Supporting Information for:

Polymorphism of Oligomers of a Peptide from β-Amyloid

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This PDF file includes:

Materials and Methods

Synthesis of macrocyclic β-sheet peptides 1–4. S5
Synthesis of linear peptide 5. S5
NMR sample preparation, data collection and data processing of peptides 1–5. S6
Modeling of the solution-state tetramer of macrocyclic β-sheet peptide 2a. S7
Diffusion-ordered spectroscopy (DOSY) experiments of macrocyclic β-sheet peptides 1–4. S8
Analytical ultracentrifugation (AUC) studies of macrocyclic β-sheet peptide 2b. S9

Supplemental Figures and Tables

Fig. S1. Key NOEs associated with folding and dimerization of macrocyclic β-sheet peptide 2a. S11
Fig. S2a. Cartoon and chemical structure illustrating the hydrogen-bonded dimer formed by macrocyclic sheet β-peptide 1 in solution. S12
Fig. S2b. Selected expansions of the NOESY spectrum of macrocyclic β-sheet peptide 1 at 2.0 mM in D2O at 500 MHz and 298 K. S12
Fig. S3. 1H NMR spectra of macrocyclic β-sheet peptide 2a at various concentrations in D2O at 500 MHz and 298 K. S13
Fig. S4. Selected expansions of the NOESY spectrum of macrocyclic β-sheet peptide 2a at 8.0 mM in D2O at 500 MHz and 300.5 K. S14

Table S1. Key NOEs associated with interlayer contacts in tetramer formation of 2a. S14

Fig. S5. Expansions of the 1H NMR spectra of macrocyclic β-sheet peptide 2a at 0.3 mM in D2O at 500 MHz and 298 K with 0 and 25 mM NaCl. S15

Table S2. Percentage of monomer and tetramer of 2a at 0.3 mM with 0 mM and 25 mM NaCl (based on relative integrals for selected 1H NMR resonances). S15

Fig. S6. Expansions of the 1H NMR spectra of macrocyclic β-sheet peptide 3 at 4.0 mM in D2O at 500 MHz and 298 K with 0, 25, and 150 mM NaCl. S16

Table S3. Percentage of monomer and tetramer of 3 at 4.0 mM with 0, 25, and 150 mM NaCl (based on relative integrals for selected 1H NMR resonances). S16

Fig. S7. 1H NMR spectra of macrocyclic β-sheet peptides at 2.0 mM at 298 K in D2O at 500 MHz: 2a (tetramer predominates), 2b (tetramer predominates), 2c (monomer predominates), and 4 (monomer predominates). S17

Fig. S8. 1H NMR spectra of macrocyclic β-sheet peptide 2a at 8.0 mM at 300.5 K in D2O at 500 MHz (tetramer predominates), macrocyclic β-sheet peptide 3 at 2.0 mM at 298 K in D2O at 500 MHz (monomer predominates), and linear peptide 5 at 1.2 mM at 298 K in D2O at 500 MHz (monomer). S18

Table S4. 1H NMR chemical shifts of the α-protons of the 2a tetramer, the 3 monomer, and linear peptide 5. S16

Fig. S9. Sedimentation coefficient distributions of macrocyclic β-sheet peptide 2b for loading concentrations at 98.7 μM, 304.0 μM, and 657.6 μM obtained from sedimentation velocity experiments performed at 344 nm. S19

Fig. S10. Sedimentation velocity data for macrocyclic β-sheet peptide 2b (98.7 μM) when fitted with a reversible model for a monomer-tetramer equilibrium using genetic-algorithm-Monte Carlo analysis. S20

Table S5. Hydrodynamic measurements for macrocyclic β-sheet peptide 2b from a genetic-algorithm Monte Carlo fit to a non-interacting model. S21

Table S6. Hydrodynamic measurements for macrocyclic β-sheet peptide 2b at 98.7 μM from a genetic-algorithm Monte Carlo fit to a reversible monomer-tetramer model. S21

References and Notes S22
| Peptide | Description |
|---------|-------------|
| **1**   | 1D $^1$H NMR spectrum in D$_2$O (500 MHz)  
2D TOCSY spectrum in D$_2$O (500 MHz)  
2D NOESY spectrum in D$_2$O (500 MHz)  
2D DOSY spectrum in D$_2$O (600 MHz) |
| **2a**  | HPLC trace and mass spectrum  
1D $^1$H NMR spectrum in D$_2$O (500 MHz)  
2D TOCSY spectrum in D$_2$O (500 MHz)  
2D NOESY spectrum in D$_2$O (500 MHz)  
1D $^1$H NMR spectrum in 9:1 H$_2$O/D$_2$O (800 MHz)  
2D TOCSY spectrum in 9:1 H$_2$O/D$_2$O (800 MHz)  
2D NOESY spectrum in 9:1 H$_2$O/D$_2$O (800 MHz)  
2D EXSY spectrum in D$_2$O (600 MHz)  
2D DOSY spectrum in D$_2$O (600 MHz) |
| **2b**  | HPLC trace and mass spectrum  
2D $^1$H NMR spectrum in D$_2$O (500 MHz)  
2D TOCSY spectrum in D$_2$O (500 MHz)  
2D COSY spectrum in D$_2$O (500 MHz)  
2D NOESY spectrum in D$_2$O (500 MHz)  
2D DOSY spectrum in D$_2$O (600 MHz) |
| **2c**  | HPLC trace and mass spectrum  
1D $^1$H NMR spectrum in D$_2$O (500 MHz)  
2D TOCSY spectrum in D$_2$O (500 MHz)  
2D NOESY spectrum in D$_2$O (500 MHz)  
2D DOSY spectrum in D$_2$O (600 MHz) |
| **3**   | HPLC trace and mass spectrum  
1D $^1$H NMR spectrum in D$_2$O at 2 mM (500 MHz)  
2D TOCSY spectrum in D$_2$O at 2 mM (500 MHz)  
2D NOESY spectrum in D$_2$O at 2 mM (500 MHz)  
1D $^1$H NMR spectrum in D$_2$O at 8 mM (500 MHz)  
2D TOCSY spectrum in D$_2$O at 8 mM (500 MHz)  
2D NOESY spectrum in D$_2$O at 8 mM (500 MHz)  
2D EXSY spectrum in D$_2$O at 4 mM (600 MHz)  
2D DOSY spectrum in D$_2$O at 2 mM (600 MHz) |
Peptide 4

HPLC trace and mass spectrum S94
1D $^1$H NMR spectrum in D$_2$O (500 MHz) S97
2D TOCSY spectrum in D$_2$O (500 MHz) S98
2D ROESY spectrum in D$_2$O (500 MHz) S99
2D DOSY spectrum in D$_2$O (600 MHz) S100

Linear Peptide 5

HPLC trace and mass spectrum S101
1D $^1$H NMR spectrum in D$_2$O (500 MHz) S104
2D TOCSY spectrum in D$_2$O (500 MHz) S105
2D ROESY spectrum in D$_2$O (500 MHz) S107
Materials and Methods:

Peptides 1–5 were prepared and studied as the trifluoroacetate (TFA) salts.

