Supporting information:
Secondary Structure of Diatom Silaffin Peptide R5 Determined by Two-Dimensional Infrared Spectroscopy

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Molecular dynamics simulations

The peptide was placed in a cubic box with 1 nm from the peptide to the box edge. For the simulation with silicate, $Si(OH)_3O^-$ was inserted 6 times at random in the simulation box using gmx insert-molecules to obtain an overall neutral charge in the system. Water molecules were then added to both simulation boxes from the spc216.gro conformation in Gromacs using gmx solvate. 6 Cl^- ions were added to the neat simulation box by replacing water molecules using gmx genion for charge neutralization. The neat simulation box was 6.84199 nm x 6.84199 nm x 6.84199 nm with 10366 water molecules. The simulation box with silicate was 6.01837 nm x 6.01837 nm x 6.01837 nm with 6986 water molecules.

Following an initial energy minimization, an NVT equilibration of 100 ps was made. Afterwards the system was equilibrated in NPT for 100 ps using the Berendsen thermostat. Two (one with silicate and one without) 2 μs production MDs were made using the leap-frog algorithm[1] for integration every 2 fs and saving the coordinates every 10 ps resulting in 200000 frames for each simulation. Neighbour searching was done using the Verlet cutoff-scheme while updating the neighbour list every 20 steps. Fast smooth Particle-Mesh Ewald (SPME)[2] was used for electrostatic interactions while a plain cut-off was used for Van der Waals interactions.
A cutoff at 1 nm was set for the short-range electrostatic and Van der Waals interactions. The Van der Waals potential was shifted with the Verlet cut-off scheme. The temperature was set to 300 K using the velocity rescaling thermostat[3,4] with a time constant of 1 ps and treating the protein and non-protein atoms separately. The pressure was set to 1.0 bar using the Parrinello-Rahman barostat[5] with an isotropic pressure coupling and a time constant of 5.0 ps. The compressibility was set to $4.5 \cdot 10^{-5}$ bar^{-1}. The bonds to hydrogen were constrained using the LINCS algorithm.[6]

Ramachandran plots

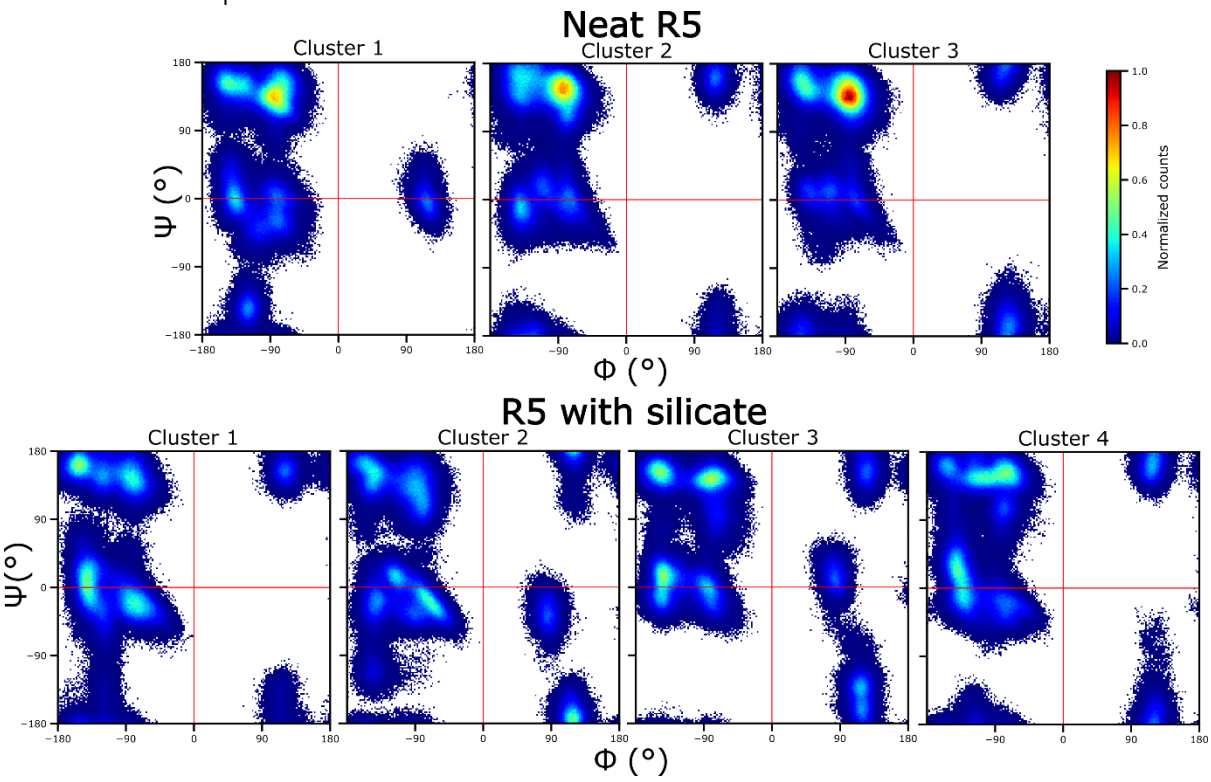

Fig S1. Ramachandran plots generated from 1 ns simulations of the representative cluster structures. Plots were made using a 2°x2° histogram and normalized to the maximum value across all plots.

