Supplementary Material for "Room temperature hyperpolarization of polycrystalline samples with optically polarized triplet electrons: Pentacene or Nitrogen-Vacancy center in diamond?"

Koichiro Miyanishi¹, Takuya F. Segawa^{2,3}, Kazuyuki Takeda⁴, Izuru Ohki⁵, Shinobu Onoda^{6, 7}, Takeshi Ohshima^{6, 7}, Hiroshi Abe^{6, 7}, Hideaki Takashima⁸, Shigeki Takeuchi⁸, Alexander I. Shames⁹, Kohki Morita⁵, Yu Wang⁴, Frederick T.-K. So^{2,6}, Daiki Terada^{2,6}, Ryuji Igarashi^{6,7,10}, Akinori Kagawa^{1,10,11}, Masahiro Kitagawa^{1,11}, Norikazu Mizuochi⁵, Masahiro Shirakawa^{2,6}, and Makoto Negoro^{6,10,11}

¹Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
²Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-Ku, Kyoto 615-8510, Japan
³Laboratory for Solid State Physics, ETH Zurich, 8093 Zurich, Switzerland
⁴Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
⁵Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan
⁶Institute for Quantum Life Science, National Institutes for Quantum and Radiological Science and Technology, 4-9-1,

Institute for Quantum Life Science, National Institutes for Quantum and Radiological Science and Technology, 4-9-1 Anagawa, Inage-Ku, Chiba 263-8555, Japan

⁷Takasaki Advanced Radiation Research Institute, National Institutes for Quantum and Radiological Science and Technology, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

⁸Department of Electronic Science and Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

⁹Department of Physics, Ben-Gurion University of the Negev, 8410501 Beer-Sheva, Israel

¹⁰JST, PRESTO, Kawaguchi, Japan

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¹¹Quantum Information and Quantum Biology Center, Institute for Open and Transdisciplinary Research Initiatives, Osaka University, Japan

Correspondence: Koichiro Miyanishi (miyanishi@qi.mp.es.osaka-u.ac.jp), Takuya F. Segawa (segawat@ethz.ch), Makoto Negoro (negoro@qiqb.otri.osaka-u.ac.jp)

1 Estimation of the electron spin polarization of NV⁻ center

Using the ESR spectrum of the nanodiamonds in Fig. 3(b), we estimated the initial electron polarization P_e^{NV} of the NV⁻ center between the $m_S = 0$ and the $m_S = -1$ states right after laser irradiation in the magnetic field sweep range. As the reference of the polarization, we use the thermally polarized signal from all S = 1/2 electron spins which exist in the nanodiamond sample. The electron polarization P_e^{NV} is calculated using the following equation

$$P_e^{\rm NV} = P_{S=1/2} \times \left(\frac{S^{\rm NV}}{S^{S=1/2}\eta^{S=1/2}}\right) \times \left(\frac{\rho^{S=1/2}}{\rho_e^{\rm NV}\eta_p^{\rm NV}}\right) = 0.0926\% \times 0.47 \times \left(\frac{177 \,\mathrm{ppm}}{3 \,\mathrm{ppm} \times 0.2}\right),\tag{1}$$

where $P^{S=1/2}$ is the polarization of the spin S = 1/2 in thermal equilibrium, S^{NV} is the area intensity of the ESR line of the NV⁻ center integrated over the field-sweep range (corresponding to the gray area in Fig. 1), $S^{S=1/2}$ is the area intensity of



Supplementary Figure 1. ESR powder spectrum of nanodiamond samples. The gray area corresponds to the magnetic field sweep range.

the ESR line of the electron spin (corresponding to the three lines in the center of the field) center integrated over the field-10 sweep range, $\eta^{S=1/2}$ is the scale factor for the signal intesity of the S = 1/2 spins and $\rho^{S=1/2} = 3.1 \times 10^{19}$ cm⁻³ (177 ppm) ($\rho_e^{\text{NV}} = 5.3 \times 10^{17}$ cm⁻³ (3 ppm)) is the density of all S = 1/2 (NV) electron spins.

2 NMR linewidth of ¹³C in PBA with and without ¹H decoupling

The ¹³C NMR of PBA with and without ¹H decoupling is shown in Fig 2. Both signals are normalized by the maximum signal intensity. The linewidth of the ¹³C NMR signal with ¹H decoupling was 1.2 kHz and that without ¹H decoupling was 5.2 kHz.

15 This signal broadening is due to the dipole–dipole interaction between ¹³C spins and ¹H spins, the interaction, which leads to the low spin diffusion coefficient in PBA.



Supplementary Figure 2. NMR spectra of 13 C in PBA. The solid line shows the 13 C NMR signals with 1 H decoupling and the dashed line without 1 H decoupling.

3 ¹³C hyperpolarization in microdiamonds at the 'high-field' horn

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Hyperpolarized ¹³C NMR is performed at a magnetic field of 0.46 T (corresponding to the 'high-field' horn of the ESR powder spectrum of the microdiamonds in Fig. 3(d)) at a Larmor frequency of $\omega_{0,C} = 4.95$ MHz and a DNP-enhanced ¹³C NMR spectrum is shown in Fig. 3(a). Buildup curves of ¹³C polarization with laser repetition frequency of R = 30, 50, 70 and 100 Hz are shown in Fig. 3(b).

The curve of longitudinal relaxation of the ¹³C spins in microdiamonds are shown in Fig. 3(c) and the longitudinal relaxation time is $T_{1,C}^{NV} = 99 \pm 14$ s. In the longitudinal relaxation measurement, we change the delay time between the DNP process and the NMR measurement.



Supplementary Figure 3. Optical hyperpolarization in microdiamonds at a magnetic field of 0.46 T (corresponding to the 'high-field' horn of the ESR powder spectrum). (a) Signal intensity dependence on the microwave power ω_{rabi}^{MW} at the high-field horn. The gray line shows the ¹³C Larmor frequency at high-field horn. (b) Buildup curves of ¹³C polarization in microdiamonds. The blue, orange, green and red denote the laser repetition frequency of 30 Hz, 50 Hz, 70 Hz and 100 Hz. (c) The relaxation curve for the ¹³C NMR signal of microdiamonds.

25 4 Sample pictures

The pictures of the three samples in the glass tubes are shown in Fig. 4.

Fig. 5 shows the effect of oxidation in air on the color of the nanodiamond powders. Both samples are electron irradiated and annealed (800° C in vacuum) nanodiamonds. Fig. 5(a) was taken before oxidation in air, while Fig. 5(b) was taken after oxidation in air. The oxidation procedure removes sp² carbon on the surface of the nanodiamonds, which was created during

30 the annealing step. The change in color from grey to white is a chemical key step to perform optical excitation of NV centers in nanodiamonds.



Supplementary Figure 4. Pictures of the three samples (a) nanodiamonds, (b) microdiamonds and (c) pentacene doped benzoic acid.



Supplementary Figure 5. Pictures of electron irradiated and annealed nanodiamonds (a) before oxidation in air ("dark") and (b) after oxidation in air ("white").