Synthesis of macrocyclic β-sheet peptides 1–4.

Macrocyclic peptide 1 was synthesized as described previously, by automated solid-phase peptide synthesis of the corresponding linear peptide on chlorotrityl resin, followed by solution-phase cyclization, deprotection, and purification.\textsuperscript{1} Macrocyclic peptides 2a-2c, 3, and 4 were synthesized in a similar fashion, using procedures previously reported for the synthesis of 1 and of other macrocyclic β-sheet peptides.\textsuperscript{1,2,3} Boc-Orn(Fmoc)-OH was used to introduce the δ-linked ornithine turn units. Fmoc-Hao-OH\textsuperscript{2} was used to introduce the unnatural amino acid Hao.\textsuperscript{4} Standard Fmoc-protected amino acids were used to introduce the other residues: Fmoc-Ala-OH, Fmoc-Asp(OtBu)-OH, Fmoc-Gln(Trt)-OH, Fmoc-Glu(OtBu)-OH, Fmoc-Leu-OH, Fmoc-Lys(Boc)-OH, Fmoc-Phe-OH, Fmoc-N(Me)-Phe-OH, Fmoc-Ser(OtBu)-OH, Fmoc-Thr(OtBu)-OH, Fmoc-Tyr(OtBu)-OH, Fmoc-Val-OH. In the synthesis of macrocyclic peptide 4, Fmoc-N(Me)-Phe-OH was introduced using normal coupling times and conditions (20 min coupling with HCTU) and the subsequent amino acid, Fmoc-Phe-OH, was introduced by double coupling with HOAT (4 equiv.), HATU (4 equiv.), and 1 hour coupling times using automated solid phase peptide synthesis.

Synthesis of linear peptide 5.

A 10 mL Bio-Rad Poly-Prep chromatography column was charged with Rink amide resin (300 mg, 0.73 mmol/g loading, 0.22 mmol) and ca. 6 mL of CH\textsubscript{2}Cl\textsubscript{2}. After 30 min, the solvent was drained and the resin was washed with ca. 3 mL of DMF. The resin was then submitted to cycles of standard Fmoc-based solid phase peptide synthesis on a PS3 automated peptide synthesizer (Protein Technologies, Inc.) using Fmoc-protected amino acid building blocks (4
equiv, with HCTU as coupling agent and 2,4,6-collidine as base). The final step of the synthesis of the protected peptide involved acetylation of the amino-terminus by treating the resin with 2 mL of acetic anhydride on the PS3 synthesizer using 2,4,6-collidine as base. The resin was stirred with 10 mL of trifluoroacetic acid/triisopropylsilane/water (38:1:1 v/v) for 4 hours under nitrogen. The solution was concentrated under vacuum. The residue was dissolved in ca. 5 mL of water/acetonitrile (1:1), and centrifuged for 5 min at 14,000 rpm. The liquid portion was decanted from the supernatant, then filtered through a 0.45 micron filter, and purified by RP-HPLC on a C18 column (elution with acetonitrile and water containing 0.1% TFA, linear gradient from 20-35% acetonitrile over 38 min). The pure fractions were lyophilized to yield 3.1 mg of acyclic control peptide 5 (1% yield based on resin loading): ESI-MS m/z for C_{64}H_{102}N_{16}O_{17} [M + 2H]^2+ calcd 683.37, found 683.34.

**NMR sample preparation, data collection, and data processing of peptides 1–5.**

$^1$H NMR experiments of macrocyclic β-sheet peptides 1–5 were performed in D$_2$O at 500 MHz and 600 MHz at varying temperatures. Solutions of the peptides were prepared gravimetrically by dissolving an appropriate weight of each peptide in an appropriate volume of solvent. In calculating molecular weights, all amino groups were assumed to be protonated as the TFA salts. The HOD peak was used as a reference after the HOD peak was calibrated based on temperature. All macrocyclic β-sheet peptides were allowed to stand for 6 hours to 36 hours to allow full hydrogen-deuterium exchange of the amide and ammonium hydrogens. 2D TOCSY, 2D COSY, 2D ROESY and 2D NOESY spectra were collected with 2048 data points in the $f_2$ domain and 512 data points in the $f_1$ domain. 2D TOCSY, 2D COSY and 2D ROESY data were processed to a 1024 x 1024 real matrix with a Qsine weighting function and with forward linear
prediction in the $f_1$ domain. 2D NOESY data were processed to a 1024 x 1024 real matrix with a Qsinc weighting function, a forward linear prediction in the $f_1$ domain, and with the parameter GB set at 0.05 in the $f_2$ and $f_1$ domain. The data were processed with the Bruker XwinNMR software.

In order to observe amide resonances for further resonance assignments, $^1$H NMR studies of macrocyclic β-sheet peptide 2a were also performed in a H$_2$O/D$_2$O mixture (9:1) at 800 MHz and 298 K using WATERGATE. 2D TOCSY and 2D NOESY data for 2a in the H$_2$O/D$_2$O mixture (9:1) were collected with 4096 data points in the $f_2$ domain and 512 data points in the $f_1$ domain. The collected data were processed with zero filling to a final matrix of 4096 x 1024 real points with a Qsine weighting function and with a forward linear prediction in the $f_1$ domain. The data were processed with the Bruker XwinNMR software.

**Modeling of the solution-state tetramer of macrocyclic β-sheet peptide 2a.**

We used the X-ray crystallographic structure of the tetramer of macrocyclic β-sheet 1 to create a model of the solution-state tetramer of macrocyclic β-sheet 2a. We generated the initial coordinates for the model in PyMOL by (1) changing the $p$-bromophenylalanine of 1 to tyrosine, (2) shifting the crystallographic dimers out of alignment by two residues toward the C-termini, and (3) moving the dimers so that they packed through the LFA faces, instead of the VF faces. The rotamer of F$_{20}$ with $\chi_1=180^\circ$ was then selected to avoid inter-chain steric clashes, and the shifted dimer layers were oriented to approximately match the observed interlayer NOEs between the methoxy group of Hao$_2$ and the methyl group of threonine.

The resulting initial structure was then imported into Maestro and a minimum-energy structure was generated by applying distance constraints to match observed NOEs as follows:
Using MacroModel with the Maestro user interface, NOE constraints to match the observed intra- and intermolecular NOEs illustrated in Figures 3, 4, 6, and 7 were applied. Distance constraints of 2.2 to 2.8 Å were applied for the following intramolecular NOEs: K$_{16}$$\alpha$–Y$_{16}$$\alpha$, F$_{20}$$\alpha$–K$_{1}$, V$_{15}$$\alpha$–Hao$_{1}$H$_{6}$, and E$_{22}$$\alpha$–Hao$_{2}$H$_{6}$ (16 constraints total within the tetramer). Distance constraints of 2.2 to 3.6 Å were applied for the following intermolecular intralayer NOEs: L$_{17}$$\alpha$–D$_{23}$$\alpha$ and F$_{19}$$\alpha$–A$_{21}$$\alpha$ (8 constraints total within the tetramer). Distance constraints of 2.2 to 5.0 Å were applied for the following intermolecular interlayer NOEs: Hao$_{2}$OMe–ThrCH$_{3}$, Hao$_{1}$H$_{4}$–Hao$_{2}$H$_{4}$, Hao$_{1}$H$_{4}$–Hao$_{2}$H$_{3}$, and Hao$_{1}$H$_{3}$–Hao$_{2}$–H$_{4}$ (16 constraints total between the layers of the tetramer). The structure was minimized with these constraints using the MMFFs force field with GB/SA water solvation. The NOE constraints were removed, and minimization was repeated using the MMFFs force field with GB/SA water solvation to generate a minimum-energy structure (local minimum).

