Supplementary Information: Zero- to Low-field Relaxometry of Chemical and Biological Fluids

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A. Experimental setup and measurement sequence

Figure S1 shows the experimental sequence (a) and experimental apparatus (b) used in ZULF NMR relaxometry. The presented traces show the time profiles of magnetic fields in all spatial directions. After thermal prepolarization in the field of the permanent magnet of 1.4 T for the time τ_{pol} (≈ 15 s), the sample was mechanically shuttled to the ZULF detection region (inside a multi-layer magnetic shielding). The spatial orientation of sample polarization inside the shield was provided by the guiding field of a solenoid extending from the magnet to the detection region and eventually piercing the shield (not to generate magnetic field outside of the solenoid in the shield). After reaching the detection region, the sample was first stored for a given storage time τ_{pol} (up to 15 s) in a magnetic field ranging between 0 and 500 µT. Then, a guiding field was switched off (within 20 µs) and, if needed, a magnetic-field pulse of optimized amplitude B_{pulse} and length τ_{pulse} was used to generate ZULF NMR signals. The additional detection field B_{det} (from 0 to 0.1 µT) was applied during the ULF NMR measurements. Nuclear-spin evolution took place inside a four-layer magnetic shielding and it was measured with the use of an atomic magnetometer [1]. Shim coils, placed inside the shield, were used to cancel residual magnetic fields and achieved ZULF conditions (see details in Ref. [2–4]), while the pulse coils provided guiding fields and DC pulses to manipulate nuclear spins.

B. T_1 relaxation of ^{15}N-methylpyridinium at high magnetic field

To further investigate atypical relaxation properties of ^{15}N-methylpyridinium in H_2O and D_2O solutions (see main text), we performed additional high-field study of T_1 relaxation of this compound. The high-field, chemical-shift-resolved ^{1}H spectra of ^{15}N-methylypridium in D_2O and in the mixture of D_2O and H_2O are shown in Fig. S2. The data reveals a ≈ 0.6 ppm shift of the main peak towards smaller values in H_2O/D_2O solution. The high-field relaxation times T_1 of ^{1}H and ^{15}N, extracted from the experimental data, are shown in Table S1. The results indicate 1.8-3.6 times longer longitudinal relaxation time T_1 when using non-deuterated water as a solvent. The increase in both ^{1}H and ^{15}N relaxation times is consistent with the ULF NMR data of strongly coupled heteronuclei presented in the main text.

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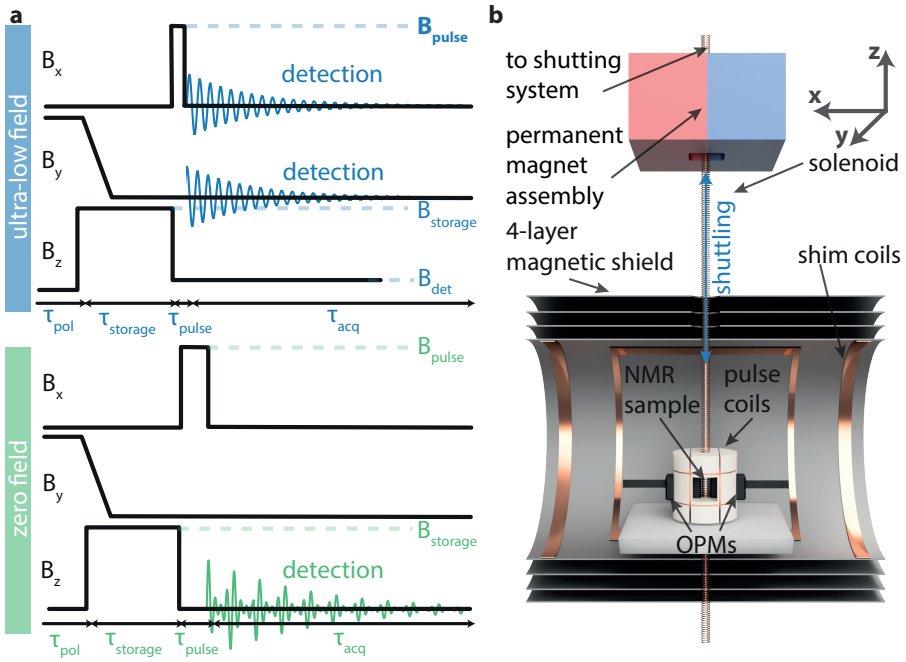

FIG. S1. (a) Measurement sequences (schematic magnetic field profiles) used in relaxometry studies performed under ultra-low field (top) and zero-field conditions (bottom). (b) Experimental setup used to perform ZULF NMR measurements.

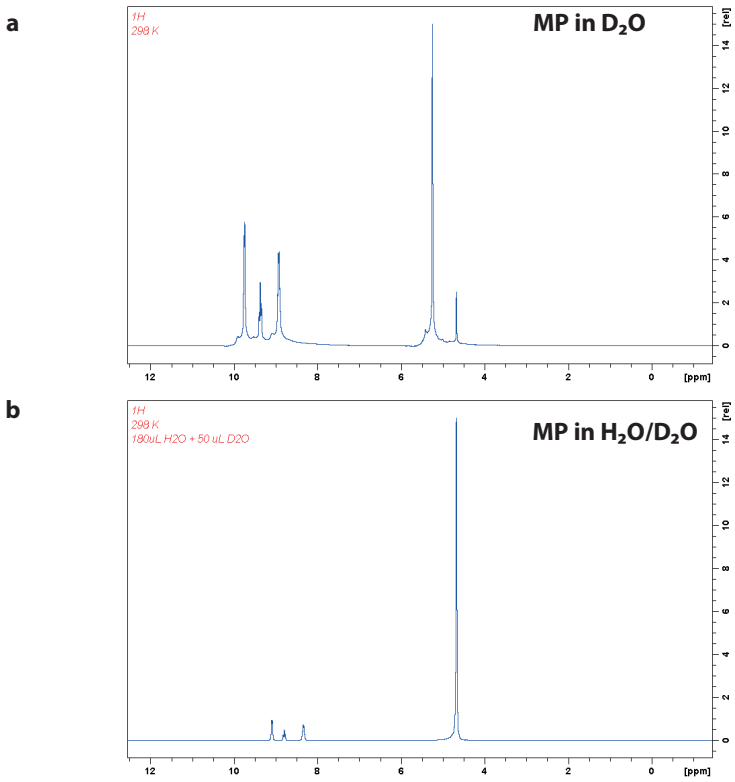

FIG. S2. ^{1}H spectra of ^{15}N-methylpyridinium in (a) D_2O and (b) H_2O/D_2O mixture in high field.

TABLE S1. Relaxation time T_1 of ^{15}N-methylpyridinium measured at high (7 T) field.

^{1}H			
in D_2O		in H_2O/D_2O	
Chemical shift (ppm)	T_1 (s)	Chemical shift (ppm)	T_1 (s)
4.67	1.8	4.67	3.2
5.2	2.0	-	-
8.9	3.4	8.3	7.0
9.3	4.1	8.8	7.4
9.75	3.4	9.1	6.5
^{15}N			
in D_2O		in H_2O/D_2O	
201	40	201	144

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