

Processing additive suppresses phase separation in the active layer of organic photovoltaics based on naphthalene diimide

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ABSTRACT

The development of non-fullerene electron acceptors for organic photovoltaics is gaining interest, as they offer the promise to overcome the light harvesting and energy tunability limitations of fullerenes. However, to fully take advantage of alternative acceptors, we must identify and achieve the needed morphologies within the active layer to maximize device performance. Here we demonstrate that the microstructure in the active layer of optimized poly(3-hexylthiophene)/naphthalene diimide devices resembles that of poly(3-hexylthiophene)/fullerene mixtures. Previously, we have reported on the synthesis of 2,6-dialkylaminonaphthalene diimides and found that the best performance was obtained with N,N'-di((thiophen-2-yl)methyl)-2,6-di(N-cyclohexylamino)-1,4,5,8-naphthalenetetracarboxydiimide (RF1). In this article, we show that suppressing the crystallization of both the donor and acceptor through the addition of 0.2% 1,8-diiodooctane (DIO) to the casting solution leads to finer morphologies in the active layer and a two-fold enhancement in the device efficiencies. Nevertheless, further increasing the DIO content of the casting solution leads to lower photocurrents and power conversion efficiencies, even though the morphology appears similar by energy-filtered TEM. We hypothesize that higher DIO content breaks up small RF1 aggregates, leading to suppression of charge separation. Continued development of novel non-fullerene acceptors must therefore take into consideration the balance between crystallization and aggregation of donors and acceptors for optimal performance.

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1. Introduction

Designing new materials for high-performance organic photovoltaics (OPVs) requires an ability to tune the optoelectronic properties of donor/acceptor systems. The process is complex because several properties must be optimized simultaneously [1]. For example, the light harvesting properties [2], molecular orbital energy levels [3], propensity for crystallization [4,5], and charge mobility [6] of donors and acceptors must be optimized. Further-

more, recent developments suggest that the miscibility [7–9], dielectric constant [10], dipole moment [11], charge delocalization [12], local charge mobilities [13] and electronic coupling at the donor/acceptor interface [14,15] must also be tuned.

The emphasis on fullerene-based acceptors in organic photovoltaics places restrictions on optimizing multiple properties at once, because of the limited synthetic versatility of fullerene. From a materials development perspective, the increase in OPV power conversion efficiencies to date is mainly due to the discovery of novel polymer donors. The acceptor in record-performing single-junction

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photovoltaic devices [16–18] is the same as the fullerene derivative identified in early seminal papers on bulk heterojunction systems, [6,6]-phenyl-C₆₁-butyric acid-methyl ester (PCBM), where the only modification is the replacement of the 60-carbon fullerene cage with C₇₀ [19,20]. New non-fullerene acceptors are warranted to take full advantage of the flexibility in organic chemistry and improve the performance characteristics of organic photovoltaics.

One critical requirement that must be considered when developing new materials for OPVs is the creation of a donor/acceptor film morphology with large interfacial area, domain sizes commensurate with the exciton diffusion length (~10 nm), and bicontinuous pathways for charge extraction of electrons and holes. There are various paradigms to achieve such a structure. The first generation of bulk heterojunction systems, based on poly(phenylene vinylene), rely on kinetically-trapped phase separation of mixtures between amorphous polymer donors and fullerenes. Because it is easier to dissolve small molecules in polymers than vice-versa due to the asymmetric entropic contributions of the polymer and small molecule [21], large fullerene contents are required to promote phase separation. Second generation materials, based on polythiophenes, rely on the crystallization of polymer donors (often self-limiting to dimensions near 10 nm) to create a microstructure of nano-crystallites surrounded by a fullerene-rich matrix [21,22]. Thus, mixtures of polythiophene and fullerene are composed of pure polymer crystallites (with some notable exceptions where polymer and fullerene co-crystallize [23]) surrounded by mixed polymer-fullerene domains. It remains a question whether acceptors beyond fullerene derivatives exhibit the same universality of morphological evolution.

