Supporting Information

Supramolecular polymorphism: Tunable electronic interactions within π-conjugated peptide nanostructures dictated by primary amino acid sequence

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General considerations

*N*-Methylpyrrolidone (NMP), *O*-((Benzotriazol-1-yl)-*N*,*N*,*N′,*N′*-tetramethyluronium hexafluorophosphate (HBTU), benzotriazol-1-yl-oxytripyrrolidinophosphonium Wang resin, and Fmoc-protected amino acids were obtained from Advanced ChemTech. hexafluorophosphate (PyBOP) was obtained from Oakwood Chemical. All other chemicals were received from Alpha Aesar or Sigma Aldrich. All reagents were used as received. 4,4′-((1*E*,1′*E*)-1,4-phenylenebis(ethene-2,1-diyl))dibenzoic acid was prepared using literature procedures. 1 DFAA and DFAF peptide characterization data matched that of Vadehra et al.1

NMR Spectroscopy: 1H NMR spectra were collected using a Bruker Avance 400 MHz FT-NMR spectrometera and processed with Bruker Topspin V 1.3 or 2.1. Chemical shifts are reported in parts per million relative to residual protio solvent: DMSO (2.50 ppm), water (4.79 ppm).

ATR-FTIR: Data obtained on dry peptides using a Thermo Nicolet NEXUS 670 FTIR.

Electrospray Ionization Mass-Spectrometry (ESI-MS): ESI data were collected on a Thermo Finnigan LCQ Deca ion trap mass spectrometer with electrospray ionization. Samples were prepared in a 1:1 methanol/water with 1% ammonium hydroxide solution and were run in negative mode.

Reverse Phase High Performance Liquid Chromatography (RP-HPLC): was performed on an Agilent Technologies 1100 Series Quaternary LC System and an
Agilent Technologies PrepStar SD-1 instrument and fitted with a Phenomenex Luna 5 mm C8 column with ammonium formate aqueous buffer (pH 8) and acetonitrile used as the mobile phase. Analytical traces were run with a linear gradient starting at 10% MeCN and ending at 40% MeCN over the course of 40 - 50 minutes.

**UV-Vis and Photoluminescence (PL):** UV-Vis spectra were collected using a Varian Cary 50 Bio UV-Vis spectrophotometer. PL data were collected using a PTI Photon Technology International Fluorometer with an Ushio Xenon short arc lamp. Micromolar concentration samples were prepared using Millipore water and the pH was adjusted by the addition of 10 µL of 1 M HCl or 1M KOH. PL spectra were obtained using an excitation wavelength corresponding to the $\lambda_{\text{max}}$ of absorption.

**Circular Dichroism (CD):** CD spectra were acquired using a Jasco J-810 spectropolarimeter. Acidic and basic samples were prepared by adding 10 µL of 1M HCl or 1M KOH, respectively, to a stock solution of the peptide in Millipore water.

**Transmission Electron Microscopy (TEM):** TEM images were acquired on a Philips EM 420 transmission electron microscope equipped with an SIS Megaview III CCD digital camera with an operating voltage of 100 kV. 200 or 300 mesh Formvar carbon coated copper grids were purchased from Electron Microscopy Sciences. Grids were prepared as follows: A stock solution of a 0.1 mg/mL peptide in Millipore water was exposed to concentrated HCl vapor for 1 min. 10 µL of this solution was pipetted onto a grid. The grid was incubated for 8 minutes. The grid was then dipped sequentially into water then into a solution of 2% uranyl acetate stain and allowed to dry in air. For peptide DFAV the stock solution was prepared in 90:10 H$_2$O:MeOH and acidified and stained as
previously described. A 0.05 mg/ mL stock solution was used for DVAG and DFVG peptides and acidified and stained as previously described.

**Molecular Simulations:** All simulations were conducted using the GROMACS 4.0.5 simulation suite.\(^2,3\) The initial structure of each DXXX monomer was generated in an elongated conformation and the PRODRG2 server used to synthesize molecular topology files employing the GROMOS96 43a2 forcefield.\(^4\)

Simulations were performed at pH 5. The pKa values of the terminal Asp residue C-terminal and side chain carboxyl groups are 2.1 and 3.9 respectively,\(^5\) from which the Henderson-Hasselbach relation predicts ratios of deprotonated to protonated forms of 800:1 and 12:1 at pH 5. Accordingly, each monomer was specified as fully deprotonated, carrying a net charge of (-4).

