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Observing Nearby Nuclei on Paramagnetic Trityls and MOFs via DNP and Electron Decoupling

Kong Ooi Tan, Luming Yang, Michael Mardini, Choon Boon Cheong, Benoit Driesschaert, Mircea Dincă, and Robert G. Griffin

Abstract: Dynamic nuclear polarization (DNP) is an NMR sensitivity enhancement technique that mediates polarization transfer from unpaired electrons to NMR-active nuclei. Despite its success in elucidating important structural information on biological and inorganic materials, the detailed polarization-transfer pathway from the electrons to the nearby and then the bulk solvent nuclei, and finally to the molecules of interest-remains unclear. In particular, the nuclei in the paramagnetic polarizing agent play significant roles in relaying the enhanced NMR polarizations to more remote nuclei. Despite their importance, the direct NMR observation of these nuclei is challenging because of poor sensitivity.

Here, we show that a combined DNP and electron decoupling approach can facilitate direct NMR detection of these nuclei. We achieved an ~80% improvement in NMR intensity via electron decoupling at 0.35 T and 80 K on trityl radicals. Moreover, we recorded a DNP enhancement factor of ε ~ 90 and ~11% higher NMR intensity using electron decoupling on paramagnetic metal-organic framework, magnesium hexa-oxytriphenylene (MgHOTP MOF).

Introduction

Dynamic nuclear polarization (DNP) is an NMR hyperpolarization technique that mediates polarization transfer from unpaired electrons to NMR-active nuclei via microwave irradiations. For an ideal two-spin electron-¹H spin system, the maximum theoretical ¹H enhancement factor can reach $\epsilon \sim 658^{[3,5]}$. The method has allowed important structural information to be extracted from small molecules, biological samples, and inorganic materials. Despite many successful applications, there is no detailed understanding of how the large electron polarization is transferred to the surrounding nuclei, or where these nuclei are located relative to the polarizing agent. Subsequently, these “nearby nuclei” are important in mediating the enhanced NMR polarizations to the target molecules via the spin diffusion mechanism. Nevertheless, not all nearby nuclei contribute to the NMR signals observed in standard DNP experiments. Although the nearby nuclei are preferentially hyperpolarized in DNP due to the larger hyperfine interactions, their enhanced polarization might not propagate to the bulk nuclei if the spin diffusion mechanism is quenched. For example, these nuclei could have excessively broadened or shifted NMR lines and/or short $T_2$ relaxation times. Consequently, they will not be efficiently in contact with the bulk nuclei.

The region in which the hyperpolarized nuclei cannot efficiently participate in spin diffusion with the bulk nuclei is known as the ‘spin diffusion barrier’.

Motivated by the earlier studies, we have recently shown, using the three-spin solid effect, that the size of the spin diffusion barrier surrounding the trityl radical in a glassy glycerol-water matrix is $< 6 \text{Å}^{[19]}$. More recent experimental findings have also reported similar values for various radicals under different DNP conditions. Nevertheless, these conclusions are derived from indirect experimental results, and further information about these near nuclei-for instance, their NMR linewidths and relaxation rates ($T_1$ and $T_2$)-remains inaccessible using the standard DNP or NMR techniques. Hence, we hypothesize that a combined DNP and electron decoupling approach using two different pulsed microwave sources (see...
Experimental Section) can enable direct NMR observations of these nearby nuclei. In this manuscript, we define nearby nuclei as any intramolecular nuclei residing on the paramagnetic molecules with a distance of ≤1 nm away from the unpaired electrons. The nearby nuclei could be either inside or outside the spin diffusion barrier.

