Supporting information for

Triplet dynamic nuclear polarization of nanocrystals dispersed in water at room temperature

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Materials

All reagents were used as received otherwise noted. Pentacene (99.999%, purified by sublimation) was purchased from TCI. *p*-Terphenyl was purchased from Wako Pure Chemical and purified by zone melting. Cetyltrimethylammonium Bromide was purchased from KISHIDA.

For sample preparation, pentacene and *p*-terphenyl were inserted into an ampule and sealed under vacuum. The sealed ampule was heated in an oil bath above 220 °C (melting point of *p*-terphenyl). The resulting liquid was rapidly cooled with liquid nitrogen. Obtained solids were taken out from ampule and ground in an agate mortar, giving bulk *p*-terphenyl crystals doped with pentacene.

The bulk *p*-terphenyl crystals doped with pentacene (300 mg), an aqueous solution of CATB (1.4 mM, 30 mL) and alumina ball (5 mm in diameter) were added into a ceramic pot and ball-milled for 3 hours at 280 rpm by using an AS ONE pot mill rotator PM-001. From the resulting milky suspension, micrometer-sized large particles were removed by centrifugation (6000 rpm, 5 min). The supernatant was collected, and the nanocrystals were settled out by centrifugation (12000 rpm, 30 min). Part of the supernatant was removed for concentrating the nanocrystals. After that, the colloids were redispersed by stirring. The final concentration of the nanocrystals in the aqueous dispersion was 5.3 wt%, which was determined by taking out the part of the dispersion, drying and measuring the weight of remained solid.

General characterizations

Dynamic light scattering (DLS) measurements were carried out by using a Malvern Nano-ZS ZEN3600. Scanning electron microscope (SEM) images were obtained by using a HITACHI FE-SEM SU9000. The nanocrystal dispersion was cast on the carbon-coated cupper grid and dried in air. UV-Vis absorption spectra were recorded on JASCO V-670 and 770 spectrophotometers. Transmission and diffuse reflection methods were employed for solution and solid samples, respectively. Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D2 Phaser (Cu-K α , 30 kV, 10 mA). The nanocrystal sample was prepared by casting the aqueous dispersion on a glass plate. Transient absorption measurements were conducted by using a UNISOKU TSP-2000 system. Time-resolved fluorescence lifetime measurements were carried out by using a time-correlated single photon counting lifetime spectroscopy system, HAMAMATSU Quantaurus-Tau C11367-02.

Triplet-DNP setup



Figure S1. Scheme of the setup for triplet-DNP.

Time-resolved ESR and triplet-DNP experiments were performed on home-built spectrometers explained below. For time-resolved ESR, the powder samples were packed in a glass capillary (FPT-220, FUJISTON, diameter 2.2 mm, inner diameter 1.4 mm) in the air. For triplet-DNP experiments, the samples were put in a sapphire capillary (ORBE PIONEER, diameter 1.9 mm, inner diameter 1.15 mm) in the air.

ESR and Triplet-DNP measurements were carried out using a home-build ~9 GHz and ~18 GHz cylindrical resonator with a window for laser irradiation and a coil for magnetic field sweep at a magnetic field generated by an electromagnet. A home-built laser was used for pentacene excitation. After triplet-DNP, the polarized sample was shuttled into an NMR coil positioned above the resonator, which was tuned for a ¹H spin. The timing control of the ISE sequence and the NMR detection were performed with an OPENCORE NMR spectrometer.

An electromagnet was purchased from Takano (MC160-60G-0.8T). The gap and pole size are 60 and 160 mm, respectively. A power supply PAG60-55 (Kikusui) with the stability of 10⁻⁴ was used. A microwave was generated from HMC-T2220 (Analog Devices) and amplified (PT188-1KW, Instruments For Industry) with the power of 1500 W. A transmission loss is -7dB. A triangle wave for field sweep was produced with a function generator (WF1945, NF Corporation) and amplified with

OPamp (PA05, Apex Microtechnology).

Microwave resonator

A cylindrical resonator was designed by using an electromagnetic simulator (CST Studio). An enclosure is a copper, and four copper rods with a diameter of 1 mm are inserted for field sweep. Diameter and height are 21 and 30 mm, respectively. The materials are put on Teflon holders. A microwave is coupled with a rectangular waveguide (WR-51) through an iris with a diameter of 6 mm which is filled with Teflon. A laser is irradiated from the opposite side. A coil for ¹H detection was put outside the resonator.

Calculation of the enhancement factor.¹

The enhancement factor (ε) was calculated by comparing the integrated intensities of the hyperpolarized ¹H NMR signal of each sample after triplet-DNP sequences (Figure 3, S8) and the ¹H NMR signal of the pentacene-doped bulk *p*-terphenyl crystals in thermal equilibrium at 0.676 T and 300 K (Figure S7).

$$\varepsilon = \frac{N_{ref} T_{DNP} g_{ref} E_{DNP}}{N_{DNP} T_{ref} g_{DNP} E_{ref}}$$
equation 1

where N is the number of ¹H spins, T is temperature and g and E are the receiver gain and the recorded signal voltage. ¹H spin polarization (P) was also determined by

$$P = \varepsilon \tanh \frac{\gamma \hbar B}{2kT} \qquad \text{equation } 2$$

where γ , \hbar , B, k, T are gyromagnetic ratio, reduced Planck constant, magnetic field, Boltzmann constant, and temperature, respectively.

