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Supporting information

Re-entrant supramolecular interactions in inverse melting α-cyclodextrin·4-methylpyridine·water mixtures: an NMR study

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Supporting Figures and tables

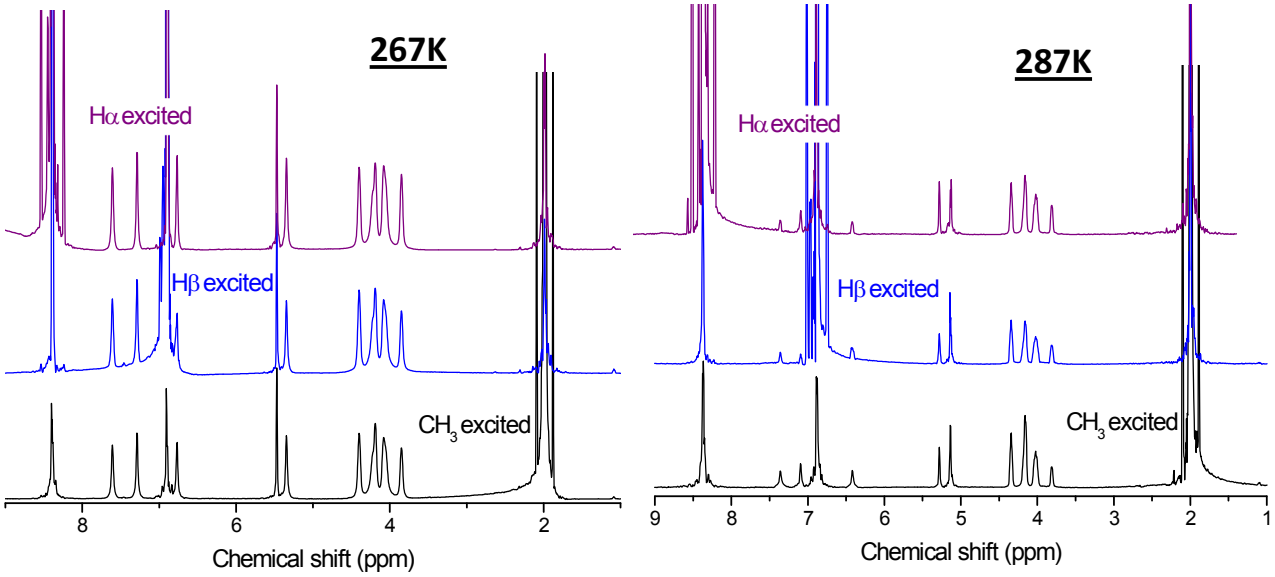

Figure S1: 1D-NOE spectra of αCD·4MP·H_2O mixture at 267K and 287K (projected from 2D-NOESY, excited protons are sighed).

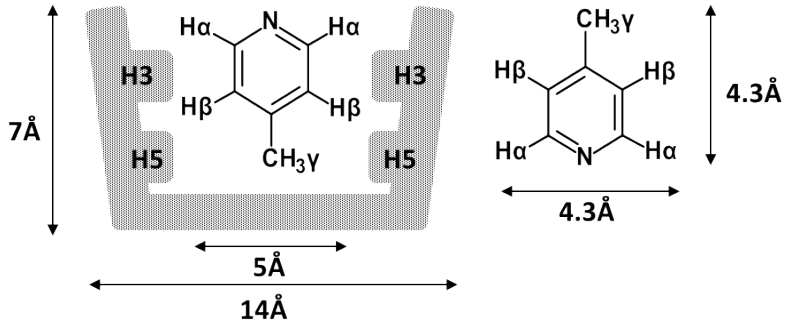

Figure S2: Two possible orientations for αCD-4MP host-guest complex; dimensions from literature[i].

