ELECTRONIC SUPPLEMENTAL INFORMATION

Sustainable, Aqueous Exfoliation of MoS_2 via Bio-Inspired Avenues

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Simulation Details

All MD simulations were conducted in the *NVT* ensemble at 340 K (for spontaneous insertion) and 300 K (for steered MD and umbrella sampling simulations). Temperatures of the systems were maintained using the Nosé-Hoover thermostat.[1,2] Long-ranged electrostatic interactions were taken into account using the particle mesh Ewald (PME) method.[3,4] A time step was 1 fs utilized in all simulations. Prior any *NVT* production MD simulations, temperatures of the systems were gradually raised from 0 to 300 K (340 K) over 1 ns through 11 steps (14 steps).

In the first approach, simulation of peptide insertion into the expanded gap in the MoS_2 stack was conducted. Under experimental conditions during the sonication, an expanded inter-sheet gap between the topmost MoS_2 nanosheet in the stack of MoS_2 and the remainder of the stack is anticipated. The spontaneous diffusion of peptides into this gap was studied. To simulate this diffusion process, two configurations of initial peptide arrangements (parallel and vertical to the MoS_2 gap, Figure S1) were set up. A stack of MoS_2 consisting of ten MoS_2 nanosheets was placed in the periodic cell filled with liquid water; each nanosheet of MoS_2 layers had dimensions ~5x5 nm. The top sheet of the MoS_2 stack was initially vertically displaced from the others by a distance of 10 Å. 12 chains of the MoSBP1 peptide (YSATFTY) were placed around the gap edges (Figure 1a). This setup probed the ability of the peptides to spontaneously infiltrate into the gap. In a second set of simulations, 12 chains of the peptides were pre-inserted into the gap, and the liquid water was equilibrated while the remainder of the system was held fixed. Following sufficient infiltration of water into the pre-inserted gap, all atoms in the system were free to move and the simulations were conducted as described above. Both capped (MoSBP1) and uncapped (CMoSBP1) versions of peptides were considered separately in the simulations. As a reference, the gap closure process in liquid water in the

absence of peptides was also conducted to provide a baseline. In this instance, again, the non-water component of the simulation system initially was held fixed to ensure the gap was sufficiently solvated – following this, all atoms were free to move and the simulations conducted as described above. All simulations in this scheme were conducted at 340 K in the *NVT* ensemble. The dimensions of the periodic cell used in spontaneous insertion are given in Figure S2. During these simulations, the bottom sheet of MoS_2 was kept fixed to maintain the initial direction of the whole MoS_2 stack.

The second set of simulations was designed to investigate the stabilization effects of peptide-decorated MoS_2 nanosheets. After sonication, MoS_2 nanosheets suspended in solution are anticipated to be decorated with peptide chains via non-covalent adsorption. Two such decorated sheets were constructed and simulated, during which the two decorated sheets were configured in a parallel arrangement and moved closer to each other along the axis perpendicular to the sheet planes. This was done to investigate if the MoSBP1 peptide chain layer on the sheets could facilitate a stable colloidal suspension in an aqueous environment.

To do so, two MoS_2 nanosheets (dimension of ~5x5 nm) were decorated with 34 MoSBP1 peptide chains each sheet (17 chains per side) and placed in a simulation cell (Figure 1c and Figure S2c) solvated with liquid water. Steered MD simulations were used to bring the upper sheet closer to the lower sheet (Figure S2c), to produce initial configurations for each window in the umbrella sampling simulations. For these steered MD simulations, the upper peptide-decorated sheet (Figure S2c) was pulled downward towards the lower peptide-decorated sheet from an initial vertical separation of ~5.0 nm. A pulling rate of 0.02 nm was applied to the top sheet by applying a pulling force with a force constant of 1000 kJ mol^{-1} nm^{-2} at 9 points in the MoS_2 upper sheet (**Figure S3**). 22 Mo atoms and 30 S atoms of the lower sulfur layer in the lower sheet were restrained with a force constant of 1000 kJ mol^{-1} nm^{-2} during the steered MD simulations to ensure that the lower sheet did not rotate. The restrained Mo and S atoms were uniformly selected in the Mo and S atom layers of the lower sheet. This steered MD simulation generated a set of configurations which was used later for the umbrella sampling simulations.

