Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Analysis of Local Molecular Motions of Aromatic Sidechains in Proteins by 2D and 3D Fast MAS NMR Spectroscopy and Quantum Mechanical Calculations

Piotr Paluch, Tomasz Pawlak, Agata Jeziorna, Julien Trébosc, Guangjin Hou, Alexander J. Vega, Jean-Paul Amoureux, Martin Dracinsky, Tatyana Polenova and Marek J. Potrzebowski.

P. Paluch, T. Pawlak, Dr. Agata Jeziorna, Prof. M. J. Potrzebowski
Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Sienkiewicza 112, PL-90-363 Lodz, Poland
E-mail: marekpot@cbmm.lodz.pl

Dr. J. Trébosc, Prof. J.-P. Amoureux Unit of Catalysis and Chemistry of Solids (UCCS), CNRS-8181, University Lille North of France, 59652 Villeneuve d'Ascq, France
E-mail: jean-paul.amoureux@univ-lille1.fr
J.-P. Amoureux Physics Department & Shanghai Key Laboratory of Magnetic Resonance, East China Normal University, Shanghai 200062, China

Dr. Guangjin Hou, Dr. Alexander J. Vega, Prof. T. Polenova Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, USA
E-mail: tpolenov@udel.edu

Dr. Martin Dracinsky, Institute of Organic Chemistry and Biochemistry, AS CR, Flemingovo nam. 2, Prague, Czech Republic
E-mail: dracinsky@uochb.cas.cz

