Supporting Information
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69451 Weinheim, Germany
Experimental Procedures

Synthesis of polyacrylamide gel

30% Acrylamide (acryl)/N,N’-methylene bisacrylamide(bisacry) solution in water with three different acry/bisacry ratio 37.5:1, 29:1 and 19:1, tetraethylidiamine, and ammonium persulfate were purchased from BioRad and used without further purification. AMUPol was obtained from the Ouari and Tordo group and synthetized according to literature. Deuterium oxide (99.9 atom % D) and acetone (HPLC grade) were purchased from Sigma Aldrich. Polyacrylamide gels synthesized from acry/bisacry ratio 37.5:1, 29:1 and 19:1, and now referred to as A, B and C were prepared according to the literature. For this study, the synthesis of the gels yields about 500 mg of the desired product. Following this precise order: D₂O (480 μL, 26 mmol) was mixed with 30 % acrylamide: N, N’-methylene bisacrylamide ratio (A 37.5:1, B 29:1, C 19:1) (500 μL), then the initiator 10 % ammonium persulfate (8 μL, 0.8 mmol) and accelerator tetramethyldiamine (1 μL, 6.7 μmol) are added in an Eppendorf. The mixture is immediately vortexed for 30 seconds and left to polymerize for 15 minutes at room temperature. Following the gel formation, it is washed by using the breathing technique introduced by Pardo-Yissar et al. This consists of two steps: (i) collapsing of the gel: 1 mL of acetone is added to 60 mg of polyacrylamide gel three times to extract/expulse the water along with the impurities APS and TEMED found inside the gel. One can see the gel become white, as shown in Figure S4 (b). That step is followed by (ii) the swelling of the gel where 200 μL of D₂O is introduced back inside and left to diffuse for fifteen minutes. D₂O fills the gel which recovers its initial clear state (Figure 4 (a, c)). The breathing cycle is repeated four times. Once the gel is clean, the polarizing agent AMUPol is diffused in the gel. This is achieved by placing the gel in a AMUPol/D₂O solution of the desired concentration (vide infra). AMUPol was allowed to diffuse inside the gel for an hour at room temperature at a volume ratio of 1:1 gel to AMUPol in D₂O. In order to get different concentrations of AMUPol in the gel, various concentrations (5, 10, 20, 40, 60 mM) of AMUPol (726 g/mol) in D₂O were used to diffuse AMUPol in the gel. The supernatant is then removed with a micropipette and used to quantify, by ¹H solution NMR, the remaining amount of AMUPol in the supernatant and thus estimate the concentration of AMUPol in the gel.

Dispersion of nanoparticles inside gel

The breathing technique was used to disperse 150 M CdTe-COOH functionalized in D₂O inside 30 mg of gel. Extraction of the D₂O by adding 500 μL of acetone three times was followed by incorporating 20 μL of CdTe-COOH solution to swell the gel and diffused for 15 minutes. This cycle was performed until the total amount of CdTe-COOH solution (145 μL) was incorporated. 30 μL of 5 mM AMUPol/D₂O was diffused in 30 mg of gel for an hour.

DNP Enhanced NMR Spectroscopy

Typically, 30-50 mg of the gel described above was transferred to a 3.2 mm o.d. sapphire rotor and capped with a teflon plug. Data were acquired at either EPFL or CRMN using 263 GHz/400 MHz Avance I or III HD Bruker DNP solid-state NMR spectrometer, respectively, equipped with a 3.2 mm Bruker triple resonance low temperature magic angle spinning (LTMAS) probe and the experiments were performed at ca. 90-100 K. The sweep coil of the main magnetic field was set for the microwave irradiation occurring at the ¹H positive enhancement maximum of the AMUPol biradical. Enhancement factor, ε, is the ratio of the signal intensity with and without microwaves.

¹³C DNP Enhanced NMR Spectroscopy.

For ¹³C NMR (νc(¹³C) = 100.6 MHz at 9.4 T), the acquisition parameters used for a CPMAS experiment are: 2 s repetition delay, a ¹H π/2 pulse length of 2.5 μs to afford 100 kHz ¹H decoupling using the SPINAL-64 method, a contact time of 3 ms at a spinning frequency of 10 kHz.

¹¹³Cd DNP Enhanced NMR Spectroscopy.