This minimum-energy was then imported into PyMOL, and PyMOL was used to generate the images in Figures 10, 11B, and 12B. A $\beta$-strand of nine glycine residues (G9) was used to generate a cartoon of the template strand Hao-K-Hao-Y-T. Specifically, the pdb coordinates from each unnatural amino acid Hao were used to generate tri-glycine segments, and the pdb coordinates of the threonine, tyrosine, and lysine residues were also used to generate three glycine residues of the G9 $\beta$-strand.

_Diffusion-ordered spectroscopy (DOSY) experiments of macrocyclic $\beta$-sheet peptides 1–4._

The diffusion coefficients of macrocyclic $\beta$-sheet peptides 1-4 were determined by DOSY experiments on a Bruker Avance 600 MHz spectrometer in D$_{2}$O at 298 K. The experiments comprised a series of 16 pulsed field gradient spin-echo experiments in which the
gradient strength was incremented to allow ca. 5–95% signal attenuation with a linear ramp. A 75-ms diffusion delay was used. Diffusion gradient lengths of 1.75 – 3.0 ms were selected to achieve appropriate attenuation of each macrocyclic β-sheet peptide. Data were processed to give a pseudo-2D spectrum. The residual HOD peak in D₂O was set as a reference (19.0 x 10⁻¹⁰ m²/s at 298 K).

Analytical ultracentrifugation studies of macrocyclic β-sheet peptide 2b.

Analytical ultracentrifugation (AUC) sedimentation velocity (SV) studies were performed on macrocyclic β-sheet 2b to further elucidate its self-association behavior. Solutions of 2b were prepared gravimetrically as 0.10, 0.30, and 0.60 mM and determined spectrophotometrically to be 98.7, 304.0, and 657.6 μM based on a molar extinction coefficient of 2897 M⁻¹cm⁻¹ at 344 nm and a molar extinction coefficient of 22,260 M⁻¹cm⁻¹ at 280 nm.a,8 Sedimentation experiments were performed with a Beckman Optima XL-I at the Center for Analytical Ultracentrifugation of Macromolecular Assemblies at the University of Texas Health Science Center at San Antonio. All measurements were made in intensity mode, measuring at 344 nm in 25 mM aqueous NaCl. The experimental data were collected at 20°C, and at 60,000 rpm, using 1.2 cm titanium 2-channel centerpieces for the 98.7 μM and 304.0 μM samples, and a 3 mm titanium 2-channel centerpiece for the 657.6 μM sample. Hydrodynamic corrections for buffer density, viscosity and partial specific volume (0.7179 ml/g for 2b)b were made according to methods outlined in Laue et al.9 and as implemented in UltraScan.10

The experimental data from SV experiments were analyzed with UltraScan v. 9.9 10,11

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a The extinction coefficient of 2b was calculated to be 22,260 M⁻¹cm⁻¹ from the extinction coefficient of Hao (9850 M⁻¹cm⁻¹) and Tyr (1280 M⁻¹cm⁻¹) at 280 nm.
b The partial specific volume of the Hao subunit was determined to be 0.65 cm³/g as described previously.8 The molar mass of the Hao subunit is 235.12 g.
and modeled with solutions of the Lamm equation.\textsuperscript{12,13} Optimization was performed by 2-dimensional spectrum analysis (2DSA)\textsuperscript{14} with simultaneous removal of time- and radially-invariant noise contributions.\textsuperscript{15} 2DSA solutions are subjected to parsimonious regularization by genetic algorithm analysis,\textsuperscript{16} and are further refined using Monte Carlo analysis to determine confidence limits for the determined parameters.\textsuperscript{17} The calculations are computationally intensive and are carried out on high-performance computing platforms.\textsuperscript{18} All calculations were performed on the Lonestar and Ranger clusters at the Texas Advanced Computing Center at the University of Texas at Austin, and on the Jacinto cluster at the Bioinformatics Core Facility at the University of Texas Health Science Center at San Antonio.

A comparison of sedimentation profiles measured at 344 nm from multiple loading concentrations (98.7 μM, 304.0 μM, and 657.6 μM) indicated a mass-action driven shift in the sedimentation profile, suggesting the presence of a reversible reaction (Figure S8). Genetic algorithm – Monte Carlo fitting of the individual concentrations suggested the presence of monomer and tetramer species at different ratios, depending on concentration. From these ratios, we estimated $K_{\text{assoc}} = 1.93 \times 10^{14}$, $5.66 \times 10^{15}$, and $8.89 \times 10^{14}$ M$^{-3}$ for the respective experiments.\textsuperscript{c} Detailed hydrodynamic fitting results for these fits are shown in Table S4. Based on these results, we fitted the lowest concentration — which displayed the largest signal for the monomer — to a reversible self-associating model for a monomer-tetramer equilibrium using a 200-iteration genetic algorithm-Monte Carlo analysis.\textsuperscript{13,19} This treatment resulted in a very good fit to the monomer-tetramer model — with random residuals (Figure S9) — and gave $K_{\text{assoc}} = 1.93 \times 10^{14}$ M$^{-3}$.

\textsuperscript{c} A $K_{\text{assoc}}$ of $1.93 \times 10^{14}$ M$^{-3}$ corresponds to a 1:1 molar ratio of monomer and tetramer at 0.086 mM total concentration of 2b and a 4:1 molar ratio of monomer and tetramer at 0.022 mM total concentration of 2b.
**Figure S1a.** Key NOEs associated with folding and dimerization of macrocyclic β-sheet peptide 2a. Interstrand main chain-main chain NOEs were observed for 2a in the NOESY 800 MHz spectrum with WATERGATE (8.0 mM in H$_2$O-D$_2$O (9:1) and 298 K).

**Figure S1b.** Key NOEs associated with folding and dimerization of macrocyclic β-sheet peptide 2a. Interstrand main chain-main chain NOEs were observed for 2a in the NOESY 800 MHz spectrum with WATERGATE (8.0 mM in H$_2$O-D$_2$O (9:1) and 298 K). Dashed lines represent weak or ambiguous NOEs.
Figure S2a. Cartoon and chemical structure illustrating the hydrogen-bonded dimer formed by macrocyclic sheet β-peptide 1 in solution. Key NOEs associated with solution-state dimerization and folding of 1 are shown with red and blue arrows.

