

Probing Exciton Delocalization in Organic Semiconductors: Insight from Time-Resolved Electron Paramagnetic Resonance and Magnetophotoselection Experiments

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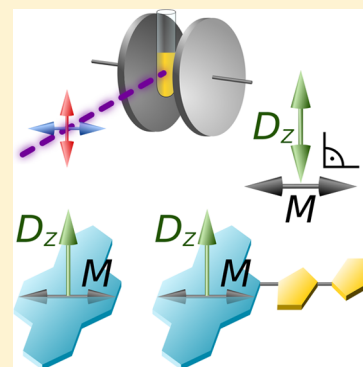
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Supporting Information

ABSTRACT: Delocalization of excited states of organic semiconductors is directly related to their efficiency in devices. Time-resolved electron paramagnetic resonance spectroscopy provides unique capabilities in this respect because of its high spectral resolution and capability to probe the geometry and extent of excitons. Using magnetophotoselection experiments, the mode of exciton delocalization, along the backbone or parallel to the π – π stacking direction of the conjugated polymers, can be revealed. We demonstrate the robustness of this approach by applying it to building blocks of a prototypical conjugated polymer showing a symmetry of their excited states being far from ideal for this experiment. This renders magnetophotoselection superior to other approaches because it is applicable to a wealth of other organic semiconductors. The insight gained into exciton delocalization is crucial to the structure–function relationship of organic semiconductors and directly relevant for developing highly efficient materials.



Organic electronics have come a long way¹ and are increasingly competing with and replacing their inorganic counterparts, particularly in the field of light-emitting diodes^{2,3} found nowadays in commercial displays and in photovoltaics.^{4,5} To gain a thorough mechanistic understanding of organic semiconductors, detailed knowledge of the electronic structure of excited states and in particular their delocalization within the molecule is of outstanding importance.^{6–8} Depending on the desired application, either localized or delocalized excited states are in demand. The importance of exciton delocalization stems from its relation to the direction of exciton migration and charge transport, hence the efficiency of conduction mechanisms. Two parameters are of particular interest: the extent of delocalization and its direction with respect to the polymer backbone, the latter either along the backbone or perpendicular to it, i.e. parallel to the π – π stacking direction. Spectroscopic methods capable of probing these parameters, ideally not requiring complicated preparation such as orienting the sample, are therefore in high demand.

Many conjugated polymers and their building blocks readily form spin-polarized triplet states when optically excited.^{9–12} Therefore, because of its molecular resolution, electron paramagnetic resonance (EPR) spectroscopy and specifically its time-resolved variant, TREPR spectroscopy,^{13,14} are particularly well-suited to probe these excited states. Generally, the local molecular environment,¹⁵ the delocalization of the excited state,^{16,17} and the orientation of the molecule with

respect to a substrate¹² can be probed. Because of the inherent anisotropy of the dipolar interactions between the two unpaired electrons of a triplet state, TREPR spectroscopy even allows the probing of the orientation of this interaction within the molecule, hence the mode of exciton delocalization. The key here is to probe the geometrical relation between the optical transition dipole moment of the molecule and the resulting triplet state by using linearly polarized light for excitation. Such magnetophotoselection experiments were performed early on for aromatic molecules¹⁸ and were crucial in revealing details of the electronic structure of chromophores taking part in photosynthesis.¹⁹

Here, we apply this method to two building blocks of a representative conjugated polymer with high relevance for organic electronics applications, namely, the n-type polymer PNDIT2, also known as P(NDI2OD-T2) or Polyera ActivInk N2200 and renowned for its high charge carrier mobility.^{20,21} Recent interest in NDI-based systems is driven by the general need for versatile electron acceptor materials and more specifically the demand for nonfullerene acceptors in organic electronics that very recently have overtaken fullerenes in terms of efficiency in organic solar cells.²² As will be detailed below, using building blocks rather than the polymer is

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