

Polarizing agents beyond pentacene for efficient triplet dynamic nuclear polarization in glass matrices[†]

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Triplet dynamic nuclear polarization (triplet-DNP),¹⁾ a means of transferring spin polarization from a electron of polarizing agents to the nuclei of a matrix material, is a technique that can obtain high nuclear polarization in low magnetic field and at high temperature. However, in order to obtain practically useful polarization, large single crystals doped with a polarizing agent must be strictly oriented with respect to the magnetic field to sharpen the electron spin resonance (ESR) spectra. Instead of a physical approach, we propose a chemical approach, *i.e.*, molecular design of polarizing agents; pentacene molecules, the most typical triplet-DNP polarizing agent, were modified to make the triplet electron distribution wider and more isotropic without loss of the triplet polarization.

The key parameters are the zero-field splitting (ZFS) parameters *D* and *E*, which represent the energy gaps between triplet sublevels in the absence of a magnetic field.¹⁾ The *D* and *E* values are related to the average distance between spins and rhombicity of the ZFS tensor, respectively. This implies that a molecular design with smaller *D* and *E* should make the triplet electron distribution more isotropic and symmetric, respectively. As a proof of concept, we designed unique polarizing agents by modifying pentacene with 5-membered rings (Fig. 1(a)), 6,13-di(benzofuran-2-yl)pentacene (DBFP), 6,13-bis(benzo[b]thiophen-2-yl)pentacene (DBTP), and 6,13-di(thiophen-2-yl)-pentacene (DTP).²⁾ The less sterically hindered furan and thiophene rings were not orthogonal to pentacene and expected to extend the conjugation.

ESR spectra were measured at X-band and room temperature (Fig. 1(b)). Each polarizing agent, pentacene, 6,13-diphenylpentacene (DPP), DBFP, DBTP, and DTP, was molecularly dispersed in β -estradiol. Compared to pentacene, DBTP and DTP exhibited much stronger and sharper ESR spectra, which was reflected in their smaller *D* and *E* values. The ESR intensity of DBFP was smaller than that of DBTP. This may be due to the lower intersystem crossing efficiency and the smaller population difference of DBFP. Quantum chemical calculations indicated that molecular vibrations that break the planar symmetry determine the spin-selectivity and ZFS parameters.

To evaluate the potential of the new polarizing agents, the ¹H-NMR signal intensities after triplet-DNP were

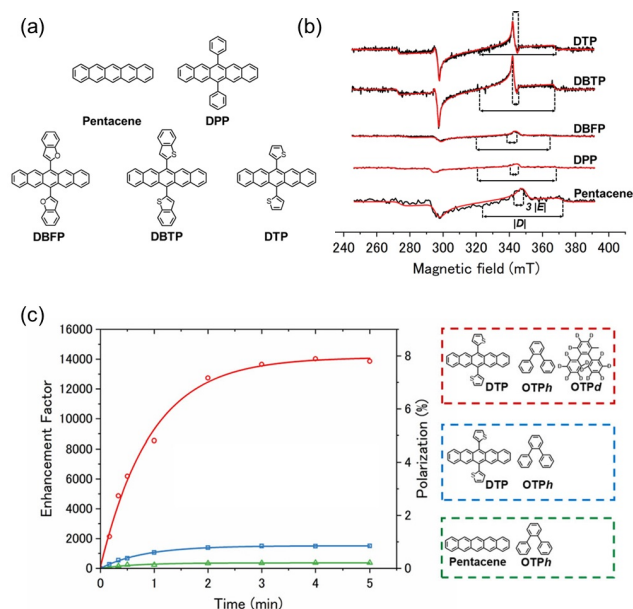


Fig. 1. (a) Chemical structures of polarizing agents: pentacene, 6,13-diphenylpentacene (DPP), 6,13-di(benzofuran-2-yl)pentacene (DBFP), 6,13-bis(benzo[b]thiophen-2-yl)pentacene (DBTP), and 6,13-di(thiophen-2-yl)pentacene (DTP). (b) Time-resolved ESR spectra doped in β -estradiol at room temperature. (c) Buildup curves of ¹H signal intensity of *o*-terphenyl (OTP) doped with pentacene (green) and DTP (blue) and partially deuterated OTP (OTP: [D14]OTP = 10: 90wt%) doped with DTP (red) in 0.65 T at 120 K.

compared between DTP and pentacene doped in *o*-terphenyl (OTP) in 0.65 T at 120 K.³⁾ The ¹H polarization and enhancement factor after 5 min of triplet-DNP reached 0.85% and 1,540 times, respectively, which were about four times larger than those of pentacene (0.21% and 370 times) (Fig. 1(c)). The polarization can be improved by reducing the density of ¹H spins. By changing the glass matrix to a mixture of OTP and fully deuterated [D14]OTP (OTP: [D14]OTP = 10: 90wt%), the ¹H polarization and enhancement factor were increased to 7.8% and 14,000 times, respectively.

The power of our chemical approach was demonstrated in an amorphous system. This indicates that a polarizing agent that exceeds the performance of pentacene, which has been considered the best over the last 30 years since triplet-DNP was first proposed, was shown to be feasible.

References

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