

**Electronic Supplementary Information for**

**Triplet dynamic nuclear polarization of crystalline ice using**

**water-soluble polarizing agents**

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## Materials

Synthesis of DAT was previously reported<sup>1</sup> and all reagents were used as received unless otherwise noted. Bromine, sodium sulfite, cesium carbonate, and sodium hydroxide were purchased from FUJIFILM Wako pure chemical, potassium hydroxide was purchased from KISHIDA, dimethyl 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate, 4-(Methoxycarbonyl)phenylboronic acid were purchased from TCI, and Tris[2-(2-methoxyethoxy)ethyl]amine and PEPPSI-IPr was purchased from Sigma Aldrich. Tris[2-(2-methoxyethoxy)ethyl]amine was purified by distillation.

## General characterizations

<sup>1</sup>H-NMR (400 MHz) spectra were measured on a JEOL JNM-ECZ400 spectrometer using TMS as the internal standard (for liquid samples). Elemental analysis was carried out by using a Yanaco CHN Corder MT-5 at the Elemental Analysis Center, Kyushu University. Dynamic light scattering (DLS) measurements were carried out by using Malvern Nano-ZS ZEN3600. UV-Vis absorption spectra were recorded on JASCO V-670 and 770 spectrophotometers. Temperature-dependent photoluminescence and excitation spectra were recorded in a cryostat (Optistat DN2, Oxford Instruments) equipped with a controller (MercuryTC, Oxford Instruments). The cryostat was mounted in the JASCO FP8500 spectrofluorometer. Low temperature quantum yield was measured in an integrating sphere using a Hamamatsu Photonics absolute quantum yield measurement system (C9920-02G) equipped with a holder for low-temperature measurement (A11238-01).

### **Triplet-DNP setup**

Time-resolved EPR and triplet-DNP experiments were performed on home-built spectrometers explained below. The aqueous dispersions were packed in glass capillaries (FPT-220, FUJISTON, diameter 2.2 mm, inner diameter 1.4 mm) in air and they were frozen in liquid nitrogen.

Triplet-DNP measurements were carried out by using a home-build ~18 GHz cylindrical resonator with a window for laser irradiation and a coil for the magnetic field sweep at a magnetic field generated by an electromagnet. A home-built laser (explained below) was used for polarizing agent excitation. After DNP, the polarized sample was shuttled into an NMR coil positioned above the resonator, which was tuned for  $^1\text{H}$  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 sizes 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. Coils for  $^1\text{H}$  detection were put outside/inside the resonator. In this experiment, we used the outer one with better sensitivity.