Our 0.35 T/15 MHz/9.8 GHz DNP spectrometer is equipped with two microwave synthesizers. The microwave frequency of the first source can be set to facilitate solid effect (SE) DNP, with two microwave synthesizers. The microwave frequency of unpaired electrons. The nearby nuclei could be either inside or magnetic molecules with a distance of

nuclei as any intramolecular nuclei residing on the para-
metered by the nitration process (Figure 1): [20] Additionally, the second microwave source is configured to perform electron decoupling, i.e., nutating EPR lines (\( \Omega_{\mu w2} = 0 \)), during the NMR detection period. Alternatively, a single frequency-agile microwave device that allows fast (microseconds) switching of \( \mu w \) frequencies can be employed. The first experimental evidence of the electron decoupling effect was demonstrated by Saliba et al. using such a device at 7 T. [21–23]

We expect that the study of nearby nuclei could not only shed light on spin diffusion and the fundamental DNP mechanism, but also help elucidate structural information of natural paramagnetic sites in functional biological molecules or inorganic materials, for example, metalloproteins or battery materials etc. [24,25] We will apply this methodology to study the metal–organic framework, magnesium 2,3,6,7,10,11-hexaoxytri-phenylene (MgHOTP MOF), which was recently demonstrated to be capable of quantum sensing Li\(^+\) ions using semiquinone-type radicals. [26] As the MOF itself is naturally paramagnetic, we show that the \( ^1H \) NMR signals can be DNP-enhanced by \( \epsilon \sim 90 \), followed by an additional \( \sim 11\% \) improvement in sensitivity via electron decoupling.

**Results and Discussions**

**Organic radicals**

A conventional solid-effect (SE) DNP experiment was applied to a Finland trityl sample dispersed in d-DNP juice using microwaves applied at the offset frequency \( \Omega_{\mu w1} = \omega_{\mu} \) at 0.35 T. [17,22–26] Subsequently, the first \( \mu w \) source was turned off and the second \( \mu w \) channel with a preset frequency \( \Omega_{\mu w2} = 0 \) was turned on (Figure 1) to facilitate electron decoupling (eDec) during the NMR acquisition. Note that eDec was applied throughout the solid echo and the FID period. We expected that the electron-decoupled \( ^1H \) NMR spectrum would have a maximum integrated intensity (less signal decay during solid echo) and narrowest lines (slower signal dephasing during FID) if efficient eDec is achieved. Indeed, the eDec frequency profile (Figure 2a) obtained by measuring the integrated intensity as a function of \( \mu w \) frequency showed that a \( \sim 80\% \) higher signal is achieved when the \( \mu w \) source is on-resonance \( (\Omega_{\mu w2} = 0) \) with the EPR line at \( \sim 9.771 \) GHz. Our results are in good agreement with those reported previously by Barnes and coworkers, despite significantly different experimental conditions. In particular, they measured \( ^13C \)-detected spectrum decoupled from electrons using frequency-chirped \( \mu w \) pulses with a gyrotrope under magic-angle spinning at 7 T fields. We also noted that the eDec performance depends on the \( T_{DNP} \) used in the polarization period. If shorter \( T_{DNP} \) values are employed, then more strongly coupled nuclei can be polarized and display a higher gain when electron decoupled. However, the NMR signal would be too weak to be observed if \( T_{DNP} \) is too short. Hence, we chose an intermediate value of \( T_{DNP} \) = 25 ms. Nevertheless, we emphasize that it is not our goal to pursue a condition (e.g., short \( T_{DNP} \)) in which the eDec is most efficient, but rather our goal is to differentiate the intramolecular nuclei from those in the solvent.

We also compared the 1D spectra (Figure 2b) with and without eDec. Although a more intense line was observed in the electron-decoupled spectrum, the normalized spectra (data

![Figure 1](image-url)
Figure 2. DNP and electron decoupling experiments performed on 5 mM Finland trityl sample in d-DNP juice at 0.35 T and 80 K. a) An EPR spectrum (blue) acquired with a field-swept spin-echo sequence is shown for reference. The electron decoupling (eDec) frequency profile (red) was obtained by varying the $\nu_{mw}$ frequency with a fixed 0.3484 T field. The frequency of the first $\nu_{mw}$ source was set to 9.786 GHz, with $\tau_{se} = 25$ ms to mediate the SE DNP using an offset frequency $\Omega_{se}/2\pi \sim 15$ MHz. Each NMR spectrum was recorded with an average of 4096 scans. b) 1D spectra acquired at the $\Omega_{se} = 0$ condition with the second $\nu_{mw}$ source used for electron decoupling turned on (red) or off (black). We have used $\tau_{se} = 10 \mu$s in these experiments. Note that switching microwave sources between the DNP and electron decoupling period can be performed in ≤5 ns.