Figure S2b. Selected expansions of the NOESY spectrum of macrocyclic β-sheet peptide 1 at 2.0 mM in D₂O at 500 MHz and 298 K. Key intermolecular interstrand NOEs associated with dimerization are highlighted in red; key intramolecular interstrand NOEs associated with folding are highlighted in blue.
**Figure S3.** $^1$H NMR spectra of macrocyclic β-sheet peptide 2a at various concentrations in D$_2$O at 500 MHz and 298 K. Noteworthy characteristic resonances of the monomer and the oligomer are labeled and highlighted with dashed lines.
Figure S4. Selected expansions of the NOESY spectrum of macrocyclic β-sheet peptide 2a at 8.0 mM in D$_2$O at 500 MHz and 300.5 K. Key interlayer NOEs associated with tetramerization are highlighted in green.

Table S1. Key NOEs associated with interlayer contacts in tetramer formation of 2a.$^a$

|       | Hao$_2$H$_3$ | Hao$_2$H$_4$ | Hao$_2$H$_6$ | Hao$_2$OMe |
|-------|-------------|-------------|-------------|------------|
| F$_{19}$Ar | weak       | strong      | -           | -          |
| L$_{17}$δ | medium     | medium      | strong      | -          |
| T$_{γ}$ | weak       | -           | -           | medium     |
| Hao$_1$H$_3$ | weak     | medium      | -           | -          |
| Hao$_1$H$_4$ | strong    | strong      | -           | strong     |
| Hao$_1$OMe | weak       | strong      | -           | -          |

$^a$Interlayer contacts are observed in Figure 6 and Figure S4.
**Figure S5.** Expansions of the $^1$H NMR spectra of macrocyclic β-sheet peptide 2a at 0.3 mM in D$_2$O at 500 MHz and 298 K with 0 mM and 25 mM NaCl. (DSA = 4,4-dimethyl-4-silapentane-1-ammonium trifluoroacetate.)

**Table S2.** Percentage of monomer and tetramer of 2a at 0.3 mM with 0 and 25 mM NaCl (based on the relative integrals for selected $^1$H NMR resonances).

| [NaCl] (mM) | L$_{17}$CH$_3$, V$_{18}$CH$_3$ (as monomer) | L$_{17}$CH$_3$ (pro-R), A$_2$V$_3$CH$_3$ (as oligomer) | % Monomer | % Tetramer |
|-------------|------------------------------------------|-------------------------------------------------|-----------|-----------|
| 0           | 0.90/H                                   | 1.13/H                                          | 44.2      | 55.8      |
| 25          | 0.26/H                                   | 1.20/H                                          | 18.1      | 81.9      |
Figure S6. Expansions of the $^1$H NMR spectra of macrocyclic $\beta$-sheet peptide 3 at 4.0 mM in D$_2$O at 500 MHz and 298 K with 0 mM, 25 mM NaCl, and 150 mM NaCl.

Table S3. Percentage of monomer and tetramer of 3 at 4.0 mM with 0, 25, and 150 mM NaCl (based on the relative integrals for selected $^1$H NMR resonances).

| [NaCl] (mM) | L$_{17}$CH$_3$, V$_{18}$CH$_3$ (as monomer) | L$_{17}$CH$_3$ ($pro$-R), A$_{21}$CH$_3$ (as oligomer) | % Monomer | % Tetramer |
|-------------|--------------------------------------------|------------------------------------------------|-----------|-----------|
| 0           | 1.19/H                                    | 1.00/H                                        | 54.3      | 45.7      |
| 25          | 0.43/H                                    | 1.00/H                                        | 29.9      | 70.1      |
| 150         | 0.25/H                                    | 1.00/H                                        | 19.7      | 80.3      |
Figure S7. $^1$H NMR spectra of macrocyclic β-sheet peptides at 2.0 mM at 298 K in D$_2$O at 500 MHz: 2a (tetramer predominates), 2b (tetramer predominates), 2c (monomer predominates), and 4 (monomer predominates). The spectrum of 4 shows multiple sets of resonances, which are associated with amide-bond rotamers.
Figure S8. $^1$H NMR spectra of macrocyclic β-sheet peptide 2a at 8.0 mM at 300.5 K in D$_2$O at 500 MHz (tetramer predominates), macrocyclic β-sheet peptide 3 at 2.0 mM at 298 K in D$_2$O at 500 MHz (monomer predominates), and linear peptide 5 at 1.2 mM at 298 K in D$_2$O at 500 MHz (monomer).

Table S4. $^1$H NMR chemical shifts of the α-protons of the 2a tetramer, the 3 monomer, and linear peptide 5.

| Residue | Peptide 2a δ (ppm) | Peptide 3 δ (ppm) | Peptide 5 δ (ppm) | $\Delta$δ (ppm) 2a - 5 | $\Delta$δ (ppm) 3 - 5 |
|---------|---------------------|-------------------|-------------------|----------------------|----------------------|
| Q$_{15}$ | 4.67                | 4.49              | 4.24              | 0.43                 | 0.25                 |
| K$_{16}$ | 4.29                | 4.31              | 4.25              | 0.04                 | 0.06                 |
| L$_{17}$ | 5.22                | 4.51              | 4.31              | 0.91                 | 0.20                 |
| V$_{18}$ | 5.03                | 4.35              | 3.99              | 1.04                 | 0.36                 |
| F$_{19}$ | 5.38                | 4.67              | 4.55              | 0.85$^a$            | 0.14$^a$            |
| F$_{20}$ | 4.88                | 4.57              | 4.51              | 0.35$^a$            | 0.04$^a$            |
| A$_{21}$ | 4.86                | 4.32              | 4.17              | 0.69                 | 0.15                 |
| E$_{22}$ | 5.10                | 4.32              | 4.35              | 0.75                 | -0.03                |
| D$_{23}$ | 5.45                | 4.59              | 4.59              | 0.86                 | 0.00                 |

$^a$ assignment of F$_{19}$ and F$_{20}$ of peptide 5 arbitrary. The average δ for F$_{19}$ and F$_{20}$ of peptide 5 was used in calculating $\Delta$δ.
Figure S9. Sedimentation coefficient distributions of macrocyclic β-sheet peptide 2b for loading concentrations at 98.7 μM (triangles), 304.0 μM (squares) and 657.6 μM (circles) obtained from sedimentation velocity experiments performed at 344 nm. The increase in sedimentation coefficient as a function of increase in loading concentration suggests the presence of a mass-action driven self-association reaction.
Figure S10. Sedimentation velocity data (black lines, lower plot) for macrocyclic β-sheet peptide 2b (98.7 μM) when fitted with a reversible model for a monomer-tetramer equilibrium\textsuperscript{13,19} using genetic algorithm-Monte Carlo analysis (red lines). Residuals are random, and shown in the upper portion of this plot. For clarity, only every fifth scan in this experiment is shown.
### Table S5. Hydrodynamic measurements for macrocyclic β-sheet peptide 2b.