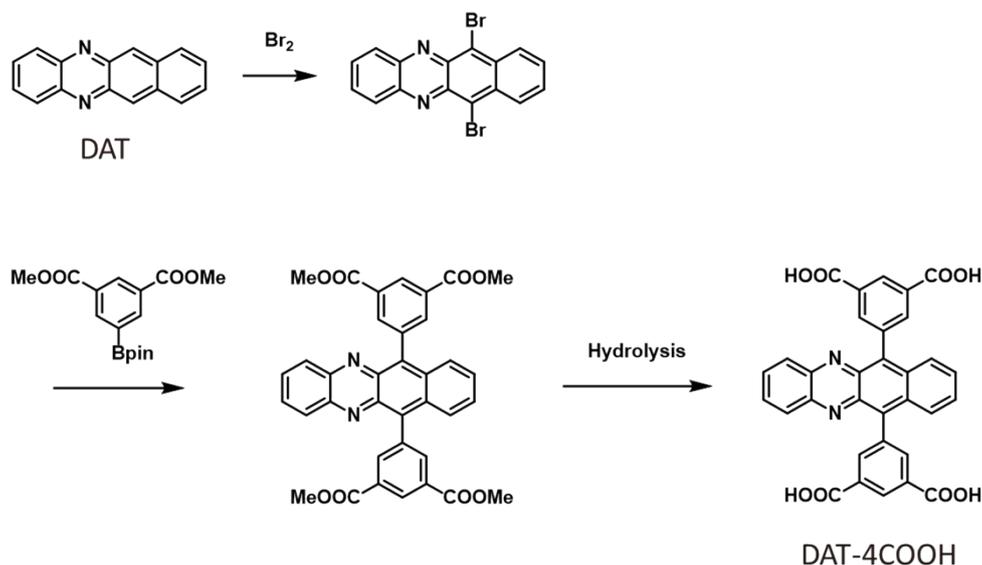
### **532 nm laser system**

The 532 nm laser system consists of a Nd-doped YAG lasers with wavelengths of 1064 nm and a  $\text{LiB}_3\text{O}_5$  (LBO) crystal for the second harmonic generation (SHG). The wavelength, pulse width, maximum repetition rate, and output power of the system are 532 nm,  $\sim 180$  ns, 3 kHz, and 0.5 mJ/pulse, respectively.

We constructed an oscillator based on a Nd-doped YAG crystal with a high-reflection flat mirror for 1064 nm, and an output coupler. A YAG rod is mounted in a chamber and pumped by laser diodes with a wavelength of 808 nm. A rotator is inserted between the chambers to minimize birefringence losses. A thin glass plate set at Brewster's angle in the oscillator is used to generate polarized light, and an aperture in the 1064-nm oscillator is used to select the  $\text{TEM}_{00}$  mode beam. An acoustic-optic Q-switch (A/O Q-sw) is employed to pulse the laser as the switch provides a high repetition frequency.

In order to generate the 532 nm light, the two infrared beams are summed in the LBO crystal. Before the beam transmitted to the crystal, the diameter and polarization of the infrared beam are precisely adjusted by telescopes and quarter-wavelength plates. The phase-matching for SHG is accomplished by controlling the crystal temperature. The optimal temperature for SFG was  $147.5^\circ\text{C}$  for our crystal and the conversion efficiency was 13%. Finally, the residual infrared beams are separated by visible-coated mirrors.

### Scheme S1. Synthesis of DAT-4COOH.



### Synthesis of 6,11-dibromobenzo[*b*] phenazine.<sup>2</sup>

1.0 g (4.3 mmol) of DAT was placed in a 300 ml flask and dissolved in 175 ml of CHCl<sub>3</sub>. After cooling in the ice bath, 0.5 ml of bromine was slowly added to the DAT solution. The resulting dark solution was kept stirred until room temperature and the reaction was monitored by TLC. Then, the solution was washed with a Na<sub>2</sub>SO<sub>3</sub> aqueous solution to quench the bromine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure after filtration. The crude product was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub> /hexane (1 : 3) and benzo[*b*]phenazine was obtained as dark purple solids (yield: 50%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\sigma$  (ppm) = 8.70-8.73 (m, 2H), 8.36-8.39 (m, 2H), 7.88-7.90 (m, 2H), 7.67-7.70 (m, 2H).

### Synthesis of tetramethyl 5,5'-(benzo[*b*]phenazine-6,11-diyl)diisophthalate.<sup>3</sup>

A mixture of 50 mL of toluene, 10 mL of ethanol and 20 mL of H<sub>2</sub>O was bubbled with N<sub>2</sub>. 388 mg (1.0 mmol) of 6,11-dibromobenzo[*b*] phenazine, 1.25 g (4.0 mmol) of dimethyl 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate, 13.6 mg (0.02 mmol) of PEPPSI-IPr, and 1.3 g (4.0 mmol) of Cs<sub>2</sub>CO<sub>3</sub> were dispersed in the above mixed solvents under an atmosphere of N<sub>2</sub>. The mixture was refluxed for 8 hours. Thereafter, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>/brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude materials was purified through column chromatography with CHCl<sub>3</sub>/methanol (100 : 1) as eluent. DAT-4COOMe was obtained as red solids including some impurities.