not shown) showed little difference. This implies that the observed peaks are still predominantly broadened by the $^1$H homonuclear dipolar couplings, and we expect that the eDec effect will be more pronounced during the solid echo period during which the $^1$H–$^1$H couplings are attenuated. To confirm this, we measured the $T_2$ relaxation times (Figure 3a) under eDec by varying the solid-echo period ($\tau_{se}$). Although an effective $T_1$ ($T_1^{eff}$) is measured here instead of the actual stochastic-process-driven $T_1$, the $T_2$ sign is omitted to streamline the notation. Contrary to our expectations, although eDec resulted in overall higher line intensities, the $^1$H's coherence lifetimes appear to be shortened, i.e., the $T_1$ value decreases from 31 to 18 $\mu$s if it is electron decoupled. This anomaly could be related to the presence of some outliers in the mono-exponential fit, which implied that multiple NMR peak components might be present underneath the broad NMR spectrum. Thus, we inspected the 1D spectra and noted that the $\tau_{se} = 10 \mu$s spectrum is significantly broader (Figure 3b, bottom) than that acquired with $\tau_{se} = 55 \mu$s. This confirms that multiple components are indeed present within the poorly resolved $^1$H peak, and the overall relaxation cannot be quantified by a single $T_2$ value. Additionally, we noted a ~100 kHz broad component that appears only in the $\tau_{se} = 10 \mu$s (blue) spectrum, and the difference between the two (black) spectra revealed a Pake-like pattern that could encode rich electron-nuclear distance information. It is evident that eDec has revealed strongly coupled, and hence severely broadened, $^1$H peaks that are otherwise not visible under conventional NMR or DNP spectroscopy. We expect these methods could be extended to determine the sizes of hyperfine interactions that contain important structural information when pulsed DNP under MAS at high field becomes feasible in the future.\cite{31} To complete the analysis, we also determined the $T_1$ of nearby nuclei to be ~11 s, and the curve is well fitted with a mono-exponential function (Figure 3c) without significant outliers.

We had planned to assign the ~100 kHz broader components to the intramolecular $^1$H's on trityl. However, the assignment is not unambiguous because there is still too much residual solvent $^1$H, possibly originating from the atmospheric moisture. Hence, we prepared new flame-sealed samples of either $^1$H-Finland or $^1$H-Finland trityl dissolved in the near ‘100%’ perdeuterated DMSO juice (see Experimental Section). Despite our best attempt to unambiguously assign the more intense $^1$H peak in the $^1$H-Finland sample (Figure 3d) to the trityl $^1$H, there are still some $^1$H signals in the $^1$H-Finland sample. We attributed the unknown $^1$H source to the 0.5% potentially protonated chemical impurity in the $d_6$-DMSO solvent.

Having realized that preparing a completely $^1$H-free sample for control is very challenging, we turned to probing intramolecular $^{19}$F in fluorinated trityl radicals, dFT15F.\cite{32} Since $^{19}$F has a similar gyromagnetic ratio as $^1$H ($\gamma_{^{19}F}/\gamma_{^1H} \approx 0.94$), the electron-nuclear and homonuclear dipolar couplings for the same distance would be slightly scaled to ~0.94 and 0.88, respectively. Given the similar strengths of dipolar interactions that drive DNP and spin diffusion, we hypothesized that the concept of spin diffusion barrier is still fundamentally applicable for the $^{19}$F system. Moreover, it is easy to adapt our experiments from $^1$H to $^{19}$F NMR because the difference in their Larmor frequencies is only 0.8 MHz at ~0.35 T. We have recorded a $^{19}$F DNP field profile (Figure S2) of $^1$H–$^{19}$F-trityl (dFT15F) in fluorinated solvent (HFB-trifluoroethanol mixture) using similar experimental conditions. The results confirm that dFT15F remains an efficient DNP polarizing agent compared to Finland or OX063 trityls.