For ¹¹³Cd NMR (νc(¹¹³Cd) = 88.7 MHz at 9.4 T) was referenced to Cd(CH₃COO)₂ 2H₂O δₚp(¹¹³Cd) = -14 ppm. The acquisition parameters used for a CP-CPMG experiment are: 3 s repetition delay, a ¹H π/2 pulse length of 2.5 μs to afford 100 kHz ¹H
decoupling using the SPINAL 64 method\(^{[3]}\), a contact time of 8 ms. For the CPMG part of the experiment a total of 500 echoes with 160 points per echo were acquired which provides spikelet separation equal to 2500 Hz at a spinning frequency of 10 kHz. 32160 points were acquired in the direct dimension. For the direct excitation CPMG experiment, the same parameters were used with the exception of 750 echoes were acquired, a longer recycle delay was necessary 300 s, and 240160 points were acquired in the direct dimension. The two-dimensional CP sideband separation in MAS (PASS) experiment the same conditions were used for the CP, and 600 steps were used.\(^{[4]}\)

![Figure S1](https://example.com/figure-s1.png)

Figure S1. Pulse sequences used to acquire Cd\(^{113}\) (I= ½, \(V_I = 88.73\) MHz) spectra, where (a) shows the CP-PASS, (b) CP-CPMG and (c) CPMG.

Quantitative solution NMR experiments.

Quantitative solution NMR experiments have been performed on a 700 MHz Bruker NMR magnet located at CRMN, equipped with an Avance III console and a TXI 5mm \(^1\)H/\(^{13}\)C/\(^{15}\)N/\(^2\)H liquid-state NMR probe. We used a gel synthetized and washed as described previously. The acry:bisacry ratio is 19:1 (gel C). After impregnation of 500 \(\mu\)L of gel with 500 \(\mu\)L of a 5 mM AMUPOL solution in D\(_2\)O, 250 \(\mu\)L of the supernatant is collected. The latter is first mixed with 300 \(\mu\)L of a solution in D\(_2\)O containing 28 mM of ascorbic acid and 1 mM of 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS). Ascorbic acid is introduced in large excess and reduces the nitroxide radicals of AMUPol. In order to make sure the reaction is complete, the solution is heated at 50°C for 10 minutes. DSS has been weighed precisely on a micro-balance (± 0.5 \(\mu\)g) and used as an internal reference for quantification. We acquired \(^1\)H spectra with a total recycling time of 47 s and 128 scans. Remaining water signals were removed using CW saturation of water peak during 4 s at 86 Hz prior to the excitation pulse (\(^1\)H pulse 34 kHz). Quantification is performed using the DSS peak at 0 ppm corresponding to Si(CH\(_3\))\(_3\) of DSS and the peak at 3.34 ppm assigned to CH\(_3\) of the reduced AMUPol. Resonance assignments of the mixture ascorbic acid, AMUPol (and their respective oxidized and reduced forms) and DSS have been done using a combination of COSY, edited HMQC and DOSY experiments. We found a concentration of AMUPOL in the supernatant of 1.19 mM and thus we can deduce the concentration of AMUPOL in the gel to be 3.81 mM. Reproducibility of this protocol has been tested using a different batch of gel and a second DSS/ascorbic acid solution (same concentration and volume), were we found a concentration of AMUPOL in the gel of 3.80 mM which is in good agreement with our hypothesis of 2.5 mM. Thus, we calculate the partition coefficient \(\mathcal{P}\) of AMUPOL between the gel and D\(_2\)O:
\[ \mathcal{P} = \frac{[\text{AMUPOL}]_{\text{gel}}}{[\text{AMUPOL}]_{\text{D2O}}} = 3.2 \]

Finally, we can estimate the concentration of AMUPOL in the gel as a function of the concentration of AMUPOL in the solution used to impregnate the gel. Note that for all gel impregnation, we used an equal volume of gel and AMUPOL solution.

<table>
<thead>
<tr>
<th>AMUPOL concentration in the solution used to impregnate the gel (mM)</th>
<th>Actual AMUPOL concentration in gel C (acryl bisacryl 19:1 ratio) (mM)</th>
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</thead>
<tbody>
<tr>
<td>60</td>
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<td>5</td>
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</table>

**Table S1.** Summary of final concentrations of optimized DNP Jelly radical concentration determined with quantitative solution NMR.