Measurement of proton spin-lattice relaxation time (T_1) by the saturation-recovery method

Proton spin-lattice relaxation time (T_1) was measured on the CP/MAS probe and a JEOL JNM-ECA400 spectrometer by the saturation recovery method. In prior to the acquisition, spin echo is applied in order to get rid of the background signal. Powder samples were dried for 24 h under reduced pressure. The MAS rate was set at 15 kHz. T_1 was determined by fitting the signal recovery curves with at least 14 time points and the last one was set to be longer than 5 times of the T_1 value.



Figure S2. Size distribution histogram of dried *p*-terphenyl nanocrystals doped with 0.5mol% pentacene from the SEM image.



Figure S3. UV-vis absorption spectra of 0.5 mol% pentacene doped in bulk *p*-terphenyl crystals (purple), 0.5 mol% pentacene doped in *p*-terphenyl nanocrystals (red) and neat pentacene powder (black).



Figure S4. Fluorescence decay ($\lambda_{ex} = 590 \text{ nm}$, $\lambda_{dt} = 610 \text{ nm}$) of bulk *p*-terphenyl crystals doped with 0.5mol% pentacene (black) and the aqueous dispersion of *p*-terphenyl nanocrystals doped with 0.5mol% pentacene (rad).



Figure S5. (a) Time-resolved ESR spectrum (black line) of bulk *p*-terphenyl crystals doped with 0.5 mol% pentacene at room temperature just after pulsed photoexcitation at 532 nm. The simulation result of ESR spectrum by using EasySpin toolbox in MATLAB is also shown (red line).² (b) Decay of the ESR peak at 348 mT under pulsed photoexcitation at 532 nm of bulk *p*-terphenyl crystals doped with 0.5 mol% pentacene. The fitting result is shown as red line according to the following equation, A $exp(-t/\tau_A) + B exp(-t/\tau_B) + C$.



Figure S6. (a) Time-resolved ESR spectrum (black line) of dried *p*-terphenyl nanocrystals doped with 0.5 mol% pentacene at room temperature just after pulsed photoexcitation at 532 nm. The simulation result of ESR spectrum by using EasySpin toolbox in MATLAB is also shown (red line).² (b) Decay of the ESR peak at 348 mT under pulsed photoexcitation at 532 nm of dried *p*-terphenyl nanocrystals doped with 0.5 mol% pentacene. The fitting result is shown as a red line according to the following equation, A exp(-t/ τ_A) + B. The negative component cannot be detected due to the large noise.

Table S1. ESR decay time of *p*-terphenyl bulk crystals and nanocrystals doped with 0.5mol% pentacene obtained by fitting the data shown in Figure S5 and S6.

| Sample | А | $	au_{\rm A}$ (µs) | В | $	au_{\mathrm{B}}\left(\mu\mathrm{s} ight)$ |
|--------|------|--------------------|-------|---|
| Bulk | 0.13 | 21 | -0.02 | 104 |
| Nano | - | 16 | - | - |

Table S2. Zero-field splitting parameters and relative zero-field populations derived from simulation of the time-resolved ESR spectra of *p*-terphenyl bulk crystals and nanocrystals doped with 0.5mol% pentacene (Figure S5, S6).

| Sample | D (MHz) | E (MHz) | P _x | $P_{\rm y}$ | $P_{\rm z}$ |
|--------|---------|---------|----------------|-------------|-------------|
| Bulk | 1364 | 24 | 0.74 | 0.09 | 0.17 |
| Nano | 1394 | 30 | 0.74 | 0.09 | 0.17 |



Figure S7. ¹H NMR spectrum of bulk *p*-terphenyl crystals doped with 0.5 mol% pentacene with 200 times accumulation (black) and its Gaussian function fitting (red).



Figure S8. ¹H NMR spectra of the bulk *p*-terphenyl crystals doped with 0.5mol% pentacene after the triplet-DNP process for different durations.



Figure S9. ¹H polarization buildup curve of the bulk *p*-terphenyl crystals doped with 0.5 mol% pentacene at 0.676 T and room temperature. The broken line is a fitting curve with the following equation, $A[1-exp(-t/T_B)]$.



Figure S10. (a) ¹H NMR spectra of the bulk *p*-terphenyl crystals doped with 0.5mol% pentacene (left) and the dried *p*-terphenyl nanocrystals doped with 0.5mol% pentacene (right) with magic angle spinning of 15 kHz. (b) Saturation recovery of bulk *p*-terphenyl crystals doped with 0.5mol% pentacene at 6.389 ppm (black) and the dried *p*-terphenyl nanocrystals doped with 0.5mol% pentacene at 6.420 ppm (red). The fitting results were shown as red lines according to the following equation, $A[1-exp(-t/T_1)] + B$.

References

- 1. K. Takeda, *Triplet State Dynamic Nuclear Polarization*, VDM Verlag Dr. Müeller, Saarbrücken, Germany, 2009.
- 2. S. Stoll and A. Schweiger, J. Magn. Reson., 2006, 178, 42-55.