Supplementary Information

Sample preparation

Peptide solutions were prepared following procedure describe by Reches and Gazit [29] Lyophilized L-diphenylalanine (FF) peptide (Sigma-Aldrich, USA) was solubilized in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Sigma-Aldrich, USA) to give a stock solution of 100 mg/ml. Stock solutions were further diluted to a working concentration of 5 mg/ml in ultra-pure water. The solution was then stored at 8° C (refrigerator) for 24 hs. The purification process consisted of centrifugation at 12,000 rpm for 15 minutes followed by remotion of the not-reacted supernatant reagent. As final step, micro/nanotubes of L-diphenylalanine sample (FF-MNTs) was kept at high vacuum (10^{-5} torr) for 24 hs at room temperature in the optical cryostat to remove the excess of HFIP and water.

Raman scattering measurements

The Raman measurements were performed in a triple spectrometer (T64000, HORIBA Jobin-Yvon) with a thermo-electrically cooled CCD detector (Synapse, HORIBA Jobin-Yvon). The 532 nm line of an optically pumped semiconductor laser (Verdi G5, Coherent) was used as excitation source. The laser power at the sample was maintained at 15 mW within a spot size of 100 µm. The samples were cooled in the cold finger of a 4 K ultra-low-vibration He closed-cycle cryostat (CS-204SF-DMX-20-OM, Advanced Research System). Measurements were performed in a near backscattering configuration in the $10 < T < 290$ K interval. Each spectrum was deconvoluted to a sum of Pseudo-Voigt lineshapes

$$I(\omega_0,\Gamma)=\left\{(1-s)\,e^{-\ln(2)\left(\frac{\omega-\omega_0}{\Gamma}\right)^2}+\frac{s}{1+\left(\frac{\omega-\omega_0}{\Gamma}\right)^2}\right\} \qquad \text{(S.1)}$$

where s is the shape parameter ($0\leqslant s\leqslant 1$), Γ is the full width at half maximum, and ω_0 the maximum frequency. Γ and ω_0 were computed for the vibrational modes of interest at each temperature.

Vibrational calculation

Density Functional Theory (DFT) [31,32] was used to obtain the equilibrium geometries and harmonic frequencies. Calculations were implemented in the Car-Parrinelo Molecular Dynamics program[33] by using the BLYP functional[34] augmented with dispersion corrections for proper description of dispersion of the interactions[35,36]. The cutoff energy of 75 Ry was set in all simulations. The Ramanactive vibrational modes calculations were performed on four subsystems of the FF-MNTs hexagonal arrangement

(i) nanochannels without water that were obtained from the crystallographic data [32] (FF-MNTs:dry on Fig. 1);

(ii) water pentamers clusters that were isolated from the nanochannel configuration ($5H_2O$ on Fig. 1);

(iii) water hexamers clusters that were isolated from the nanochannel configuration ($6H_2O$ on Fig. 1);

(iv) FF peptide bonded to one molecule of water (FF:$1H_2O$ on Fig.1).

due to prohibitive computational cost to perform calculation on overall system. The atomic connectivity between the atoms in the simulation box was fixed in each subsystem. Table S1 summarizes the calculations findings in the low frequency ($\omega<170\ \mathrm{cm}^{-1}$) region.

Table S1. Calculated vibrational modes frequencies and the corresponding assignment for FF-MNTs structure studied in the present work for $\omega<170\ \mathrm{cm}^{-1}$.

