Supporting Information for:

A Nobel Polypseudorotaxane Composed of Cyclic β-Peptide as Bead Component

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General procedure. All reagents were purchased from commercial sources and used as received. The NMR measurements were performed by a Bruker DPX-400 NMR spectrometer (400 MHz). IR spectra were measured on a Nicolet 6700 FT-IR spectrometer. MALDI-TOF MS was performed on a JEOL JMS-ELITE spectrometer. Circular dichroism (CD) spectra were measured at room temperature on a JASCO J-600 CD spectropolarimeter using an optical cell of 0.1 cm path length.

Synthesis of cyclic hexa-β-peptide (1). Acetyl protected cyclic hexa-β-peptide (39 mg, 21 μmol) was dissolved in DMSO (6.0 mL) and then 1 N NaOH (420 μL) was added. After stirring at room temperature for 12 h, the mixture was neutralized with 1 N HCl. Ethanol and diethyl ether was added to the solution until the insoluble part appeared. The precipitate was dissolved in methanol and was purified by a Sephadex LH20 column with methanol as eluant to afford **1** (17 mg, 72 %).: ^{1}H NMR (400MHz, DMSO-d_6) δ 7.88–7.64 (3H, m, N*H*), 7.51–7.20 (3H, m, N*H*), 5.16–4.90 (9H, m, 4-O*H* and 3-O*H*), 4.80–4.32 (9H, m, 6-O*H* and 3-O*H*), 4.18–3.85 (12H, m, H-1 and H-3), 3.73–3.62 (6H, m, H-6a), 3.55-3.42 (6H, m, H-6b), 3.25–2.92 (18H, m, H-2, H-4 and H-5); IR (KBr) 3439, 2937, 2886, 1675, 1539, 1417, 1370, 1298, 1097, 1030, 997 cm^{-1}; MS (MALDI-TOF, matrix: dithranol) : *m/z* 1157.4 (calcd. for $C_{42}H_{66}N_6O_{30}Na$ [$(M + Na)^+$], 1157.3).

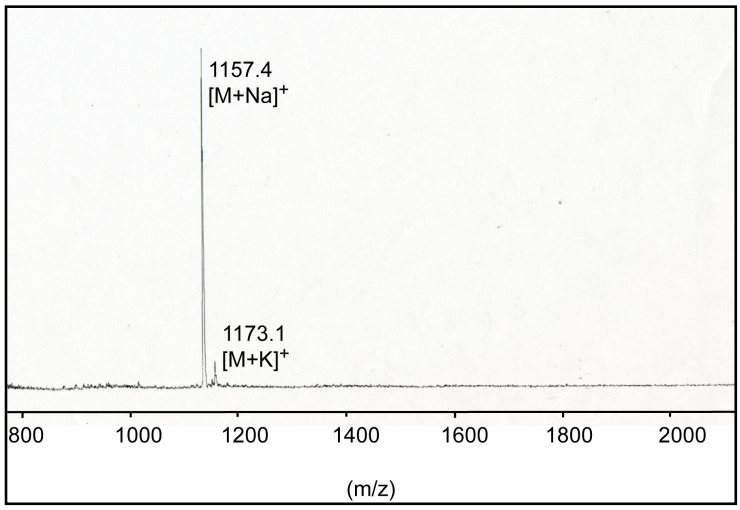

Figure S1. MALDI-TOF mass spectrum of cyclic hexa-*β*-peptide **1**.

