

Photovoltaic and charge transfer analysis of perylene diimide dimer systems

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ARTICLE INFO

Keywords:

Organic photovoltaic
PDI
PBDDT-TSI
Fused
Bridge

ABSTRACT

The dimerization of perylene diimide (PDI) with a bridge separating each monomer has been of interest recently due to notable increases in device efficiencies. We aim to further investigate the impact this bridge has on the photovoltaic and charge transfer properties of an organic photovoltaic using electronic structure methods. Calculations were performed on a variety of heteroatom substituted bridge units in both fused and unfused PDI dimers to directly compare with the previously studied thiophene bridge unit. The systems consist of bridged PDI dimers as an acceptor, coupled with a known polymer donor. Using Marcus theory, the rates of intermolecular charge recombination (k_{CR}) and charge transfer (k_{CT}) were calculated using the Gibbs free energies, reorganization energy and electronic coupling for each system. Fused systems exhibit a k_{CT}/k_{CR} ratio up to 10^6 times higher than unfused systems, decreased reorganization energy, and had more favorable Gibbs free energies. Larger heteroatom substitutions, like silicon and phosphorus, have improved photovoltaic and Marcus theory parameters, and show potential to perform better than typical thiophene linkers.

1. Introduction

Organic photovoltaics (OPVs) are among a new generation of solar cell technologies. These devices have grown in popularity due to their low-cost, flexibility, and simple synthetic process [1–3]. Power conversion efficiencies (PCEs) are a primary focus for OPV research. Recently, efficiencies over 14% have been reached [4,5]. Thus far, the most efficient OPVs utilize a bulk-heterojunction (BHJ), which is a blend of donor and acceptor materials throughout the active layer. Most OPVs have been designed around a fullerene acceptor, which debuted in OPV BHJs in 1995 [7–9], due to efficient charge separation and the ability to transport electrons in three dimensions. However, fullerenes have many shortcomings, including difficulty in tuning the electronic properties, high cost of production, and questionable long-term stability [10,11]. This has led to OPVs made with non-fullerene acceptors to become a subject of interest. Non-fullerene replacements, such as perylene diimide (PDI) [12], have improved stability and easily tuned molecular energy levels and absorption spectra, while also having a significantly lower production cost [13]. PDI systems suffer from low efficiencies due to aggregation of PDI and phase separation from the donor polymer due to strong π - π stacking [14]. Nonplanar PDI molecules were developed to combat this issue by the dimerization of PDI. This has been done with, and without, a bridge unit and have been studied previously [13,15–19].

A fused PDI dimer bridged by an ethylene group was synthesized,

which improved charge separation and transfer in BHJ OPVs [20]. This led to the idea of substituting ring structures to act as bridges. This was done using a single bond connected to the bay region of each PDI, or using two bonds and effectively fusing the units together with the bridge. Typically, the ring system was benzene, but thiophene has gained increased interest. Substituting different chalcogens into the fused bridge unit to modulate the electronic and geometric properties was achieved and produced a PCE of 6.72% for the sulfur substituted system [6]. A majority of bridge units that have been investigated consist of chalcogen rings, most often thiophene, and conjugated carbon systems [6,21]. To our knowledge, no studies have investigated the properties of pnictogen-ring species, particularly five membered rings, as bridge units for PDI dimers, and few have directly compared the properties between fused and unfused systems. Details regarding the synthesis of the fused and unfused PDI dimers using chalcogens in the bridge unit have been described by Zhong et al. [6]. This study aims to thoroughly investigate these pnictogen-ring species as bridge units for these PDI dimers and compare them to the more common chalcogen and carbon-ring systems.

Typically, the donor molecule is a conjugated polymer system. Recently, polymers have been extensively researched to optimize the photovoltaic properties [22]. This includes optimizing molecular energy levels to match a wide variety of acceptors, broadening and red-shifting the absorption band, and increasing hole mobility [23]. One subunit shown to improve charge transport efficiencies in polymers is

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<https://doi.org/10.1016/j.jphotochem.2018.07.048>

Received 6 April 2018; Received in revised form 6 June 2018; Accepted 21 July 2018

Available online 20 August 2018

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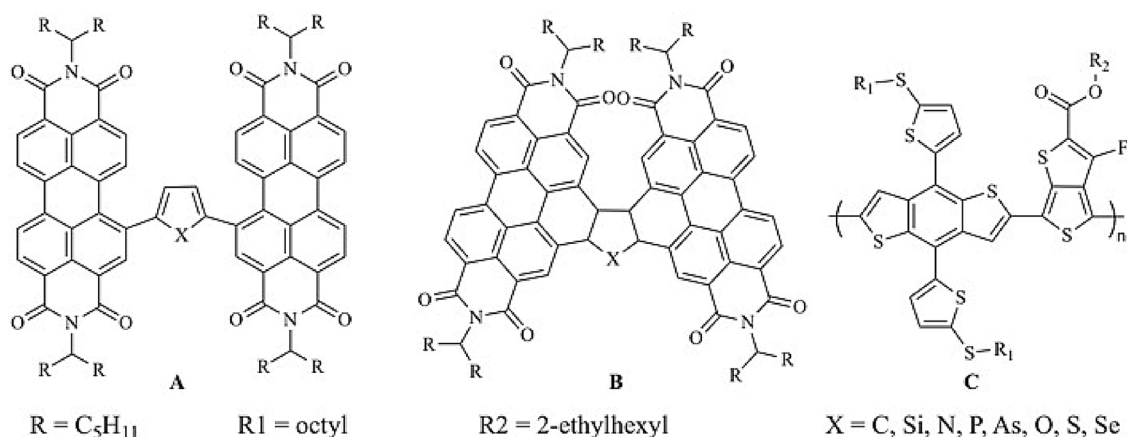


Fig. 1. Chemical structures of studied systems: A) Unfused PDI B) Fused PDI and C) PBDDT-TS1 donor polymer.

benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT), which is easily tunable, features high hole mobility and can be readily synthesized. The substitution of 2-alkylthienyl to BDT has helped bring OPV efficiencies to new heights, being featured in many of the highest performing polymers [24]. One example is PBDDT-TS1 (Fig. 1), which is a proven polymer used in high PCE OPV's and will be used as the donor molecule for this study [25].