ω (cm^{-1})	Structure (refer to Fig. 1)	Assignment
33	$5H_2O$	$H^{donator} \cdots O$ stretching
41	FF:$1H_2O$	skeletal torsion+asymmetric twisting H_2O
54	FF:$1H_2O$	C^{β},C^{γ},C^{δ} out of plane + $CHCH_2$ stretching
65	FF:$1H_2O$	C^{β},C^{γ},C^{δ} out of plane + $CHCH_2$ stretching
82	$5H_2O$: $6H_2O$	$(H_2O)_4HOH \cdots O^{acceptor}H_2(H_2O)_5$ water dimer acceptor bend*
105	FF-MNTs:dry	Phe-Phe twisting
115	$5H_2O$	torsion in the plane
130	$6H_2O$	H-O-H in phase wagging
143	FF:$1H_2O$	H-C^{δ}; amine, $H^{donator}$ wagging
171	FF:$1H_2O$	H-C^{δ}; amine, $H^{donator}$ wagging

*This vibration assignment was based on experimental determination in $(D_2O)_2$ presented on ref. 37. This mode was absence in our calculations since it is possibly related to pentamer-hexamer water link.

Goodness of fit of Raman data

Figure S1 shows the deconvoluted experimental Raman data at 10 K (Fig. S1a) and 290 K (Fig S1b). The open circles are the experimental data. The solid line across the experimental data is the best fit to the sum of 10 pseudo-Voigt lines and a

Gaussian-like background (dashed line). The temperature dependence of the 5 (~ 82 cm^{-1}) and 8 (113 cm^{-1}) bands was studied in detail in this work. The excellent agreement between experimental data and fitted curve is a indicative of the good quality of the fit. The R^2 parameter was 0.980 and 0.996 for 10 K and 290 K data, respectively. The best parameters found are shown on Table S1.

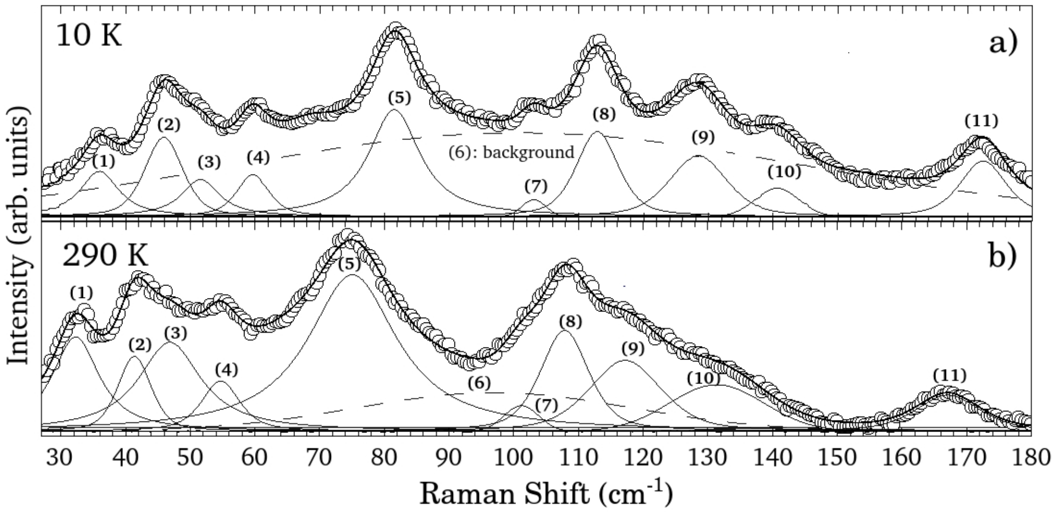

FIG. S1. Experimental Raman data (open circles) for FF MNTs at 10 K (a) and 290 K (b). The solid line across the experimental data represents the best fit to the sum of pseudo-Voigt profiles, including a Gaussian background, as described in the text.

Table S2. Best fitting parameters obtained from data shown on Fig. S1. $\delta\omega_0$ and δs are the errors on the last significant digit estimated from the fitting.

