Kinetics of charge transfer processes in organic solar cells: Implications for the design of acceptor molecules

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ARTICLE INFO

ABSTRACT

We report the electronic properties of a new class of non-fullerene electron acceptor molecules with electron affinities tunable over an approximately 1 eV range. This tunability allows us to vary the thermodynamic driving force for electron transfer (ΔG°) such that it is equal-and-opposite-to the reorganization energy for the ionized states (λ). We utilize this design principle, derived from Marcus–Hush theory, to optimize the rate of charge transfer in blends of these acceptors with poly(3-n-hexylthiophene-2,5-diyl) (P3HT) – a standard organic solar cell donor material. We show that computationally inexpensive calculations can be used to parameterize Marcus–Hush theory so as to correctly predict whether quenching will occur. Arguments based solely on energetics are common in the literature and we show that such theories do not predict the trends observed in our photoluminescence quenching experiments. This is the case whether the energies determined from experiments [cyclic voltammetry (CV) and the optical gap] or calculated from density functional theory for the solid state. We predict essentially barrier-less photoelectron transfer (PET) from P3HT to the acceptor 2-[{7-(9,9-di-n-propyl-9H-fluoren-2-yl)benzo[c][1,2,5] thiadiazol-4-yl}methylene]malononitrile (or K12), consistent with the experimental photoluminescence quenching efficiencies found for P3HT:K12 blends. Our results clearly show that energetics alone is not sufficient to predict PET between the acceptor–donor pair, and that kinetics are an important determining factor.

1. Introduction

Organic photovoltaic (OPV) devices are rapidly approaching market release with private corporations having already achieved certified solar power (AM 1.5) conversion efficiencies of 10% [1], and literature values reported over 8% [2,3]. Conventional organic solar cells based upon the heterojunction concept require an electron accepting material to facilitate photoinduced electron transfer (PET) from the photoexcited donor material and to transport the resultant separated electrons to the external circuit [4]. The upper limit for the device photovoltage (the open circuit V_{oc}) is given by the difference between the donor ionization energy (IE) and acceptor electron affinity (EA) [5,6]. It is believed that to improve device efficiency further, an open circuit voltage above 1 V is required.

To date the best performing material blends are composed of narrow optical gap donor polymers and the fullerene derivatives [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) or the C_{70} analogue ($PC_{71}BM$) as acceptors [2,3,7]. Non-fullerene acceptor materials are of interest for a number of reasons including: (i) potential for tuning the electronic states to deliver a higher V_{oc}; (ii) potential for more versatile processability and cheaper fabrication; and (iii) providing insight into why the fullerene systems work so well as acceptors. Although the number of

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non-fullerene acceptors is growing [8–17], their performance has yet to match that of the fullerenes in a bulk heterojunction (BHJ) device. A number of possible reasons for this have been proposed including: (i) poorly formed donor–acceptor nanoscale phases and morphology resulting in a lack of a bi-continuous charge transport network and resultant low charge carrier mobility [18–22] (ii) a low static permittivity of the blend resulting in stronger Coulomb interactions and greater recombination losses [23–27]; and, (iii) poor charge carrier generation efficiencies via PET at the donor–acceptor interface. The latter being the focus of this report.

The thermodynamic driving force for PET is derived from the Gibbs energy of electron transfer ($\Delta G°$) and can be approximated by the difference between the ionization energy of the photoexcited donor (I_D^*) and the EA of the acceptor. In discussions framed in terms of molecular orbital theory this is often referred to as the difference between the donor and acceptor lowest energy unoccupied molecular orbitals (LUMO) ΔE_{LUMO}, but this is both inexact and inaccurate [28]. Nevertheless, it has been proposed that a minimum ΔE_{LUMO} is necessary to overcome the Coulomb binding energy of the photoexcited donor electron–hole pair (the 'exciton binding energy' E_b) [29,30].