The initial coordinates of each monomer stack were generated by replicating 35 DXXX monomers along the z-dimension (Figure 6a). Energy minimization calculations informed an initial inter-monomer spacing of 0.46 nm, and each successive monomer was rotated 10° clockwise to generate a twisted ribbon as the initial simulation geometry. Employing the right-handed screw convention along the positive z-axis, we define this twist angle as (-10)°. To simulate an infinite ribbon, the stack was placed in a cuboidal simulation cell of size 6×6×16.1 nm with periodic boundaries. This configuration preserved a spacing of 0.46 nm and relative twist angle of (-10)° between the monomers on either side of the periodic wall. The ribbon was then solvated by SPC/E water molecules at a density of 1.0 g/cm\(^3\), 140 of which were replaced with Na+ counter ions to maintain charge neutrality.\(^6\)

Lennard-Jones interactions were switched smoothly to zero at a 1.4 nm, and Coulomb interactions treated using Particle Mesh Ewald with a real-space cutoff of 1.5 nm and a
0.12 nm Fourier grid spacing. Bond lengths were fixed to improve simulation efficiency. Equations of motion were integrated using a leap-frog algorithm with a 1 fs time step. Simulations were conducted in the NPT ensemble at 298 K and 1 bar, employing a Nosé-Hoover thermostat and Parrinello-Rahman barostat. In analogy with simulations of membranes, semi-isotropic pressure coupling – in which the length of the box in the z-dimension is decoupled from the x-y box area – was employed. The system was relaxed by performing steepest descent energy minimization, followed by a 20 ns equilibration run after which time the side lengths of the box (which were free to change under the action of the barostat) reached a stationary value, and the global structure of the ribbon no longer changed. Snapshots were saved for analysis every 1 ps during a subsequent 10 ns production run.

The unit vector defining the axis of the ribbon was defined as the leading eigenvector of the gyration tensor of all heavy atoms in the ribbon. The principal axis of each monomer was defined as the leading eigenvector of the gyration tensor of the heavy atoms within the oligophenylene vinylene linker. Twist angles between neighboring monomers, \( \Delta \theta \), were calculated from the dot product of the component of principal axis of each monomer perpendicular to the ribbon axis. Interplanar spacings between neighboring monomers, \( \Delta r \), were defined as the minimum image distance between the centers of mass of the oligophenylene vinylene linker region. In the event that the periodic ribbon severed during the course of the simulation (DFAI, DFAV, DAAG, DGAG, DIAG, DVAG), twist angles and distances between the monomers constituting the ends of the ribbon were neglected in the computation of \( \Delta \theta \) and \( \Delta r \).
Experimental details and characterization data

General synthesis of peptides. All peptides were synthesized using standard solid phase 9-fluorenlymethoxycarbonyl (Fmoc) chemistry on a Wang resin preloaded (0.8 mmol/g) with the Fmoc-protected leading amino acid. Fmoc deprotection was performed by mixing the resin in a piperidine/DMF (2:8) solution for 10 minutes (2x), followed by rinsing with DMF, MeOH, and CH\textsubscript{2}Cl\textsubscript{2}. For all standard amino acid couplings, 3.0 eq. (relative to the resin substitution) of Fmoc protected amino acid was activated externally with 2.9 eq. of HBTU and 10 eq. of diisopropylethylamine (DIPEA) dissolved in NMP. The activated Fmoc-protected amino acid was then added to a peptide chamber containing the Wang resin and mixed for 3 hours. The resin was then drained and rinsed with NMP, MeOH, and CH\textsubscript{2}Cl\textsubscript{2} then allowed to dry. All coupling and deprotection steps were monitored by performing a Kaiser test.

