Singlet fission as a polarized spin generator for dynamic nuclear polarization†

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Singlet fission (SF), converting a singlet excited state into a spin-correlated triplet-pair state, is an effective way to generate a spin quintet state in organic materials. Although its application to photovoltaics as an exciton multiplier has been extensively studied,[1] the use of its unique spin degree of freedom has been largely unexplored. Here, we demonstrate that the spin polarization of the quintet multiexcitons generated by SF improves the sensitivity of magnetic resonance through dynamic nuclear polarization (DNP),[2] which is a method that transfers hyperpolarization from electron spins to nuclei.

To construct supramolecular assemblies that exhibit SF, we used sodium 4,4'-(pentacene-6,13-diyl) dibenzoate (NaPDBA) in water-glycerol (Fig. 1). Molecular dynamics (MD) simulation showed that the structure splits into multiple dimers and a few monomers. To systematically change the assembly structure and excitonic interaction, we added γ-cyclodextrin (γCD). The absorption peak of NaPDBA was red-shifted and broadened by cooling to 143 K after the inclusion was allowed to fully progress by letting the solution stand at 243 K in the presence of γCD. This suggests that the excitonic interaction between pentacenes was enhanced by the formation of the inclusion complex between NaPDBA and γCD at low temperature. The 2 : 2 inclusion complex of NaPDBA-γCD in water-glycerol at 243 K was supported by MD simulation.

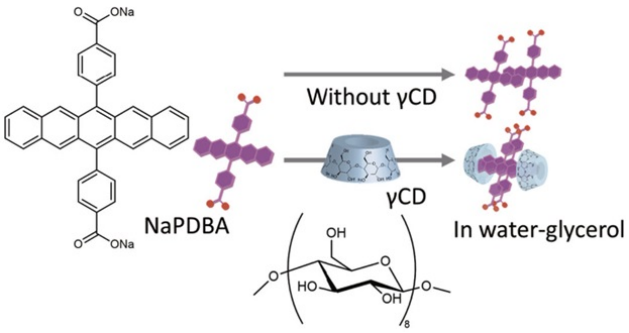

Fig. 1. Molecular structures of NaPDBA and γCD. Supramolecular assembly of only NaPDBA and the NaPDBA-γCD inclusion complex.

To investigate the SF properties of these systems, we conducted pump-probe transient absorption spectroscopy and electron spin resonance (ESR) measurements at 143 K on both bare NaPDBA dimers and the NaPDBA-γCD complex. Results suggest that both aggregated and isolated NaPDBA coexisted in the water-glycerol glass system, and both SF-derived and Intersystem crossing-derived triplets were generated with light irradiation.

DNP was performed using the polarized electron spins produced in these supramolecular assemblies. With NaPDBA and NaPDBA-γCD, signal enhancement of 30% and 46%, respectively, was observed in the magnetic field corresponding to the quintet ESR peak compared to the magnetic field corresponding to the triplet ESR peak, respectively (Fig. 2). We also investigated the dependence of the microwave intensity irradiated during the DNP sequence using the quintet and triplet electron spin polarizations. The NMR signal was maximized at a weaker intensity with the quintet than with the triplet. This is because the Rabi frequency of electrons in the quintet state is $\sqrt{3}$ times higher than that in the triplet state.[3] This result further confirms that the SF-derived polarized quintet state is successfully utilized for the DNP application.

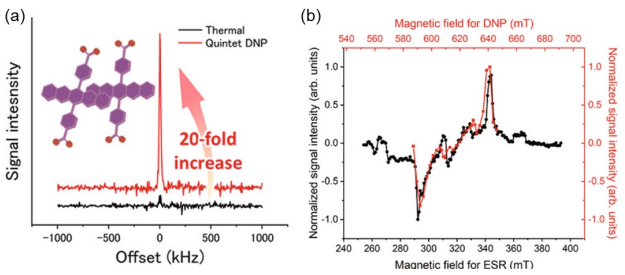

Fig. 2. DNP using SF-born quintet electron spin polarization. (a) ^{1}H-NMR signals under thermal conditions (black) and after quintet-DNP for 5 min (red) of water-glycerol (glycerol-d_8 : D_2O : H_2O = 5 : 4 : 1) containing NaPDBA. (b) Magnetic field dependence of ^{1}H-NMR by DNP and ESR spectra.

† Condensed from the article in Nat. Commun. **14**, 1056 (2023)

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DOI:10.34448/RIKEN.APR.57-202

To date, the application of SF has been mainly limited to the field of energy. This study opens a new potential application of SF to quantum biotechnology based on the unique multiexcitons exhibited by organic chromophores.

References

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