For the umbrella sampling simulations, a periodic cell was filled with 71756 TIPS3P[5,6] water molecules and subjected to 55 x 100 ns simulations (one for each of the 55 configurations along the reaction coordinate). Umbrella sampling simulations were performed for both the capped CMoSBP1 and uncapped MoSBP1 peptide systems. Each umbrella sampling

simulation involved ~55 windows with spacing of 0.05 nm along the reaction coordinate (the vertical distance between the centers of the upper and lower sheets), and every window was simulated for 100 ns. The weighted histogram analysis method (WHAM[7]) was used to analyze the potential of mean force (PMF). The last 50 ns of umbrella sampling simulations were used to calculate the mass density along the reaction coordinate and the sheet contact data of residues. The residues in contact with the MoS_2 surface were defined based on their vertical distance (less than a cutoff of 0.5 nm) between the sulfur atom layer of the MoS_2 sheet and a pre-assigned atom or group of atoms in the site-chain of each residue.[8] These atoms and groups of atoms are given Table S1.

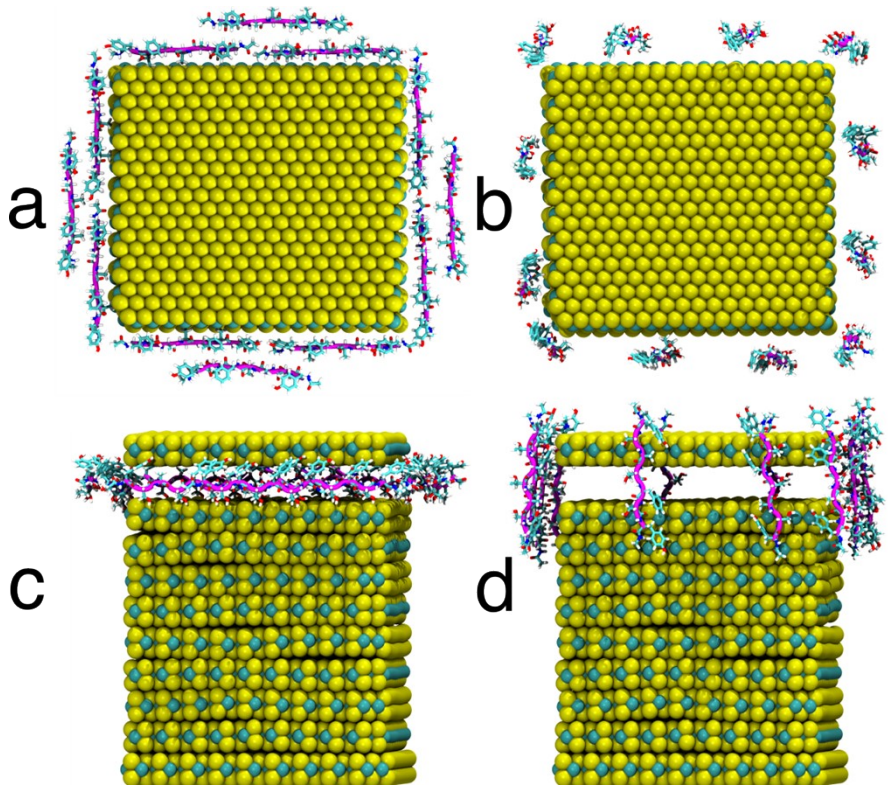

Figure S1. Top and side views of two initial arrangements of peptide chains used for simulation of spontaneous insertion of peptides into the expanded gap of the MoS_2 stack. Top views are in panels (a) and (b), side views are in panels (c) and (d). Water not shown for clarity.