In certain polymer-fullerene donor–acceptor systems the internal quantum efficiency (IQE), can approach 100% [31], evidence that the PET step in the photon harvesting process can generate free carriers with high efficiency. However, many donor–acceptor material combinations exhibit a much lower free carrier generation efficiency [32–34]. Although it is difficult to decouple the other losses in the photon harvesting process, proposed explanations have focused on an insufficient driving force ($\Delta E_{LUMO} < E_b$), and fast recombination of the Coulomb bound charge transfer (CT) state (geminate recombination). The latter has been rationalized by the observation of strong donor photoluminescence (PL) quenching but with a reduced free carrier yield [32,34,35]. Recently Street et al. [36] argued that geminate recombination may not be a major loss mechanism in P3HT:PC$_{61}$BM and PCDTBT:PC$_{71}$BM OPV devices. Further, Gong et al. [37] recently observed PET between poly(3-n-hexylthiophene-2,5-diyl) (P3HT) and the small molecule acceptor 9,9′-bifluorenylidene despite having an apparent driving force of only ∼0.1 eV – a value much less than the expected exciton binding energy of P3HT (∼0.7 eV for free carrier generation [38]). This suggests that explaining PET only on energetic grounds may be an over simplification. Furthermore, it is well known from Marcus–Hush theory that kinetics can limit the PET efficiency [29,39,40]. Additionally, errors in the measurement or calculation of energy levels and differences between measurement methods can lead to incorrect expectations for the thermodynamics of the donor–acceptor system [28].

In this contribution we investigate the role of kinetics by focusing on the PET process between P3HT and a series of solution processable small molecule acceptors. The members of this family of acceptor molecules each incorporate a fluorene-benzothiadiazole (FBT) moiety with simple structural variations enabling the tuning of the EA over a wide range. This has enabled us to undertake a systematic study of the energetics and thermodynamics of the

donor–acceptor system. PET was detected by quenching of the P3HT steady state PL upon blending with each acceptor in thin films characteristic of operating solar cells. The acceptor strength was compared to the expectations from two energetic analyses, one based on cyclic voltammetry (CV), the other considering solid state EA as calculated using density functional theory (DFT).

We find that energetics alone cannot explain the observed trend in the PL quenching across the series of molecules. However, by calculating the electron transfer rate from Marcus–Hush theory and DFT, we show electron transfer is limited by the kinetics of the PET process. Using this relatively low cost computational technique we also demonstrate that PET is highly efficient for a particular acceptor molecule (K12), consistent with PL quenching efficiency measurements [9]. Our results show that in order to achieve rapid electron transfer the energetics must be matched to the reorganization energy of the molecule and its environment due to the transfer of charge. We conclude by presenting some important design considerations for organic electron acceptors.

2. Materials and methods

2.1. Materials

The molecular structures for all compounds in this study are shown in Fig. 1. The FBT unit, listed as compound K13, is common to all the compounds. The benzothiadiazole unit (BT) has been exploited in donor–acceptor type narrow optical gap donor polymers and small molecules [41–43], but we use it as a versatile design platform and functional basis for a new class of electron acceptors [44]. By further functionalizing the benzothiadiazole unit, the EA can be tuned over a range of ∼1 eV as detailed in Table 1. To provide solution processability, each new acceptor molecule contains two n-propyl groups attached to the fluorene moiety. For DFT calculations the n-propyl groups were replaced by methyl groups to decrease computation time (details in the experimental section). Likewise, for computational efficiency, P3HT was modeled as octa(3-methylthiophene) (P3MT). In both cases this approximation is justified since the alkyl groups only perturb the electronic structures by a small amount.

2.2. P3HT photoluminescence quenching (PET detection)

A simple method to experimentally determine if PET has occurred is to observe quenching of the donor PL (inhibition of the radiative decay pathway) upon blending with the acceptor in the solid-state. Although both the donor and acceptor can contribute to photo-carrier generation [45,46], we chose to measure PET from the donor P3HT to each acceptor by monitoring the P3HT PL and its subsequent quenching. This allows us to experimentally isolate charge transfer from the donor, thus dramatically simplifying the calculations required to accurately model the experiment. This method is useful for detecting whether PET has occurred, but does not resolve the nature of the charge transfer state, that is, whether the state is bound