

# Ultrafast Spectroscopy Reveals Bulk Heterojunction Morphology

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**Abstract:** We propose a new technique to probe the nanosized morphology in polymer-fullerene bulk heterojunctions by ultrafast spectroscopy. The method reveals the size of fullerene clusters in an all-optical way and is applicable “on-the-fly” to functional photovoltaic devices.

**OCIS codes:** 300.6530 Spectroscopy, ultrafast; 160.4890 Organic materials; 180.4315 Nonlinear microscopy.

## 1. Introduction

The morphology of the bulk heterojunction – the nanoscale texture of polymer and fullerene constituents – is one of the key ingredients for optimization of the efficiency of modern plastic solar cells [1]. The particular morphology emerges from self-organization of polymer and fullerene fractions into an interpenetrating network. This first maximizes the interface area where optically excited excitons are separated into charges, and second, provides pathways of charge transport to the device electrodes. Morphology is a challenging property not only to control but even to characterize as this generally requires chemical selectivity combined with nanometer spatial resolution. Standard methods for studying nanostructures – such as AFM, STM, TEM, SAXS, etc. – either lack adequate spatial resolution or require special sample preparation (or both).

Here we show how ultrafast spectroscopy can be used to obtain information on morphology by making use of fullerene excitons [2]. Our approach (Fig.1a) is based on the fact that the soluble fullerene derivative PC<sub>71</sub>BM, currently used in the overwhelming majority of novel organic photovoltaic blends, exhibits a substantial visible light absorption. First, a pump pulse selectively creates an exciton in the PC<sub>71</sub>BM domain which after diffusion to the interface dissociates into a hole on the polymer and an electron on the fullerene. The hole modifies the vibronic structure of the polymer leading to the so-called polaron absorption which is probed by a delayed IR pulse [3]. From the delay of the IR response and efficiency of exciton-to-hole generation, a characteristic size of the PC<sub>71</sub>BM domains is retrieved via the ratio of short-time interfacial and long-time diffusion-mediated contributions. The key advantage of the proposed all-optical technique over its rivals lies in its potential applicability to functional photovoltaic devices at no additional materials preparation.

## 2. Experimental

As donor polymers we selected MDMO-PPV (known for extreme phase segregation), regiorandom (RRa-) P3HT (good miscibility with PC<sub>71</sub>BM) and regioregular (RRe-) P3HT (formation of crystalline structure). Selective PC<sub>71</sub>BM excitation was performed by choosing appropriate pump energies (1.82 eV for P3HT and 1.97 eV for MDMO-PPV) below the polymer absorption bandgap where the PC<sub>71</sub>BM absorption dominates to warrant high contrast between fullerene and polymer responses. Different weight ratios of constituents were used to decipher direct and diffusion-mediated hole transfer. IR spectra of the polaron response were measured in the 1-10 μm range (not shown); the wavelength of the probe was chosen near the low-energy peak at 3 μm.

## 3. Results

Figure 1b shows a few representative transients for two of the polymers used. At low PC<sub>71</sub>BM concentrations, the fullerene molecules are well dispersed in the polymer matrix so that the polymer response is delayed only by the

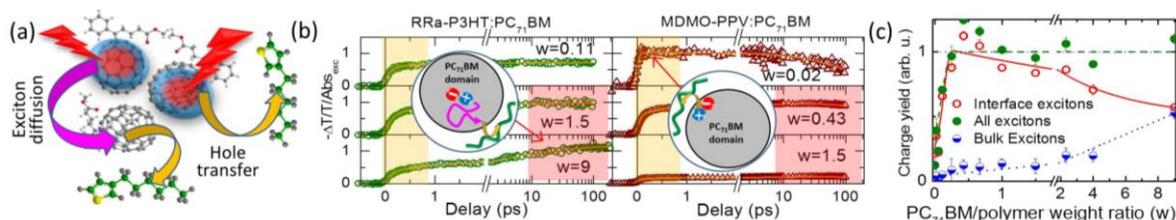


Fig. 1. a) Concept of the technique. Lightning bolt: PC<sub>71</sub>BM excitation, magenta arrow: PC<sub>71</sub>BM exciton diffusion, yellow arrow: exciton dissociation via hole transfer to the polymer. b) Representative (out of 30) transients for two polymers at different PC<sub>71</sub>BM concentrations (indicated by PC<sub>71</sub>BM/polymer weight ratio  $w$ ). Symbols: experimental data, solid curves: fits from Monte-Carlo simulations. Yellow and red shaded areas indicate characteristic times for interfacial and diffusion-mediated exciton dissociation, respectively. (c) Charge yield at 1 ps (red dots), 80 ps (green dots), and their difference (blue dots) for blends with different PC<sub>71</sub>BM/RRa-P3HT weight ratios.

hole transfer time (<100 fs). At high PC<sub>71</sub>BM concentrations, the fullerene molecules begin to form phase-separated domains. This results in a slowly raising response in the 10-200 ps range since now (a part of) the PC<sub>71</sub>BM excitons need to diffuse further to reach the interface where they can charge separate. In the MDMO-PPV case, the PC<sub>71</sub>BM domains grow to such size that most excitons cannot reach the interface within their lifetime (~500 ps) which leads to a decreased amplitude of the response (lowest transient, w=1.5). Therefore, transient amplitudes at short times (~1 ps) indicate direct interfacial charge yield while the long-time amplitudes give both interfacial and diffusion mediated charge yield.