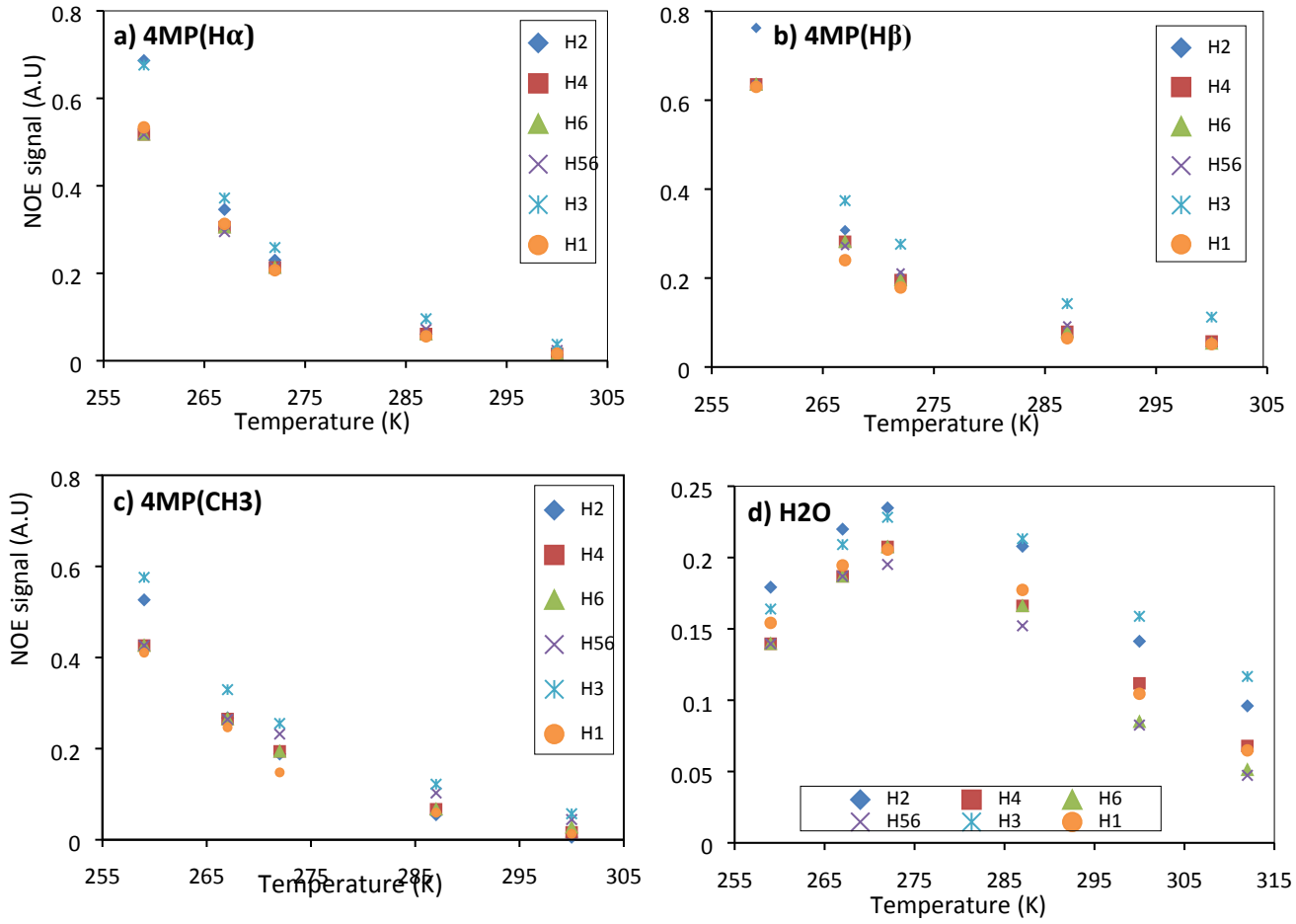

Figure S3: Relative integration of NOE signals vs. temperature of (a) 4MP(Hα) , (b) 4MP(Hβ), (c)4MP(CH_3) and (d) H_2O with αCD(H_1-H_6) for host-guest investigation in αCD·4MP·H_2O mixture.