After fullerenes, perhaps the second-most studied acceptor systems are based on rylene derivatives. Rylenes possess high electron affinity, good electron mobilities, and have a high degree of chemical flexibility through functionalization at the core and imide positions [24]. Unfortunately, rylenes have a strong tendency to crystallize, often leading to morphologies that are dominated by the crystallization of the acceptor. Given that most commonly used donors, such as poly(3-hexylthiophene), are designed for fullerene derivatives which themselves are less likely to crystallize due to either kinetic or thermodynamic reasons, coarse morphologies often contribute to the limited performance of rylene derivatives.

One strategy to control the morphology in donor/acceptor mixtures involves adding a solvent additive, generally at 0.1–10% of the solvent volume [16,25]. Solvent additives studied include 1,8-diiodooctane (DIO), 1-chloronaphthalene, 1,8-octanedithiol, and alkylthiophenes. These additives can enhance the morphology in polymer/fullerene systems and thereby improve photovoltaic device performance by either promoting or suppressing phase segregation [16]. Nevertheless, the role of solvent additives on the morphology of polymer/rylene derivative systems has not been widely explored [26–32]. Recently, power conversion efficiencies in the 2–5% range have been demonstrated with rylene diimide acceptors by tuning the film morphology when blended with an electron donor [29,30,33–37].

We previously showed that 2,6-dialkylaminonaphthalene diimides (2,6-dialkylamino-NDI) are promising acceptors for OPVs with light absorption up to 700 nm [38]. By tuning the substituents we can tune a variety of properties, including the propensity for crystallization. In a recent structure–property study, we compared a series of 2,6-dialkylamino-NDI compounds where the imide substituents consisted of a linker connected to a thiophene group, where the linker was phenyl, methyl, or ethyl. The linker affected the dihedral angle between the thiophene group and the NDI core, which then influenced morphology in blend films with the common polymeric donor regioregular poly(3-hexylthiophene)(P3HT). That angle was calculated to be 114°, 45–61° and 8° for the methyl, phenyl, and ethyl linkers, respectively. The acceptor that combined the methyl linker and the cyclohexylamino core substituent, N,N'-di((thiophen-2-yl)methyl)-2,6-di(N-cyclohexylamino)-1,4,5,8-naphthalenetetracarboxydiimide (RF1, Fig. 1), gave the best performance when blended with P3HT [39]. Interestingly, the blend morphology did not appear ideal, showing large crystalline domains. Here we show that the morphology of the P3HT:RF1 system can be further tuned with a processing additive. By adding 1,8-diiodooctane at 0.2% by volume in the casting solvent, we were able to suppress the large-scale phase separation in the active layer. Enacting control of the crystallization with molecular design and phase separation with a processing additive leads to microstructures observed in energy-filtered TEM micrographs that resemble morphologies of P3HT:PCBM films. As a consequence, the device performance was enhanced approximately two-fold to near 1%. Our results demonstrate that the optimum morphology of P3HT:RF1 is similar to the morphology of P3HT:PCBM, suggesting an universality in the microstructure of the active layer for optimizing device performance in polymer/small molecule photovoltaic devices.

2. Experimental section

2.1. Materials

P3HT was synthesized following the published procedure [40]. ¹H NMR (CDCl₃): δ = 6.96 (s, 1H), 2.79 (t, 2H), 1.69 (m, 2H), 1.47–1.25 (m, 6H), 0.90 (m, 3H); GPC

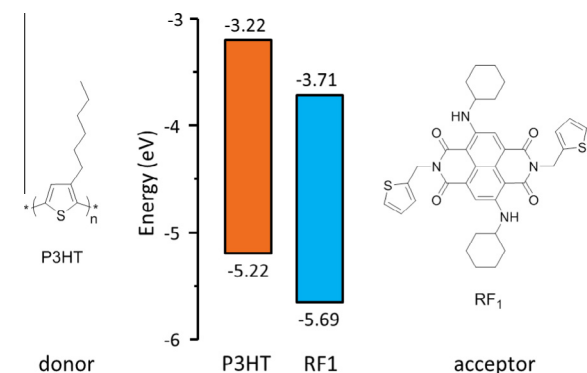


Fig. 1. Chemical structure and estimated energy levels for donor and acceptor studied.

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