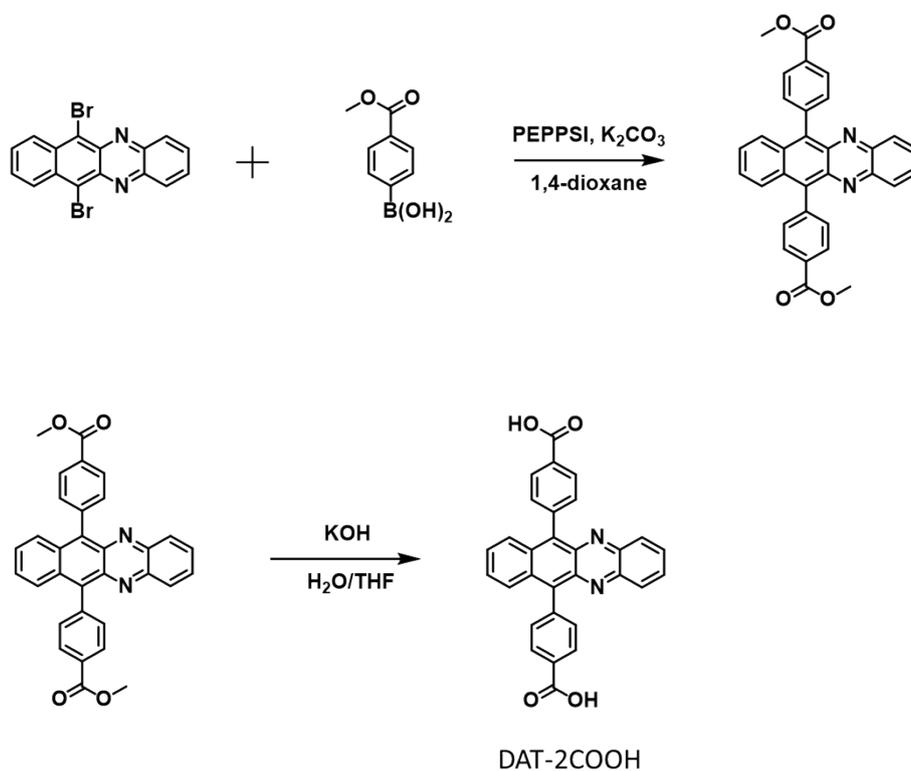
### Synthesis of 5,5'-(benzo[b]phenazine-6,11-diyl)diisophthalic acid (DAT-4COOH).

To a suspension of 400 mg (0.65 mmol) of DAT-4COOMe in the mixture of 50 ml THF, 50 ml methanol and 25 ml 4N NaOH aqueous solution was added. The mixture was stirred overnight. The mixture formed by acidification with 4N aqueous HCl was collected by centrifugation and washed several times with methanol. The filtrate was recrystallized in THF and DAT-4COOH was obtained as red solids by filtration. (total yield: 15%)

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ ):  $\sigma$  (ppm) = 13.4 (br, 4H), 8.72-8.73 (t, 2H), 8.35 (m, 4H), 7.98-8.01 (dd, 2H), 7.82-7.87 (m, 4H), 7.60-7.62 (dd, 2H).

Elemental analysis for  $\text{C}_{32}\text{H}_{18}\text{N}_2\text{O}_8$ : calculated (%) H 3.25, C 68.82, N 5.02; found (%) H 3.44, C 68.67, N 4.95.

### Scheme S2. Synthesis of DAT-2COOH.



### **Synthesis of dimethyl 4,4'-(benzo[b]phenazine-6,11-diyl)dibenzoate**

300 mg (0.77 mmol) of 6,11-dibromobenzo[b] phenazine, 694.3 mg (3.9 mmol) of 4-(methoxycarbonyl)phenylboronic acid, 43.3 mg (0.037 mmol) of PEPPSI-IPr and 490 mg (3.5 mmol) of potassium carbonate were placed in a 300 ml three-necked flask. 1,4-dioxane was dehydrated by molecular sieve and degassed by the bubbling of N<sub>2</sub>. Then, 1,4-dioxane was added in the three-necked flask under N<sub>2</sub>. The dispersion was refluxed for 17 hours. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>/brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was recrystallized in toluene and filtrated. The filtrate was purified through column chromatography with CHCl<sub>3</sub>/methanol (20 : 1) as eluent. DAT-2COOMe was obtained as red solids including some impurities.