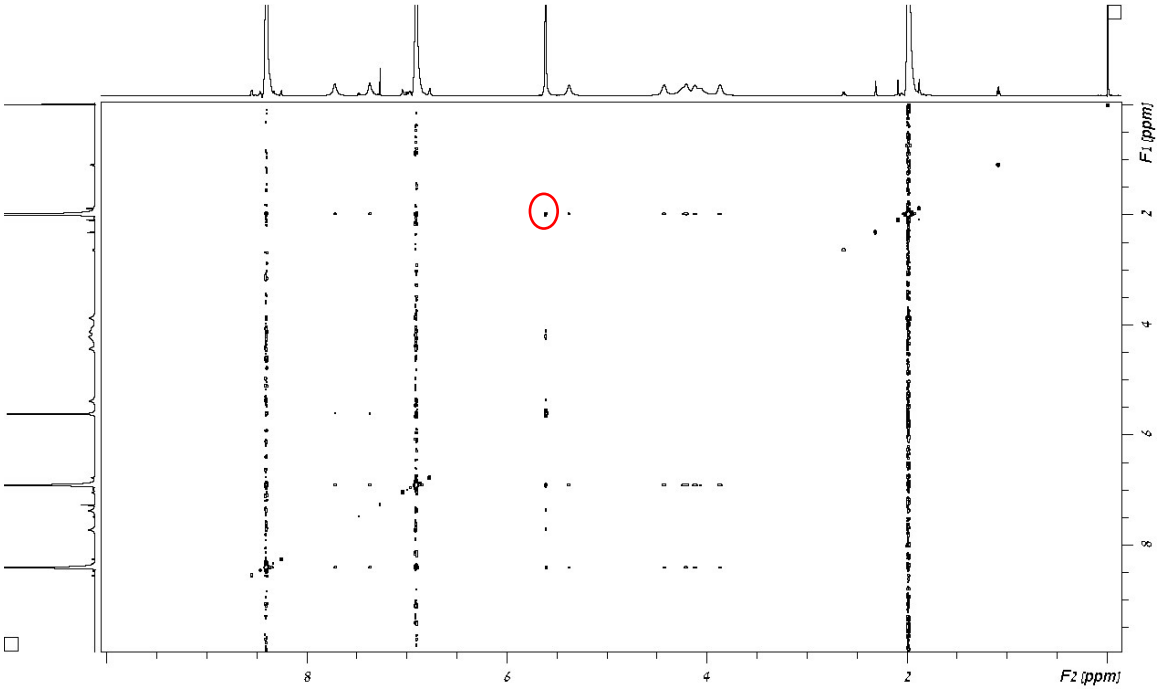

Figure S4: 2D-NOESY spectra of αCD·4MP·H_2O mixture at 259K. 4MP(CH_3)-H_2O cross peak is sighed.