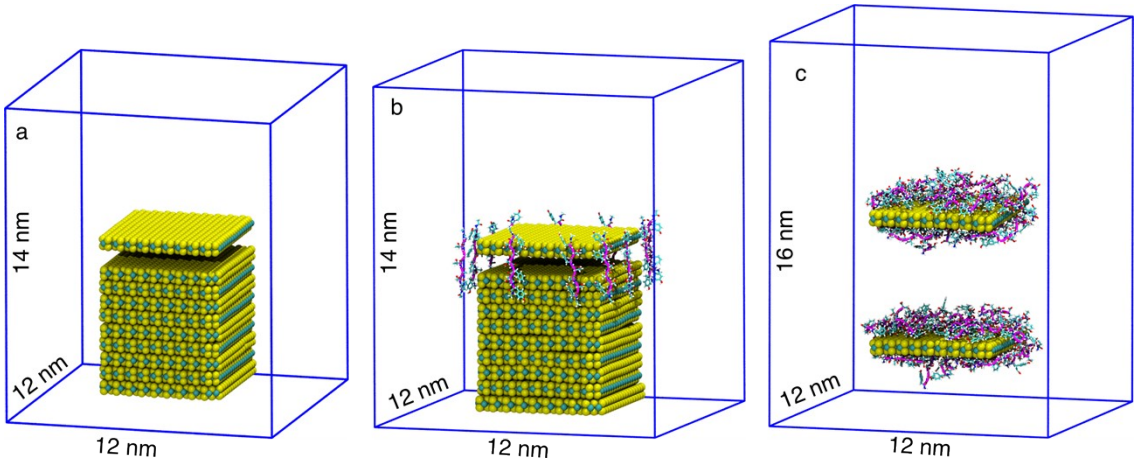

Figure S2. Dimensions of simulation cells used in the two simulation schemes. (a) Simulation cells without (a) and with (b) peptides. (c) dimensions of the cell used for the umbrella sampling simulations. Water not shown for clarity.

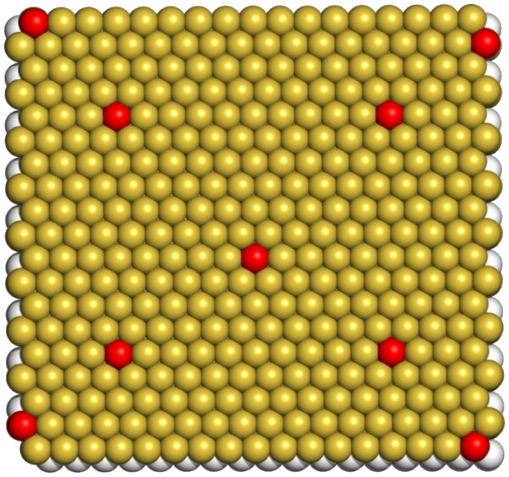

Figure S3 Pulling points (red) in the top sheet where forces were applied to pull the top sheet downward during the steered MD simulations.