General on-resin dimerization procedure. Followed procedure from Vadehra et al. \textsuperscript{1} 4,4'-(1\textsuperscript{E},1'\textsuperscript{E})-1,4-phenylenebis(ethene-2,1-diyl))dibenzoic acid (0.3 eq.) and PyBOP (0.6 eq.) were dissolved in 2:1 NMP:CH\textsubscript{2}Cl\textsubscript{2}. DIPEA (7.0 eq.) was added and mixed for approximately one minute. The solution was then added to the deprotected Wang resin (1.0 eq.) in a peptide chamber, and the reaction was mixed for 18 hours. The chamber was drained, and the resin was washed with CH\textsubscript{2}Cl\textsubscript{2}, MeOH, and NMP. A second round of coupling was then performed: 4,4'-(1\textsuperscript{E},1'\textsuperscript{E})-1,4-phenylenebis(ethene-2,1-diyl))dibenzoic acid (0.2 eq.) and PyBOP (0.4 eq.) were dissolved in 2:1 NMP:CH\textsubscript{2}Cl\textsubscript{2}. DIPEA (7.0 eq.) was added and mixed for approximately one minute. The solution was then added to deprotected Wang resin (1.0 eq.) in a peptide chamber, and the reaction was mixed for 18 hours. The chamber was drained, and the resin was washed with
CH₂Cl₂, MeOH, and NMP.

**General Procedure for peptide cleavage from the resin.** A (2:1) solution of 9.5:0.25:0.25 Trifluoroacetic acid/H₂O/triisopropylsilane and CH₂Cl₂ were added to the peptide chamber and mixed with the resin for 3 hours. The resin was removed by filtration, and the filtrate was then concentrated via solvent evaporation under reduced pressure. Cold Et₂O was added to the solution and the peptide was collected via centrifugation. After decanting the Et₂O, the crude peptide was dissolved in water and ammonium hydroxide was added until peptide was completely dissolved and then lyophilized. The obtained peptide was purified via Reverse Phase High Performance Liquid Chromatography (RP-HPLC).

**DFAG-OPV3-GAFD Peptide.** Yellow powder. 0.080 g, 0.063 mmol, 42 % yield. ¹H NMR (400 MHz, d6-DMSO) δ: 8.72 (1H, m), 8.16 (1H, m), 8.03 (1H, m), 7.90 (4H, d, J = 8.2 Hz), 7.71 (4H, d, J = 8.6 Hz), 7.68 (4H, s), 7.42 (2H, d, J = 16.2 Hz), 7.36 (2H, d, J = 16.1 Hz), 7.24 (10H, m), 4.45 (2H, m), 4.48 (2H, m), 3.91 (2H, m), 3.08 (2H, m), 2.83 (4H, m), 1.19 (6H, d, J = 7.2 Hz). MS (ESI) m/z 1149.7 (M-H)⁻ (calc. 1149.4), m/z 574.5 (M-2)²⁻ (calc. 574.2). ν max(solid) cm⁻¹ 1635, 1535, 1394, 1292, 1234, 1189, 1114, 995, 960, 844, 746, 698.
**DFAA-OPV3-AAFD Peptide.** Yellow powder. 0.030 g, 0.020 mmol, 30 % yield. $^1$H NMR (400 MHz, D$_2$O) δ: 7.80 (4H, d, $J = 8.0$ Hz), 7.70 (4H, d, $J = 8.0$ Hz), 7.67 (4H, s), 7.51 (2H, d, $J = 16.4$ Hz), 7.35 (4H, d, $J = 16.8$ Hz), 4.39 (2H, m), 4.26 (2H, m), 4.15 (2H, m), 3.87 (4H, m), 2.20 (4H, m), 2.01 (4H, m), 1.86 (2H, m), 1.76 (2H, m). 1.22 (6H, d, $J = 6.8$ Hz), 0.82 (24H, m). MS (ESI-) m/z 1177.7 (M-H$^-$) (calc. 1177.5), m/z 588.3 (M-2H$^2-$) (calc. 588.2). $\nu_{\text{max}}$(solid) cm$^{-1}$ 1641, 1527, 1452, 1396, 1288, 1234, 1186, 962, 846.

