Supporting Information

Peptide and Protein Dynamics and Low-Temperature/DNP Magic Angle Spinning NMR

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Notes:

1. GAMMA simulation parameters.

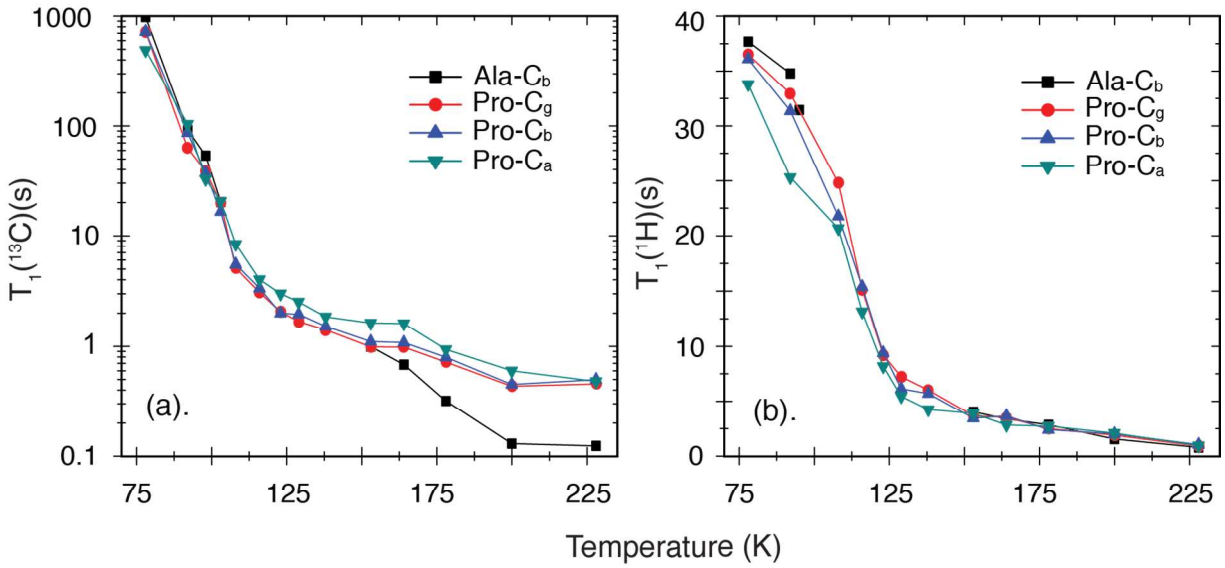

Figure S1: ^{13}C CP MAS Spin lattice relaxation, T_1 values at different temperatures for ^{13}C (right) and ^{1}H (left) measured with saturation recovery experiments. The T_1 values were acquired with $\omega_r/2\pi$ = 4.83 kHz, $\omega_{1H}/2\pi$ = 83 kHz for TPPM decoupling and $\omega_{0H}/2\pi$ □□□□□□Hz.

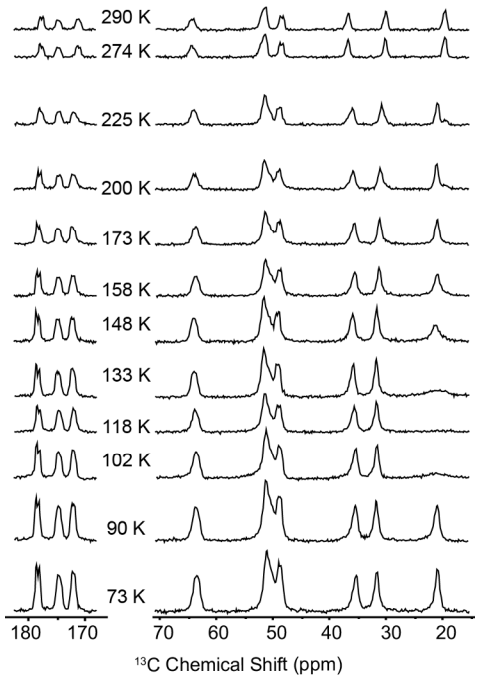

Figure S2. Temperature-dependent direct ^{13}C spectra of [U-^{13}C,^{15}N] APG. The spectral changes are plotted in **Figure 3c**. The spectra were acquired with $\omega_r/2\pi$ = 4.83 kHz, $\omega_{1H}/2\pi$ = 83 kHz for TPPM decoupling and $\omega_{0H}/2\pi$ □□□□□□Hz.