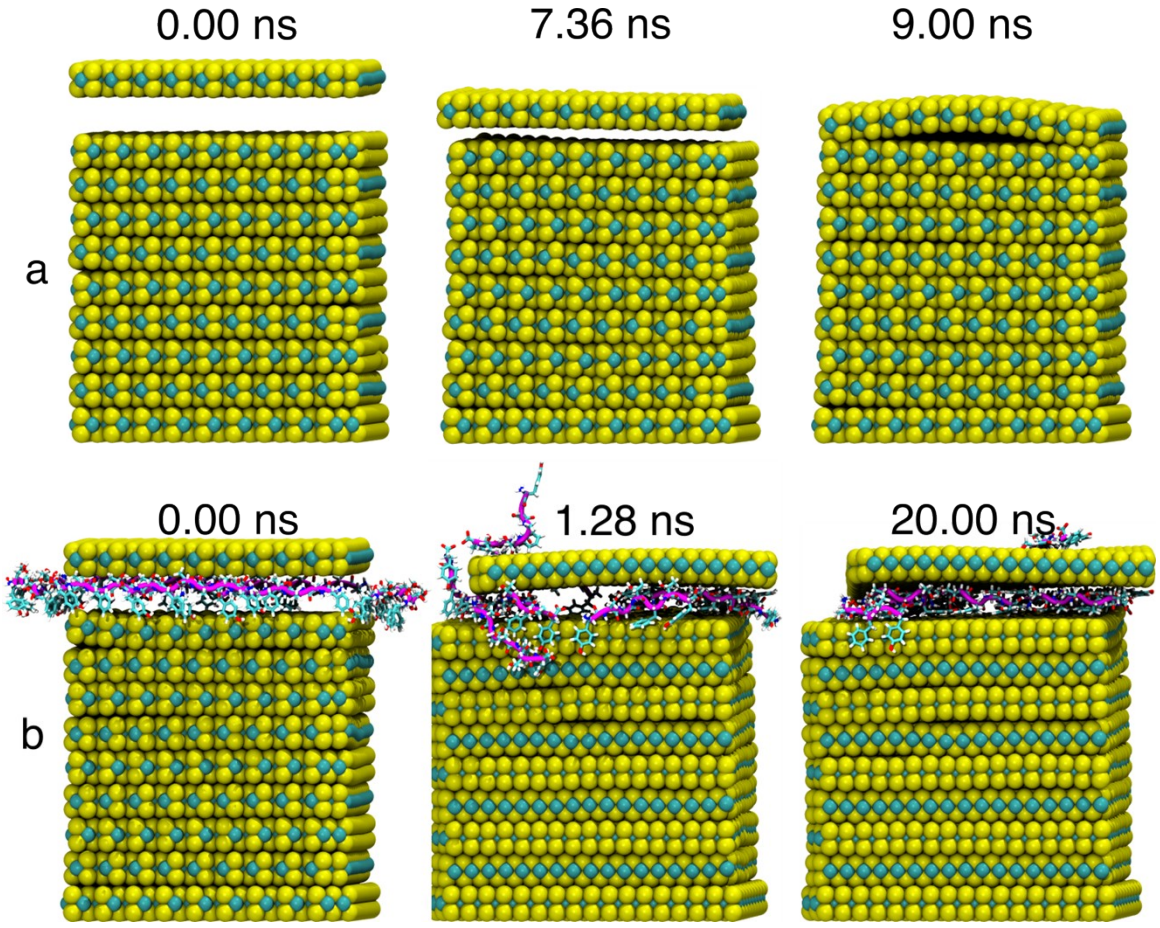

Figure S4 Snapshot showing gap closure in neat water only (a), and spontaneous insertion of MoSBP1 peptides into the gap starting from parallel arrangement configurations. Gap closure times in panel (a) and ingress times in panel (b) were averaged from three simulations. Water molecules not shown for clarity.