![DFAA-OPV3-AAFD Peptide](image)

**DFAV-OPV3-VAFD Peptide.** Yellow powder. 0.052 g, 0.044 mmol, 29 % yield. $^1$H NMR (400 MHz, d6-DMSO) δ: 8.24 (2H, d, $J = 8.5$ Hz), 8.04 (2H, d, $J = 7.1$ Hz), 7.89 (4H, d, $J = 8.5$ Hz), 7.70 (4H, d, $J = 8.4$ Hz), 7.68 (4H, s), 7.41 (2H, d, $J = 16.6$ Hz), 7.35 (2H, d, $J = 16.9$ Hz), 7.21 (10H, m), 4.48 (2H, m), 4.30 (2H, m), 3.04 (2H, m), 2.80 (2H, m), 2.10 (2H, m) 1.21 (6H, m), 0.88 (12H, m). MS (ESI) m/z 1233.6 (M-H$^-$) (calc. 1233.5), m/z 616.5 (M-2)$^2-$ (calc. 616.3), m/z 410.8 (M-3)$^3-$ (calc. 410.5). $\nu_{\text{max}}$(solid) cm$^{-1}$ 1612, 1525, 1442, 1382, 1299, 1220, 1186, 1155, 964, 842.

![DFAV-OPV3-VAFD Peptide](image)

**DFAF-OPV3-FAFD Peptide.** Yellow powder. 0.043 g, 0.030 mmol, 35% yield. $^1$H NMR (400 MHz, d6-DMSO) δ: 7.78 (4H, d, $J = 8.4$ Hz), 7.66 (8H, m), 7.36 (4H, m), 7.23 (12H, m), 7.15 (8H, m), 4.70 (2H, m), 4.48 (2H, m), 4.29 (4H, m), 3.06 (5H, m), 2.95 (2H, m), 2.8 (4H, m), 1.25 (6H, d, $J = 7.2$ Hz). MS (ESI-) m/z 1329.5 (M-H$^-$) (calc.
1329.5), m/z 664.2 (M-2H)^2+ (calc. 664.3). ν_max(solid) cm⁻¹ 1633, 1531, 1456, 1400, 1232, 1191, 964, 846, 746.

**DFAI-OPV3-IAFD Peptide.** Yellow powder. 0.089 g, 0.047 mmol, 47% yield. ¹H NMR (400 MHz, d6-DMSO) δ: 8.29 (2H, d, J = 8.6 Hz), 8.10 (2H d, J = 8.4 Hz), 8.05 (2H, d, J = 7.6 Hz), 7.89 (4H, d, J = 8.4 Hz), 7.70 (4H, d, J = 8.5 Hz), 7.67 (4H, s), 7.41 (2H, d, J = 16.5 Hz), 7.37 (2H, d, J = 16.5 Hz), 7.20 (10H, m), 4.46 (2H, m), 4.32 (2H, m), 3.05 (2H, dd, J = 14.2, 4.5), 2.8 (2H, dd, J = 14.6, 9.3), 1.88 (2H, m), 1.48 (2H, m), 1.20 (6H, d, J = 7.3), 0.83 (6H, m). MS (ESI-) m/z 1261.7 (M-H⁻)⁻ (calc. 1261.6), m/z 630.5 (M-2H⁻)^2+ (calc. 630.3). ν_max(solid) cm⁻¹ 1623, 1510, 1452, 1382, 1216, 1184, 1155, 1093, 1056, 960, 844, 695.

**DFFG-OPV3-GFFD Peptide.** Yellow powder. Following HPLC purification, 0.009 g, 2.3% yield. ¹H NMR (400 MHz, d6-DMSO) δ: 8.67 (1H, t, J = 5.7 Hz), 8.30 (1H, d, J = 8.3 Hz), 7.98 (1H, d, J = 8.2 Hz), 7.88 (1H, d, J = 8.4 Hz), 7.71 (2H, d, J = 8.5 Hz), 7.67 (2H, s), 7.42 (1H, d, J = 16.4 Hz), 7.36 (1H, d, J = 16.4 Hz), 7.29-7.22 (4H, m), 7.21-7.12 (6H, m), 4.55-4.48 (2H, m), 4.31 (1H, s), 3.89-3.75 (2H, m), 3.07 (1H, dd, J = 13.9, 4.5 Hz), 2.99 (1H, dd, J = 13.8, 4.0 Hz), 2.84 (1H, dd, J = 13.9, 9.4 Hz), 2.75 (1H, dd, J = 13.8, 9.3 Hz), 2.61-2.45 (2H, m). MS (ESI-) m/z 1301.8 (M-H⁻)⁻ (calc. 1301.5), m/z 650.8
(M-2H\(^{2+}\)) (calc. 650.2), m/z 433.8 (M-3H\(^{3+}\)) (calc. 433.2). \(\nu_{\text{max}}\) (solid) cm\(^{-1}\) 1718, 1641, 1531, 1290, 1232, 1186, 1085, 1045, 960, 846.

