Electronic Supporting Information for "Non-aqueous solvents for DNP Surface Enhanced NMR Spectroscopy."

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Experimental Details

DNP Solid-state NMR Experiment Details. All experiments were done on a commercial Bruker Avance 400 MHz DNP spectrometer, equipped with a 263 GHz gyrotron microwave system ($B_0 = 9.4$ T, $\omega_H/2\pi = 400$ MHz, $\omega_C/2\pi = 100$ MHz, $\omega_{Si}/2\pi = 79.5$ MHz).[1] The experiments done on the model hybrid mesoporous material containing surface phenolic groups (**I**)[2] were recorded using a double resonance CPMAS probe at a spinning frequency of 8 kHz. The NMR experiments recorded on compound **II** (Figure 3) were done using a triple resonance ^{1}H/^{13}C/^{15}N CPMAS probe at a spinning frequency of 12 kHz. All experiments were done with a sample temperature of ~ 105 K (± 10 K). Sapphire rotors were used in order to allow for better MW penetration into the sample. In the following tables all the acquisition parameters for all solid-state NMR experiments are listed. In all CP and 2D HETCOR, SPINAL-64 decoupling was applied during acquisition.[3] 2D HETCOR spectra were recorded with eDUMBO-1_{22} homonuclear decoupling in t_1 and a scaling factor of 0.56 was applied to correct the ^{1}H chemical shift scale.[4]

Synthesis and characterization of the materials. Anhydrous solvents were purchased from Aldrich and were used without further purification. The synthesis of the bTbK biradical was performed as previously described.[5] Compound **I** was synthesized according to previously described methods.[2]

Sample preparation for the quenching measurements. Samples for DNP SSNMR experiments were prepared by placing between 6.1 and 7.7 mg of dry material onto a disposable weigh boat (m_{dry}). 12 µL of the bTbK 1,1,2,2-tetrachloroethane radical solution was added to the material (m_{liq}) with a micro-pipette. The total mass of this impregnated material was then recorded. The material was then mixed by hand with a glass stir rod in order to homogeneously distribute the solution over the powdered sample. This impregnated material was then packed into a sapphire rotor. The rotors were weighed before and after packing of the impregnated material (which gives access to the mass of wet material inside the rotor, m_{in}). A polyfluoroethylene plug was then inserted. The mass of dry material was then determined by calculating the fraction of material inside the rotor which corresponded to dry material ($\mathrm{m}_{\text{dry,in}}$) using the formula:

$$m_{\text{dry,in}} = \frac{m_{\text{in}} m_{\text{dry}}}{m_{\text{dry}} + m_{\text{liq}}}$$

The knowledge of this mass is necessary to calculate the overall gain in sensitivity obtained by using the SENS approach compared to traditional NMR methods applied to dry powders. This is because the introduction of a paramagnetic radical in the porous material leads to a reduction in the signal intensities of the ^{29}Si CPMAS spectra due a variety of paramagnetic effects (see below).

Table S1. Acquisition parameters for solvent evaluation solid-state NMR experiments.

Pulse Sequence	CP/MAS	Pulse-Acquire
Nucleus	^{29}Si	^{1}H
MW On/ MW Off	MW On/Off	MW On/Off
Number of scans	512	8
Recycle delay (s)	1.0	1.0
Dwell time(μs)	5.6	3.3
Spectral width (kHz)	89.3	150
Spinning frequency (Hz)	8000	8000
Acquisition length (number of points)	800	2068
^{1}H 90° pulse width [π/2] (μs)	2.50	2.50
CP contact time (ms)	2.5	-
^{1}H rf field during CP contact pulse (kHz)	80	-
(Ramp 90-100)		
^{29}Si rf field during CP contact pulse (kHz)	50	-
^{1}H rf field during decoupling (kHz)	89	-
(SPINAL 64)[3]		

Table S2. Acquisition parameters for quenching (q_{Si}) measurement solid-state NMR experiments.