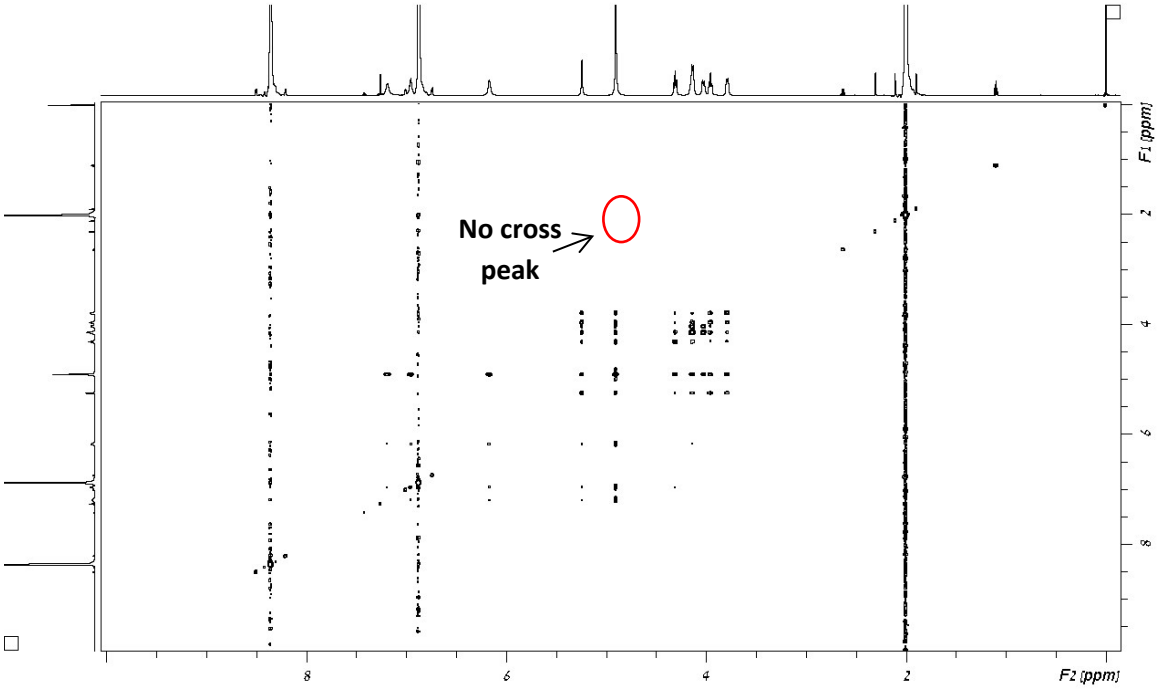

Figure S5: 2D-NOESY spectra of αCD·4MP·H_2O mixture at 300K, with no 4MP(CH_3)-H_2O cross peak.

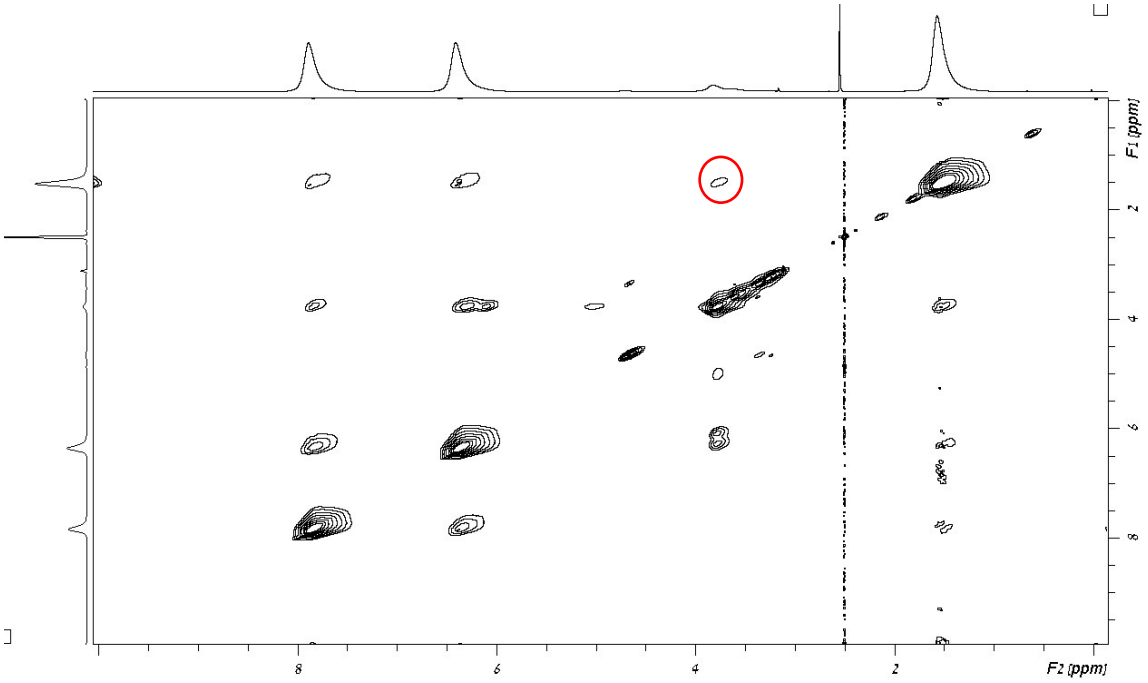

Figure S6: 2D-NOESY spectra of αCD·4MP·H_2O mixture at 335K. 4MP(CH_3)-H_2O cross peak is sighed.

