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DIPOLAR EPR SPECTROSCOPY OF FULLERENE AND PORPHYRIN SYMMETRIC PAIRS

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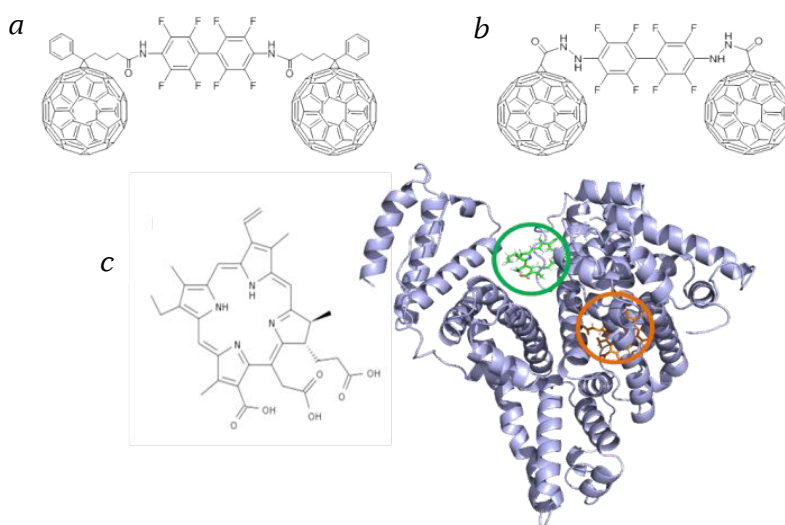
Abstract

This work introduces a dipole electron paramagnetic resonance (EPR) approach for measuring distances in symmetric non-orthogonal photoexcited spin pairs, aiming to enhance sensitivity of pulsed EPR techniques. Using fullerene and porphyrin-based pairs, the study explores intermolecular distances, spectral features, proposing a methodology for nanometer-scale distance measurements in such systems with potential applications in biological contexts.

In this work, we introduce for the first time a dipole electron paramagnetic resonance (EPR) approach for measuring distances in symmetric non-orthogonal photoexcited spin pairs. Previous research has effectively explored spin pairs consisting either of a photoexcited triplet state of a molecule paired with a stable radical [1, 2], or two photoexcited triplet states of different natures [3]. The subsequent phase involves examining a coupled system containing two photoexcited triplet states to potentially enhance the sensitivity of pulsed EPR techniques through the intensified hyperpolarized signal emanating from two identical components of the pair. Furthermore, such symmetrical systems are increasingly utilized in the efficient conversion of solar energy into electrical energy. Despite the theoretical efficiency limit of contemporary solar cells being only 34 %, utilizing the singlet fission process in such symmetric spin pairs could elevate this efficiency to 44 %. This increase is facilitated by the generation of two charge carriers rather than one, a process hindered by intersystem crossing (ISC) in spin pairs, which does not contribute to an efficiency gain in solar cells [4].

The aim of this work is to develop an approach for measuring nanometer-scale distances using electron paramagnetic resonance (EPR) in symmetric photoexcited spin pairs based on fullerene and porphyrin. The investigations were conducted using molecules of bisfullerene connected by a fluorinated linker, and pairs of chlorin e6 molecules in complex with human serum albumin.

The echo-detected spectra of the bisfullerene molecules revealed several noteworthy effects and distinctions compared to the monomeric form of PCBM. The spectrum of the bisfullerene was notably broader and featured a distinct set of spectral lines. Utilizing a theoretical framework that involves strongly interacting spins within fullerene pairs,



Structures of the studied spin pairs: *a* — bisfullerene with a long linker, *b* — bisfullerene with a short linker, *c* — chlorine molecule e6 and its complex with human serum albumin

coupled with considerably weaker dipolar interactions between the fullerenes, enabled the simulation of the echo-detected spectrum and the estimation of inter-fullerene distances using the point dipole approximation. Data derived from nutation experiments and subsequent modeling suggest that the formation of the two triplet states in the system under investigation occurs not via inter-combination conversion, but through the mechanism of singlet fission.

However, not all transitions within the triplet state spectra were accurately described by the existing model. During experiments with a delayed interval post-laser pulse, a spectral line emerged, associated with the coherence transfer of transitions having closely matched frequencies. Throughout the course of the experiments, a general decline in the intensity of the echo-detected spectrum was observed, alongside a notable peak at the center. Additionally, a resolution of the two extreme lines of the original triplet spectrum and a reversal in the sign of one of the spectrum lines were detected. These observed effects could be further modeled by considering an exchange interaction between the paired fullerenes.

We proposed a methodology for measuring distances in symmetric photoexcited spin pairs using the relaxation-induced dipole modulation enhancement (RIDME) pulsed EPR technique. The experimental label spacing determined in bisfullerene aligns with estimates derived from ED spectrum modeling. Additionally, this approach enabled the first-time measurement of the distance between two binding sites of chlorin e6 with albumin. The RIDME technique has thus proven effective for probing nanometer-scale distances in symmetric photoexcited spin pairs, including applications in biological systems. This method utilizes the high quantum yield of photoexcited triplet states and overcomes a significant limitation of dipolar methods — the presence of a broad echo-detected spectrum.

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