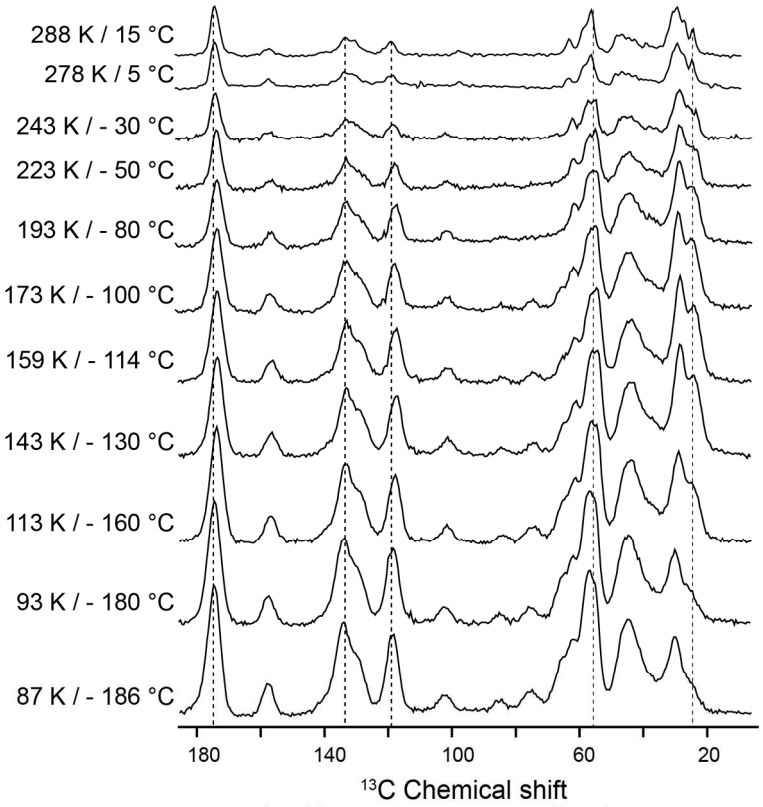

Figure S3. Temperature-dependent ^{1}H-^{13}C CP spectra of [^{13}C,^{15}N- FVYL]-PI3-SH3 amyloid fibrils. Sample was cryoprotected in d_8-glycerol/D_2O/H_2O (60/30/10 volume ratio). $\omega_r/2\pi$ = 7 kHz, $\omega_{1H}/2\pi$ = 100 kHz for TPPM decoupling and $\omega_{0H}/2\pi$ □□□□□□Hz.