### **Synthesis of 4,4'-(benzo[b]phenazine-6,11-diyl)dibenzoic acid (DAT-2COOH)**

To a suspension of 70 mg (0.14 mmol) of DAT-2COOMe in a mixture of 75 ml THF and 15 ml methanol, 1.0 ml 2N NaOH aqueous solution was added. The mixture was refluxed for 4.5 hours. A precipitate was filtered and potassium 4,4'-(benzo[b]phenazine-6,11-diyl)dibenzoate was obtained as red solid. (total yield: 6.9%)

<sup>1</sup>H-NMR of potassium 4,4'-(benzo[b]phenazine-6,11-diyl)dibenzoate (400 MHz, D<sub>2</sub>O):  $\sigma$  (ppm) = 7.92-8.00 (d, 4H), 7.67-7.69 (br, 2H), 7.51-7.54 (br, 2H), 7.42-7.44 (br, 2H), 7.26-7.32 (br and d, total 6H).

DAT-2COOH was obtained by acidification of potassium 4,4'-(benzo[b]phenazine-6,11-diyl)dibenzoate. However, due to poor solubility in common organic solvent, the NMR measurement of DAT-2COOH could not be conducted.

**Calculation of the enhancement factor.<sup>4</sup>**

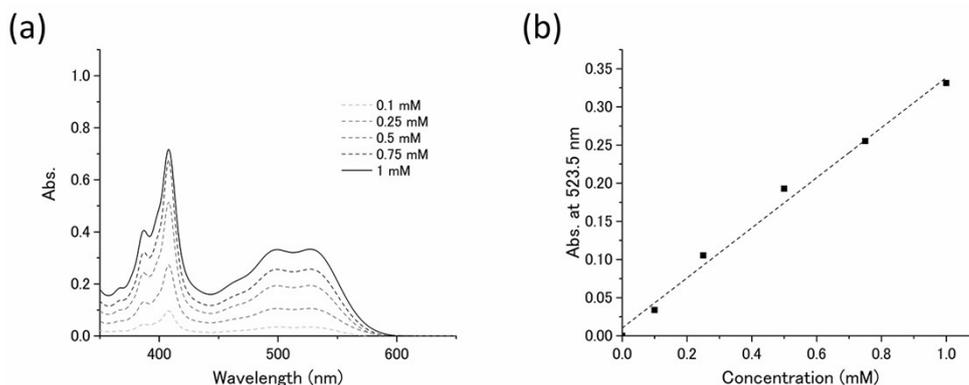
The enhancement factor ( $\varepsilon$ ) was calculated by comparing the integrated intensities of the hyperpolarized  $^1\text{H}$  NMR signal of DAT-4COOH/MEEA system after the triplet-DNP sequence and the  $^1\text{H}$  NMR signal of methanol in thermal equilibrium at 0.664 T and 140 K.

$$\varepsilon = \frac{N_{ref} T_{DNP} g_{ref} E_{DNP}}{N_{DNP} T_{ref} g_{DNP} E_{ref}} \quad (1)$$

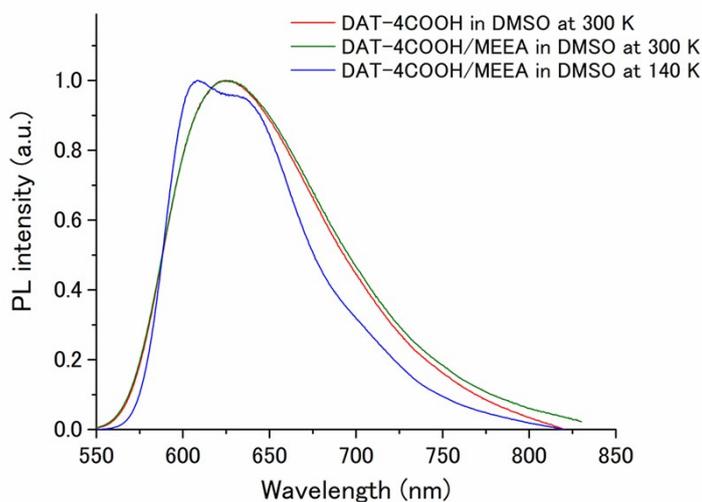
where  $N$  is the number of  $^1\text{H}$  spins,  $T$  is temperature and  $g$  and  $E$  are the receiver gain and the recorded signal voltage. The  $^1\text{H}$  spin polarization ( $P$ ) was also determined by