Pulse Sequence	CP/MAS[a]	CP/MAS[b]	Pulse-Acquire
Nucleus	^{29}Si	^{29}Si	^{1}H
MW On/ MW Off	MW On/Off	MW On/Off	MW On/Off
Number of scans	32/64	4/128	8
Recycle delay (s)	2.0	45.0	6.0
Dwell time(μs)	5.6	5.6	2.5
Spectral width (kHz)	89.3	89.3	200
Spinning frequency (Hz)	8000	8000	8000
Acquisition length (number of points)	800	800	512
^{1}H 90° pulse width [π/2] (μs)	2.80	2.80	2.80
CP contact time (ms)	2.5	2.5	-
^{1}H rf field during CP contact pulse (kHz) (Ramp 90-100)[3]	80	80	-
^{29}Si rf field during CP contact pulse (kHz)	50	50	-
^{1}H rf field during decoupling (kHz) (SPINAL 64))[4]	89	89	-

[a] Spectra acquired to measure ε. [b] Spectra acquired to quantify the quenching factor (q_{Si}). The "MW off" spectrum was acquired on **I** impregnated with pure solvent. A 45 s recycle delay was used to allow for full longitudinal relaxation.

Table S3. Acquisition parameters for ^{13}C solid-state NMR spectra of **II**.

Pulse Sequence	CP/MAS	HETCOR
MW On/ MW Off	MW On	MW On
Number of scans	1024	512
Recycle delay (s)	1.5	1.5
Dwell time (μs)	10	10
Spectral width (kHz)	50	50
Spinning frequency (Hz)	12000	12000
Acquisition length (number of points)	800	900
^{1}H 90º pulse width [π/2] (μs)	2.8	2.8
CP contact time (ms)	1.0	1.0
^{1}H rf field during CP contact pulse (kHz) (Ramp 90-100)[3]	70	70
^{13}C rf field during CPcontact pulse (kHz)	51	51
^{1}H magic pulse width (μs)	1.1	-
^{1}H rf field during DUMBO decoupling (kHz)	89	-
^{1}H rf field during SPINAL-64 decoupling (kHz))[4]	89	89
Number of increments in the indirect dimension.	50	-
Size of increment (μs) (STATES-TPPI)	67.2	-

*Calculation of enhancement and quenching factors***.** The different silicon-29 enhancement factors (ε, Σ and $\Sigma^{\dagger}$) and the quenching factor (q) used in the text are defined in this section. The DNP enhancement factor ε is measured from:

$$\varepsilon = \frac{I_{\text{on}}}{I_{\text{off}}}$$

where I_{on} and I_{off} are the integrated intensity of the isotropic resonances of the MW on and off spectra, respectively.

The presence of radicals in the pores of the material results in a reduction of signal via a number of different paramagnetic effects. We refer to the reduction in signal intensity as "quenching" and describe the magnitude of signal reduction with a quenching factor (θ):

$$\theta = \frac{I_{\text{on,[bTbK]}}}{I_{\text{EtCl4}}\,\varepsilon}\,\frac{m_{\text{dry, EtCl4}}}{m_{\text{dry,in}}}$$

where I_{on} and I_{EtCl4} are the integrated intensity of the spectra of the material impregnated with the bTbK solution and irradiated by MW at low temperature and of the spectra of the material impregnated with pure solvent respectively. e and $m_{\text{dry, in}}$ are the same as above, and $m_{\text{dry, EtCl4}}$ corresponds to the mass of dry SiO_2 material inside the rotor which was packed with material impregnated with pure tetrachloroethane.

The overall sensitivity enhancement (Σ), is defined as:

$$\Sigma = \frac{S/N_{\text{DNP}}}{S/N_{\text{dry,LT}}}\sqrt{\frac{T_{1,\text{wet}}}{T_{\text{DNP}}}}$$

Where S/N_{DNP} is the signal-to-noise ratio of a DNP spectrum of the impregnated material acquired with MW irradiation; $S/N_{\text{dry,LT}}$ is the signal-to-noise ratio in the spectrum of the dry material, recorded at low temperature. T_{DNP} is the DNP enhanced longitudinal relaxation time constant for material impregnated with radical solution. $T_{1,\text{ wet}}$ is the longitudinal relaxation time constant for the material impregnated with pure solvent. The T_1 of the material impregnated with pure solvent was chosen for the calculation of S due to the presence of molecular oxygen inside the pores of the pristine material. When the pristine material is spun with cold N_2 gas, the amount of oxygen in the pores varies. T_1 of the impregnated material was used as the reference point for Σ calculations. It was determined that impregnation with pure solvent only alters longitudinal relaxation rates and does not cause any substantial reduction in signal intensities.