We repeated the eDec experiments on dFT15F in $^{19}$F-free $d_7$-TCE, and the results (Figure 4a) allow us to confidently assert that the intramolecular $^{19}$F on the trityl molecules have been directly observed. The fact that their peaks can be directly observed and not excessively broadened (linewidths of ~40 kHz) indicate that the intramolecular $^{19}$F nuclei are outside the spin diffusion barrier and, thus, contribute to the overall bulk $^{19}$F signal. This is not a surprising result as our DFT calculations show that the mean $e^{-\lambda t}$ distance is ~7.6 Å (see Table S1 in Supporting Information), which is clearly outside the spin diffusion barrier determined in previous studies.\cite{17} Additionally, a similar ~80% signal improvement (Figure 4b and c) was achieved during eDec, showing again that the intramolecular nuclei on the radical can be efficiently decoupled from the unpaired electron.
The intramolecular $^{19}$F nuclei is anticipated in future work, such as to study their structures, their roles in DNP, and spin diffusion to the bulk.

Metal-organic frameworks

Following the DNP and eDec study on intramolecular nuclei on the organic radicals, we applied the same techniques on other...
paramagnetic materials whose hyperfine-coupled nuclei might play important roles in material science applications. For instance, MgHOTP MOF is one of the paramagnetic materials that shows promising applications in quantum sensing of Li ions via EPR.\[26\] However, the exact binding mechanism of the Li ions to the MOF is not yet known, and we proposed that DNP and electron decoupling could answer this question by elucidating the structures of the native MOF. First, we note that the paramagnetic MOF has a narrow EPR linewidth (~ 18 MHz, Figure 5a), and the spin counting technique suggests that the radical concentration is ~ 30 mM, which is within the range typically used for DNP applications. As expected, the MOF featured a standard SE DNP profile (Figure 5a) with an enhancement of ε ~ 90 using short buildup times (t\text{1DNP} ~ 0.4 s). A possible reason for the short DNP buildup time of this MOF—about 20 times shorter than those in trityls—are that the electrons and/or ¹H nuclei have fast relaxation rates. Indeed, Figure 5(c–e) shows that the electron T\text{1e} is ~ 24 µs, and the ¹H relaxation times are T\text{1} ~ 0.22 s and T\text{2} ~ 16 µs, respectively. The similarity between the T\text{1} and t\text{1DNP} values imply that the DNP enhancement of 90 is achieved.

Figure 5. ¹H-DNP and EPR measurements performed on paramagnetic MgHOTP MOF at 0.35 T and 80 K. We also determined the DNP build-up time constant to be τ\text{1DNP} ~ 0.2 s. a) DNP frequency profile (red) acquired with t\text{DNP} = 400 ms features a typical solid effect DNP profile that agrees with the EPR spectrum (blue) with an arbitrarily scaled EPR intensity. b) Electron decoupling frequency profile obtained with t\text{DNP} = 15 ms. Measurement of the MOF ¹H's c) T\text{1} ~ 0.22 s and d) T\text{2} ~ 16 µs obtained from mono-exponential fits (red). e) An electron T\text{1e} ~ 24 µs was measured using an inversion recovery sequence and a mono-exponential fit (blue). f) EPR Mims ENDOR spectrum with the x-axis referenced to the ¹H Larmor frequency of ω0/2π = 14.84 MHz.
process is in the relaxation-limited regime, and any additional DNP polarization built up past $t_{\text{DNP}}$ time will be limited via spin-lattice relaxation.

Besides DNP, the eDec performance on $^1$H near the paramagnetic organic linker was measured to be $\approx 4\%$ (Figure 5b), significantly lower than the $\approx 80\%$ observed in trityls. The weaker decoupling performance could be due to several reasons: 1) the $^1$H's are strongly coupled in the fully protonated MOF's ligands, hence, the $^1$H's polarization are more efficiently spin-diffused to the bulk and less affected by nearby electrons, 2) the EPR linewidths in MOF are twice as broad those in trityls, which resulted in a more difficult saturation of EPR lines (shorter $T_{1e}$ and higher radical concentration), 3) stronger hyperfine interactions in MOF. To confirm the last hypothesis, a Mims ENDOR experiment was performed, and it showed a $\approx 2$ MHz broad $^1$H peak (Figure 5f), which is about an order of magnitude larger than that exhibited by trityl in $d$-DNP juice. Thus, we expect that the eDec performance can be significantly improved if higher microwave power is available and frequency-chirped pulses can be applied to frequency-sweep through the EPR spectrum.

