Spin exchange between triplet ^{3}CS and ^{3}LE states in NI-PXZ dyad revealed by TR EPR

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The control over the photoexcited triplet state formation plays a key role in quantum information science and spintronics. Moreover, the development of the ways of increasing the singlet-triplet transition quantum yield is important for photodynamic therapy and design of new triplet-triplet annihilation upconversion based devices. There are several mechanisms of intersystem crossing (ISC) within organic molecules: spin-orbit ISC – the most common one, which quantum yield can be enhanced by heavy atom effect; radical pair (RP) ISC and spin-orbit charge transfer (SOCT) ISC. The latter two occur within donor-bridge-acceptor (DbA) chromophore dyads as a result of a charge separation (CS) and following charge recombination from the ^{3}CS to a triplet locally excited (^{3}LE) state. The SOCT ISC is the most promising mechanism since it requires only synthesis of purely organic compounds, readily tunable for a particular application. However, SOCT ISC is understudied. There is no model of it that covers all its features observed in experiments. One of the phenomena will be discussed in this report.

We studied a naphthalimide-phenoxazine (NI-PXZ) dyad by time-resolved EPR spectroscopy – a technique providing various information about a short-lived triplet state. The unique spectral lineshape of ^{3}(NI-PXZ) and its dynamics correspond well to a spin exchange between its ^{3}CS and ^{3}LE [1]. This conclusion concurs with the findings of other experimental techniques and DFT calculations provided by our colleagues. Thus, for the best of our knowledge, it is the first observation of the spin exchanging ^{3}CS and ^{3}LE in a DbA dyad, an important one for the further design of the SOCT ISC compounds.

The measurements were performed at 80 K using a homemade X-band TR EPR spectrometer based on Bruker EMX. The molecules dissolved in 2MeTHF:TOL (1:3, v/v) mixture were efficiently excited by 355 nm laser light.

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