As T_1 only changes by 1.5 s for **I** impregnated with pure solvent to the highest radical concentration, Σ is calculated here as the ratio of the signal-to-noise ratios. The total sensitivity enhancement ($\Sigma^{\dagger}$) takes into account the Boltzmann factor of 2.8 gained by doing the experiments at low temperature and is defined as:

$$\Sigma^{\dagger} \approx \frac{\Theta_{\text{rt}}}{\Theta_{\text{DNP}}}\Sigma = \frac{\Theta_{\text{rt}}}{\Theta_{\text{DNP}}}\frac{S/N_{\text{DNP}}}{S/N_{\text{dry,RT}}}\sqrt{\frac{T_{1,\text{wet}}}{T_{\text{DNP}}}}$$

Where Θ_{rt} is room temperature (298 K) and Θ_{DNP} is the sample temperature for the DNP experiments (ca. 105 K); $S/N_{dry,RT}$ is the signal-to-noise ratio in the spectrum of the dry material, recorded at room temperature.

DNP in frozen solution of tetrachloroethane

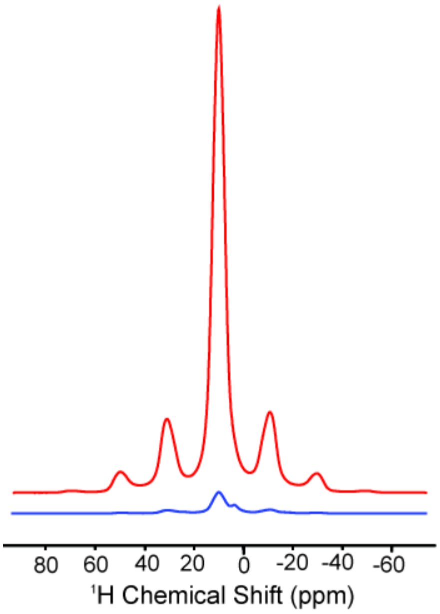

Figure S1. ^{1}H MW OFF (bottom) and ON (top) spectra of pure solvent in a frozen 16 mM solution of bTbK in tetrachloroethane (no material added). ε_H and ε_C values of 22 were obtained, consistent with the enhancements observed for surfaces, indicating there is no particular surface effect (this mixture should be a good all-purpose DNP polarizing solution).

Table S4. Proton to electron ratio for biradical solutions of varying concentration and different solvents.

Solvent	H:D Ratio	^1H Concentration (M)	$[^1H]/[e-]$ for 16 mM biradical solution	ε_{Si}
tetrachloroethane	100:0	18.9	5906	21
	75:25	14.2	4438	28
	50:50	9.5	2969	8
	7:93	1.3	413	6
Water	10:90	10.2	3188	-