Conclusion

We have demonstrated that a combined DNP and electron decoupling approach allows an $\approx 80\%$ improvement in NMR signal intensity of intramolecular trityls' $^1$H and $^{19}$F nuclei. This was achieved via electron decoupling with $\approx 2$ MHz microwave Rabi field at 0.35 T. Electron decoupling has revealed some broad components ($\geq 100$ kHz) that are not easily visible in conventional DNP technique. These components might contain important distance or structural information, i.e., it could become a new method in studying paramagnetic biomolecules or materials with upcoming pulsed DNP technology. We would like to emphasize that the DNP buildup time required for observing only the nearby nuclei is in the order of $T_{1e}$ ($\mu$-ms) because the slower nuclear-nuclear spin diffusion process is less relevant in this context. Thus, high-sensitivity nearby nuclei spectroscopy can already be envisaged at high-field DNP with short $t_{\text{DNP}}$. Furthermore, direct detection of intramolecular trityl $^{19}$F nuclei facilitated by DNP and eDec affirms that these nearby nuclei could participate in spin diffusion with the bulk nuclei during DNP. Finally, we extended the methodology to MgHOTP MOF, and the high DNP performance ($\epsilon \approx 90$) suggests that the MOF could be used for promising potential quantum sensing applications via DNP NMR.

Experimental Section

Sample preparation: In contrast to procedures in standard DNP experiments, we have not used $d_2$-glycerol/D$_2$O/H$_2$O (in a 6:3:1 ratio by volume) formulation because the deuteration factor of the commercially available $d_2$-glycerol (Cambridge Isotope Laboratories, 99.5% deuterated) $^1$H can be insufficient high; that is, any residual solvent $^1$H can overshadow the signal arises from the intramolecular $^1$H on trityls. Thus, we turned to the mixture $d_2$-DMSO/D$_2$O mixture in a 6:4 ratio (by volume) which forms glassy matrices suitable for DNP. Despite the high deuteration factor (99.9% of these solvents, the chemical purity of $d_2$-DMSO is only 99.5%). Hence, any chemical impurities, if protonated, might complicate our attempts to directly observe the intramolecular $^1$H. Furthermore, a small amount of $d_2$-glycerol was added because we observed an unusual EPR lineshape and the nutation curve suggesting that the Finland trityls are more prone to aggregation in pure $d_2$-DMSO/D$_2$O than in glycerol/H$_2$O. This observation agrees with our previous finding that the trityl and glycerol preferentially associate over other solvent components. Hence, we prepared a 5 mM Finland trityl in a $d_2$-DMSO/D$_2$O/glycerol mixture in a 57:38:5 ratio by volume, and this sample was used for the results presented in Figures 2 and 3(a-c).

To further minimize the $^1$H contamination in the sample from atmospheric water, we improved the sample preparation procedures. First, the radicals were mixed with solvents in a nitrogen-filled glove box, where the sample was syringed into a quartz EPR tube (Wilmad-LabGlass). Subsequently, the quartz tube was connected to a 3-way tap fitted with a 3D-printed adapter (Figure S1) enclosed with an O-ring before being transported out of the glove box. The glass tap was immediately fitted to a vacuum line, the headspace before the tap pumped and backfilled to remove contaminating atmospheric water from the transport. The tubes were then placed under vacuum and subsequently flame sealed. The DNP samples were kept frozen in liquid nitrogen (to avoid trityl aggregation) during the flame seal, and the frozen sample was $\approx 10$ cm away from the flame. These samples were used for the experiments shown in Figure 3(d).