DSSP plots

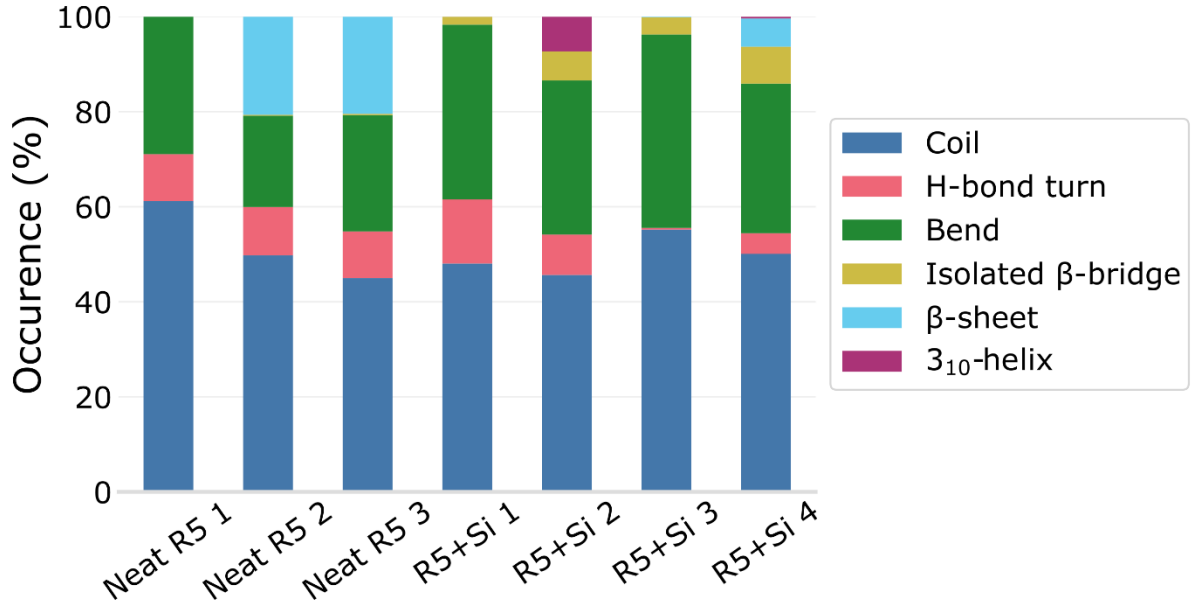

Fig. S2 DSSP occurrences calculated from each 1 ns simulation of the representative cluster structures.

Spectral overlap

The following equation was used to calculate the spectral overlap in every fitting iteration.[7]

$$S^{2D} = \sum_{i,j} \left(I_{\text{calc}}(\omega_i, \omega_j) I_{\text{exp}}(\omega_i, \omega_j) \right) / \sqrt{\left(\sum_{i,j} I_{\text{calc}}(\omega_i, \omega_j) I_{\text{calc}}(\omega_i, \omega_j) \right) \times \left(\sum_{i,j} I_{\text{exp}}(\omega_i, \omega_j) I_{\text{exp}}(\omega_i, \omega_j) \right)}$$

Here $I_{calc}(\omega_i, \omega_j)$ is the intensity of the calculated spectrum at frequencies (ω_i, ω_j) and $I_{exp}(\omega_i, \omega_j)$ is the intensity of the experimental spectrum. An overlap S^{2D} of zero means that there is no overlap and an overlap of 1 means that the spectra are identical.

Experimental 2DIR pump slices

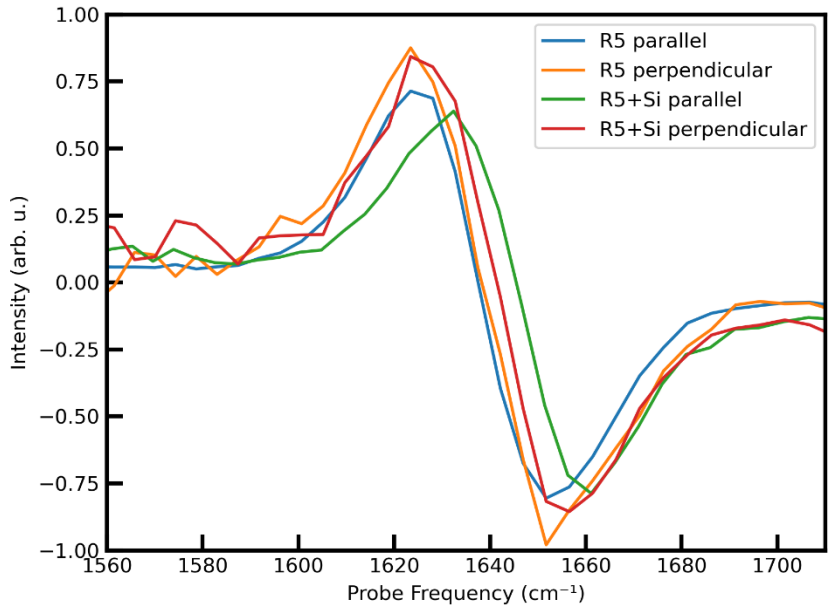

Fig. S3 Slices of normalized experimental 2DIR spectra at pump frequencies 1646 ±1 cm^{-1}

1 W. F. van Gunsteren and H. J. C. Berendsen, *Molecular Simulation*, 1988, **1**, 173–185.

2 U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee and L. G. Pedersen, *The Journal of chemical physics*, 1995, **103**, 8577–8593.

3 G. Bussi, T. Zykova-Timan and M. Parrinello, *The Journal of chemical physics*, 2009, **130**, 074101.

4 G. Bussi, D. Donadio and M. Parrinello, *The Journal of chemical physics*, 2007, **126**, 014101.

5 M. Parrinello and A. Rahman, *Journal of Applied physics*, 1981, **52**, 7182–7190.

6 B. Hess, H. Bekker, H. J. C. Berendsen and J. G. E. M. Fraaije, *Journal of computational chemistry*, 1997, **18**, 1463–1472.

7 J. F. Kruiger, C. P. van der Vegte and T. L. C. Jansen, *The Journal of Chemical Physics*, 2015, **142**, 054201.