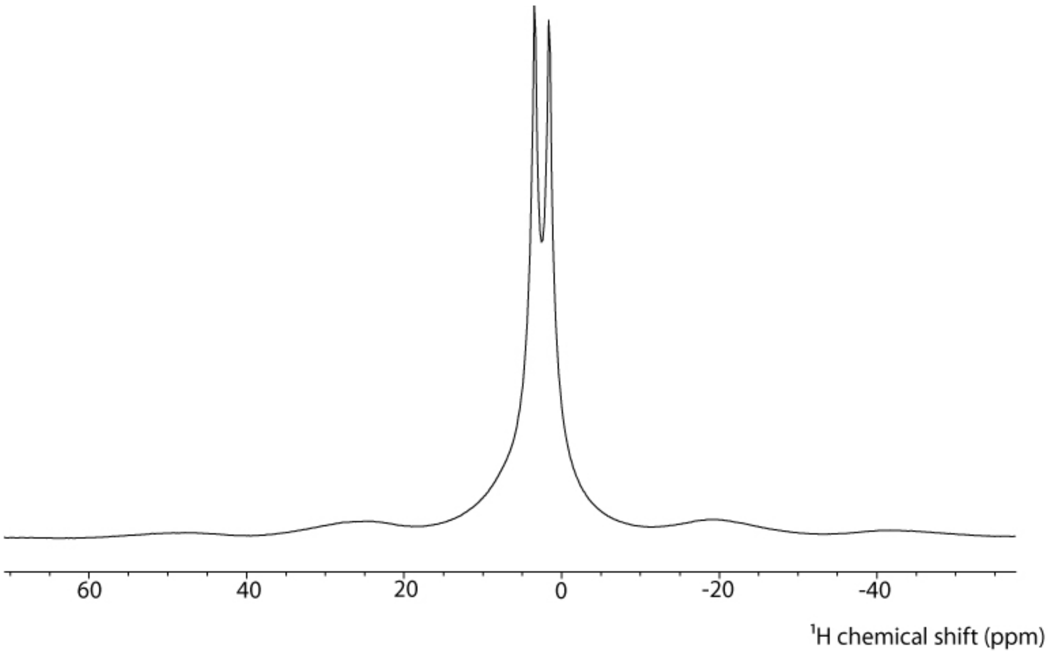

Fig. S2 Spectrum of **I** impregnated with THF acquired at a sample temperature of ca. 105 K with n_{rot} = 8000 Hz (8 scans, 1 s recycle delay).

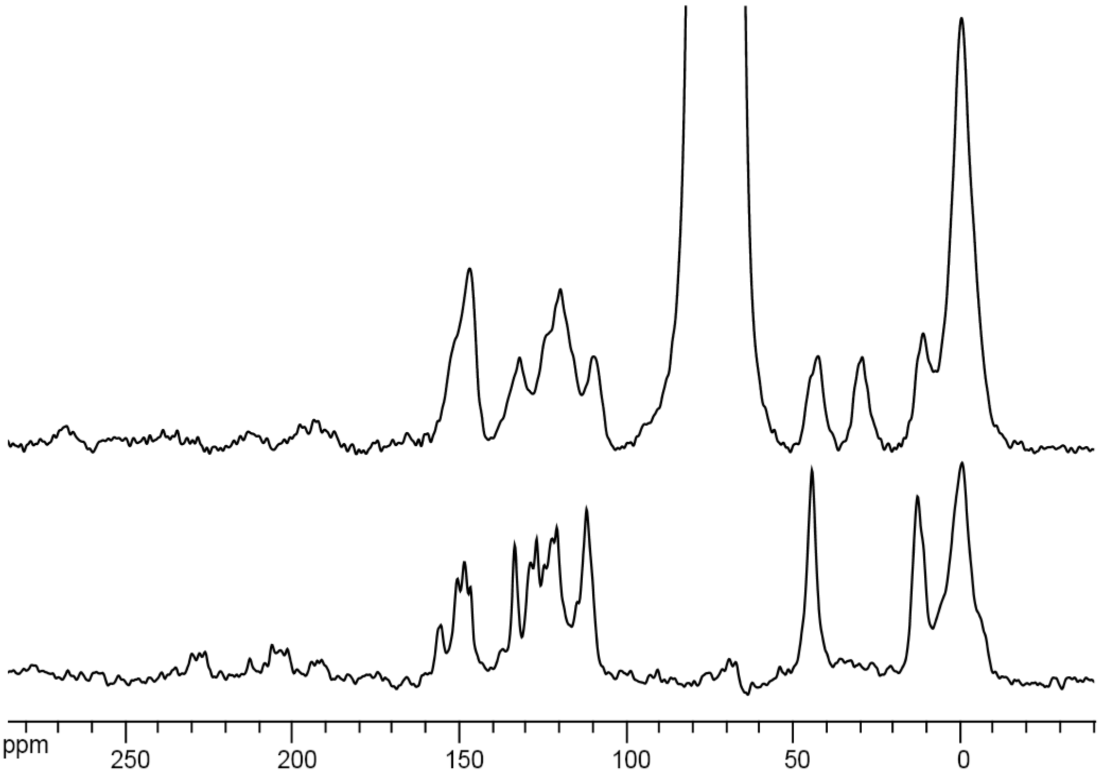

Fig. S3 (top) DNP ^{13}C CPMAS spectrum of **II** impregnated with a 14.8 mM bTbK tetrachloroethane solution. Experimenal details are provided in the main text. (lower) ^{13}C CPMAS of dry powdered **II** acquired on a 4 mm double resonance probe with a spinning frequency of 10 kHz and a CP time contact of 2 ms. 16000 scans were acquired with a 5 s delay in between scans (total experiment time of ca. 23 hours).

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