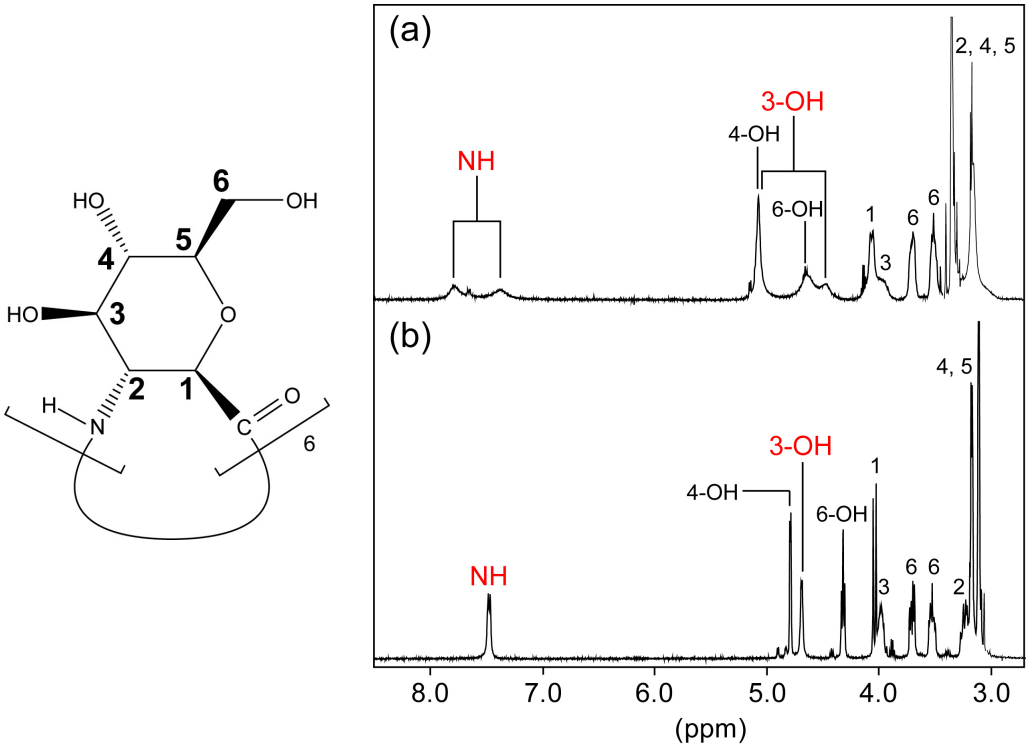

Figure S2. ^{1}H NMR spectra of **1** in DMSO (a) at room temperature and (b) at 60 °C.

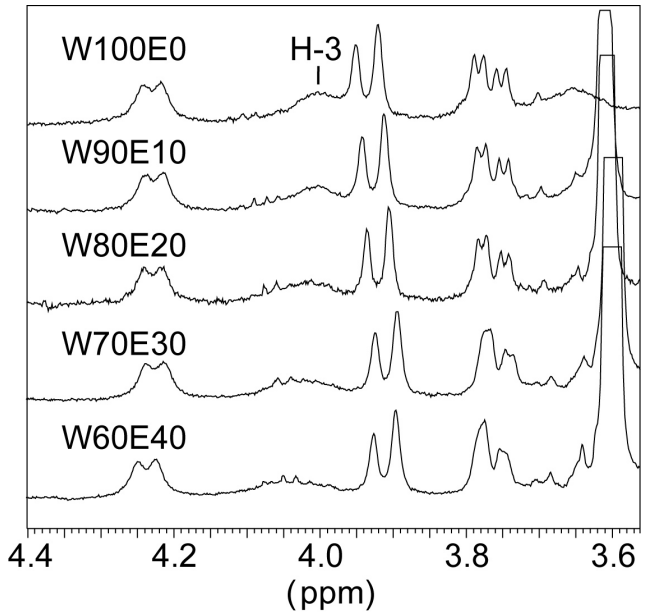

Figure S3. ^{1}H NMR spectra of **1** in a mixed solution of water and ethanol; W and E represent water and ethanol, respectively, and the numbers after these letters show volume ratios of water and ethanol.

Geometry optimization. The initial geometry of the compound was generated by the Fujitsu CAChe WorkSystem 6.1.1 software, and it was optimized by the semiempirical Austin Model 1 (AM1) method in the MOPAC 2002 package.[S-1] The obtained geometries are shown in Figure S4.