DFGG-OPV3-GGFD Peptide. Yellow powder. Following HPLC purification, 0.008 g, 2.4% yield. \(^1\)H NMR (400 MHz, d\(_6\)-DMSO) \(\delta\): 8.80 (1H, t, \(J = 5.6\) Hz), 8.10 (1H, t, \(J = 5.9\) Hz), 8.09 (1H, d, \(J = 8.4\) Hz), 7.91 (1H, d, \(J = 8.5\) Hz), 7.71 (2H, d, \(J = 8.5\) Hz), 7.67 (2H, s), 7.42 (1H, d, \(J = 16.5\) Hz), 7.35 (1H, d, \(J = 16.0\) Hz), 7.27-7.13 (6H, m), 4.53-4.47 (1H, m), 4.16 (1H, s), 3.90 (2H, d, \(J = 5.2\) Hz), 3.77-3.61 (2H, m), 3.07 (1H, dd, \(J = 16.5\) Hz), 7.36 (1H, d, \(J = 16.4\) Hz), 7.25-7.13 (6H, m), 4.56-4.50 (1H, m), 4.26 (1H, s), 4.17 (1H, dd, \(J = 7.2\), 1.3 Hz), 3.96-3.86 (2H, m), 3.08 (1H, dd, \(J = 13.9\), 4.6 Hz), 2.80 (1H, dd, \(J = 13.9\), 9.7 Hz), 2.47-2.41 (1H, m), 1.70-1.64 (1H, m), 1.33-1.26 (1H, m), 1.05-0.94 (1H, m), 0.77-0.71 (6H, m). MS (ESI-) m/z 1121.7 (M-H\(^{-}\)) (calc. 1121.4), m/z 1143.7 (M-2H+Na\(^{-}\)) (calc. 1143.4), m/z 560.9 (M-2)\(^{2-}\) (calc. 560.2). \(\nu_{\text{max}}\) (solid) cm\(^{-1}\) 1641, 1533, 1401, 1305, 1230, 1187, 1025, 993, 962, 844.

DFIG-OPV3-GIFD Peptide. Yellow powder. Following HPLC purification, 0.018 g, 4.9% yield. \(^1\)H NMR (400 MHz, d\(_6\)-DMSO) \(\delta\): 8.77 (1H, t, \(J = 5.8\) Hz), 8.15 (1H, d, \(J = 8.4\) Hz), 7.90 (2H, d, \(J = 8.4\) Hz), 7.80 (1H, d, \(J = 8.7\) Hz), 7.72 (2H, d, \(J = 8.5\) Hz), 7.68 (2H, s), 7.42 (1H, d, \(J = 16.5\) Hz), 7.36 (1H, d, \(J = 16.4\) Hz), 7.25-7.13 (6H, m), 4.56-4.50 (1H, m), 4.26 (1H, s), 4.17 (1H, dd, \(J = 7.2\), 1.3 Hz), 3.96-3.86 (2H, m), 3.08 (1H, dd, \(J = 13.9\), 4.6 Hz), 2.80 (1H, dd, \(J = 13.9\), 9.7 Hz), 2.47-2.41 (1H, m), 1.70-1.64 (1H, m), 1.33-1.26 (1H, m), 1.05-0.94 (1H, m), 0.77-0.71 (6H, m). MS (ESI-) m/z 1233.8 (M-H\(^{-}\))
DFVG-OPV3-GVFD Peptide. Yellow powder. Following HPLC purification, 0.015 g, 4.1% yield. $^1$H NMR (400 MHz, d6-DMSO) $\delta$: 8.78 (1H, t, $J = 5.6$ Hz), 8.25 (1H, d, $J = 8.3$ Hz), 7.91 (2H, d, $J = 8.4$ Hz), 7.77 (1H, d, $J = 8.9$ Hz), 7.71 (2H, d, $J = 8.5$ Hz), 7.67 (2H, s), 7.42 (1H, d, $J = 16.4$ Hz), 7.36 (1H, d, $J = 16.3$ Hz), 7.25-7.13 (5H, m), 4.53-4.47 (1H, m), 4.17 (1H, dd, $J = 8.9, 6.6$ Hz), 4.10-4.05 (1H, m), 4.00-3.86 (2H, m), 4.00 (1H, d, $J = 16.6$ Hz), 7.90 (2H, m), 7.41 (2H, d, $J = 16.6$ Hz), 7.35 (2H, d, $J = 16.4$ Hz), 4.35 (2H, m), 4.21 (2H, m), 4.02 (2H, m), 3.90 (2H, m), 3.70 (2H, m), 1.27 (2H, d, $J = 7.2$ Hz), 1.23 (2H, d, $J = 7.2$ Hz). MS (ESI-) m/z 1205.8 (M-H) $^-$ (calc. 1205.5), m/z 1227.8 (M-2H+Na) $^-$ (calc. 1227.5), m/z 603.0 (M-2) $^{2-}$ (calc. 602.3). $\nu_{\text{max}}$ (solid) cm$^{-1}$ 1641, 1544, 1388, 1066, 1047, 962, 846, 804.