|                      | Monomer (98.7 μM) | Tetramer (98.7 μM) | Monomer (304.0 μM) | Tetramer (304.0 μM) | Monomer (657.6 μM) | Tetramer (657.6 μM) |
|----------------------|-------------------|--------------------|---------------------|--------------------|-------------------|-------------------|
| Partial concentration (% of total OD) | 31.06% | 68.94% | 12.02% | 87.98% | 2.73% | 97.27% |
| Molecular weight (Da)         | 2752.8 | 8946.4 | 3316.4 | 8947.7 | 2548.6 | 8507.2 |
| Sedimentation Coefficient (x 10^{-13} s) | 0.60   | 1.30  | 0.59   | 1.27   | 0.65   | 1.25   |
| Diffusion Coefficient (x 10^{-7} cm²/s) | 18.75  | 12.50 | 15.22  | 14.33  | 21.94  | 15.60  |
| Anisotropy (f/f₀)          | 1.24   | 1.26  | 1.44   | 1.24   | 1.09   | 1.21   |
| K_{assoc} (M⁻³)            | 1.93 x 10^{14} | 5.66 x 10^{15} | 8.89 x 10^{14} |

Hydrodynamic measurements for macrocyclic β-sheet 2b from a genetic algorithm-Monte Carlo fit to a non-interacting model with 50 iterations, fitting each loading concentration individually. Only two species were detected in each sample, corresponding in molecular weight to the monomer and tetramer of 2b. The shift in partial concentration is consistent with a reversible self-association model for a monomer-tetramer equilibrium. K_{assoc} is estimated based on the relative amounts of monomer and tetramer determined in the genetic algorithm-Monte Carlo analysis, but due to the low amount of monomer in the two higher concentrations, the K_{assoc} from the lowest concentration is considered to be the most reliable.

### Table S6. Hydrodynamic measurements for macrocyclic β-sheet peptide 2b at 98.7 μM from a genetic algorithm-Monte Carlo fit to a reversible monomer-tetramer model.

|                      | Monomer | Tetramer |
|----------------------|---------|----------|
| Molecular weight (Da)         | 2137.0 (2116.5, 2157.6) | 8548.0 (8466.0, 8630.4) |
| Sedimentation Coefficient (x 10^{-13} s) | 0.514 (0.511, 0.518) | 1.223 (1.220, 1.225) |
| Diffusion Coefficient (x 10^{-7} cm²/s) | 21.27 (21.17, 21.36) | 12.64 (12.54, 12.74) |
| Anisotropy (f/f₀)          | 1.18 (1.17, 1.19) | 1.25 (1.24, 1.26) |
| K_{assoc} (M⁻³)            | 1.93 (1.80, 2.05) x 10^{14} |  |

Hydrodynamic measurements for macrocyclic β-sheet 2b from a genetic algorithm-Monte Carlo fit to a reversible self-association model for a monomer-tetramer with 200 iterations. The K_{assoc} observed in this fit matched well the K_{assoc} observed with the non-interacting fit. Values in parenthesis reflect the 95% confidence intervals for each parameter.
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1D $^1$H NMR spectrum of macrocyclic $\beta$-sheet 1

2 mM in $D_2O$, 500 MHz, 298 K

tetramer predominates, monomer denoted with asterisk (*)
2D TOCSY spectrum of macrocyclic β-sheet 1 as tetramer
2 mM in D$_2$O, 500 MHz, 298 K, 150-ms spin-locking mixing time
tetramer predominates, monomer denoted by asterisk (*)
2D TOCSY spectrum of macrocyclic β-sheet 1 as tetramer
2 mM in D₂O, 500 MHz, 298 K, 150-ms spin-locking mixing time
tetramer predominates, monomer denoted by asterisk (*)
2D TOCSY spectrum of macrocyclic β-sheet 1 as tetramer
2 mM in D₂O, 500 MHz, 298 K, 150-ms spin-locking mixing time
tetramer predominates
2D NOESY spectrum of macrocyclic β-sheet 1 as tetramer
2 mM in D$_2$O, 500 MHz, 298 K, 200-ms spin-locking mixing time
tetramer predominates, monomer denoted by asterisk (*)
2D NOESY spectrum of macrocyclic β-sheet 1 as tetramer
2 mM in D$_2$O, 500 MHz, 298 K, 200-ms spin-locking mixing time
tetramer predominates, monomer denoted by asterisk (*)
*select NMR crosspeaks are labeled
2D NOESY spectrum of macrocyclic β-sheet 1
2 mM in D$_2$O, 500 MHz, 298 K, 200-ms spin-locking mixing time
tetramer predominates, monomer denoted by asterisk (*)
*select NMR crosspeaks are labeled
2D DOSY spectrum of macrocyclic β-sheet 1
2 mM in D₂O, 600 MHz, 298 K
tetramer predominates

Calculation for 1 at 2.0 mM

\[ DC_{\text{HOD}} = 19.0 \times 10^{-10} \text{ m}^2/\text{s} \]
\[ \log DC_{\text{HOD}} = -8.721 \]

For 1 tetramer, \( \log DC (\text{m}^2/\text{s}) = -9.99(7) \),
\[ DC = 10^{-9.997} \text{ m}^2/\text{s} = 10.1 \times 10^{-11} \text{ m}^2/\text{s} = 10.1 \times 10^{-7} \text{ cm}^2/\text{s} \]

\(^a\) Longsworth, L. G. J. Phys. Chem. 1960, 64, 1914–1917.
macrocyclic \( \beta \)-sheet peptide 2a (as the TFA salt)

molecular weight calculated for \( C_{101}H_{141}N_{25}O_{29} \cdot 4CF_3CO_2H \) (TFA salt of 2a): 2625.44
molecular weight calculated for \( C_{101}H_{141}N_{25}O_{29} \) (free base of 2a): 2169.35
exact mass calculated for \( C_{101}H_{141}N_{25}O_{29} \) (free base of 2a): 2168.03

Analytical RP-HPLC of macrocyclic \( \beta \)-peptide 2a

Signal 1: VWD1 A, Wavelength=214 nm

| RetTime | Area   | Height | Width | Type | Area   | *s | %    |
|---------|--------|--------|-------|------|--------|----|------|
| 8.744   | 7939.88721 | 494.81061 | 100.0000 |

Totals: 7939.88721 494.81061
Macrocyclic \(\beta\)-sheet peptide 2a

MS (ESI) of macrocyclic \(\beta\)-sheet peptide 2a calculated m/z for

- \([\text{M+2H}]^{+}\) : 1085.02
- \([\text{M+3H}]^{+}\) : 723.67
- \([2\text{M+3H}]^{+}\) : 1446.35

\([\text{M+H}]^{+}\)

\([\text{M+Na+2H}]^{3+}\)