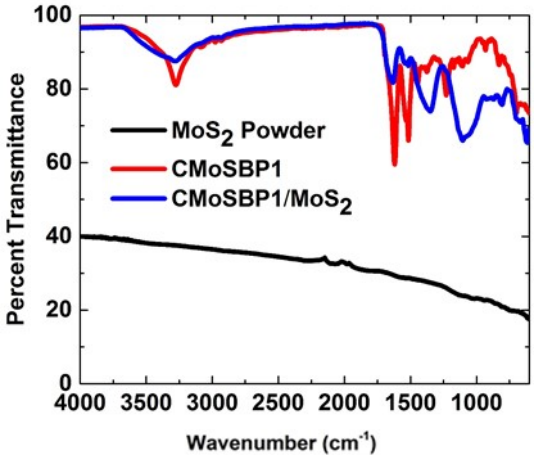

Figure S5 the FT-IR spectrum of the CMoSBP1-exfoliated MoS_2 nanosheets

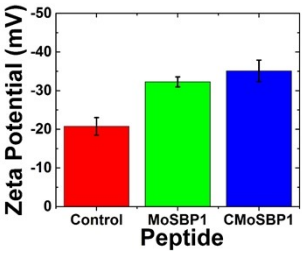

Figure S6 Zeta of MoSBP1 and CMoSBP1 sheets

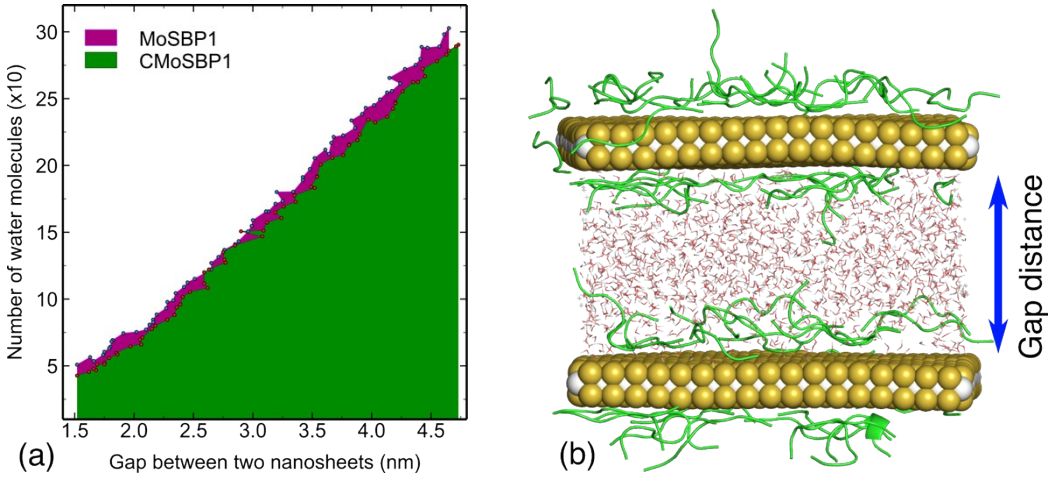

Figure S7 Number of water molecules in the gap (a) of two MoS_2 nanosheets decorated with MoSBP1 and CMoSBP1 peptides at several gap distances. A snapshot showing water molecules inside the gap (b).

Total furthest reaching distances of capped and uncapped peptides in the middle regions of gaps at two different gap distances of ~4.0 nm and ~3.10 nm are plotted in Figure S8. The furthest distance is defined as the longest vertical distance of heavy peptide atoms to the sulphur atom layers of MoS_2 nanosheets. The total furthest reaching distance is the sum of longest vertical distances measured on both top and bottom sheets. At the gap distance of 3.10 nm, one can see that uncapped peptides have longer total reaching distance (blue line).

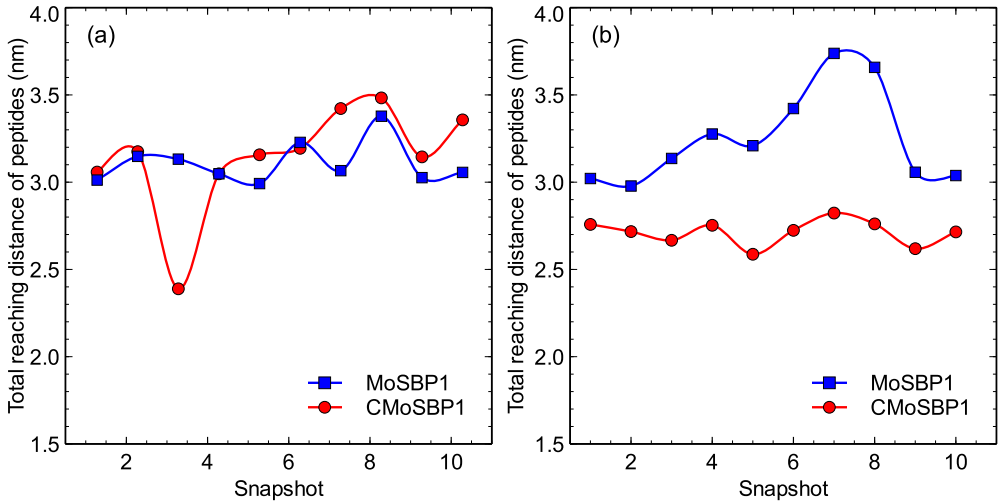

Figure S8 The total furthest reaching vertical distance of peptides measured in 1ns of umbrella sampling simulations at the gap distances of ~4.00 nm (a) and ~3.10 nm (b).