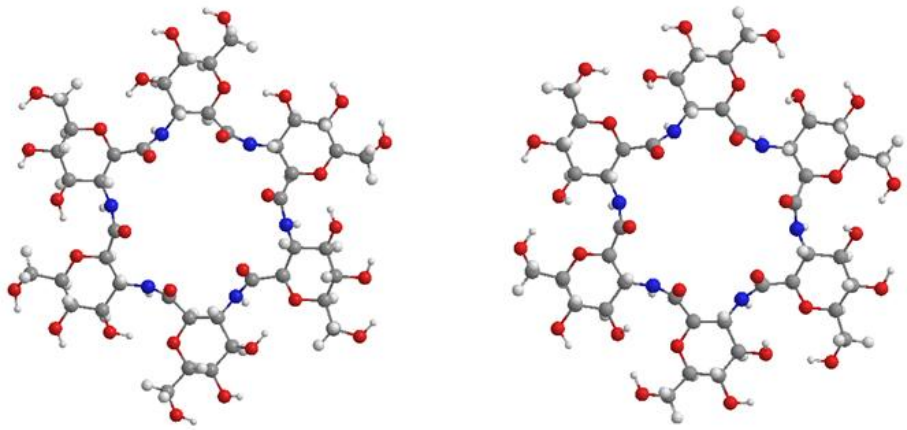

Figure S4. Two geometry-optimized structures of compound **1.** The models between left and right are different in the manner of intramolecular hydrogen bonds at O–H of C3.

CD measurement. CD spectra were measured at the residue concentration of 1.3×10^{-4} M. In a mixed solution of water and ethanol, ethanol contents were changed from 0 to 50 %. CD spectra of a mixture of **1** and PEG were obtained by changing the ratio of **1** and the monomeric (–CH_2CH_2O–) unit of PEG in water and water/ethanol solutions. The obtained spectra are shown in Figures S5–7.

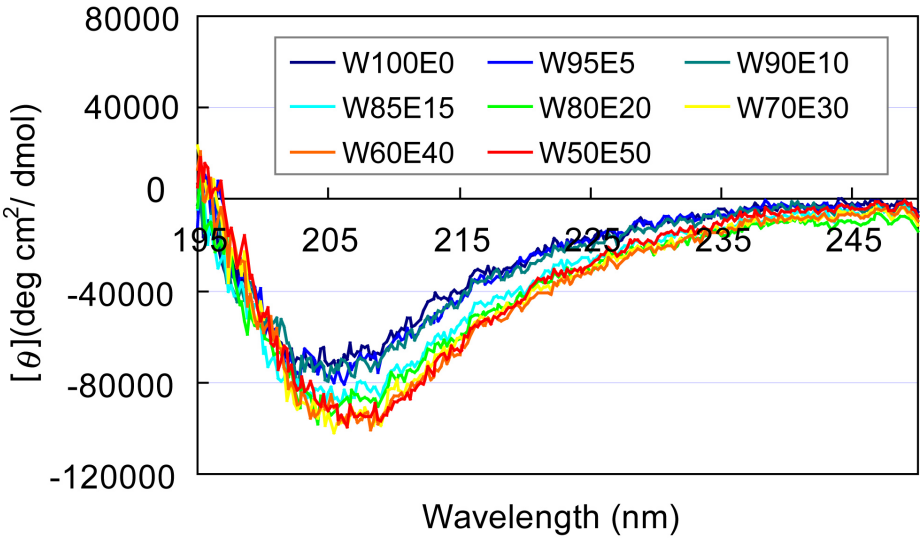

Figure S5. CD spectra of **1** in a mixed solution of water and ethanol; W and E represent water and ethanol, respectively, and the numbers after these letters show volume ratios of water and ethanol.