$$P = \varepsilon \tanh \frac{\gamma \hbar B}{2kT} \quad (2)$$

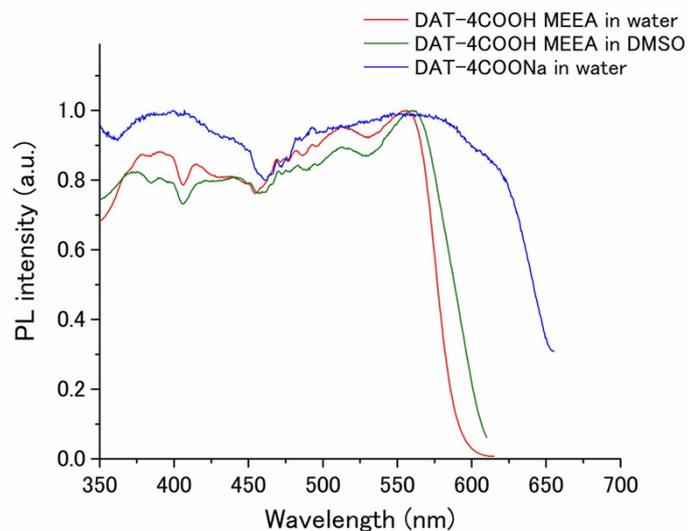
where  $\gamma$ ,  $\hbar$ ,  $B$ ,  $k$ ,  $T$  are gyromagnetic ratio, reduced Planck constant, magnetic field, Boltzmann constant, and temperature, respectively.



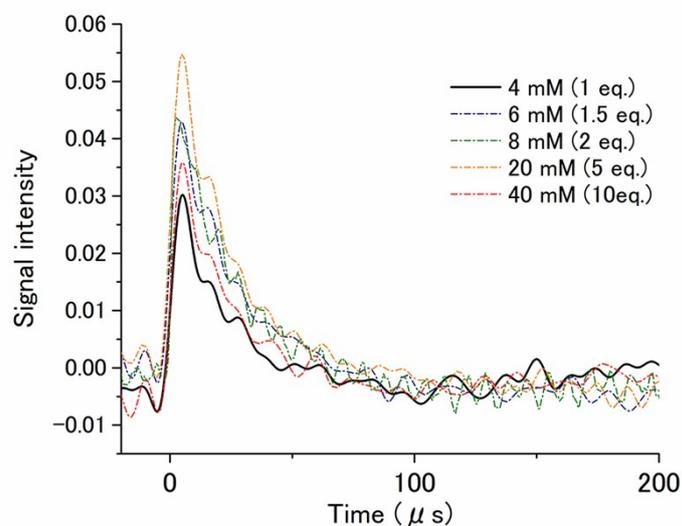
**Figure S1.** (a) Concentration-dependent absorption spectra of DAT-4COOH/MEEA (1:4) in DMSO at room temperature. (b) The absorbance of DAT-4COOH/MEEA (1:4) in DMSO at 523.5 nm with different DAT-4COOH concentrations. The fitting result is shown as a black line according to be following equation,  $y = Ax+B$ . The observed linearity supports the molecularly-dispersed state of DAT-4COOH/MEEA in DMSO at room temperature in the examined concentration range.