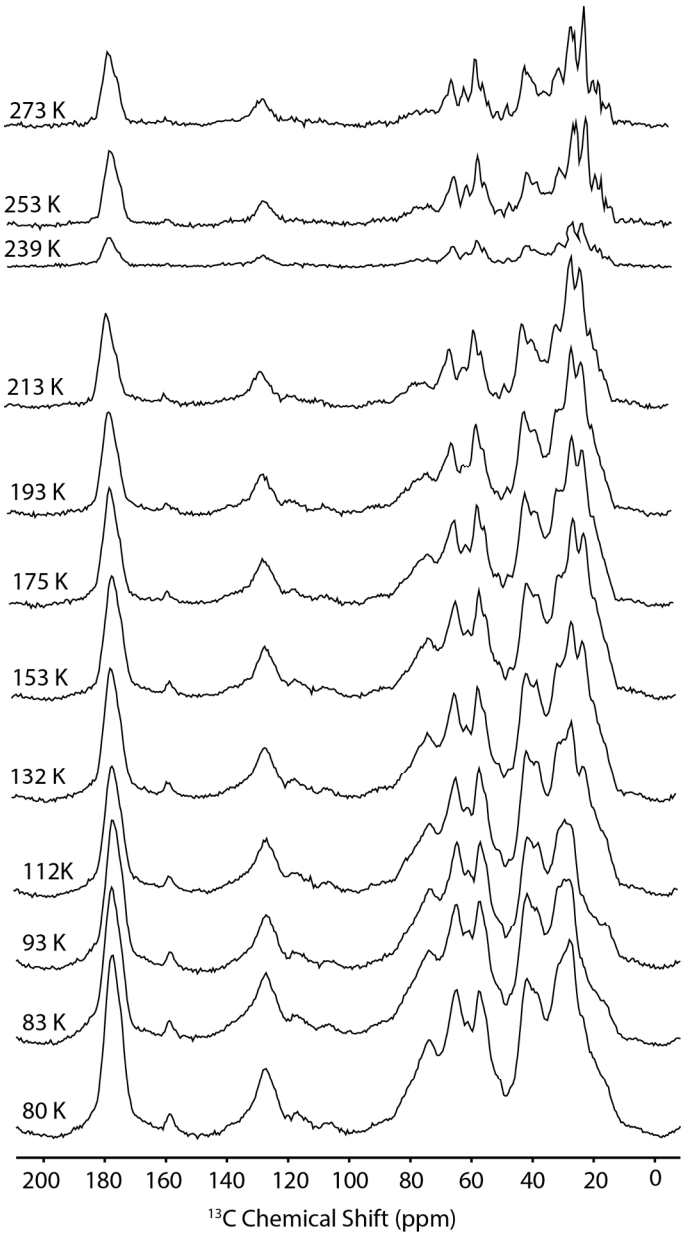

Figure S4. Temperature-dependent ^{1}H-^{13}C CP spectra of [^{13}C,^{15}N]- bacteriorhodopsin. Sample was cryoprotected in d_8-glycerol/D_2O/H_2O (60/30/10 volume ratio). $\omega_r/2\pi$ = 4.83 kHz, $\omega_{1H}/2\pi$ = 100 kHz for TPPM decoupling and $\omega_{0H}/2\pi$ □□□□□□Hz.

