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Liquid-State Polarization of 30% through Photo-Induced Non-Persistent Radicals on $^{13}$C Pyruvic Acid

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Hyperpolarization via dissolution Dynamic Nuclear Polarization (dDNP) [1] is crucial to significantly increase magnetic resonance imaging (MRI) sensitivity, opening up for in vivo real-time MRI using in particular $^{13}$C-labelled substrates such us pyruvic acid (PA) [2]. The range of applications is however limited by the relatively fast decay of the nuclear spin polarization together with the constraint of having to polarize the spins near the MRI magnet. As recently demonstrated, the employment of UV-induced non-persistent radicals, generated via irradiation of frozen samples containing a fraction of PA and immersed in liquid nitrogen, represents an elegant solution to tackle these drawbacks. Indeed these labile paramagnetic centers showed to pave the way to hyperpolarized (HP) samples’ storage and transport far away from their production site [4, 5, 6]. Nevertheless, since its introduction, the spread of the technique has been prevented by the relatively low achievable polarization ($\approx 10\%$), slow buildup time ($\approx 3\ h$) and time-consuming sample preparation ($\approx 1\ h$). In the present work, thanks to a thorough investigation of the radical generation process and distribution of the photo-induced paramagnetic centers inside the DNP samples, we provide a robust protocol to enhance the efficiency and performances of the UV-radical technique. A new sample irradiation setup was designed to work in a moister free environment (see Fig 1). The set-up provides a fast generation of the UV-induced radicals thanks to a high power ($20\ W/cm^2$) broad-band UV-source (Dymax BlueWave 75) shining light on the tail of a quartz cold finger placed inside a reflecting aluminum chamber. On a sample containing a mixture of PA:H$_2$O 1:1 (v/v) we were able to induce more than 50 mM of radicals in about 5 min, thus doubling the maximum yield and reducing the irradiation time by a factor of 30 compared to the current state of the art [5, 6].

The distribution of the paramagnetic centers inside the DNP samples was investigated via ESR by changing the radical precursor (PA) concentration, in a solvent mixture of glycerol:water 60:40 (GW64), and the dimension of the frozen pellets. Taking into account the strong absorption of the UV-light while travelling through the spherical frozen samples, a radicals’ distribution profile with exponential dumping ($\sim e^{-x/d}$) from the surface to the core of the pellet was assumed and verified experimentally (see Fig 2). The attenuation parameter $d$ increased from about 0.1 mm to 3 mm by decreasing the PA concentration from 90% to 10% of the total sample volume. DNP wise the best compromise between PA concentration and homogeneity of the radicals’ distribution was found to be a mixture of PA:GW64 1:1 (v/v). In this sample $^{13}$C nuclei polarized up to 30% in about 1 h working at 6.7 T and 1.1 K. These values represent a clear improvement compared to the current state of the art making the UV-radical technique useful for the most recent demanding metabolic imaging applications.

References