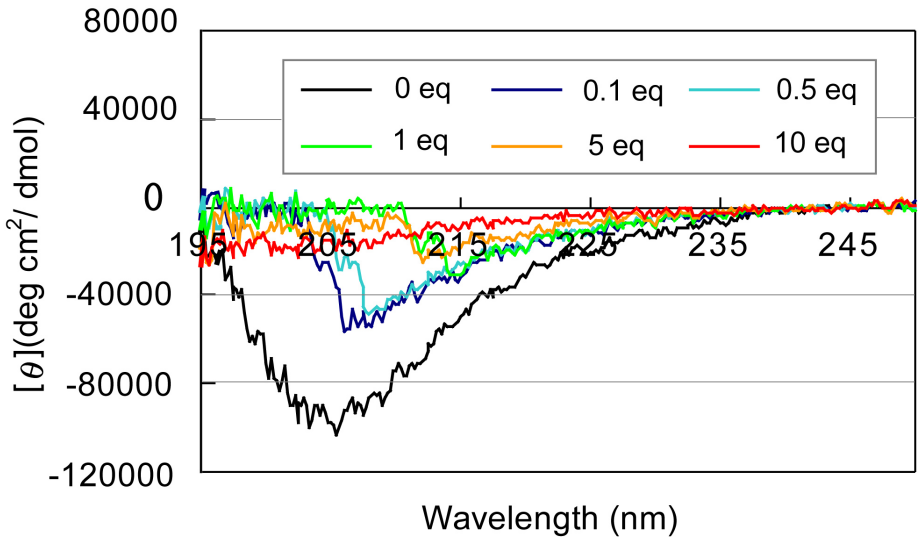

Figure S6. CD spectral change of **1** in water with the addition of PEG600. The spectra were recorded right after the mixing of **1** and PEG. The numbers represent the amount of PEG600 in ethylene glycol units vs. the concentration of the cyclic peptide.

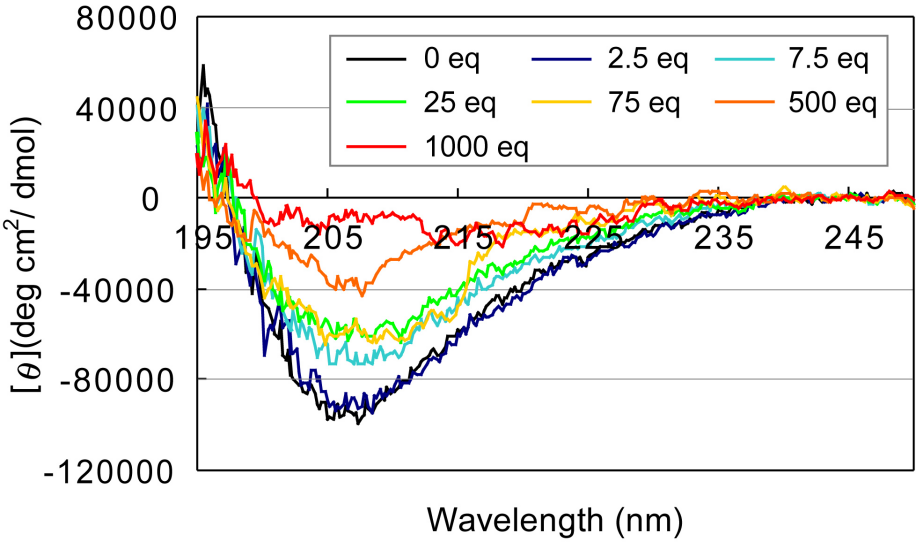

Figure S7. CD spectral change of **1** in a solution of water and ethanol (1/1 v/v) with the addition of PEG. Spectra were recorded after treatments of sonication and standing for 24 h. The numbers represent the amount of PEG600 in ethylene glycol units vs. the concentration of the cyclic peptide.