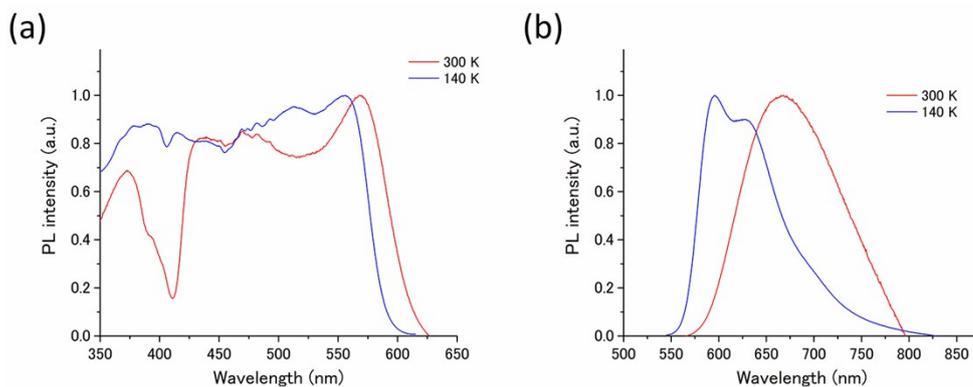
**Figure S2.** Photoluminescence (PL) spectra ( $\lambda_{ex} = 532$  nm) of DAT-4COOH (1 mM) in DMSO at 300 K (red), DAT-4COOH (1 mM)/MEEA (4mM) mixture in DMSO at 300 K (green) and DAT-4COOH (1 mM)/MEEA (4mM) mixture in DMSO at 140 K (blue). The absence of any significant shift by decreasing the temperature below the glass transition temperature of DMSO (292 K) indicates the molecularly dispersed state of DAT-4COOH/MEEA in glassy DMSO.



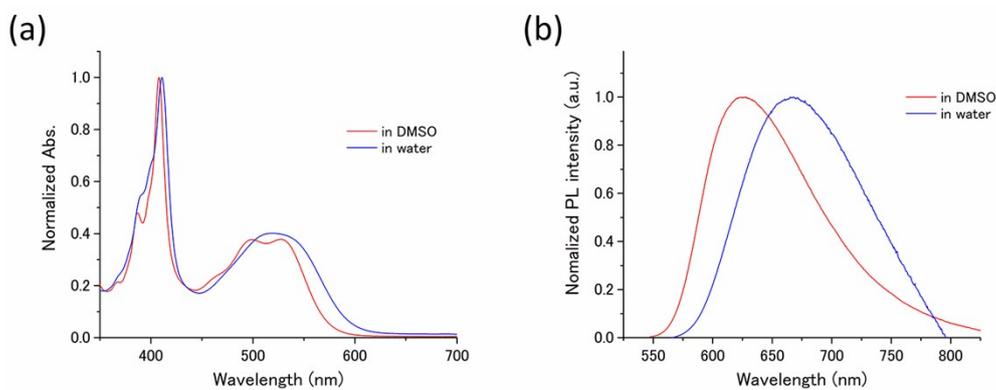
**Figure S3.** Excitation spectra of DAT-4COOH/MEEA in water at 140 K (red, [DAT-4COOH] = 1 mM, [MEEA] = 4 mM,  $\lambda_{dt}$  = 630 nm), DAT-4COOH/MEEA in DMSO at 140 K (green, [DAT-4COOH] = 1 mM, [MEEA] = 4 mM,  $\lambda_{dt}$  = 625 nm), and DAT-4COONa in water at 140 K (blue, [DAT-4COONa] = mM,  $\lambda_{dt}$  = 670 nm).



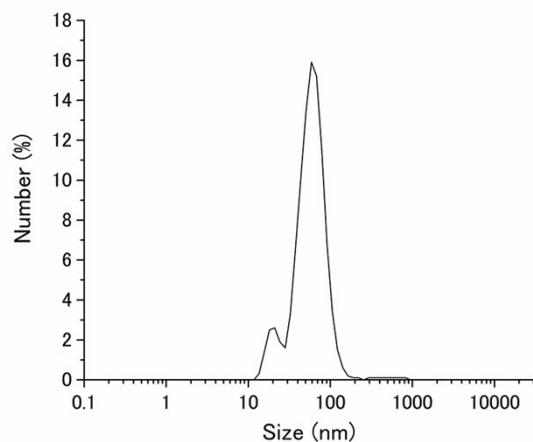
**Figure S4.** Time-resolved EPR signal intensity of DAT-4COOH (1 mM)/MEEA in water at 140 K with different MEEA concentrations of 4, 6, 8, 20, and 40 mM.