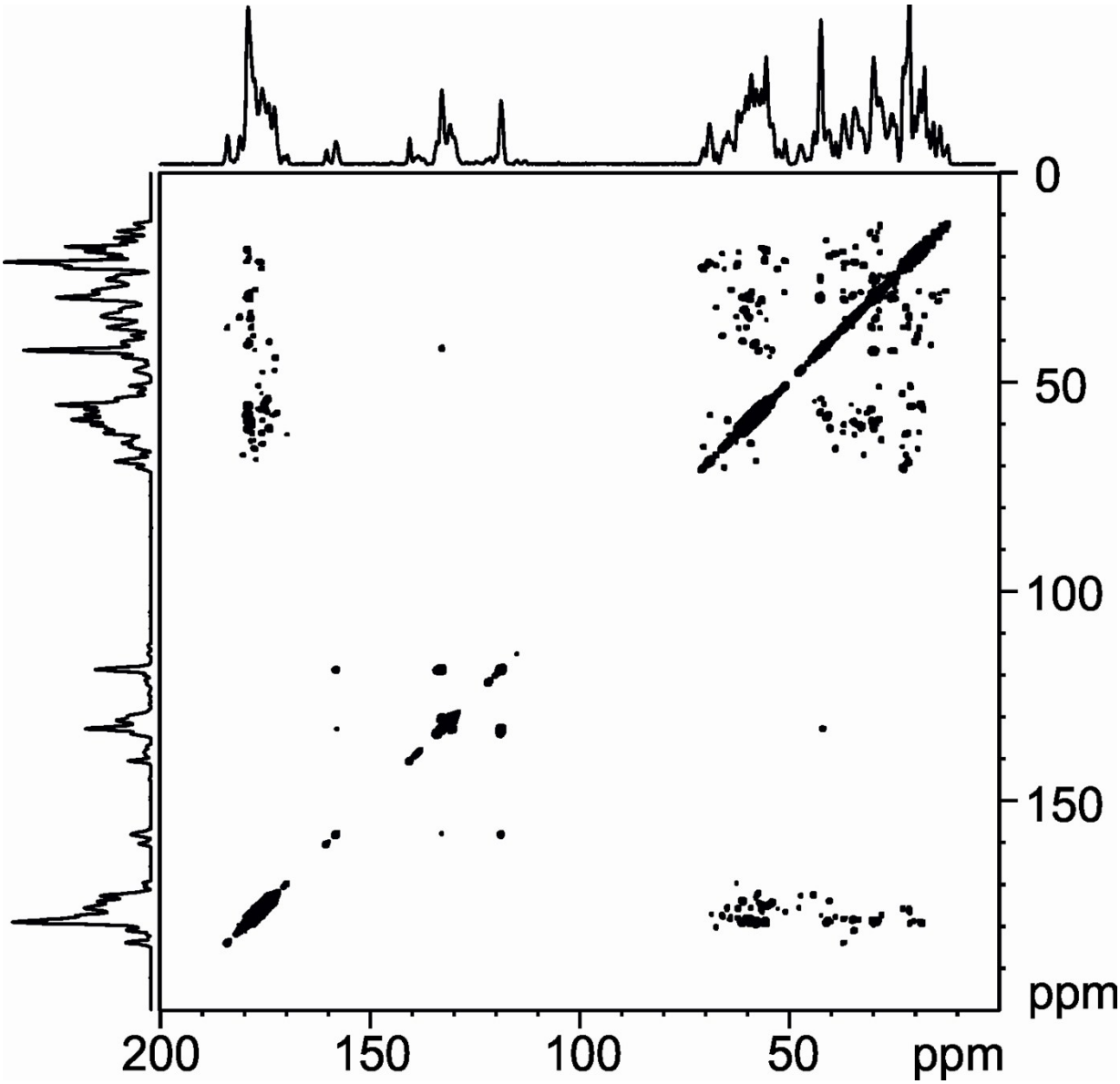

Figure S1. 2D ^{13}C-^{13}C RFDR spectrum of LC8 acquired with the mixing time of 16 ms.