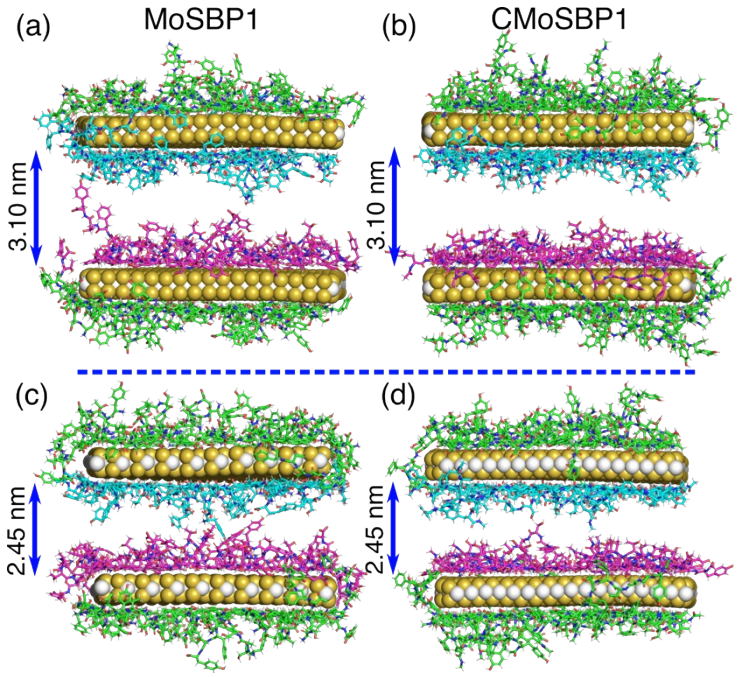

Figure S9 Snapshots showing peptides (MoSBP1 and CMoSBP1) between two MoS_2 nanosheets at different gap distances of 3.10 nm (panels a and b), and of 2.45 nm (panels c and d). In-gap peptides attached to the bottom (top) sheet are in magenta (cyan). Water molecules are hidden for clarity.