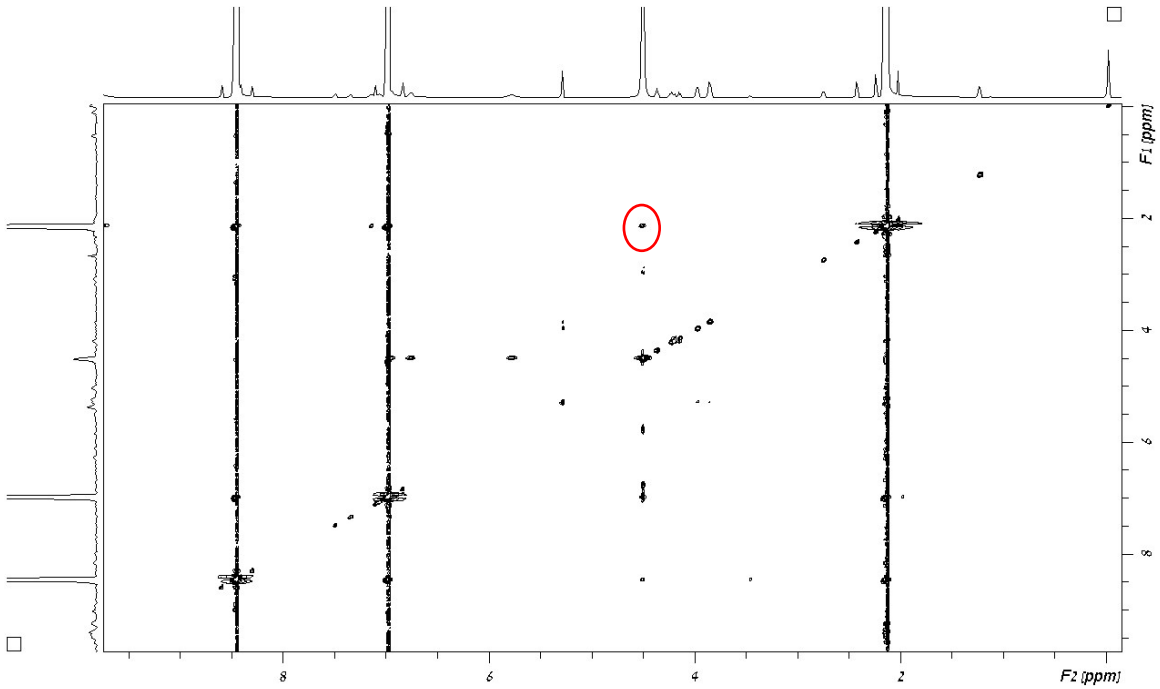

Figure S7: HRMAS 2D-NOESY spectra of αCD·4MP·H_2O mixture at 335K. 4MP(CH_3)-H_2O cross peak is sighed.