**DNP Data Processing.**

DNP enhancements were determined by comparing the integration of the resonance of interest for the spectra acquired with and without microwave using MatLab software v7.10. Proton spin lattice relaxation measurements were measured using saturation recovery experiment. Data are fit using a mono-exponential of the form: 

\[ S(\tau) = A \left( 1 - m \cdot e^{-\frac{\tau}{T_B}} \right) \]

where, \( A \) is the equilibrium signal intensity with microwave irradiation, \( S(\tau) \) is the integrated intensity at recycle delay time \( \tau \), and \( T_B \) is the build-up value acquired with microwave off. The CP-CPMG train of echoes were co-added using RMN software and the CP-PASS isotropic dimension was also treated in RMN.
Figure S2. Breathing technique used to wash the gel. The freshly synthesized gel is placed in acetone which has the effect to collapse and have a white aspect (shown by black arrows) (b). Then the gel (a) is placed in D$_2$O, and swells back to its original translucent form (b).

Figure S3. (a) $^{13}$C CPMAS DNP enhanced spectra of polyacrylamide gels A, B and C after a diffusion step with a 20 mM AMUPol solution in D$_2$O. The two $^{13}$C signals at 30 ppm and 175 ppm were assigned to the alkyl and amide carbons of the polyacrylamide gel. (b) Reproducibility tests performed on three different batch (CI, CII and CIII) of polyacrylamide gel C after a diffusion step with a 5 mM AMUPol in D$_2$O. After diffusion, the concentration of AMUPOL is 3.8 mM in the gel. Spectra with microwaves are represented with a solid line whereas spectra recorded without microwaves are plotted with dashed lines. All spectra were acquired with MAS rate set to 10 kHz and a 2 s repetition delay, where * denotes spinning side bands.
The $^1$H relaxation time measured with μwave off ($T_B$ off) as a function of the AMUPol concentration is plotted in Figure 1 (b). Build-up experiments with μwave off measure the average between short and long spin-lattice relaxation delays of protons in DNP jelly and in water. Protons in close proximity to the radical will have shorter $T_B$ compared to protons situated further away. As the concentration in radical decreases, the average relaxation weights less towards the protons in proximity to the radical. Hence, our results follow the expected trend that the $T_B$ decreases with increasing radical concentration, as relatively more protons are closer to radicals. Our experimental results are in agreement with previously reported studies for different formulations such as TOTAPOL in DMSO-d6/D$_2$O/H$_2$O (6/3/1 v/v),$^{11}$ TEMPO in glycerol-d8/D$_2$O (6/4 v/v)$^{5}$ or bTbK in tetrachloroethane.$^6$

![Figure S4](image1.png)

**Figure S4.** (a) DNP $\varepsilon_H$ (blue) and $\varepsilon_C$, CP (orange) of 10 mM AMUPol in glycerol-d8/D$_2$O/H$_2$O (6/3/1 v/v), glycerol-d8/D$_2$O (6/4 v/v) and D$_2$O/H$_2$O (9/1 v/v).

![Figure S5](image2.png)

**Figure S5.** Polyacrylamide gel at (a) room temperature, and (b) after flash frozen in liquid nitrogen. The glassing properties and transition of a polymer gel are not straightforward at 100 K. However, we observe good DNP $\varepsilon$ for frozen DNP jelly. The white opaque color might correspond to micro-domains of water crystalizing. The DNP process is not affected since they are micro-domains, i.e. radical concentrated zones are minimal.
Figure S6. (a) $^{13}$C CPMAS and (b) $^1$H DNP spectra of polyacrylamide gel C with dispersed CdTe-COOH NP acquired with 3.8 mM AMUPol/D$_2$O. MAS rate was set to 10 kHz and a 2 s repetition delay was used. Spectra with microwaves are represented with a solid line whereas spectra recorded without microwaves are plotted with dashed lines. * denotes spinning side bands. The $^{13}$C signal in (a) at 213 ppm was assigned to the C=O resonance of acetone (its presence is due to the breathing procedure).

Figure S7. $^{113}$Cd DNP CP$\cdot$CPMG acquired with microwave irradiation on (black) and off spectra of CdTe-COOH NP dispersed in gel C. Spinning sidebands can be depicted (MAS of 10 kHz) in the (CP$\cdot$)CPMG experiments.

Figure S8. 2D CP-PASS (orange) spectrum of CdTe-COOH NP dispersed in gel C.
References