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A narrow line UV-induced non-persistent radical to generate highly polarized transportable glucose solid samples

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The main limitation of dissolution DNP [1] concerns the need to place the polarizer as close as possible to the MRI scanner (or high resolution spectrometer) where the actual hyperpolarized (HP) magnetic resonance experiment is performed. Indeed, after dissolution the life-time of the HP liquid is limited by spin-lattice relaxation that brings the nuclear spin populations back to thermal equilibrium, generally in less than a minute. It was demonstrated that photo-induced radicals, generated via UV-light irradiation of frozen solutions containing a fraction of pyruvic acid (PA), are suitable to perform DNP on several substrates [2, 3]. The unique property of this polarizing agent is their non-persistence: they suffer from thermal stress and they are naturally scavenged if the temperature of the DNP sample is raised above 190 K. Thus, they can be eliminated while the sample is still frozen inside the polarizer through a fast thermalization process, yielding radical-free highly polarized solid samples [4]. The latter, because of the absence of paramagnetic species, can be extracted from the polarizer, stored in appropriate conditions of temperature and magnetic field, transported and dissolved with negligible polarization loss at another location and time [4, 5]. In the present work, we tackled the main drawback associated to DNP photo-induced non-persistent radicals: the low achievable ¹³C polarization (up to 12% at 7 T and 1 K) [4], when compared to Trityl radicals [6]. This is due to the fairly large ESR line width of the radical when PA is the precursor. A precursor with a narrower ESR line (see Fig. 1A) and not involved in any metabolic process is the object of the present study. The DNP properties of the new radical precursor, i.e. trimethyl pyruvic acid (Tri-PA), were tested on ¹³C-glucose, a substrate showing increasing interest among the dissolution DNP community [7].

Tri-PA was added in concentration of 1.6 M to a solution containing 3 M of [U²H, U¹³C] dissolved in a mixture H₂O:glycerol 1:1 (v/v). 20 frozen pellets were prepared pouring 4.0±0.5 µL droplets of the sample’s solution into a transparent quartz dewar (Wilmad-LabGlass WG-850-B-Q) filled with liquid nitrogen. The sample was UV-irradiated for 120 s only with a high power (20 W/cm²) broad-band UV source (Dymax BlueWave 75). X-band ESR measurements (Magnetette MiniScope 5000) showed a radical concentration of 30±5 mM. DNP was performed using a 6.7 T/1.1 K polarizer. Shining microwaves on the frozen sample in optimal conditions (188.18 GHz with 25 MHz/1 kHz modulation), ¹³C was polarized up to 50±5 % in about 1 h (see Fig 1B). After dissolution and transfer (about 10 s) to a 9.4 T high resolution vertical NMR magnet a polarization of 15.3±0.1 % was measured (see Fig 1C). As comparison an identical sample containing 30 mM Trityl, instead of the UV-radical precursor, was prepared. ¹³C nuclei polarized up to 60% under the same DNP conditions of temperature and field.

The promising DNP performances of UV-induced Tri-PA are in good agreement with its sharper ESR spectrum, when compared to UV-induced PA. Since the unpaired electron is localized on the beta carbon of these photoactive molecules, “pushing” the methyl groups further away reduces the hyperfine coupling between the electron and the molecule’s nuclear environment, providing a DNP radical with features closer to Trityl.

Figure 1A. X-band ESR spectra of UV-irradiated Tri-PA (top) and UV irradiated PA (bottom) at 77 K. B Carbon DNP buildup measured shining microwaves at a frequency of 188.18 GHz with a 25 MHz/1 kHz modulation. C After dissolution ¹³C spectrum of glucose at room temperature in a Varian 400 MHz high resolution NMR spectrometer (C).

References