The synthesis of $^{19}$F-trityl radical, dFT15F ($C_{12}H_{17}D_2F_3N_3O_2S_{27}$, molecular weight: 1429.8) was performed in one step from the deuterated Finland trityl (dFT, Finland trityl-$d_2$) (Figure 6). Briefly, dFT sodium salt (dFT-Na) (100 mg, 0.09 mmol, 1 equivalent) was dissolved in dry DMSO (10 mL) under argon. N,N-Diisoproplyltyramine (95 mL, 0.54 mmol, 6 equivalent) was added followed by PyBOP (283 mg, 0.54 mmol, 6 equivalent). The green solution immediately turned red; the solution was stirred for 5 min. Next, 2,2,3,3,3-pentafluoropropylamine ($97\mu$L, 0.90 mmol, 10 equivalent) was added, and the solution was stirred overnight. Water (10 mL) was then added, the organic layer was separated, and the aqueous layer was extracted with DCM (3×10 mL). The organic layers were combined, dried over MgSO$_4$, and filtered. The solvent was evaporated under reduced pressure and the crude was purified by flash chromatography (Combiflash RF) on silica gel (12 g) using a gradient from $n$-hexane to DCM to isolate 106 mg (82% yield) of dFT15F as a dark green solid. HRMS (ESI) m/z [M]$: calculated for $C_{12}H_{17}D_2F_3N_3O_2S_{27}$ 1428.2130, found 1428.2113. The $^{19}$F-trityl radical was dissolved in either deuterated tetrachloroethane (d-TCE) or hexafluorobenzene (HFB)-trifluoroethanol mixture (95:5 v/v) to give a 5 mM solution. For the control experiment (Figure 4), OX063 trityl was dissolved in $d$-DMSO juice because the radical is insoluble in TCE.

The synthesis of MgHOTP MOF was described in the literature. Note that the precursor of the MOF, i.e., the free ligand 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), is diamagnetic in solvents, the chemical purity of 6-DMSO is only 99.5% because the slower nuclear-nuclear spin diffusion process is less relevant in this context. Thus, high-sensitivity nearby nuclei spectroscopy can already be envisaged at high-field DNP with short $t_{\text{DNP}}$. Furthermore, direct detection of intramolecular trityl $^{19}$F nuclei facilitated by DNP and eDec affirms that these nearby nuclei could participate in spin diffusion with the bulk nuclei during DNP. Finally, we extended the methodology to MgHOTP MOF, and the high DNP performance ($\epsilon \approx 90$) suggests that the MOF could be used for promising potential quantum sensing applications via DNP NMR.
EPR and DNP NMR Spectroscopy

All EPR and DNP experiments were performed using the Bruker X-band (0.35 T) instrument described in previous publications. The instrument was equipped with two microwave sources capable of performing pulsed electron-electron double resonance (PELDOR/DEER) or ELDOR-detected NMR experiments. A 10 W microwave amplifier with a 100% duty cycle was used in all experiments, and generated a Rabi field $\omega_{1S}/2\pi \approx 2$ MHz. In the experiments described here, we used the microwave pulse forming unit (MPFU) for DNP and the ELDOR channel for electron decoupling. This configuration was chosen because the frequency of the latter $\mu\nu$ channel can be directly configured in the PulseSPEL pulse program, which facilitates the acquisition of the electron decoupling profile. The RF circuitry was also improved for better sensitivity, and 128 saturation pulses were employed to ensure that any enhanced NMR signal from previous scans was fully saturated. This is crucial because the signal intensity gain ($\approx 1.8 \times$) observed in electron-decoupled signal could be overshadowed by the sensitivity gain from DNP ($\approx 100 \times$). Note that the DNP enhancement factor represents only an estimated value based on previous studies performed on partially protonated DNP juice. The actual DNP enhancement on the nearby nuclei could not be determined because the $^1$H thermal equilibrium signal was not observable despite long acquisition periods. To directly observe only the nearby nuclei, a short $\tau_{\text{DNP}}$ time ($\approx 25$ ms) and a recycle delay of $\approx 0.25$ s was used.

Supporting Information Available

Additional information about the 3D-printed Adapter, $^{19}$F-DNP, the HRMS spectrum and DFT calculations of the $^{19}$F trityl are available in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: dynamic nuclear polarization · electron decoupling · hyperpolarization · metal-organic framework
Electron decoupling (eDec) attenuates the electron-nuclei hyperfine interaction (depicted as the magenta sphere) and, thus, improves the NMR sensitivity by ~80%. Furthermore, the combined DNP and eDec technique reveals that the intramolecular nuclei in trityl and paramagnetic MgHOTP MOF are outside the spin diffusion barrier.

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Observing Nearby Nuclei on Paramagnetic Trityls and MOFs via DNP and Electron Decoupling