\([\text{M+2Na+H}]^{3+}\)
Macrocyclic β-sheet peptide 2a

TOF MS ES+
3.82e3

[M+2H]^{2+} and [2M+4H]^{4+}

[2M+Na+3H]^{4+}
1D $^1$H NMR spectrum of macrocyclic β-sheet 2a
8 mM in D$_2$O, 500 MHz, 300.5 K
tetramer predominates
2D TOCSY spectrum of macrocyclic β-sheet 2a
2 mM in D₂O, 500 MHz, 300.5 K, 150-ms spin-locking mixing time
tetramer predominates, monomer denoted with an asterisk (*)
2D TOCSY spectrum of macrocyclic β-sheet 2a
2 mM in D$_2$O, 500 MHz, 300.5 K, 150-ms spin-locking mixing time
tetramer predominates, monomer denoted with an asterisk (*)
2D TOCSY spectrum of macrocyclic β-sheet 2a
2 mM in D₂O, 500 MHz, 300.5 K, 150-ms spin-locking mixing time
tetramer predominates, monomer denoted with an asterisk (*)
2D NOESY spectrum of macrocyclic β-sheet 2a
8 mM in D$_2$O, 500 MHz, 300.5 K, 150-ms spin-locking mixing time
tetramer predominates
2D NOESY spectrum of macrocyclic β-sheet 2a
8 mM in D$_2$O, 500 MHz, 300.5 K, 150-ms spin-locking mixing time
tetramer predominates
*select NMR crosspeaks are labeled
2D NOESY spectrum of macrocyclic β-sheet 2a
8 mM in D$_2$O, 500 MHz, 300.5 K, 150-ms spin-locking mixing time
tetramer predominates
2D NOESY spectrum of macrocyclic β-sheet 2a
8 mM in D₂O, 500 MHz, 300.5 K, 150-ms spin-locking mixing time
tetramer predominates
*select NMR crosspeaks are labeled
with WATERGATE
8 mM in 9:1 H$_2$O/D$_2$O, 800 MHz, 298 K
tetramer predominates
2D TOCSY spectrum of macrocyclic β-sheet 2a with WATERGATE
8 mM in 9:1 H₂O/D₂O, 800 MHz, 298 K
75-ms spin-locking mixing time
tetramer predominates
2D TOCSY spectrum of macrocyclic β-sheet 2a with WATERGATE

8 mM in 9:1 H₂O/D₂O, 800 MHz, 298 K

75-ms spin-locking mixing time
tetramer predominates
2D TOCSY spectrum of macrocyclic β-sheet 2a with WATERGATE
8 mM in 9:1 H₂O/D₂O, 800 MHz, 298 K
75-ms spin-locking mixing time
tetramer predominates
2D NOESY spectrum of macrocyclic β-sheet 2a with WATERGATE
8 mM in 9:1 H₂O/D₂O, 800 MHz, 298 K
225-ms spin-locking mixing time
tetramer predominates
2D NOESY spectrum of macrocyclic β-sheet 2a with WATERGATE
8 mM in 9:1 H₂O/D₂O, 800 MHz, 298 K
225-ms spin-locking mixing time
tetramer predominates
2D NOESY spectrum of macrocyclic β-sheet 2a with WATERGATE
8 mM in 9:1 H₂O/D₂O, 800 MHz, 298 K
225-ms spin-locking mixing time
tetramer predominates
*select NMR crosspeaks are labeled
$^1$H NMR 2D EXSY (ROESY spectra showing exchange crosspeaks)
Peptide 2a, 2 mM in D$_2$O, 600 MHz, 350 K
200 ms spin-locking time
Exchange crosspeaks shown in red; ROE crosspeaks shown in black
$^1$H NMR 2D EXSY (ROESY spectra showing exchange crosspeaks)
Peptide 2a, 2 mM in D$_2$O, 600 MHz, 350 K
200 ms spin-locking time
Exchange crosspeaks shown in red; ROE crosspeaks shown in black
$^1$H NMR 2D EXSY (ROESY spectra showing exchange crosspeaks)
Peptide 2a, 2 mM in D$_2$O, 600 MHz, 350 K
200 ms spin-locking time
Exchange crosspeaks shown in red; ROE crosspeaks shown in black
$^1$H NMR 2D EXSY (ROESY spectra showing exchange crosspeaks)

Peptide 2a, 2 mM in D$_2$O, 600 MHz, 350 K

200 ms spin-locking time

Exchange crosspeaks shown in red; ROE crosspeaks shown in black
2D DOSY spectrum of macrocyclic \( \beta \)-sheet 2a

2 mM in \( \text{D}_2\text{O} \), 600 MHz, 298 K
tetramer predominates

Calculation for 2a at 2.0 mM

\[
\text{DC}_{\text{HDO}} = 19.0 \times 10^{-10} \text{ m}^2/\text{s}^a
\]

\[
\log \text{DC}_{\text{HDO}} = -8.721
\]

For 2a tetramer, \( \log \text{DC} \) (m\(^2\)/s) = -10.00(1), \( \text{DC} = 10^{-10.001} \text{ m}^2/\text{s} = 10.0 \times 10^{-11} \text{ m}^2/\text{s} = 10.0 \times 10^{-7} \text{ cm}^2/\text{s} 

\(^a\) Longsworth, L. G. J. Phys. Chem. 1960, 64, 1914–1917.
2D DOSY spectrum of macrocyclic β-sheet 2a
8 mM in D₂O, 600 MHz, 298 K
tetramer predominates

Calculation for 2a at 8.0 mM

\[ DC_{HOD} = 19.0 \times 10^{-10} \text{ m}^2/\text{s} \]
\[ \log DC_{HOD} = -8.721 \]

For 2a tetramer, log DC (m²/s) = -9.99(4), DC = \(10^{-9.994}\) m²/s = \(10.1 \times 10^{-11}\) m²/s = \(10.1 \times 10^{-7}\) cm²/s

\[ ^*\text{Longsworth, L. G. J. Phys. Chem. 1960, 64, 1914–1917.} \]
macrocyclic β-sheet peptide 2b (as the TFA salt)

molecular weight calculated for C_{100}H_{139}N_{25}O_{31} • 4CF_3CO_2H (TFA salt of 2b): 2643.42
molecular weight calculated for C_{100}H_{139}N_{25}O_{31} (free base of 2b): 2187.32
exact mass calculated for C_{100}H_{139}N_{25}O_{31} (free base of 2b): 2186.01

Analytical RP-HPLC of macrocyclic β-peptide 2b

Signal 1: VWD1 A, Wavelength=214 nm

Peak RetTime Type Width Area Height Area %
# [min] [min] mAU *s [mAU ]
-----|-----|-----|-----|-----|-----|-----|
 1  8.744 VV  0.2105  7939.88721  494.81061 100.0000

Totals : 7939.88721  494.81061

S56
Macrocyclic β-sheet peptide 2b

MS (ESI) of macrocyclic β-sheet peptide 2b calculated m/z for

[M+2H]^{2+} : 1094.01
[M+3H]^{3+} : 729.67
Macrocyclic β-sheet peptide 2b

$[M+2H]^{2+}$ and $[2M+4H]^{4+}$

$[2M+Na+3H]^{4+}$

$[M+Na+H]^{2+}$
1D $^1$H NMR spectrum of macrocyclic $\beta$-sheet 2b
2 mM in $D_2O$, 500 MHz, 285 K
tetramer predominates
2D TOCSY spectrum of macrocyclic β-sheet 2b as tetramer
2 mM in D$_2$O, 500 MHz, 285 K
150-ms spin-locking mixing time
tetramer predominates
2D COSY spectrum of macrocyclic β-sheet 2b as tetramer
2 mM in D₂O, 500 MHz, 285 K
tetramer predominates
2D NOESY spectrum of macrocyclic β-sheet 2b as tetramer
2 mM in D$_2$O, 500 MHz, 285 K
150-ms spin-locking mixing time
tetramer predominates
2D NOESY spectrum of macrocyclic β-sheet 2b as tetramer
2 mM in D$_2$O, 500 MHz, 285 K
150-ms spin-locking mixing time
tetramer predominates

