1-1-9. Time-Resolved ESR Spectroscopy

Overview

Time-Resolved Electron Spin Resonance (Time-Resolved ESR) detects the nanosecond time evolution of spin states of short-lived paramagnetic species (radicals, triplets, radical pairs, etc.) generated by photochemical processes. Non-equilibrium spin state distributions and correlations immediately after formation are observed by microwave. Anisotropic microwave absorption (A) and emission (E) due to spin correlations after photoinduced charge separation ($PD^{+}Pheo_{D1}^{-}$) from chlorophyll and pheophytin were observed in the photosynthetic membrane protein PSII in 2017, and the three-dimensional structure of this state was first shown from magnetic anisotropy with respect to the external magnetic field (B_0) direction (Fig. 1).

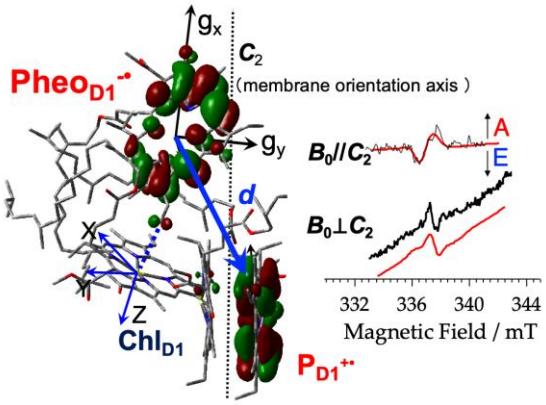

Figure 1. Determination of photoinduced charge separation geometry using time-resolved ESR.

Current Status and Frontiers

Time-resolved ESR studies of photochemistry have been conducted out of basic scientific interest and have led to the development of spin chemistry. In Japan, measurements were pioneered by Obi, Murai and by Hirota, Yamauchi, Terashima in the early 1980s. Kuwata, Ikegami, Tero, Higuchi, Azumi, and many other prominent researchers joined, and this research was expanded to quantum manipulation of photoreactions by Murai, Maeda, and others in the 1990s. In recent years, time-resolved ESR measurements have been useful not only for functional evaluation of photoenergy conversion in organic solar cells, functional expression of photoreceptor proteins, and exciton pair formation by singlet fission, but also in various fields such as spin quantum technology using light as input and readout as a qubit and chirality-induced spin selection.

1. Functional evaluation of light energy conversion

Organic photovoltaic cells (OPVs) and organic light-emitting devices (OLEDs) are regarded as next-generation devices that are lightweight, thin, flexible, and low-cost, etc. For OPVs, long-range charge-separation structures were first demonstrated by time-resolved ESR (Kobori et al. 2013), and the causes of photocurrent and voltage losses are also being clarified (Imahori and Kobori et al. and Yamada and Kobori et al.), and for OLEDs, time-resolved ESR has been used to observe triplets that cause thermally activated delayed fluorescence, revealing the electronic states and activation details (Ikoma et al. and Aizawa et al.) The ESR were also used to elucidate intermediate functions for the synthesis using organic photocatalysts (Kanai, Mitsunuma, Kobori,

et al.).

2. Functional expression by photoreceptor proteins

In 2021, structure of a photoreceptor intermediate involved in magneto-photoreception and its role in the fluctuation of protein-bound water were investigated by time-resolved ESR. The electronic function inside the protein that expresses magneto-compass properties was clarified (Kobori, et al.).

3. Spin conversion of exciton pairs in singlet fission (SF) and triplet-triplet annihilation (TTA)

Time-resolved ESR measurements on molecular assemblies and dimers have been performed since 2018 for the formation and annihilation of quintet excitons and spin-correlated triplet pairs (Fig. 2), which are important processes for SF efficiency enhancement, and the details of molecular vibrations and electronic effects were shown in 2022 (Nagashima and Kobori et al). As for TTA upconversion (TTA-UC), which is the reverse process of SF, the spin conversion process was shown by ESR in 2024, and the ultrafast kinetic effect was also shown in 2025 (Okamoto, Ikoma, Kobori et al.)

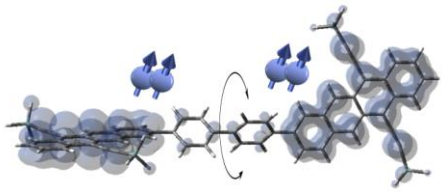

Figure 2. Geometry of spin-correlated excitons induced by triplet pair activation motion in intramolecular singlet fission.

4. Development of novel spin quantum manipulation techniques in photochemical reactions

After 2020, optical spin qubit manipulation has become the focus of attention, and the following research projects were carried out: reaction control by electromagnetic irradiation and waveforms (Maeda et al., Kanemoto et al., Wakikawa and Ikoma et al.), measurement of excited quartets in chromophore-radical systems (Teki et al., Asano et al.) and their intramolecular vibronic effects (Kobori et al.), observation of giant electron spin magnetization and hyperpolarization produced by spin conversion in the quartet (Kawai et al., Yanai et al.).

References

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Future Perspectives and Directions

Issues to be solved and realized by the end of the next decade: Development of devices combining OPV with quantum technology, development of quantum life science, quantum spin manipulation and quantum sensing using light as input and readout, and its application to the medical field.

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