AFM observation. AFM was performed in the non-contact mode using an UNISOKU USM 1100-SA (UNISOKU Co., Ltd.) under high vacuum (< 10^{-7} Torr) at room temperature. A SII cantilever was used with a typical resonance frequency of 300 Hz. Samples were prepared by casting dilute aqueous solutions on a freshly-cleaved mica surface and dried under ambient conditions. The AFM images and the height profiles of polypseudorotaxane (colored image) and cyclic peptide **1** are shown in Figure S8 and Figure S9, respectively.

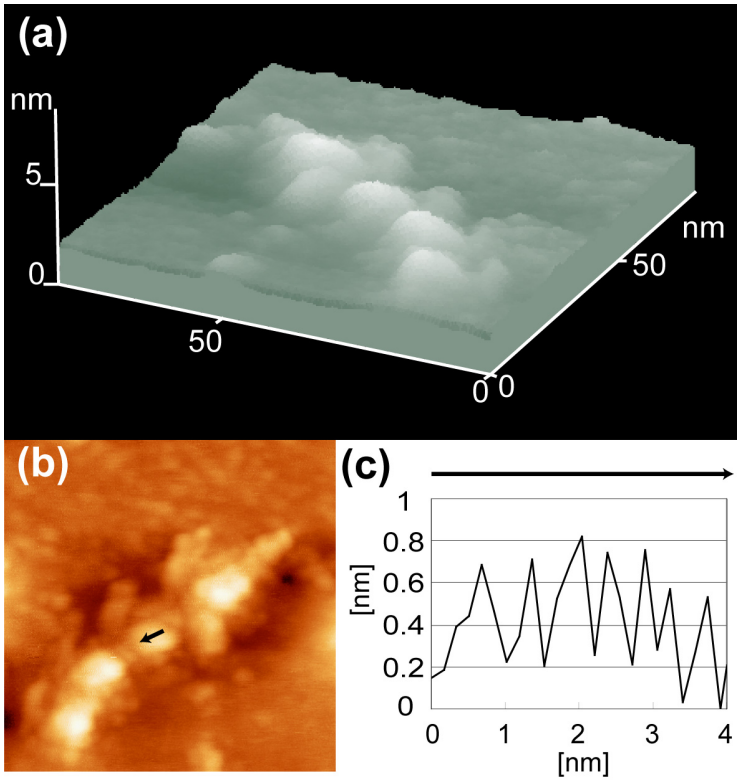

Figure S8. (a) 3-D and (b) 2-D AFM images (81 nm×81 nm) of the prepared polypseudorotaxane; (c) the height profile along the arrow shown in (b) (colored image of Figure 3).

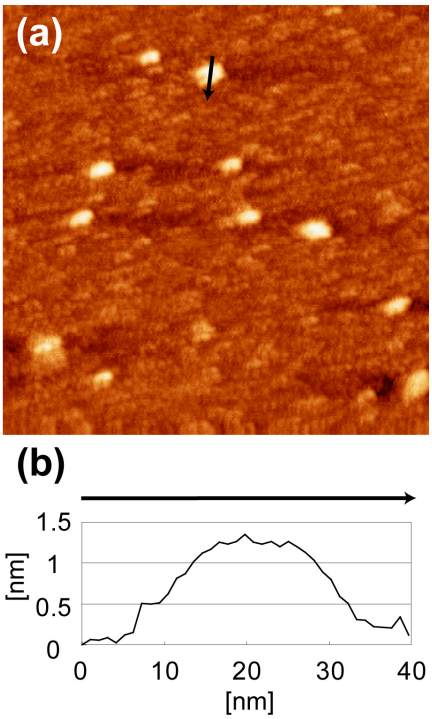

Figure S9. (a) AFM topographic image (500 nm×500 nm) of **1** on mica; (b) the height profile along the arrow shown in (a).

Supporting Reference

(S-1) Cache Worksystems Pro Version 6.1.1; Fujitsu Limited: Tokyo, J., 2003.