#select NMR crosspeaks are labeled
2D NOESY spectrum of macrocyclic β-sheet 2b as tetramer
2 mM in D$_2$O, 500 MHz, 285 K
150-ms spin-locking mixing time
tetramer predominates
#select NMR crosspeaks are labeled
2D DOSY spectrum of macrocyclic β-sheet 2b
2 mM in D_2O, 600 MHz, 298 K
tetramer predominates

Calculation for 2b at 2.0 mM

\[ DC_{\text{HOD}} = 19.0 \times 10^{-10} \text{ m}^2/\text{s}^a \]
\[ \log DC_{\text{HOD}} = -8.721 \]

For 2b tetramer, \( \log DC \ (\text{m}^2/\text{s}) = -9.98(6) \), \( DC = 10^{-9.986} \text{ m}^2/\text{s} = 10.3 \times 10^{-11} \text{ m}^2/\text{s} = 10.3 \times 10^{-7} \text{ cm}^2/\text{s} \)

\(^a\) Longsworth, I. G. J. Phys. Chem. 1960, 64, 1914–1917.

S65
2D DOSY spectrum of macrocyclic β-sheet 2b
8 mM in D₂O, 600 MHz, 298 K
tetramer predominates

Calculation for 2b at 8.0 mM

\[ DC_{\text{HOD}} = 19.0 \times 10^{-10} \text{ m}^2/\text{s} \]
\[ \log DC_{\text{HOD}} = -8.721 \]

For 2b tetramer, \( \log DC \) (m\(^2\)/s) = -9.99(4), \( DC = 10^{-9.994} \text{ m}^2/\text{s} = 10.1 \times 10^{-11} \text{ m}^2/\text{s} = 10.1 \times 10^{-7} \text{ cm}^2/\text{s} \)

* Longsworth, L. G. J. Phys. Chem. 1960, 64, 1914–1917.
macrocyclic β-sheet peptide 2c (as the TFA salt)

molecular weight calculated for C_{101}H_{141}N_{25}O_{31} \cdot 4CF_3CO_2H (TFA salt of 2c): 2657.44
molecular weight calculated for C_{101}H_{141}N_{25}O_{31} (free base of 2c): 2201.35
exact mass calculated for C_{101}H_{141}N_{25}O_{31} (free base of 2c): 2200.02

Analytical RP-HPLC of macrocyclic β-sheet peptide 2c

Signal 1: VWD1 A, Wavelength=214 nm

| Peak | RetTime | Type | Width | Area | Height | Area  | %     |
|------|---------|------|-------|------|--------|-------|-------|
| 1    | 7.234   | BV   | 0.0780| 4340.98779 | 798.37006 | 100.0000 |

Totals: 4340.98779 798.37006
Macrocyclic $\beta$-sheet peptide $2c$

MS (ESI) of macrocyclic $\beta$-sheet peptide $2c$ calculated m/z for

$[2M+4H]^{4+} : 1101.01$

$[M+3H]^{3+} : 734.34$

$[2M+4H]^{4+}$
Macrocyclic β-sheet peptide 2c

\[ [M+2H]^2+ \text{ and } [2M+4H]^4+ \]

\[ [2M+Na+3H]^4+ \]

\[ [2M+2Na+2H]^4+ \]

\[ [2M+3Na+H]^4+ \]

\[ [2M+4Na]^4+ \]
2D TOCSY spectrum of macrocyclic β-sheet 2c
2 mM in D₂O, 500 MHz, 298 K
150-ms spin-locking mixing time
2D TOCSY spectrum of macrocyclic β-sheet 2c
2 mM in D$_2$O, 500 MHz, 298 K
150-ms spin-locking mixing time
2D TOCSY spectrum of macrocyclic β-sheet 2c
2 mM in D$_2$O, 500 MHz, 298 K
150-ms spin-locking mixing time
2D NOESY spectrum of macrocyclic β-sheet 2c
2 mM in D₂O, 500 MHz, 298 K
250 ms spin-locking time
2D DOSY spectrum of macrocyclic β-sheet 2c
2 mM in D₂O, 600 MHz, 298 K
monomer predominates

Calculation for 2c at 2.0 mM

DC_{HOD} = 19.0 \times 10^{-10} \text{ m}^2/\text{s}^a

\log \text{DC}_{\text{HOD}} = -8.721

For 2c tetramer, \log \text{DC} (\text{m}^2/\text{s}) = -9.78(3), \text{DC} = 10^{-9.781} \text{ m}^2/\text{s} = 16.5 \times 10^{-11} \text{ m}^2/\text{s} = 16.5 \times 10^{-7} \text{ cm}^2/\text{s}

^a Longsworth, L. G. J. Phys. Chem. 1960, 64, 1914–1917.
macrocyclic β-sheet peptide 3 (as the TFA salt)

molecular weight calculated for C_{103}H_{146}N_{26}O_{28} \cdot 5\text{CF}_3\text{CO}_2\text{H} (TFA salt of 3): 2766.54
molecular weight calculated for C_{103}H_{146}N_{26}O_{28} (free base of 3): 2196.42
exact mass calculated for C_{103}H_{146}N_{26}O_{28} (free base of 3): 2195.08

Analytical RP-HPLC of macrocyclic β-sheet peptide 3

Signal 1: VWD1 A, Wavelength=214 nm

| # | RetTime | Type | Width | Area | Height | Area % |
|---|---------|------|-------|------|--------|-------|
| 1 | 8.181   | VV   | 0.1970| 5600.01514 | 403.11060 | 100.000 |

Totals: 5600.01514 403.11060
Macrocyclic β-sheet peptide 3

MS (ESI) of peptide 3 calculated m/z for
[M+2H]^+ : 1098.54
[M+3H]^+ : 732.69
Macrocyclic β-sheet peptide 3