Theoretical calculations play an important role in the field of organic semiconductors and OPV devices by providing a guideline for the rational synthesis, thus avoiding expensive trial-and-error attempts. The use of computational methods allows one to rapidly screen novel molecules and determine the viability in an OPV device. Throughout the years computational techniques have deepened the understanding of the mechanisms involved in determining device efficiency and been at the forefront in the development of novel donor and acceptor molecules [26–29].

Using an ab initio approach to directly calculate the PCE ($=V_{OC}J_{SCFF} / P_{in}$) of an OPV is a difficult task. The main factors that contribute to PCE are the short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}) and fill factor (FF). There are routes for improving the contributions to PCE that ab initio methods can readily provide. These include increasing the energy gap between the highest occupied molecular orbital (HOMO) of the donor and lowest occupied molecular orbital (LUMO) of the acceptor to increase V_{OC} , and decreasing the band gap of the donor molecule to more closely match the solar spectrum and boost J_{SC} . Furthermore, the LUMO energy difference between donor and acceptor ΔE_{L-L} , denoted as the energetic driving force, should be greater than 0.3 eV to overcome coulombic attraction and allow efficient charge separation [3]. There are two main processes at the D/A interface, intermolecular charge transfer (CT) and intermolecular charge recombination (CR). To improve J_{SC} , FF, and to increase the effective exciton dissociation, the rate of charge transfer (k_{CT}) should be as fast as possible. Also, the rate of charge recombination (k_{CR}) should be kept at a minimum. This can be readily analyzed using the ratio of the transfer rates for each system (k_{CT}/k_{CR}).

This study aims to provide a comprehensive ab initio analysis of the electronic and optical properties of PDI dimers, both fused and unfused, with 5-membered ring systems acting as bridge units. These rings will have one site substituted with various heteroatoms, which include the pnictogens, chalcogens, carbon and silicon as shown in Fig. 1. Firstly, the ground state energies and UV spectra will be calculated for both the fused and unfused PDI dimers, from which the photovoltaic properties will be calculated. A charge transfer complex will be built using PDI and PBDDT-TS1 to calculate the electronic coupling. The electronic coupling, reorganization energy and free energies will be combined to provide a picture for charge transfer and recombination rates via Marcus theory.

2. Methods

All optimization and time-dependent calculations are done using DFT and the 6–31 G(d) Pople basis set, which has been shown to yield reliable results for evaluating the photovoltaic properties of OPV systems [30]. To determine the most appropriate functional for this system, both ground and excited state energies were run using several DFT functionals including B3LYP, HSE06, PBE0, ω B97xD and CAM-B3LYP. All geometry and time dependent calculations were done in gas phase using the Gaussian09 software package [31]. Geometries from Gaussian09 were then used by the electron transfer module in NWChem [32] for the calculation of the electronic coupling (V_{AB}) using the 6-31 + G(d) basis set. The carbon chains branching off the imide ends of PDI, shown in Fig. 1, impact the solubility and active layer morphology but have little impact on the electronic structure [33,34]. These are replaced by a methyl group to ease computational expense.

In determining k_{CT} and k_{CR} , the Marcus rate equation was employed [35]:

$$k = \sqrt{\frac{4\pi^3}{h^2\lambda k_b T}} |V_{AB}|^2 \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda k_b T}\right) \quad (1)$$

where ΔG is the Gibbs free energy change, λ is the reorganization energy and V_{AB} is the electronic coupling between the donor and acceptor. T is the temperature, which is set to 298 K, while k_b and h are the Boltzmann and Planck constants, respectively. The ΔG of charge recombination and charge transfer are expressed as ΔG_{CR} and ΔG_{CT} , respectively. Generally ΔG is calculated as [36]:

$$\Delta G = E_{IP}(D) - E_{EA}(A) \quad (2)$$

where $E_{IP}(D)$ is the ionization potential of the donor, and $E_{EA}(A)$ is the electron affinity of the acceptor. The free energy changes are commonly estimated as the difference in orbital energies [36], thus for charge recombination, ΔG_{CR} is taken as the donor HOMO energy minus the acceptor LUMO. By employing the Rehm-Weller equation, ΔG_{CT} can be calculated as [36,37]:

$$\Delta G_{CT} = -\Delta G_{CR} - \Delta E_{0-0} - E_b \quad (3)$$

where ΔE_{0-0} is the donor's lowest excited state energy (i.e., the excitation energy, E_{exc} , from the donor HOMO to S1). The exciton binding energy, E_b , incorporates the electron-hole Coulomb attraction and can be estimated as the difference between the electronic and optical band gaps [38,39]. Another important parameter is ΔE_{L-L} , the energy difference between the LUMO's of the donor and acceptor. A ΔE_{L-L} of approximately 0.3 eV is considered adequate for efficient electron injection to occur [40,41]. These energies are visualized in Fig. 2.

The total reorganization energy, λ_{tot} , is the energy required to reorganize the nuclei from the reactant to product geometries without

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