Supplementary Information:

Liquid State DNP of Water at 9.2 T:
An Experimental Access to Saturation

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S1: Temperature distribution over the sample:

The temperature distribution over the sample in the MW cavity can be estimated by investigating the lineshape of the DNP enhanced signal (inverted peaks) with respect to the reference signal (left figure). A schematic distribution of the electric component (E-field) and the magnetic component (B-field) of the TE_{011} mode in MW cavity which leads to heating and to DNP enhancement, respectively, is indicated (right figures). The E-field component of the MW field vanishes at the MW cavity axis, which is the preferable position for an aqueous sample with high dielectric losses. Any portion of the sample placed off the cavity axis will be exposed to the E-field component of the MW field, resulting in heating. The larger the capillary ID the larger the portion of the sample will be exposed to the E-field component of the MW field, resulting in a stronger sample heating. The signal lineshape is determined by the cylindrical shape of the DNP sample and its transversal orientation to the applied magnetic field B_0. At 25°C the signal is about 0.56 ppm broad, whereas after applying MW the signal becomes broader according to applied MW power. At 50°C and at 100°C the signal is about 0.71 ppm and 1.07 ppm broad, respectively. This corresponds approximately to a temperature gradient ΔT over the sample of 17°C and 55°C. However, the main part of the DNP enhanced signal remains in the 0.56 ppm region. We expect that this could be due to molecular diffusion along the sample which smoothes the temperature gradient. Peak positions have been used as estimates for the sample temperature. Since the peak
represents the central, and hence hottest, part of the sample, the given temperature values should be considered upper boundaries.

**S2: Additional experimental data:**

![Graphs showing MW power vs. integrated enhancement and NMR line shift](image)

Integrated enhancements (A,C) and corresponding NMR line shifts (B,D) plotted against the irradiation MW power, for 1 M (top) and 100 mM (bottom) $^{14}$N-TEMPOL in water samples, as well as pure water samples for NMR line shift comparison, for three ID capillary sizes: 50 µm (▲), 30 µm (■) and 20 µm (★). Sample in the capillaries of different ID is exposed differently to the E-field component of the MW field resulting in different heating of the sample. It is evident for the results in figures (A) and (C) for 50; 30 and 20 µm capillaries, that samples in the largest capillary of 50 µm can be heated up to 100°C with MW power below 100 mW while in case of 20 µm capillary more than 400 mW is necessary to reach the same sample temperature. The size of the paramagnetic contribution to the NMR lineshift of 1 M sample with respect to 100 mM sample is evident from figure (B) and (D).
**S3: Reference signal:**

Normalized reference signal amplitude as a function of $^{14}$N-TEMPOL concentration (left). Corresponding equidistantly spaced experimental spectra show the paramagnetic shift altogether with the reference signal broadening (right). Due to this strong amplitude dependence of the reference signal on the $^{14}$N-TEMPOL concentration we restrict our self to integral values, which remain the same for all used concentrations, for the DNP enhancement calculation.

**S4: Temperature calibration:**

In order to assign the sample temperature to each DNP experiment we perform a temperature calibration based on the relative shift ($\Delta \delta$) of the water peak and the CH$_2$ peak of ethylene glycol (inset figure A). Figure A shows the evolution of $\Delta \delta$ in a Bruker BBI liquid probe compared to a DNP probe upon gas heating in very good correspondence. Figure B shows the $\Delta \delta$ under MW irradiation.

NOTE: In the classical NMR probe the sample temperature could not be raised above 100°C because of boiling. Only with the very tiny DNP sample capillary super-heated water could be obtained by
microwave irradiation. Within the classical temperature range the differential chemical shift of both probes could be compared and gave very similar results. The DNP probe could be only heated by gas flow up to 60 °C, due to thermal expansion of delicate components of the home build DNP probe. Therefore the predictions of the superheated temperatures above 100°C result from linear extrapolations of the temperature calibration curves at lower temperatures and might not be quantitatively exact.

**S5: Coupling factors $\xi$ from NMRD:**

![Graph showing coupling factors $\xi$ from NMRD at different temperatures and proton Larmor frequencies.](image)

<table>
<thead>
<tr>
<th>NMR / EPR freq.</th>
<th>25 °C</th>
<th>35 °C</th>
<th>45 °C</th>
<th>55 °C</th>
<th>62 °C</th>
<th>72 °C</th>
<th>80 °C</th>
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</thead>
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<tr>
<td>15 MHz / 9.9 GHz</td>
<td>0.3501</td>
<td>0.3846</td>
<td>0.4064</td>
<td>0.4220</td>
<td>0.4276</td>
<td>0.4348</td>
<td>0.4384</td>
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<tr>
<td>140 MHz / 92 GHz</td>
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<td>0.0634</td>
<td>0.0856</td>
<td>0.1114</td>
<td>0.1304</td>
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<tr>
<td>400 MHz / 263 GHz</td>
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<td>0.0185</td>
<td>0.0255</td>
<td>0.0311</td>
<td>0.0419</td>
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<tr>
<td>600 MHz / 395 GHz</td>
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<td>0.0161</td>
<td>0.0221</td>
<td>0.0266</td>
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<tr>
<td>950 MHz / 625 GHz</td>
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<td>0.0074</td>
<td>0.0102</td>
<td>0.0124</td>
</tr>
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</table>

Coupling factors calculated at different proton Larmor frequencies using the parameters reported in Table 2.