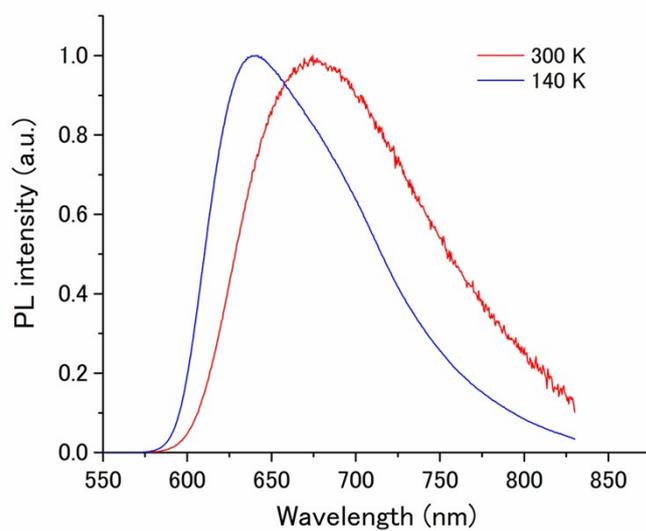
**Figure S5.** (a) Excitation spectra of DAT-4COOH/MEEA in water ( $[\text{DAT-4COOH}] = 1 \text{ mM}$ ,  $[\text{MEEA}] = 4 \text{ mM}$ ) at 300 K (red,  $\lambda_{\text{dt}} = 665 \text{ nm}$ ) and 140 K (blue,  $\lambda_{\text{dt}} = 630 \text{ nm}$ ). (b) Photoluminescence (PL) spectra ( $\lambda_{\text{ex}} = 532 \text{ nm}$ ) of DAT-4COOH (1 mM)/MEEA (4 mM) mixture in water at 300 K (red) and 140 K (blue).



**Figure S6.** (a) Absorption spectra of DAT-4COOH (1 mM)/MEEA (4 mM) mixture in DMSO (red) and in water (blue) at 300 K. (b) Photoluminescence (PL) spectra ( $\lambda_{\text{ex}} = 532 \text{ nm}$ ) of DAT-4COOH (1 mM)/MEEA (4 mM) mixture in DMSO (red) and in water (blue) at 300 K.



**Figure S7.** DLS profile of DAT-4COOH/MEEA in water at room temperature ( $[\text{DAT-4COOH}] = 1$  mM,  $[\text{MEEA}] = 4$  mM).



**Figure S8.** Photoluminescence (PL) spectra ( $\lambda_{\text{ex}} = 532$  nm) of DAT-2COOH (1 mM)/MEEA (2mM) mixture in water at 300 K (red), 140 K (blue).

**Table S1.** Zero-field splitting parameters and relative zero-field populations derived from simulation of the time-resolved EPR spectra of 0.05mol% DAT in *p*-terphenyl at room temperature<sup>1</sup> and DAT-4COOH/MEEA ([DAT-4COOH] = 1 mM, [MEEA] = 4 mM) in water at 140 K. D and E were assumed to be both positive.

	D  (MHz)	E  (MHz)	$P_x$	$P_y$	$P_z$
5,12-diazatetracene (DAT)	1598	153	0.71	0.11	0.18
DAT-4COOH/MEEA	1484	133	0.56	0.21	0.23

**Table S2.** EPR decay time of 0.05 mol% DAT in *p*-terphenyl at room temperature<sup>1</sup> and DAT/4COOH MEEA ([DAT-4COOH] = 1 mM, [MEEA] = 4 mM) in water at 140 K. The fitting was according to be following equation:  $A \exp(-t/\tau_A) + B \exp(-t/\tau_B) + C$ .

	A	$\tau_A$ ( $\mu$ s)	B	$\tau_B$ ( $\mu$ s)
5,12-diazatetracene (DAT)	0.22	11	-0.023	98
DAT-4COOH/MEEA	0.031	37	-0.0094	108

## References

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