Improving the Efficiency of Triplet Dynamic Nuclear Polarization of Biomolecules Based on Zero-Field Splitting Control of Polarizing Agent Molecules

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Dynamic nuclear polarization (DNP) improves the sensitivity of nuclear magnetic resonance (NMR) by transferring the spin polarization of electron spins to nuclear spins. However, common DNP based on radicals requires cryogenic temperatures (~1 K) to obtain a high electron spin polarization (~100%) at thermal equilibrium. In contrast, DNP using photoexcited triplet electron spins (triplet-DNP) can produce hyperpolarization at milder conditions since the triplet spin polarization is high (~70%) independent of temperature.[1]

However, conventional polarizing agents such as pentacene show broaden ESR spectra in the random orientation due to the dipole interaction between triplet electron spins (zero field splitting, ZFS), and this leads to a lower polarization transfer efficiency to target molecules. In this study, we developed new water-soluble polarizing agents with controlled ZFS and succeeded in improving the nuclear spin polarization of water molecules.

ZFS parameters of two novel water-soluble pentacene derivatives, (pentacene-6,13-diylbis(thiophene-5,2-diyl))dimethanol (PTDM) and (pentacene-6,13-diylbis(4,1-phenylene))dimethanol (PPDM), were compared (Fig. 1). ESR spectrum of photo-excited triplet state of PTDM was sharper than that of PPDM thanks to its smaller *D* and *E* values (Fig. 2). The polarization transfer from PTDM and PPDM to water molecules by triplet-DNP will also be reported.

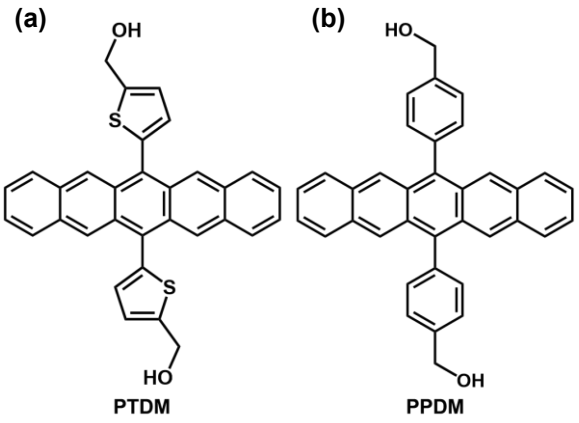

Figure 1. Chemical structures of (a) PTDM and (b) PPDM.

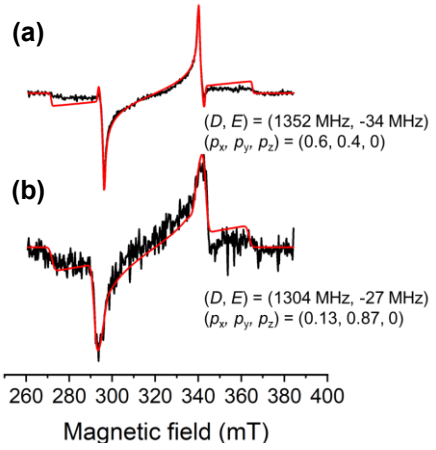

Figure 2. ESR spectra of (a) PTDM and (b) PPDM.

1) a) W. Th. Wenckebach et al., *Chem. Phys. Lett.*, **1990**, *165*, 6-10. b) N. Yanai et al., *Chem. Commun.*, **2020**, *56*, 7217-7232.

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