Interfacial and diffusion-mediated charge yields are summarized in Fig. 1c. At weight ratios lower than ~0.5, the charge yield increases because of increased contrast between PC<sub>71</sub>BM and still-noticeable polymer excitation (which yields mainly polymer excitons but few polarons). At higher concentrations, the total charge yield levels off, i.e. each absorbed photon eventually produces a charge pair. However, the preceding dissociation pathways are very different: the contribution of interfacial excitons decreases while the share of diffusion-mediated excitons increases.

Knowing the fractions of interface and diffusion mediated excitons, we can readily estimate the typical size of PC<sub>71</sub>BM clusters (Fig. 2a) assuming these to be spherical, by simple surface-to-volume argument. From this we find that the PC<sub>71</sub>BM cluster diameter varies from ~1 nm (single PCBM molecule) to ~7 nm in RRa/RRe-P3HT:PC<sub>71</sub>BM blends and ~4 nm in MDMO-PPV:PC<sub>71</sub>BM blends. Hence, the first two polymers exhibit reasonable good miscibility with optimal domain sizes for both polymer and fullerene exciton harvesting. In contrast, MDMO-PPV:PC<sub>71</sub>BM blends demonstrate explosive growth of the domain size at weight ratios higher than 1.5 resulting in a catastrophic decrease of PC<sub>71</sub>BM exciton yield (Fig. 1b).

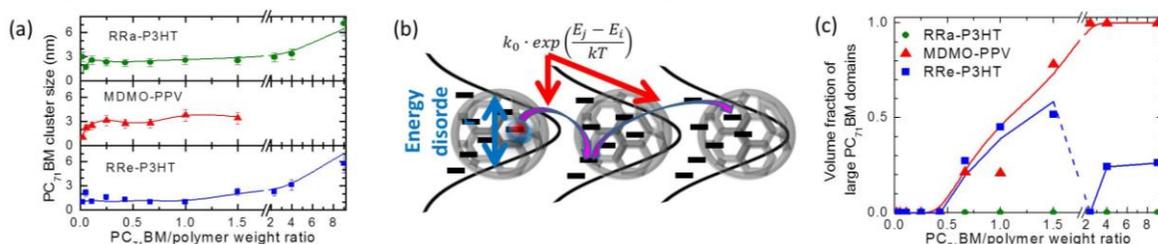


Fig. 2. a) PC<sub>71</sub>BM aggregate sizes at different PC<sub>71</sub>BM/polymer ratios for the three investigated polymers. Closed symbols are obtained with the surface-to-volume model while solid curves resulted from Monte-Carlo simulations. b) Schematics of the exciton diffusion model. Equilibrium hopping rate is  $k_0 = 5 \text{ ps}^{-1}$ . c) Volume fraction of large (>15 nm) PC<sub>71</sub>BM domains which do not contribute to separated charges.

To verify the validity of our simple approach, we performed Monte-Carlo simulations to elucidate the experimental data. The fullerene cluster was modelled by 1-nm spherical molecules placed in a 3D hexagonal matrix. To account for energy disorder in the fullerene domains, each PC<sub>71</sub>BM molecule was assigned a random energy from a Gaussian distribution with SD=0.07 eV. The exciton hopping rate between PC<sub>71</sub>BM molecules was scaled with a Boltzman factor [4]. The initial exciton was randomly placed in the PC<sub>71</sub>BM domain, after which its diffusional trajectory was calculated until it either reached the interface or dies after its 500-ps lifetime. The simulations were run over 100,000 realizations for each PC<sub>71</sub>BM/polymer weight ratio.

The results of the simulations excellently reproduce the experimental data (Fig. 1b, solid lines). Interestingly, due to energetic disorder, the effective diffusion coefficient of PC<sub>71</sub>BM excitons decreases in time because the probability of being captured at local energetic minimum for a longer time increases for the low-energy states. This is necessary to adequately reproduce the growing segment of the transients. Figure 2a demonstrates that the simple surface-to-volume rationale used here is fully consistent with the Monte-Carlo simulations.

Figure 2c shows the volume fraction of PC<sub>71</sub>BM domains which are so large that they do not contribute to charge separation. Because of this fact, their appearance is unfavorable for organic photovoltaics applications. The size of these large domains cannot be exactly evaluated by the current method but we can certainly assign a lower limit of ~15 nm. Nonetheless, we are capable of obtaining such subtle changes in morphology as formation and further disruption of RRe-P3HT nanocrystals at weight ratio ~2 (Fig. 2c, blue dots).

Summarizing, the main advantage of the proposed method lies in its capability to resolve nm-sized PC<sub>71</sub>BM clusters “on-the-fly”. Furthermore, it allows estimating the PC<sub>71</sub>BM exciton dissociation yield which is highly relevant for initial charge generation in organic photovoltaics blends.

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