DGAG-OPV3-GAGD Peptide. Yellow powder. 0.033 g, 0.035 mmol, 23% yield. $^1$H NMR (400 MHz, d6-DMSO) $\delta$: 8.70 (2H, m), 8.31 (2H, m), 7.90 (4H, d, $J = 8.7$ Hz), 7.71 (4H, d, $J = 8.6$ Hz), 7.67 (4H, s), 7.41 (2H, d, $J = 16.6$ Hz), 7.35 (2H, d, $J = 16.4$ Hz), 4.35 (2H, m), 4.21 (2H, m), 4.02 (2H, m), 3.90 (2H, m), 3.70 (2H, m), 1.27 (2H, d, $J = 7.2$ Hz), 1.23 (2H, d, $J = 7.2$ Hz). MS (ESI-) m/z 484.5 (M-2H$^+$)$^{2-}$ (calc. 484.2). $\nu_{\text{max}}$ (solid) cm$^{-1}$ 1635, 1533, 1380, 1295, 1236, 1106, 1012, 995, 964, 848.
**DAAG-OPV3-GAAD Peptide.** Yellow powder. 0.047 g, 0.048 mmol, 32% yield. $^1$H NMR (400 MHz, d6-DMSO) δ: 8.44 (2H, s), 7.86 (4H, d, $J = 8.3$ Hz), 7.71 (4H, d, $J = 8.4$ Hz), 7.67 (4H, s), 7.40 (2H, d, $J = 16.4$ Hz), 7.45 (2H, d, $J = 16.4$ Hz), 4.34 (2H, m), 4.22 (2H m), 3.77 (4H, s), 1.25 (4H, m). MS (ESI-) m/z 498.5 (M-2H$^+$) (calc. 498.2), m/z 332.2 (M-3)$^3$ (calc. 331.8). $\nu_{\text{max}}$(solid) cm$^{-1}$ 1631, 1533, 1382, 1292, 1230, 1187, 1105, 995, 962, 846.

![DAAG-OPV3-GAAD Peptide](image)

**DVAG-OPV3-GAVD Peptide.** Yellow powder. 0.055 g, 0.052 mmol, 45% yield. $^1$H NMR (400 MHz, d6-DMSO) δ: 8.73 (2H, m), 8.08 (2H, d, $J = 7.4$ Hz), 8.01 (2H, d, $J = 8.6$ Hz), 7.90 (4H, d, $J = 8.5$ Hz), 7.71 (4H, d, $J = 8.5$ Hz), 7.67 (4H, s), 7.42 (2H, d, $J = 16.4$ Hz), 7.36 (2H, d, $J = 16.9$ Hz), 4.43 (2H, m), 4.08 (4H, m), 3.98 (4H, m), 3.85 (2H, m), 2.41 (2H, m), 2.07 (2H, m), 1.28 (6H, d, $J = 7.2$ Hz). MS (ESI-) m/z 526.7 (M-2H$^+$)$^2$- (calc. 526.2). $\nu_{\text{max}}$(solid) cm$^{-1}$ 1631, 1531, 1388, 1305, 1220, 1087, 993, 962, 844.

