Photo-generated extremely long-lived spin-polarized radicals in Metal-Organic Frameworks

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The generation and control of the electron spin polarization (ESP) is a crucial foundation not only for a wide range of quantum technologies but also for dynamic nuclear polarization (DNP), which is a technique to enhance the signal intensity of NMR and MRI. In addition to the generation of ESP, elongated spin-lattice relaxation times of the electron spin (T_{1e}) is desired for expanding the scope of future quantum technology and DNP. However, in conventional systems, T_{1e} has been limited to less than a few μs at room temperature. In this work, we have discovered photo-generated spin-polarized radicals with extremely long lifetime in acene-based metal-organic frameworks (MOFs).

To obtain large ESP at room temperature, we employed 5,12-diazatetracene (DAT) which can produce polarized triplets by photo-irradiation. We synthesized new ligand DPyDAT by modifying DAT with pyridine as a coordination site to the metal. Pillared-layer type of the MOF was synthesized with DPyDAT, Zn ion and carboxylic ligand. DAT moieties are aligned one-dimensionally with relatively close distance in the skeleton of the MOF. ESP formation in the MOF was evaluated by time-resolved ESR measurements at room temperature. The ESR spectrum of the MOF showed, in addition to the DAT triplet-derived pattern, a relatively sharp emissive peak of radical origin around 342 mT. Significantly, spin-lattice relaxation time T_{1e} was found to be as long as 275 μs by pulsed ESR inversion recovery sequence at 342 mT at room temperature. We will also show the relationship between assembly structure of acenes and the T_{1e} value by comparing different MOF structures.

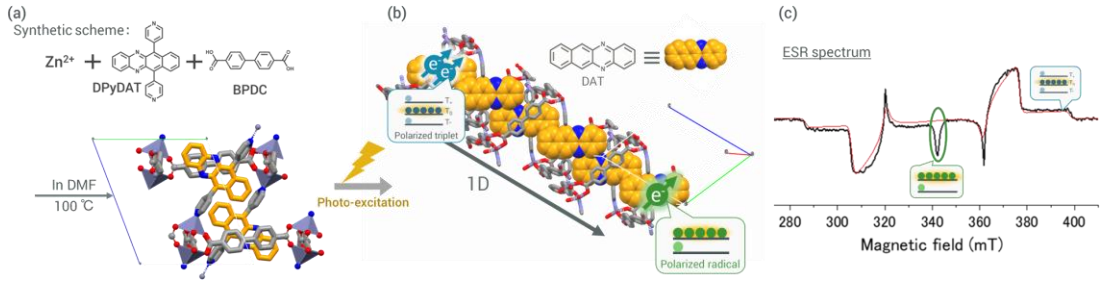

Fig. 1 (a) Synthetic scheme and structure of the MOF. (b) Schematic image of this work. (c) Tr-ESR spectrum of the MOF.

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