band	$\omega_0(\delta\omega_0)$ (cm^{-1})		$\Gamma(\delta\Gamma)$ (cm^{-1})		$s(\delta s)$	
	10K	290 K	10 K	290 K	10K	290K
1	36(1)	32(1)	3.6(5)	4.4(5)	0.9 (9)	1.0(9)
2	46 (1)	41(1)	3.5 (9)	3.0(2)	0.44(9)	0.44(2)
3	51.6(9)	47(1)	3.5(6)	5.8(3)	1.0(5)	1.0(5)
4	59.7 (8)	54.7(5)	2.9(3)	3.5(5)	0.7(5)	0.65(1)
5	81.5(1)	75.1(1)	4.8(2)	8.3 (6)	1.0 (3)	0.97(5)
6	100(10)	96 (10)	52(8)	25(10)	background	
7	103(2)	101(2)	2.2(8)	3.1(1)	0.0 (1)	0.0(1)
8	113 (1)	108(1)	3.9 (2)	4.4(4)	0.5(2)	0.5(2)
9	128.4 (2)	117(3)	5.2(4)	6(1)	0.4(2)	0.4(2)
10	141(1)	131.4(9)	4.0(5)	9.0(4)	0.0 (5)	0.0(5)
11	172(1)	167(2)	4.2 (2)	5.9(5)	0.5(2)	0.54(4)

Temperature dependence of 1,031/1,038 and 3,037 cm^{-1} modes

The hypothesis of hydrogen bond (HB) fluctuations be responsible for the dynamical transition observed in FF MNTs was tested by analyzing $\Gamma(T)$ of the 1,031/1,038 cm^{-1} benzene rings doublet and 3,037 cm^{-1} N-H stretching vibrational modes. The data is present in the Fig. S2. We notice the absence of crossover for these modes around T_W = 204 K. Moreover, the 1,031 cm^{-1} followed an Arrhenius behavior in the 10-290 K temperature range. As discussed in the main text, these facts excludes the effect on HB fluctuations in the Arrhenius-non-Arrhenius transition in the FF MNTs case.

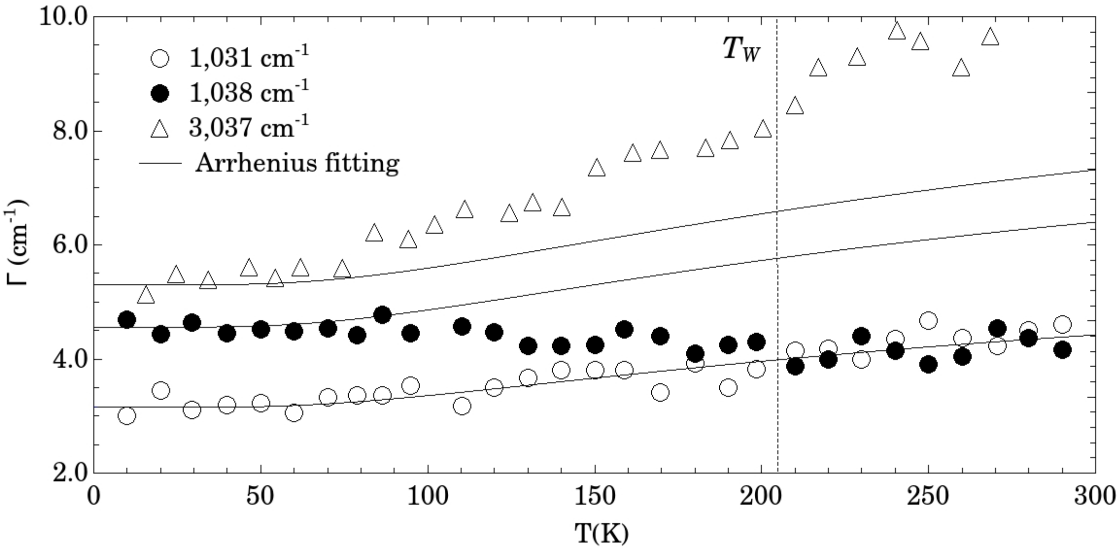

FIG. S2. Γ(T) for 1,031 (open circles)/ 1,038 (closed circles) cm^{-1} benzene rings vibrational mode doublet and 3,037 (open diamond) cm^{-1} N-H stretching. The solid and dashed lines are the Arrhenius fit to the experimental data. The vertical line indicates T_w=204 K.