



Investigating charge generation in polymer:non-fullerene acceptor bulk heterojunction films

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ABSTRACT

Non-fullerene acceptors are now capable of being used in high efficiency bulk heterojunction (BHJ) donor-acceptor organic solar cells. Acceptors comprising single or multiple linked chromophores have been used. We have developed a new non-fullerene molecular acceptor as well as two non-polymeric macromolecular materials that contain four equivalents of a similar chromophore, but can adopt different spatial arrangements of the chromophores. We compare the effect of having single and multiple chromophores within a macromolecule on the charge generation processes in P3HT:non-fullerene acceptor BHJ films using Transient Absorption Spectroscopy (TAS) and Time Resolved Microwave Conductivity (TRMC) measurements. It was found from the TAS measurements that at low weight percent (5 wt%) the single chromophore formed more polarons than the acceptors in which chromophores were linked, due to it having a more even distribution within the film. At higher concentrations (50 wt%) the trend was reversed due to the single chromophore forming crystalline domains, which reduced the interface area with the P3HT donor. The TRMC measurements showed that more mobile carriers were formed in the macromolecular acceptors when used at low concentrations in the blend and, independent of concentration, mobile carriers had a longer lifetime when compared to films containing the molecular material, which we ascribe to the charges being able to sample more than one chromophore and thus reduce recombination events.

1. Introduction

Two important optoelectronic criteria that need to be considered for high-performance organic solar cells are that firstly, the photoactive layer must be able to generate charges efficiently, and secondly, the charges generated must be collected at the electrodes. In the most efficient organic solar cells the photoactive layer comprises a blend of two or more materials to form a bulk heterojunction (BHJ) [1–4]. To generate charges efficiently in a BHJ layer the materials must be chosen so that they have appropriately aligned electron affinities (EAs) and ionization potentials (IPs). Materials that have the lowest IP are generally defined as the 'donor', with compounds having the higher EA called the 'acceptor'. Donor materials can be photoexcited and transfer electrons to the acceptor or the acceptor(s) can be excited and transfer holes to the donor materials. These two mechanisms are defined as Channels I and II respectively [5], and in principle give rise to the same charge transfer state. Additionally, to ensure effective collection of the generated charges, the

donor and acceptor materials are required to have sufficient hole and electron mobilities in their respective phases, and the blend microstructure needs to be such that the charges have an unencumbered path to the electrodes. Significant effort has been expended in order to understand these processes for non-polymeric:fullerene and polymer:fullerene blends, which, up to recently, have given the most efficient bulk heterojunction organic solar cells [6–12]. More recently, non-fullerene acceptor-based organic solar cells have shown a remarkable improvement in efficiency with the best having efficiencies of around 10–12% [13–16]. Non-fullerene acceptors have a number of attractive features including the ability to molecularly engineer a wide range of optoelectronic properties, e.g., to give complementary absorption to the donor material, manipulate the dimensionality, and control of the physical properties. However, at this stage it is unclear why some non-fullerene organic solar cells work well and others do not, and in particular what governs and controls the charge generation process in the bulk heterojunction layer. Fang et al. reported the use of Time Resolved

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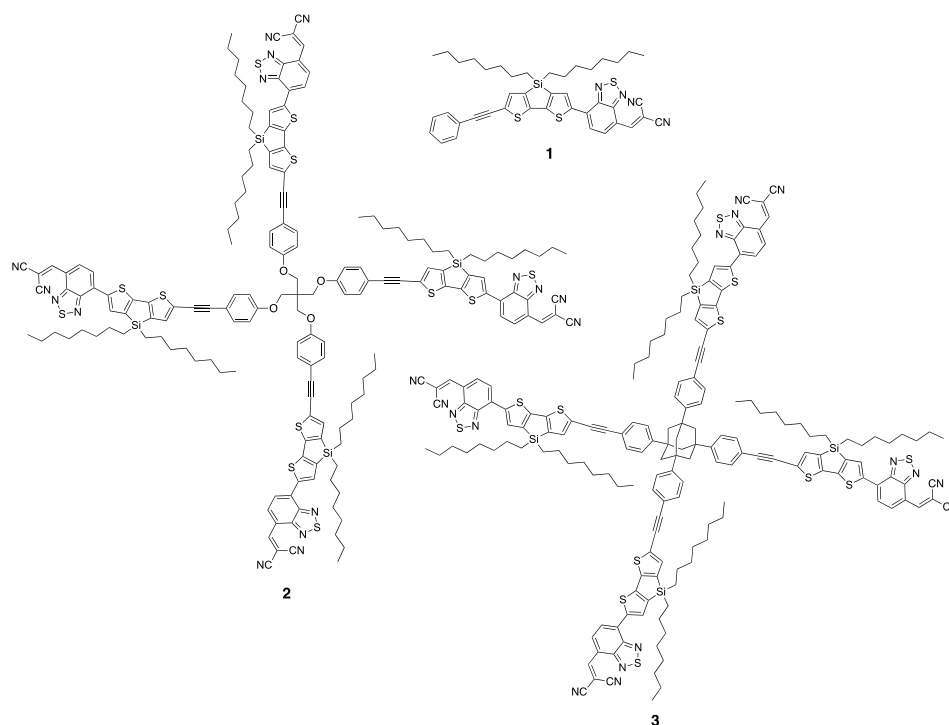


Fig. 1. Structures of the compounds used in this study.