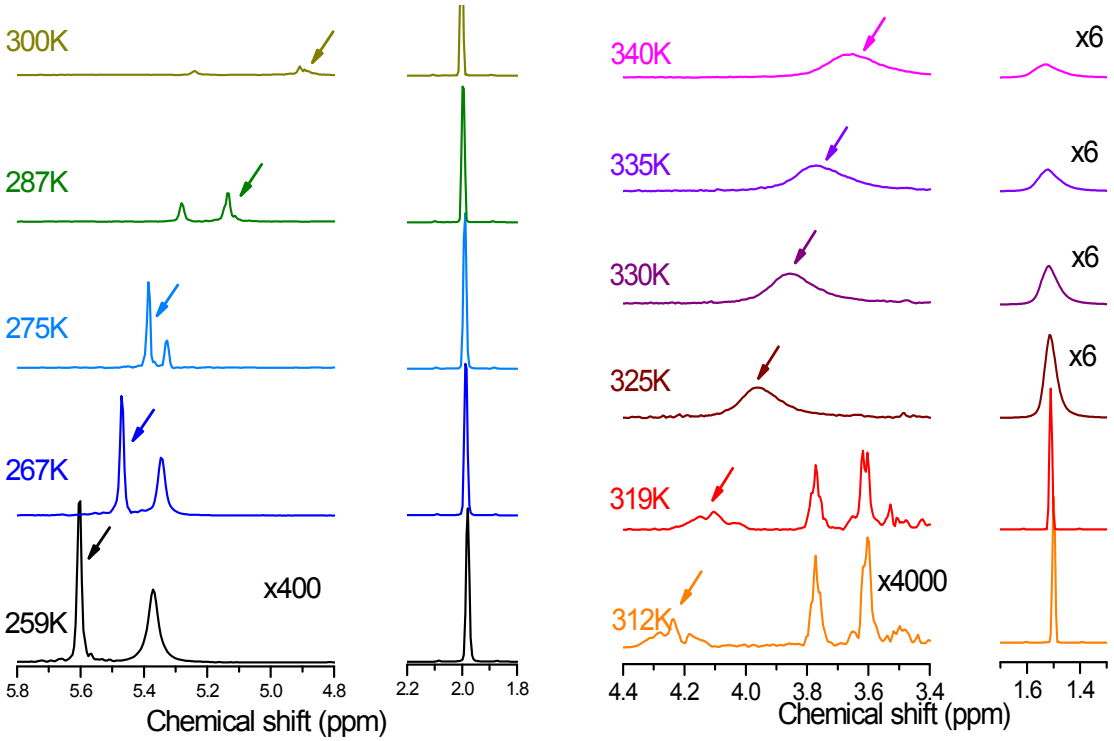

Figure S8: 1D-NOE spectra focused on 4MP(CH_3)→H_2O cross peak in αCD·4MP·H_2O mixture at different temperatures (projected from 2D-NOESY spectra, 4MP(CH_3) is excited). 4MP(CH_3) peak is at 1.5-2.0 ppm and its cross peak with water is sighed with an arrow. These cross peak were integrated and their normalized values at different temperature are shown in Figure 3 in the main article.

Table S1: Spin lattice relaxation time (T_1) values (in seconds) for the protons in αCD·4MP·H_2O mixture.

Temperature	4MP(CH_3)	DMSO	H_2	H_4	H_6	$H_{5,6}$	H_3	H_2O	H_1	4MP(H_β)	4MP(H_α)
293K	3.22 (0.14)[a]	2.3	1.03	1.04	1.03	1.03	1.03	1.03	1.02	4.84	4.43
312K	4.19 (0.15)[a]	3.6	1.03	1.03	1.02	1.03	1.03	1.03	1.03	5.85	5.94

[a] Long and (short) relaxation time due to bi-exponential fitting.