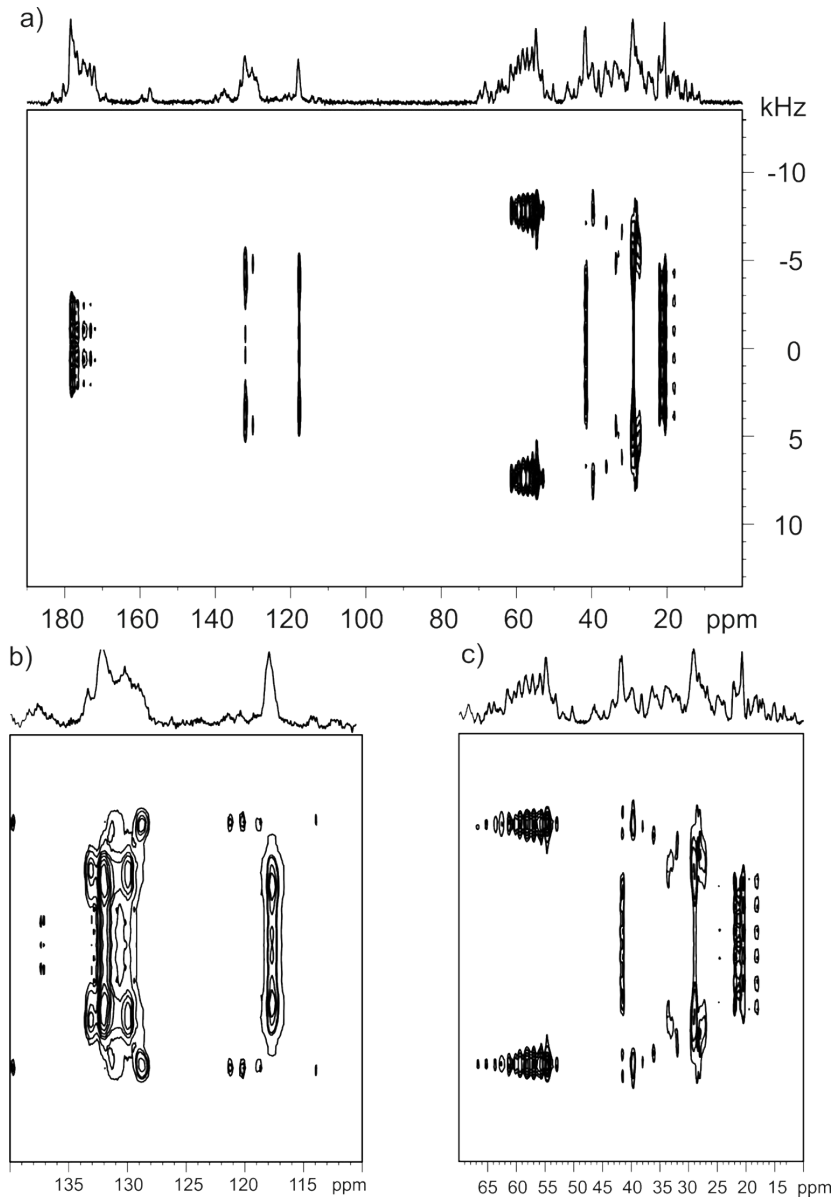

Figure S2. The 2D CPVC spectra of LC8 (a) and expansion around aromatic (b) and aliphatic (c) regions. The acquisition time was of 38.4 ms, the recycle delay of 2 s, the number of transients per *t1* step of 40, the number of *t1* steps of 128, thus giving a total experiment time of 3h. We used Swept-Frequency TPPM decoupling with RF = 10 kHz.

Table S1. ^{13}C Chemical Shifts of Aromatic Residues in LC8.

Residue	Cα	Cβ	C'	Cγ	Cδ1	Cδ2	Cε1	Cε2	Cε3	Cζ	Cζ2	Cζ3	Cη2	Cη2' (second conformer)
Y32	-	-	-	-	-	-	-	-	N/A	-	N/A	N/A	N/A	N/A
Y41	61.6	38.3	177.2	128.3	133.2	133	117.7	117.7	N/A	157.2	N/A	N/A	N/A	N/A
Y50	58.3	40.2	176.7	-	-	-	-	-	N/A	-	N/A	N/A	N/A	N/A
Y65	61	39.7	173	131.2	132.2	132.2	117.7	117.7	N/A	157.2	N/A	N/A	N/A	N/A
Y75	54.6	40.4	174.2	129.3	131.8	131.8	117.4	117.4	N/A	157	N/A	N/A	N/A	N/A
Y77	55.9	41.7	176.3	-	131.5	131.5	117.8	117.8	N/A	156.6	N/A	N/A	N/A	N/A
H55	55	33.9	174.4	136.2	N/A	119.4	138.9	N/A	N/A	N/A	N/A	N/A	N/A	N/A
H68	55.0	38.3	172.3	-	N/A	-	-	N/A	N/A	N/A	N/A	N/A	N/A	N/A
H72	53.9	40.2	174.0	-	N/A	-	-	N/A	N/A	N/A	N/A	N/A	N/A	N/A
F46	64	34.52	178.3	144	130.1	130.1	overlap with Cδ	overlap with Cδ	N/A	overlap with Cδ	N/A	N/A	N/A	N/A
F62	57.4	39.9	173.5	137.2	132.1	132.1	129.6	129.6	N/A	-	N/A	N/A	N/A	N/A
F73	57.92	42.3	172.5	137.5	131.2	131.2	129.9	129.9	N/A	-	N/A	N/A	N/A	N/A
F76	54.9	43.1	169.6	136.9	131.8	131.8	129.7	129.9	N/A	128.8	N/A	N/A	N/A	N/A
F86	56.4	42.3	172.3	138.4	131.7	131.7	130.8	130.8	N/A	129.1	N/A	N/A	N/A	N/A
W54	56	30	173.9	112.1	129.5	131		137.6	120.3	N/A	114.1	121.1	123.5	124.8

Table S2. Dipolar Interaction Parameters for the Aromatic Residues in YAF, GB1, and LC8 Obtained by 3D CPVC-RFDR NMR Spectroscopy.