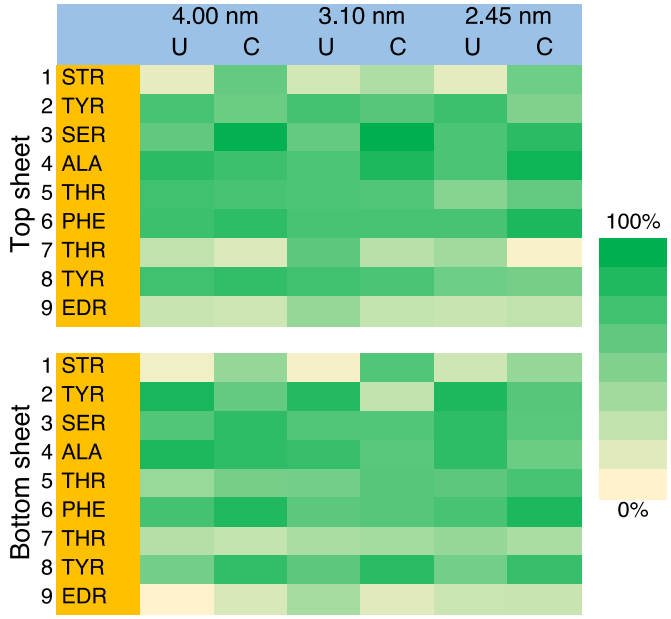

Figure S10 Residue contact heatmap of in-gap peptides observed at three gap distances of ~4.00, 3.10, and 2.45 nm. U and C are abbreviation of uncapped MoSBP1 and capped CMoSBP1 peptides. Residue order numbers of peptides are provided on the left. STR and EDR are the terminal groups of capped and uncapped peptides, which are ACE and NME in the capped peptides, and are $NH3^{+}$ and COO^{-} in the uncapped ones. The label "top sheet" refers to the peptides on the underside of the top sheet (exposed to gap) and "bottom sheet" refers to the peptide layer on the top of the bottom sheet (exposed to gap).

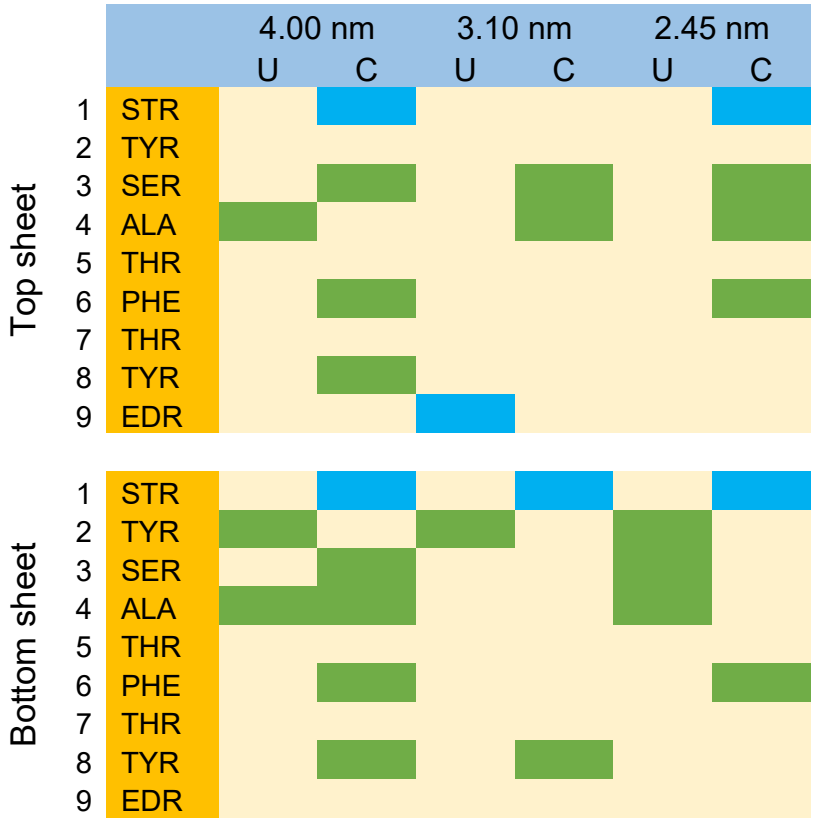

Figure S11 Strongest-contact residues with > 80% contact time highlighted in green. Terminal groups with > 50 % contact time in blue and the rest residues in light orange. U and C are abbreviation of uncapped MoSBP1 and capped CMoSBP1 peptides. Residue order numbers of peptides are provided on the left. STR and EDR are the terminal groups of capped and uncapped peptides, which are ACE and NME in the capped peptides, and are $NH3^{+}$ and COO^{-} in the uncapped ones.

Table S1 Individual atoms or groups of atoms in side-chain of residues used to measure the vertical distances between their reference points to the sulphur atom layer.