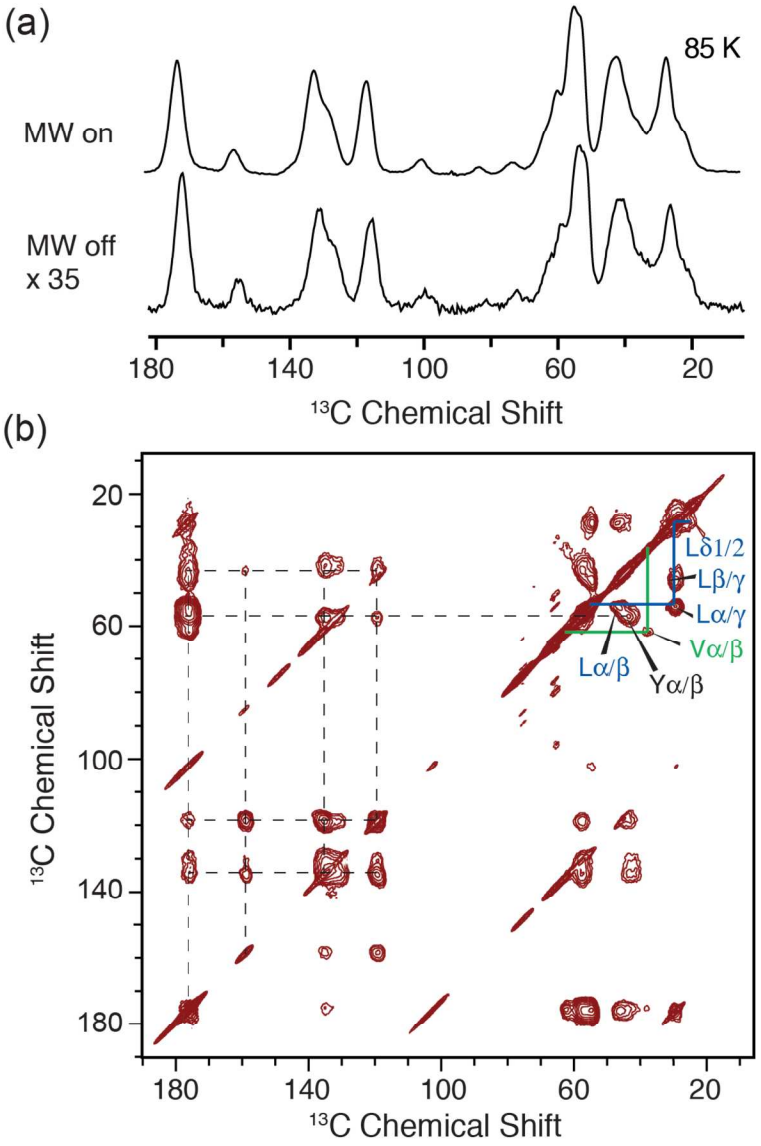

Figure S5. DNP-enhanced 1D and 2D spectra of [^{13}C,^{15}N-FVYL]-PI3-SH3 fibrils. (a) ^{1}H-^{13}C CP MAS NMR spectra at 88 K measured with (top) and without (bottom) DNP, an enhancement of 35 was obtained. The fibril was hydrated in 60/30/10 volume ratio of d_8-glycerol/D_2O/H_2O supplemented with 15 mM TOTAPOL. (b) DNP-enhanced 2D ^{13}C-^{13}C RFDR acquired with 1.6 ms of mixing time and a total experiment time of 4 hours. The dashed lines indicate the spin systems of tyrosine residues. The spectra were acquired with $\omega_r/2\pi$ = 7 kHz, $\omega_{1H}/2\pi$ = 83 kHz for TPPM decoupling, and $\omega_{0H}/2\pi$ =380 MHz.

The enhanced intensity greatly accelerates the acquisition of multidimensional spectra and allows the investigation of low-temperature structural and dynamic behaviors such as conformational disorder, polymorphism, and backbone and side chain motions. In the 2D RFDR spectrum of [^{13}C,^{15}N-FVYL]-PI3-SH3, methyl containing valine and leucine residues are recovered at 85 K.

Notes: GAMMA Simulation of 3-Site Hopping Mechanism

The details of the simulation performed for the results in Figure 7 will be discussed here.

The equation of motion for the density operator $\hat{\sigma}(t)$ is given as

$$\frac{d}{dt}\hat{\sigma}(t) = -i\hat{\hat{L}}\hat{\sigma}(t) \tag{1}$$

with the solution

$$\hat{\sigma}(t) = \exp\left(-i\hat{\hat{L}}t\right)\hat{\sigma}(0) \tag{2}$$

where

$$\hat{\hat{L}} = \hat{\hat{H}} - i\hat{\hat{K}} \tag{3}$$

while $\hat{\hat{\mathrm{L}}}$, $\hat{\hat{\mathrm{H}}}$ and $\hat{\hat{\mathrm{K}}}$ are the Liouvillian, Hamiltonian and exchange superoperators in the Liouville space. The Hamiltonian superoperator $\hat{\hat{\mathrm{H}}}$ can be constructed from the Hamiltonian $\hat{\mathrm{H}}$ in the Hilbert space as follows

$$\hat{\hat{H}} = \hat{H} \otimes \hat{1} - \hat{1} \otimes \hat{H} \tag{4}$$

In the context of this paper, the Hamiltonian $\hat{H}$ contains information about dipolar couplings, chemical-shifts and more importantly, the parameters used in ^{1}H decoupling. We have chosen a natural set of bases to represent the density operator $\hat{\sigma}$ of the four-spins methyl group, namely

$$\hat{\sigma} = |m_S m_{I1} m_{I2} m_{I3}, m_S' m_{I1}' m_{I2}' m_{I3}' > \tag{5}$$

where $m_S = \pm 1/2$ for the ^{13}C spin, and $m_I = \pm 1/2$ for the ^{1}H spin or $m_I = 0, \pm 1$ for the ^{2}H spin. The number of dimension N spanned by the density operator can be calculated easily, i.e. $N = (2 \times 2^3)^2 = 2^8 = 256$ for the CH_3 group and $N = (2 \times 3^3)^2 = 2916$ for the CD_3 group. The exchange superoperator $\hat{\hat{K}}$ in a hopping mechanism can be setup by considering all the possible permutations $\hat{\hat{P}}$ exhibited by the molecule.

$$\hat{\hat{K}}\hat{\sigma}_0 = \frac{k_{ex}}{M}(-n\hat{\sigma}_0 + \sum_{i=1}^{n} \hat{\hat{P}}_i\hat{\sigma}_0) \tag{6}$$

where $\hat{\hat{P}}$ is the permutation superoperator, M=3 for three-site hopping, n is the number of possible permutations, and k_{ex} is the hopping rate. For instance, when spin 1 hops and exchanges with spin 2, the spin states m_{I1} and m_{I2} exchanges and can be formulated as

$$\hat{\hat{P}}_{12}|m_S m_{I1} m_{I2} m_{I3}, m_S' m_{I1}' m_{I2}' m_{I3}' >= |m_S m_{I2} m_{I1} m_{I3}, m_S' m_{I2}' m_{I1}' m_{I3}' > \tag{7}$$

if $m_{I1} \neq m_{I2}$ and $m_{I1}' \neq m_{I2}'$.