Making Triplet Dynamic Nuclear Polarization More Accessible and Feasible

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Nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging (MRI) are powerful and versatile methods in modern chemistry and biology fields. Nevertheless, they suffer from intrinsically limited sensitivity due to the low nuclear spin polarization at ambient temperature. One of the promising methods to overcome this limitation is dynamic nuclear polarization (DNP) that transfers spin polarization from electrons to nuclei. In particular, DNP based on photo-excited triplet (triplet-DNP) is promising, since it allows the hyperpolarization at room temperature.[1] In typical scheme of triplet-DNP (Fig. 1a), the spin-selective intersystem crossing (ISC) produces the large electron spin polarization in the excited triplet state sublevels, and this polarization is effectively transferred to nuclear spins by a pulsed microwave irradiation for satisfying Hartmann-Hahn condition, so-called integrated solid effect (ISE).

Previous studies of triplet-DNP have been limited to dense crystalline and amorphous materials, and it remains difficult to hyperpolarize biology-relevant probes. To overcome this limitation, we introduce the chemistry of metal-organic frameworks (MOFs) to the field of triplet-DNP (Fig. 1b).[2] The nanoporous structure of MOFs allows the accommodation of polarizing agents as well as other guest molecules. This work paves the way towards the hyperpolarization of various probe molecules at room temperature for imaging applications.

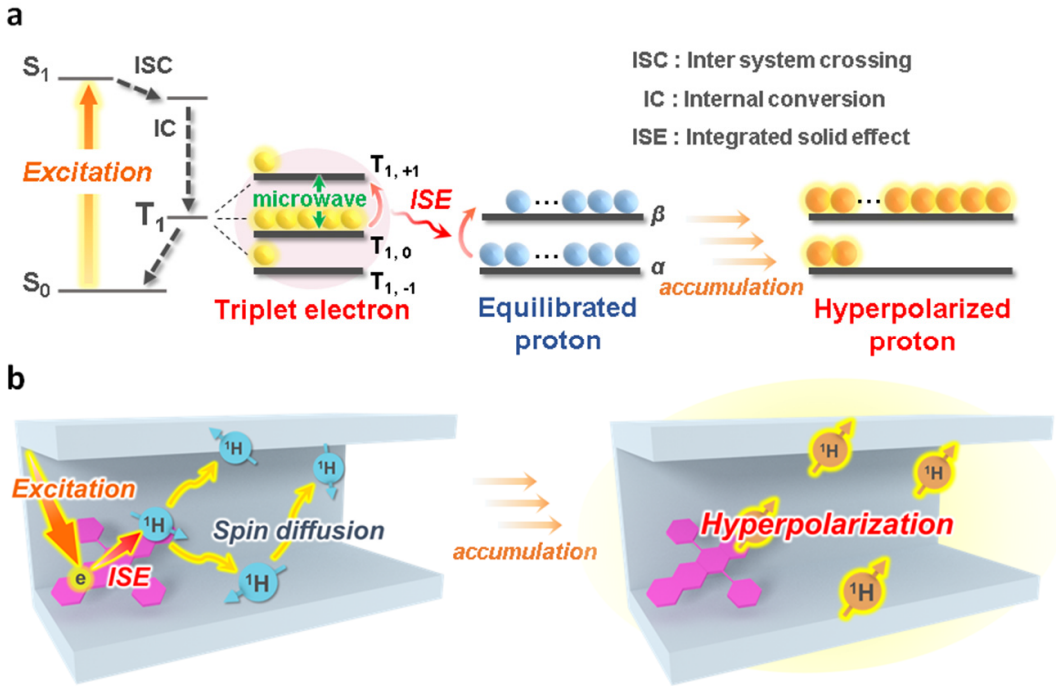

Fig. 1 (a) Typical scheme of Triplet-DNP. (b) Schematic illustration of Triplet-DNP in MOFs accommodating polarizing agents.

Another important challenge of triplet-DNP is to develop air-stable polarizing agents. Since the first report of room-temperature triplet-DNP in 1990,[1] pentacene has been the only and best option of triplet polarizing agents. However, the poor air-stability of pentacene has severely limited the applicability of triplet-DNP. We demonstrate new polarizing agents with significant air-stability as well as high polarizing ability comparable to pentacene.

References:

1. A. Henstra, T.-S. Lin, J. Schmidt, W. Th. Wenckebach, *Chem. Phys. Lett.* **1990,** *165*, 6-10.
2. S. Fujiwara, M. Hosoyamada, K. Tateishi, T. Uesaka, K. Ideta, N. Kimizuka, N. Yanai, *J. Am. Chem. Soc.*, **2018**, *140*, 15606-15610.