![DVAG-OPV3-GAVD Peptide](image)

**DIAG-OPV3-GAID Peptide.** Yellow powder. 0.055 g, 0.051 mmol, 34% yield. $^1$H NMR (400 MHz, D$_2$O) δ: 8.54 (2H, s), 7.86 (4H, d, $J = 8.0$ Hz), 7.70 (4H, d, $J = 8.0$ Hz), 7.62 (4H, s), 7.31 (2H, d, $J = 16.2$ Hz), 7.23 (2H, d, $J = 16.0$ Hz), 4.5 (4H, m, 4.34 (2H, m), 4.16 (4H, m), 2.71 (4H, m), 1.50 (10H, d, $J = 6.8$ Hz), 1.23 (2H, m), 0.96 (12H, m). MS (ESI-) m/z 540.6 (M-2H$^+$)$^2$- (calc. 540.2). $\nu_{\text{max}}$(solid) cm$^{-1}$ 1560, 1384, 1303, 970, 846.
Figure S1 HPLC trace of DFAG peptide.

Figure S2 HPLC trace of DFAV peptide.

Figure S3 HPLC trace of DFAI peptide.
Figure S4 HPLC of DFGG peptide.

Figure S5 HPLC of DFVG peptide.

Figure S6 HPLC of DFFG peptide.
Figure S7 HPLC of DFIG peptide.

Figure S8 HPLC of DGAG peptide.

Figure S9 HPLC trace of DAAG peptide.
Figure S10 HPLC of DVAG peptide.

Figure S11 HPLC trace of DIAG peptide.
FTIR

Figure S12 ATR-IR of DFAG peptide.

Figure S13 ATR-IR of DFAV peptide.
Figure S14 ATR-IR of DFAI peptide.

Figure S15 ATR-IR of DFGG peptide.

Figure S16 ATR-IR of DGAG peptide.
Figure S17 ATR-IR of DFVG peptide.

Figure S18 ATR-IR of DFFG peptide.
Figure S19 ATR-IR of DFIG peptide.

Figure S20 ATR-IR of DAAG peptides.
Figure S21 ATR-IR of DVAG peptides.

Figure S22 ATR-IR of DIAG peptide.
Figure S23 ESI of DFAG peptide.

Figure S24 ESI of DFAV peptide.
Figure S25 ESI of DFAI peptide.

Figure S26 ESI of DFGG peptide.
Figure S27 ESI of DFVG peptide.

Figure S28 ESI of DFFG peptide.
Figure S29 ESI of DFIG peptide.

Figure S30 ESI of DGAG peptide.
Figure S31 ESI of DAAG peptide.

Figure S32 ESI of DVAG peptide.
Figure S33 ESI of DIAG peptide.

NMR

Figure S34 NMR of DFAG peptide.
Figure S35 NMR of DAV peptide.

Figure S36 NMR of DFAI peptide.
Figure S37 NMR of DFGG peptide.

Figure S38 NMR of DFVG peptide.
Figure S39 NMR of DFFG peptide.

Figure S40 NMR of DFIG peptide.
Figure S41 NMR of DGAG

Figure S42 NMR of DAAG peptide.
Figure S43 NMR of DVAG peptide.

Figure S44 NMR of DIAG.
MD

DFAAX MD simulation structural results:

Table S1: Mean and standard deviation in the twist angles (Δθ) and interplanar spacings (Δr) between neighboring monomers in the 1-D DFAAX peptide ribbons computed from molecular dynamics simulations. a

<table>
<thead>
<tr>
<th>peptide</th>
<th>Δθ / ° (mean ± std)</th>
<th>Δr / nm (mean ± std)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFAG</td>
<td>-12 ± 20</td>
<td>0.59 ± 0.18</td>
</tr>
<tr>
<td>DFAA</td>
<td>-10 ± 25</td>
<td>0.59 ± 0.20</td>
</tr>
<tr>
<td>DFAI</td>
<td>-13 ± 34</td>
<td>0.61 ± 0.15</td>
</tr>
<tr>
<td>DFAV</td>
<td>-13 ± 19</td>
<td>0.52 ± 0.17</td>
</tr>
<tr>
<td>DFAF</td>
<td>-8 ± 20</td>
<td>0.52 ± 0.12</td>
</tr>
</tbody>
</table>

aNote that the Δθ distributions had multiple local maxima (cf. Figure S45); the tabulated values reflect averages over the entire range.