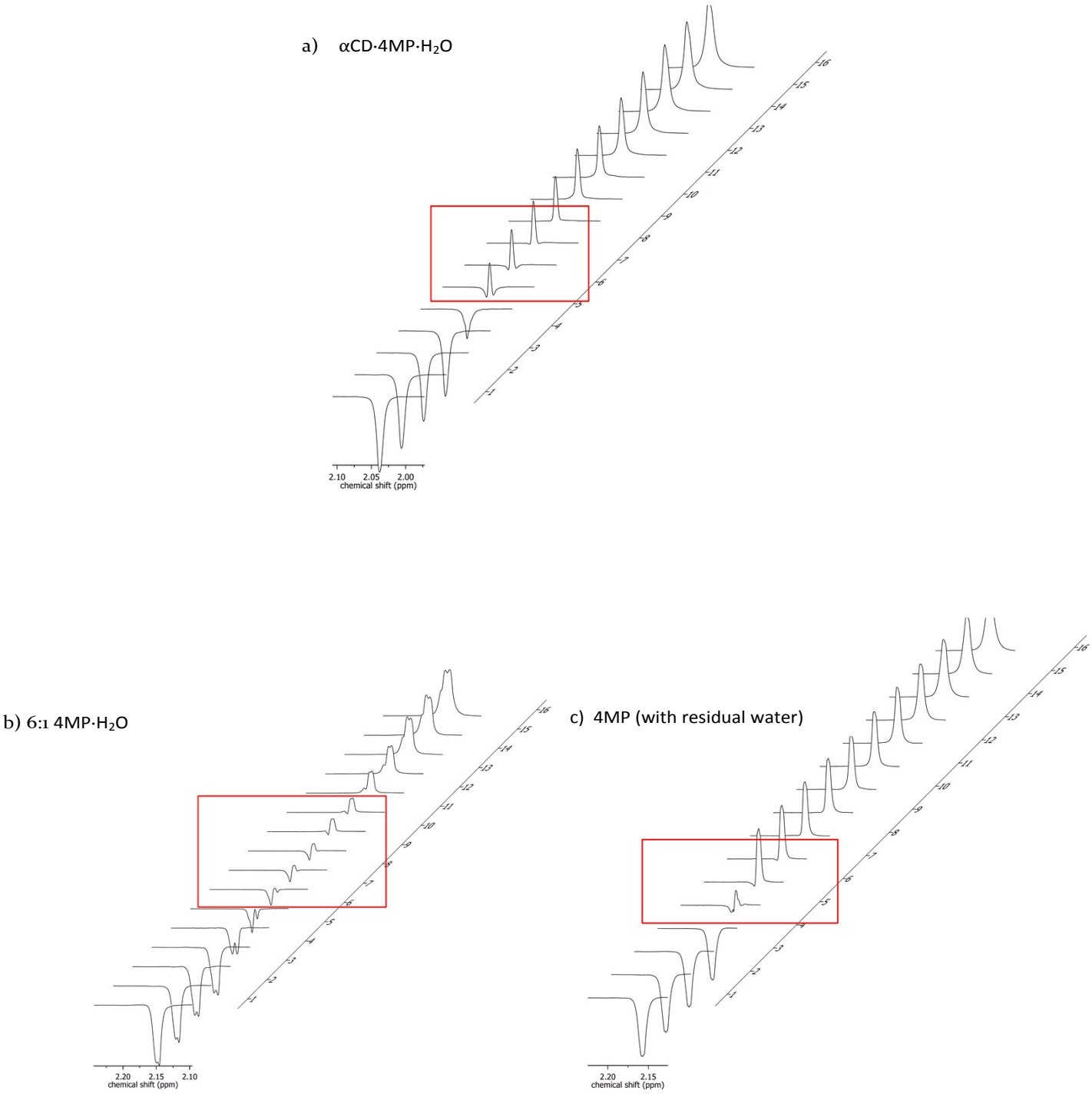

Figure S9: Inverse-recovery measurements of 4MP(CH_3) in a) αCD·4MP·H_2O, b) 6:1 4MP·H_2O and c) 4MP at 278±3K. Several populations with different relaxation times are clearly shown and sighed.

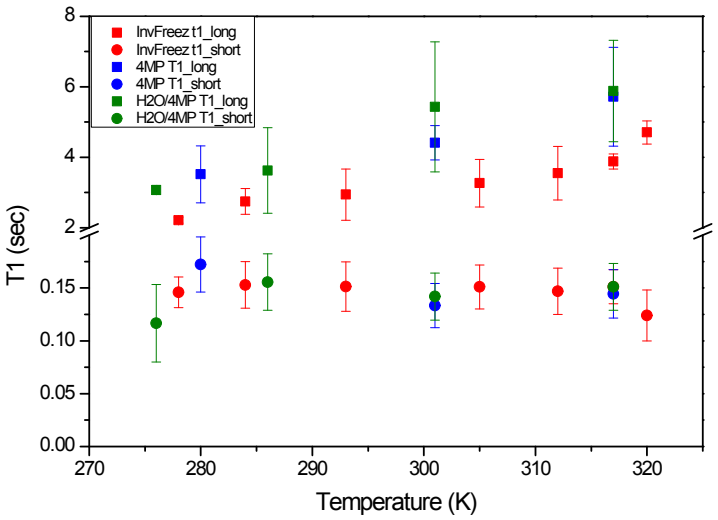

Figure S10: Temperature dependence of 4MP(CH_3) long (square) and short (circle) T_1 values of αCD·4MP·H_2O (red), 6:1 4MP·H_2O (green) and 4MP (blue). Error bars represent errors in fitting bi-exponential curves to data.

T_1 analysis of a peak with several populations was done by fitting the inverse recovery integration points to $Mz = \sum_{i=1}^{n} M_{0,i}(1 - 2\exp(-t / T_{1,i}))$. We found that bi-exponential fitting $Mz = M_{0,long}\left[1 - 2\exp(-t / T_{1,long})\right] + M_{0,short}\left[1 - 2\exp(-t / T_{1,short})\right]$ is sufficient, meaning that the 4MP(CH_3) populations could be divided to two main groups: with long and short relaxation times.

SI REFERENCES

[i] F. B. T. Pessine, A. Calderini and G. L. Alexandrino, in Book: *Magnetic Resonance Spectroscopy*, ed. D-H. Kim, InTech, Shanghai, 2012, 12, p. 237.