Exciton diffusion length, delocalization range and the energetic disorder in organic semiconductors

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We present a new method to evaluate the exciton diffusion length and the delocalization range of photoexcitations in organic semiconductors based on photoinduced charge generation directly probed from the internal quantum efficiency (IQE). By doping organic semiconductors with materials which are able to quench excitons at very low densities, and using appropriate 3D analytical and numerical models we were able to develop an approach to decouple the diffusive part of exciton quenching from its instantaneous component which corresponds to exciton delocalization. For three different organic semiconductors, PC70BM, P3HT, and PCDTBT, our results indicate typical exciton diffusion lengths on the order of several nm but substantial delocalization lengths on the order of few nm. Furthermore, we present a new means to measure energetic disorder in neat organic semiconductors by measuring the IQE as a function of the incident photon excess energy.

Quantifying electronic bandgap, exciton binding energy, and energetic disorder from the IQE

Here we propose that the IQE spectra of devices made of a single layer of neat organic semiconductors is indicative of the energetic disorder and electronic bandgap. Using kinetic Monte-Carlo (KMC) simulations, we demonstrate how energetic disorder determines the spectral shape of the IQE. Based upon the KMC simulations the energetic disorder can be determined by fitting an error function to the experimental IQE data. We predict that the disorder can enhance charge separation in neat materials through creating a relative "hotness" between the organic semiconducting molecules in the density of state with the help of photon excess energy. We also predict that the amount of energetic disorder in the materials, measured experimentally, is larger than that previously thought. Very importantly, the results also explain the mechanism of charge generation in neat organic semiconductors.
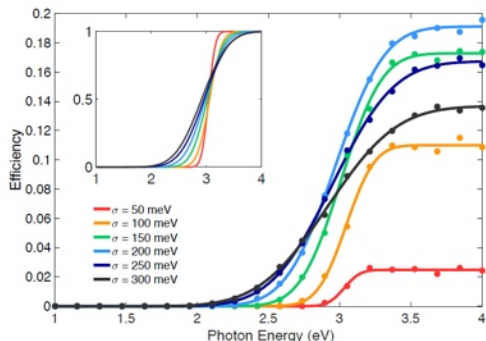
Polymer	Disorder (meV)	Mean electronic energy (eV)	Electronic gap (eV)	Optical gap (eV)	Exciton binding energy (eV)
PCPDTBT	200	2.8	2.0	1.5	0.5
PTB7	250	3.0	2.3	1.6	0.7
P3HT	190	3.2	2.6	1.9	0.7
MEHPPV	190	3.4	3.0	2.1	0.9
DPP-DTT	230	2.5	2.0	1.4	0.6
PCDTBT	250	3.2	2.5	1.8	0.7
PB-TTT	240	3.3	2.7	1.9	0.8
Super Yellow	210	3.3	2.7	2.2	0.5

Table 1. Experimental fitting results. The energetic disorder values are determined from the width of the onset of the IQE and the mean electronic energy indicates the position of the middle of the IQE. The electronic gap can be thought of as the point at which charge generation begins to happen (the beginning of the IQE onset), and the optical gaps are from absorption. The difference between the electronic gaps gives the exciton binding energy for each material.

Quantifying the exciton diffusion length and the delocalisation range in organic semiconductors

In this contribution, we also show that under operational steady state condition, excitons in a matrix of an electron acceptor or a donor can be quenched through long-range delocalisation and diffusion, and we evaluate the branching fraction between these two processes. The approach is based upon applying a 3D model of the exciton quenching yield (QY) in slightly doped donors with acceptors (or vice versa) in the regimes where the charge generation occurs at the single molecular level, provided that a quencher molecule is almost isolated from other quenchers. We quantify the diffusion length and the delocalisation range for three different systems. The diffusion lengths range between 5-10 nm (depending on the system) in agreement with previous reports where a comparison is possible. Strikingly, we estimate the delocalisation range to be also of several nm. The results presented here indicate that only a limited fraction of excitons (10-20 %) can undergo quenching through delocalisation, and therefore, diffusion is mainly responsible for exciton dissociation.

The approach is based on considering a matrix of an organic semiconductor slightly doped with an exciton quencher. Each quencher located at position has a quenching volume around it; being the region in which the generated exciton at position is quenched with the probability of . The observable QY is obtained by averaging over the initial position of the exciton, which we assume is uniformly distributed within a simulation volume :

$$. \qquad\qquad (1)$$

Figure 2a schematically shows how QY changes as the quencher concentration increases. The probability function is different for diffusive and delocalised excitons. We analytically calculate this function for diffusive excitons undergoing a random walk and confirm its validity using MC simulations. For delocalised excitons we assume a Gaussian function for . Figure 2b shows QY versus the quencher concentration for three cases of diffusion-only, delocalisation-only and a combinational case. By measuring the quenching yield in a broad range of quencher concentration using this novel technique, we can fit our model to experimental data and evaluate the diffusion length, delocalisation range and the branching fraction () between the excitons quenched through these two pathways.
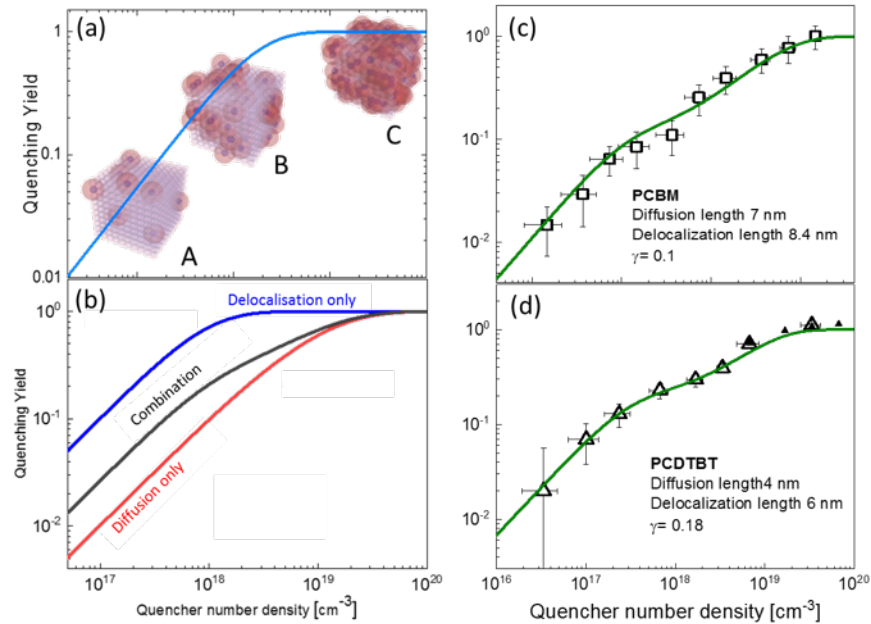

Figure 2. *(a) Demonstration of quenching yield as a function of quencher concentration. (b) Quenching yield through delocalisation, diffusion and combination (c) and (d) fitting the model on the experimental data for PC70BM and PCDTBT.*