TOF MS ES+ 152
1D $^1$H NMR spectrum of macrocyclic $\beta$-sheet 3
2 mM in D$_2$O, 500 MHz, 298 K
monomer predominates, small resonances are from tetramers
2D TOCSY spectrum of macrocyclic β-sheet 3, 2 mM in D₂O, 500 MHz, 298 K
150-ms spin-locking mixing time
monomer predominates, small resonances from tetramer
2D TOCSY spectrum of macrocyclic β-sheet 3, 2 mM in D₂O, 500 MHz, 298 K
150-ms spin-locking mixing time
monomer predominates, small resonances from tetramer
2D TOCSY spectrum of macrocyclic β-sheet 3, 2 mM in D₂O, 500 MHz, 298 K
150-ms spin-locking mixing time
monomer predominates, small resonances from tetramer
2D NOESY spectrum of macrocyclic β-sheet 3
2 mM in D₂O, 500 MHz, 298 K
200-ms spin-locking mixing time
monomer predominates, small resonances are from tetramers
2D NOESY spectrum of macrocyclic β-sheet 3, 2 mM in D$_2$O, 500 MHz, 298 K
200-ms spin-locking mixing time
monomer predominates, small resonances are from tetramers
2D NOESY spectrum of macrocyclic β-sheet 3, 2 mM in D₂O, 500 MHz, 298 K
200 ms spin-locking time
monomer predominates, small resonances are from tetramer
40/60 ratio of monomer to tetramer resonances from tetramer are labeled.
2D TOCSY spectrum of macrocyclic β-sheet 3, 8 mM in D₂O, 500 MHz, 298 K
150-ms spin-locking mixing time
40/60 ratio of monomer to tetramer
resonances from tetramer are labeled
2D NOESY spectrum of macrocyclic β-sheet 3, 8 mM in D₂O, 500 MHz, 298 K
200-ms spin-locking mixing time
40/60 ratio of monomer to tetramer resonances from tetramer are labeled
$^1$H NMR 2D EXSY (ROESY spectra showing exchange crosspeaks)
Peptide 3, 4 mM in D$_2$O, 600 MHz, 340 K
200 ms spin-locking time
Exchange crosspeaks shown in red; ROE crosspeaks shown in black
$^1$H NMR 2D EXSY (ROESY spectra showing exchange crosspeaks)
Peptide 3, 4 mM in D$_2$O, 600 MHz, 340 K
200 ms spin-locking time
Exchange crosspeaks shown in red; ROE crosspeaks shown in black
$^1$H NMR 2D EXSY (ROESY spectra showing exchange crosspeaks)
Peptide 3, 4 mM in D$_2$O, 600 MHz, 340 K
200 ms spin-locking time
Exchange crosspeaks shown in red; ROE crosspeaks shown in black
$^1$H NMR 2D EXSY (ROESY spectra showing exchange crosspeaks)
Peptide 3, 4 mM in D$_2$O, 600 MHz, 340 K
200 ms spin-locking time
Exchange crosspeaks shown in red; ROE crosspeaks shown in black
2D DOSY spectrum of macrocyclic β-sheet 3
2 mM in D₂O, 600 MHz, 298 K
monomer predominates,
small resonances from tetramer

Calculation for 3 at 2.0 mM

\[
\text{DC}_{\text{HOD}} = 19.0 \times 10^{-10} \text{ m}^2/\text{s}^a
\]
\[
\log \text{DC}_{\text{HOD}} = -8.721
\]

For 3 tetramer, log DC (m²/s) = -9.78(5), DC = 10^{-9.785} m²/s = 16.4 \times 10^{-11} m²/s = 16.4 \times 10^{-7} cm²/s

\(^a\) Longsworth, L. G. J. Phys. Chem. 1960, 64, 1914–1917.
macrocyclic β-sheet peptide 4 (as the TFA salt)

molecular weight calculated for $\text{C}_{102}\text{H}_{143}\text{N}_{25}\text{O}_{29} \cdot 4\text{CF}_{3}\text{CO}_{2}\text{H}$ (TFA salt of 4): 2639.47
molecular weight calculated for $\text{C}_{102}\text{H}_{143}\text{N}_{25}\text{O}_{29}$ (free base of 4): 2183.38
exact mass calculated for $\text{C}_{102}\text{H}_{143}\text{N}_{25}\text{O}_{29}$ (free base of 4): 2182.04

Analytical RP-HPLC of macrocyclic β-peptide 4

Signal 1: VWD1 A, Wavelength=214 nm

| # | RetTime | Type | Width | Area  | Height | Area   | %    |
|---|---------|------|-------|-------|--------|--------|------|
| 1 | 8.098   | VV   | 0.1003| 5771.48926 | 812.59326 | 100.0000 |

Totals: 5771.48926 812.59326
Macrocyclic β-sheet peptide 4

MS (ESI) of macrocyclic β-sheet peptide 4 calculated m/z for
[M+2H]⁺: 1092.02
[M+3H]⁺: 728.35
[M+4H]⁺: 546.51

S95
$\text{1D } ^1\text{H NMR spectrum of macrocyclic } \beta\text{-sheet peptide 4}$

$2 \text{ mM in D}_2\text{O, 500 MHz, 298 K}$
2D TOCSY spectrum of macrocyclic β-sheet peptide 4 as monomer
2 mM in D$_2$O, 500 MHz, 298 K
150 ms spin-locking time
2D ROESY spectrum of macrocyclic β-sheet peptide 4
2 mM in D$_2$O, 500 MHz, 298 K
200 ms spin-locking time
2D DOSY spectrum of macrocyclic $\beta$-sheet 4
2 mM in D$_2$O, 600 MHz, 298 K
monomer predominates

Calculation for 4 at 2.0 mM

$D_{\text{HOD}} = 19.0 \times 10^{-10}$ m$^2$/s$^a$

$log D_{\text{HOD}} = -8.721$

For 4 tetramer, log DC (m$^2$/s) = -9.75(4), DC = $10^{-9.354}$ m$^2$/s = $17.6 \times 10^{-11}$ m$^2$/s = $17.6 \times 10^{-7}$ cm$^2$/s

$^a$ Longsworth, L. G. J. Phys. Chem. 1960, 64, 1914–1917.
linear peptide 5 (as the TFA salt)

molecular weight calculated for C_{64}H_{100}N_{16}O_{17} • 3CF_3CO_2H (TFA salt of 5): 1707.65
molecular weight calculated for C_{64}H_{100}N_{16}O_{17} (free base of 5): 1365.58
exact mass calculated for C_{64}H_{100}N_{16}O_{17} (free base of 5): 1364.75

Analytical RP-HPLC of linear peptide 5

Signal 1: VWD1 A, Wavelength=214 nm

| Peak | RetTime | Type | Width | Area | Height | Area |
|------|---------|------|-------|------|--------|------|
| #    | [min]   |      | [min] | mAU  *s | [mAU]   | %   |
|      |---------|------|-------|-------|--------|------|
| 1    | 7.692   | VV   | 0.0657| 2891.74707 | 698.99927 | 100.0000 |

Totals: 2891.74707 698.99927
Linear peptide 5

MS (ESI) of acyclic peptide 5 calculated m/z for
[M+2H]^{2+} : 683.37
[M+3H]^{3+} : 455.91
[2M+3H]^{3+} : 910.83

TOF MS ES+ 8.87e3

TOF MS ES+ 8.95e3
Linear peptide 5

TOF MS ES+ 3.68e3

TOF MS ES+ 707

S103
1H NMR spectrum of linear peptide 5 as control

1.2 mM in D2O, 500 MHz, 298 K
2D TOCSY NMR spectrum of linear peptide 5 as control
4.95 mM in D$_2$O, 500 MHz, 298 K
150 ms spin-locking time
2D TOCSY NMR spectrum of linear peptide 5 as control
4.95 mM in D₂O, 500 MHz, 298 K
150 ms spin-locking time
2D ROESY NMR spectrum of linear peptide 5 as control
4.95 mM in D₂O, 500 MHz, 298 K
200 ms spin-locking time
2D ROESY NMR spectrum of linear peptide 5 as control
4.95 mM in D$_2$O, 500 MHz, 298 K
200 ms spin-locking time