Residue (Cross peak)	δ_{iso} (ppm)	ω_D (kHz)	η_D
YAF			
Y2 (Cδ1,Cδ2)	132.6	23.2	0.20
Y2 (Cε1,Cε2)	115.8	22.8	0.16
F3 (Cδ1,Cδ2)	129.4	12.3	0.42
F3 (Cε1,Cε2)	127.0	12.2	0.45
F3 (Cζ)	125.8	22.9	0.00
GB1			
Carbons on mobile residues			
Y3 (Cδ1,Cδ2)	133.3	14.5	0.46
Y33 (Cδ1,Cδ2)	132.1	14.3	0.04
Y33 (Cδ1,Cδ2-Cζ)	132.1	14.1	0.01
Y33 (Cε1,Cε2)	132.4	14.1	0.04
Y33 (Cε1,Cε2-Cγ)	132.4	13.9	0.05
Y33 (Cε1,Cε2-Cζ)	132.4	14.3	0.03
Y45 (Cε1,Cε2)	117.5	14.2	0.12
Carbons on rigid residues			
W43 (Cδ1)	127.0	22.2	0.10
W43 (Cδ1-Cγ)	127.0	22.7	0.03
W43 (Cε3)	120.1	22.6	0.10
W43 (Cε3-Cδ2)	120.1	22.4	0.08
W43 (Cε3-Cε2)	120.1	22.6	0.13
W43 (Cε3-Cγ)	120.1	22.6	0.07
W43 (Cε-Cη)	117.9	22.6	0.00
W43 (Cη2)	122.7	22.9	0.23
W43 (Cη2-Cε3)	122.7	22.8	0.01
W43 (Cη2-Cζ)	122.7	22.8	0.01
W43 (Cζ)	114.1	22.4	0.03
W43 (Cζ-Cδ)	114.1	23.3	0.19
W43 (Cζ-Cε)	114.1	22.9	0.01
W43 (Cζ-Cη)	114.1	23.3	0.19
F52 (Cε1,Cε2,Cζ)	131.0	21.8	0.00
F52 (Cε1,Cε2,Cζ-Cγ)	131.0	22.0	0.06
Carbons that do not carry a hydrogen			
W43 (Cε2)	138.2	2.7	0.42

W43 (Cε2-Cζ)	138.2	1.5	0.22
Y3 (Cζ)	158.4	3.6	0.49
Y3 (Cζ-Cε1,Cε2)	158.4	5.5	0.16
Y33 (Cζ)	158.4	5.0	0.80
Y33 (Cζ-Cε1,Cε2)	158.4	5.2	0.07
Y45 (Cζ)	157.3	5.6	0.11

LC8			
Carbons on mobile residues			
Y41 (Cε1,Cε2)	117.3	11.6	0.49
Y41 (Cε1,Cε2-Cζ)	117.3	12.4	0.69
Y41 (Cδ1,Cδ2)	132.8	14.0	0.32
Y41 (Cδ1,Cδ2-Cε1,Cε2)	132.8	14.2	0.27
Y41 (Cδ1,Cδ2-Cγ)	132.8	14.4	0.30
Y65 (Cδ1,Cδ2)	131.4	12.0	0.75
Y65 (Cδ1,Cδ2-Cε1,Cε2)	131.4	10.9	0.67
Y65 (Cδ1,Cδ2-Cζ)	131.4	13.1	0.46
Y65 (Cδ1,Cδ2)	131.4	12.0	0.75
Y75 (Cε1,Cε2)	117.0	11.9	0.76
Y75 (Cε1,Cε2-Cδ1,Cδ2)	117.0	10.4	0.59
Y75 (Cδ1,Cδ2)	131.5	12.2	0.70
Y75 (Cδ1,Cδ2-Cε1,Cε2)	131.5	11.2	0.66
Y75 (Cδ1,Cδ2-Cε1,Cε2)	131.5	12.3	0.60
Y77 (Cδ1,Cδ2-Cζ)	131.5	10.8	0.48
Y77 (Cε1,Cε2-Cζ)	131.3	11.6	0.66
F76 (Cδ1,Cδ2-Cε1,Cε2)	131.4	14.6	0.05
F76 (Cζ-Cγ)	128.8	21.9	0.26
Carbons on rigid residues			
W54 (Cζ2)	113.6	21.8	0.20
W54 (Cε3)	120.4	22.0	0.06
H55 (Cδ2)	118.4	21.7	0.17
H55 (Cδ2-Cγ)	118.4	21.9	0.14
H55 (Cε1)	139.2	22.0	0.06
H55 (Cε1)	139.3	22.1	0.14

*The carbon atom whose dipolar lineshape is recorded is listed first; diagonal peaks are labeled with a single frequency.