Figure S45: Molecular simulations of DFAAX peptide stacks. Histograms of the distribution of twist angles between neighboring peptides over the 10 ns molecular dynamics production run for 1-D ribbons of (a) DFAG, (b) DFAA, (c) DFAI, (d) DFAV, and (e) DFAF.
DFXG MD simulation structural results:

Table S2: Mean and standard deviation in the twist angles ($\Delta \theta$) and interplanar spacings ($\Delta r$) between neighboring monomers in the 1-D DFXG peptide ribbons computed from molecular dynamics simulations.\(^a\)

<table>
<thead>
<tr>
<th>Peptide</th>
<th>$\Delta \theta / ^\circ$ (mean ± std)</th>
<th>$\Delta r / \text{nm}$ (mean ± std)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFGG</td>
<td>$-9 \pm 18$</td>
<td>$0.59 \pm 0.18$</td>
</tr>
<tr>
<td>DFAG</td>
<td>$-12 \pm 20$</td>
<td>$0.59 \pm 0.18$</td>
</tr>
<tr>
<td>DFIG</td>
<td>$1 \pm 44$</td>
<td>$0.53 \pm 0.15$</td>
</tr>
<tr>
<td>DFVG</td>
<td>$-10 \pm 21$</td>
<td>$0.56 \pm 0.13$</td>
</tr>
<tr>
<td>DFGG</td>
<td>$-8 \pm 39$</td>
<td>$0.55 \pm 0.14$</td>
</tr>
</tbody>
</table>

\(^a\)Note that the $\Delta \theta$ distributions had multiple local maxima (cf. Figure S46); the tabulated values reflect averages over the entire range.

Figure S46: Molecular simulations of DFXG peptide stacks. Histograms of the distribution of twist angles between neighboring peptides over the 10 ns molecular dynamics production run for 1-D ribbons of (a) DFGG, (b) DFAG, (c) DFIG, (d) DFVG, and (e) DFGG.
DXAG MD simulation structural results:

Table S3: Mean and standard deviation in the twist angles (Δθ) and interplanar spacings (Δr) between neighboring monomers in the 1-D DXAG peptide ribbons computed from molecular dynamics simulations. a

<table>
<thead>
<tr>
<th>peptide</th>
<th>Δθ /° (mean ± std)</th>
<th>Δr /nm (mean ± std)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGAG</td>
<td>-8 ± 18</td>
<td>0.59 ± 0.20</td>
</tr>
<tr>
<td>DAAG</td>
<td>-8 ± 27</td>
<td>0.59 ± 0.18</td>
</tr>
<tr>
<td>DIAG</td>
<td>-11 ± 23</td>
<td>0.59 ± 0.11</td>
</tr>
<tr>
<td>DVAG</td>
<td>-5 ± 44</td>
<td>0.60 ± 0.18</td>
</tr>
<tr>
<td>DFAG</td>
<td>-12 ± 20</td>
<td>0.59 ± 0.18</td>
</tr>
</tbody>
</table>

aNote that the Δθ distributions had multiple local maxima (cf. Figure S47); the tabulated values reflect averages over the entire range.

Figure S47: Molecular simulations of DXAG peptide stacks. Histograms of the distribution of twist angles between neighboring peptides over the 10 ns molecular dynamics production run for 1-D ribbons of (a) DGAG, (b) DAAG, (c) DIAG, (d) DVAG, and (e) DFAG.
Figure S48: TEM image of DFFG peptide nanostructures imaged with a 100 kV operating voltage on 200 mesh Formvar carbon coated copper grid and stained with 2% uranyl acetate.
References