 1050          | 197   | 1064          | ring deformation, C-C asymmetric stretching |
| 1182          | 228   | 1217          | ring twist, CH$_2$ twisting |
| 1239          | 243   | 1263          | ring twist, CH$_2$ twisting |
| 1266          | 257   | 1308          | ring twist, CH$_2$ twisting |
| 1327          | 279   | 1364          | CH$_2$ wagging |
| 1344          | 292   | 1388          | CH$_2$ wagging |
| 1427          | 301   | 1444          | $^a$amide II |
| 1450          | 317   | 1502          | $^c$CH$_2$ scissoring |
| 1479          | 336   | 1530          | $^c$CH$_2$ scissoring |
| 1650          | 345   | 1708          | $^c$amide I |

$^a$represents characteristic frequencies of the band (see Table S3-2)
| Band            | Mode #s                      | Simulated frequencies / cm⁻¹                      |
|-----------------|------------------------------|--------------------------------------------------|
| Amide II+       | 303-310                      | 1455.2−1475.0                                    |
| CH₂ scissoring  |                              |                                                  |
| CH₂ scissoring  | 311-340                      | 1494.3−1536.9                                    |
| Amide I         | 341,342,343, **344, *345,    | 1698.1,1698.5,1702.1, **1703.9, **1707.9,       |
|                 | 346,347,348,349,350          | 1709.0,1717.5,1720.3, 1728.9,1736.2              |

* and ** represent the largest and the second largest Raman intensities in the band, respectively.

Note collective motions in the lower frequency region (< 500 cm⁻¹) may need more detailed analysis (see Fig. S10).
Table S4. Vibrational mode of the PPII form of P12 and their assignments based on Gaussian 09 calculations.

| \( \omega \text{expt.} \) | \( \omega \text{calc.} \) | Assignment |
|----------------|----------------|------------|
| 261            | 266            | CH\(_2\) rocking |
| 310            | 321            | CH\(_2\) rocking, NC out-of-plane bending (plane: pyrrolidine ring plane) |
| 334            | 354            | CH\(_2\) rocking, NC out-of-plane bending, CO in-plane bending |
| 404            | 409            | NC out-of-plane bending |
| 499            | 503            | NC in-plane bending |
| 529            | 537            | NC bending, CO bending |
| 730            | 747            | CO out-of-plane bending |
| 762            | 788            | CH\(_2\) twist |
| 833            | 848            | ring deformation |
| 875            | 898            | ring twist |
| 898            | 920            | ring twist |
| 925            | 937            | ring twist |
| 1050           | 1085           | ring deformation, C-C stretching |
| 1098           | 1132           | ring twist |
| 1168           | 1185           | ring deformation, CH\(_2\) twist |
| 1177           | 1211           | CH\(_2\) twisting |
| 1203           | 1228           | CH\(_2\) wagging |
| 1248           | 1285           | CH\(_2\) twisting |
| 1270           | 1313           | CH\(_2\) twisting |
| 1328           | 1381           | CH\(_2\) wagging |
| 1350           | 1393           | CH\(_2\) wagging |
| 1424           | 1460           | amide II |
| 1454           | 1531           | CH\(_2\) scissoring |
| 1482           | 1550           | CH\(_2\) scissoring |
| 1650           | 1643           | amide I |
**Table S5.** Vibrational mode of the PPI form of P12 and their assignments based on Gaussian 09 calculations.

| ω_{expt} | ω_{calc} | Assignment                                      |
|----------|----------|-------------------------------------------------|
| 320      | 332      | CH$_2$ wagging                                  |
| 365      | 361      | ring-CO scissoring (CO bending out of helix axis) |
| 412      | 395      | pyrrolidine ring twist                          |
| 499      | 513      | CH$_2$ rocking                                  |
| 583      | 603      | CH$_2$ rocking                                  |
| 660      | 642      | CO bending of terminal COO’, ring twist          |
| 731      | 719      | CO out-of-plane bending                         |
| 842      | 802      | ring twist                                      |
| 865      | 839      | ring twist                                      |
| 895      | 895      | ring twist, CH$_2$ rocking                      |
| 920      | 940      | ring deformation                                |
| 960      | 977      | ring deformation                                |
| 1050     | 1071     | ring deformation, C-C asymmetric stretching     |
| 1092     | 1130     | ring twist                                      |
| 1165     | 1193     | ring deformation, CH$_2$ wagging                |
| 1182     | 1214     | CH$_2$ twisting                                 |
| 1193     | 1239     | CH$_2$ wagging                                  |
| 1240     | 1284     | CH$_2$ twisting                                 |
| 1270     | 1335     | CH$_2$ wagging                                  |
| 1302     | 1356     | CH$_2$ wagging                                  |
| 1330     | 1375     | CH$_2$ wagging                                  |
| 1350     | 1388     | CH$_2$ wagging                                  |
| 1425     | 1450     | Am II                                           |
| 1449     | 1533     | CH$_2$ scissoring                               |
| 1479     | 1546     | CH$_2$ scissoring                               |
| 1650     | 1625     | Am I                                            |