Residue	Side-Chain Site
ALA	Beta carbon
TYR	Centre-of-mass of ring heavy atoms
SER	Side-chain oxygen
THR	Side-chain oxygen
PHE	Centre-of-mass of ring heavy atoms
ACE	Centre-of-mass of all atoms
NME	Centre-of-mass of all atoms
NH_3^+	Centre-of-mass of all atoms
COO^-	Centre-of-mass of all atoms

Table S2. Gap closure time of MoS_2 nanostack in pure water (bare nanosheet), and peptide ingress times (for simulations in the presence of the peptides). All time in ns. Parallel and vertical refer to the initial arrangement of the peptide chains.

no.	bare nanosheet			MoSBP1		CMoSBP1	
	start	step 1	step 2	parallel	vertical	parallel	vertical
1	7.74	7.80	9.80	1.50	2.10	1.79	2.58
2	9.95	10.03	10.48	1.61	2.24	2.73	2.82
3	4.41	4.49	6.71	0.95	2.18	1.80	1.50

Table S3. Residue contact data (%) of in-gap peptides observed at three gap distances of ~4.00, 3.10, and 2.45 nm. U and C are abbreviation of uncapped MoSBP1 and capped CMoSBP1 peptides. Residue order numbers of peptides are provided on the left. STR and EDR are the terminal groups of capped and uncapped peptides, which are ACE and NME in the capped peptides, and are $NH3^+$ and COO^- in the uncapped ones.

	Distance		4.00 nm		3.10 nm		2.45 nm		average	
	order	residue	U	C	U	C	U	C	U	C
Top sheet	1	STR	29	66	35	45	30	63	33	54
	2	TYR	74	64	75	70	77	58	76	64
	3	SER	67	93	66	94	73	82	70	88
	4	ALA	82	77	72	86	73	90	73	88
	5	THR	76	74	72	71	56	66	64	69
	6	PHE	77	81	74	74	74	86	74	80
	7	THR	40	32	68	42	49	24	59	33
	8	TYR	76	80	76	73	63	61	70	67
	9	EDR	38	36	52	39	38	40	45	40
Bottom sheet	1	STR	26	52	25	71	36	52	31	62
	2	TYR	87	66	84	40	86	70	85	55
	3	SER	71	81	71	71	81	69	76	70
	4	ALA	86	81	79	69	81	64	80	67
	5	THR	51	61	62	70	68	74	65	72
	6	PHE	75	85	68	70	74	86	71	78
	7	THR	43	39	46	48	52	46	49	47
	8	TYR	62	80	68	82	62	79	65	81
	9	EDR	22	33	47	31	37	38	42	35

Average contact data (%) of terminal groups:

COO^- = 32
NH_3^+ = 43.5
ACE = 58
NME = 37.5

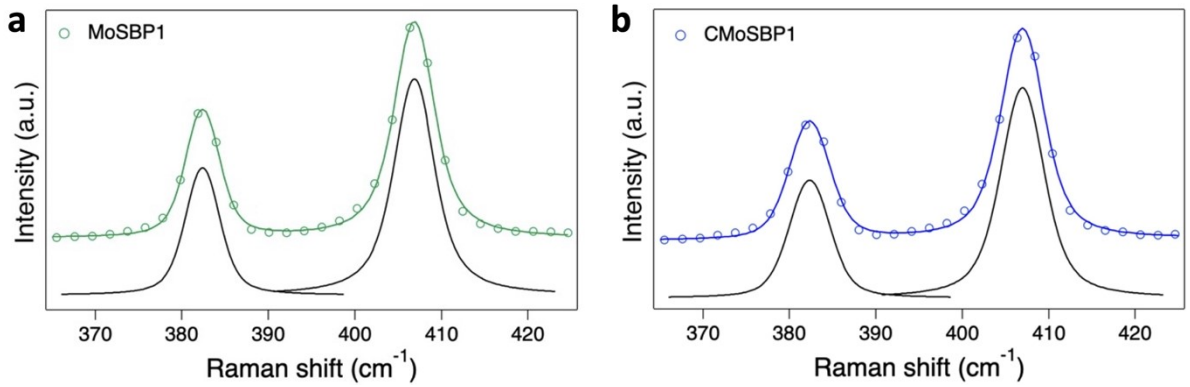

Figure S12. Voigt lineshape fitting of the MoS_2 peaks for the materials exfoliated with (a) MoSBP1 and (b) CMoSBP1.

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