Microwave Conductivity (TRMC) to assess how free charges were formed upon photoexcitation of poly(3-*n*-hexyl)thiophene (P3HT):YF25 blends [17], with YF25 [2-(7-(4,4-di-*n*-propyl-4*H*-silolo(3,2-*b*:4,5-*b'*)dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)methylene]malononitrile] being one of the early non-fullerene acceptors that gave moderately efficient BHJ solar cells. Zhong et al. have used Transient Absorption Spectroscopy (TAS) to study charge generation mechanisms in blends of poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene)-2-carboxylate-2,6-diyl] (PBDTT-TT) and a helical perylene diimide (PDI) [18]. Holiday et al. have also reported the use of TAS to study blends of P3HT and FBR [(5*Z*,5'*Z*)-5,5'-([9,9-di-*n*-octyl-9*H*-fluorene-2,7-diyl]bis[benz(*c*)(1,2,5)thiadiazole-7,4-diyl])bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one)] [19] as well as blends of P3HT and IDTBR [(5*Z*,5'*Z*)-5,5'-([4,4,9,9-tetra-*n*-octyl-4,9-dihydro-*s*-indaceno(1,2-*b*:5,6-*b'*)dithiophene-2,7-diyl]bis[benzo[*c*][1,2,5]thiadiazole-7,4-diyl])bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one)] [20]. For the P3HT:FBR blends the authors concluded that both exciton quenching and polaron formation were faster in a P3HT:FBR blend than a comparable P3HT:PCBM blend, but that the P3HT:FBR blend also experienced faster charge recombination losses [19]. For the P3HT:IDTBR blends, polaron growth kinetics were observed on a similar timescale to acceptor exciton decay, indicating efficient charge generation, and that the polaron generation kinetics were limited by the kinetics of exciton diffusion in the pure IDTBR domains [20]. P3HT:non-fullerene BHJ devices have now reached efficiencies of over 5% [21,22].

It is well known that fullerene acceptors have a propensity to aggregate when blended with the donor, even at low concentration [21]. TRMC measurements show that when this occurs then photoexcitation of the blend leads to mobile electrons within the fullerene clusters. Many of the best performing non-fullerene acceptors contain multiple linked perylene diimide (PDI) chromophores [24,25]. To a first approximation such a macromolecular non-fullerene acceptor structure could be thought to be equivalent to a cluster of fullerenes and that this is an important design criteria. However, there have now been reports that 'single' chromophore non-fullerene acceptors have also given efficient devices [13–16]. Hence, there is a need to understand whether linking chromophores within a macromolecular acceptor material or

whether having similar concentrations of 'single' chromophores can give rise to the same degree of charge generation.

In this report we discuss the synthesis and properties of three new acceptor materials 1–3 (Fig. 1) that contain one or four chromophores of 1. In the case of the acceptors comprising four chromophores we have utilized a pentaerythritol (2) and an adamantyl (3) centre-linking unit to form macromolecular structures in which the four chromophores of 1 are held in spatially different geometries. In the case of the adamantyl-containing compound, the four units are displayed tetrahedrally, whilst for the pentaerythritol there is flexibility in the arrangement of the chromophores although they are physically held close together. We demonstrate that the optical properties of the materials are similar, as are their IPs and EAs. Blends of P3HT with the non-fullerene materials and PC70BM were prepared with acceptor loadings of 5 and 50 wt % and X-ray diffraction showed that 1, 2, and 3 did not disrupt the semicrystalline regions of P3HT in BHJ films, and that while 1 crystallized in the blend film at the higher acceptor concentration, 2 and 3 were non-crystalline under all conditions. TAS and TRMC were then employed to probe charge generation and recombination in the blends and showed that all three materials could act as electron acceptors, and that in the cases of 2 and 3 the formed charges could hop between the four chromophores.

2. Materials and methods

2.1. Materials synthesis

All reagents were purchased from commercial sources and were used as received unless otherwise stated. Tetrahydrofuran, diethyl ether, and toluene were dried on an LC Systems solvent purification system prior to use. Triethylamine was dried and distilled over calcium hydride prior to use. Solvents for chromatography were distilled prior to use. Column chromatography was performed with Davisil LC60A 40–63 μm silica gel. Thin layer chromatography (TLC) was performed using aluminum backed silica gel 60 F254 plates. Medium pressure liquid chromatography (MPLC) was performed on a Grace Reveleris X2 system using silica cartridges. ^1H and ^{13}C NMR were performed using Bruker Avance 300, 400 or 500 MHz spectrometers in deuterated

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