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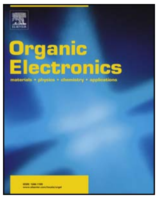

Novel thienoisoindigo-based dyes for near-infrared organic photovoltaics - A combination of theoretical and experimental study

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ABSTRACT

A series of thienoisoindigo (TII)-based dyes (**TII 1–4**) using different electron-donating moieties (D) and π-linkers were synthesized. The experimental results show that the maximum absorption band of **TII 1–4** was located at 611–749 nm. Moreover, their absorption onset was extended to 741–901 nm that covers the near infrared (NIR) region. The bulk-heterojunction solar cell device fabricated by using **TII 3**/$PC_{61}BM$ as the active layer exhibited a power conversion efficiency (PCE) of 0.82%, showing the potential of **TII**-based dyes for NIR organic photovoltaics (OPVs). In order to study the structural effect of dyes on the PCE of solar cells, we further designed four **TII**-based dyes (**TII 5–8**) and the photophysical and photovoltaic properties for **TII 1–8** were investigated through theoretical calculations. Calculated results demonstrate that carbazole group, whose has strong electron-donating ability than D moieties in this study, leads to generate long lifetime of the first excited state and whose generate large short-circuit current (J_{sc}). Thiophene group, whose has weak resonance energy than other π-linkers, can improve the π delocalization effect throughout whole molecule and generate large open-circuit voltage (V_{oc}). According to these results, **TII 3** and **TII 8** with the carbazole as D moiety and thiophene as π-linker should be useful in development of a new SM-OPV device.

1. Introduction

Recently, as potential candidates for application as renewable energy source, organic photovoltaics (OPV_S) have attracted a great deal of attention from researchers because of their significant advantages such as suitability for solution processes, low cost and light weight, which increase their potential to replace conventional silicon-based solar cells [1–8]. Many investigators have employed a molecular design approach with the goal of increasing the power conversion efficiency (PCE) of OPVs, and with rapid progress having occurred over recent years. PCEs over 9% have been achieved by introducing novel conjugated polymers as the active layers of OPVs [9–16]. Among OPVs, small molecular organic photovoltaics (SM-OPVs) have been considered as a promising alternative due to their well-defined molecular structures, easy synthetic procedures, and the high purity and crystallinity of the small molecules [17–24]. Recently, SM-OPVs using single bulk-heterojunction devices have achieved PCEs in the range of 6–10% and SM-OPVs using tandem devices have achieved PCEs in the range of 12% [25–31]. Considering the solar spectrum, common electron-donating dyes used for SM-OPVs, such as oligothiophene-, triarylamine-, BODIPY-, and isoindigo-based dyes, usually lack the ability to absorb NIR solar photons with energy lower than ~1.8 eV, which provide almost 50% of sunlight's intensity [32–37]. Some examples of NIR electron-donating dyes can be found in the literature, including the merocyanes, phthalocyanines, aza-dipyrromethenes, squarines, cyanine salts, and dithienosiloes [38–46]. However, these electron-donating dyes show poor photovoltaic properties which may limit their application. Therefore, it is necessary to develop better NIR-absorbing electron-donating dyes for SM-OPVs. The low photovoltaic properties can be found in these electron-donating dyes, and this property may limit the application. Therefore, it is necessary to develop many of the NIR absorbing electron-donating dyes for SM-OPVs.

In SM-OPVs, the selection of D and A not only determines E_g of the electron-donating dyes, which can have an effect upon the intramolecular charge transfer between the D and A moieties of the electron-donating dye, but also influences their absorption wavelength

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region [47–51]. Electronic and photophysical properties can be adjusted by selecting a different D moiety to meet the requirements of SM-OPVs. Thus, the most useful strategy for designing an appropriate electron-donating dye is to select a D moiety with good electron-donating and hole-transport ability. Triarylamine groups are the well-known candidates to serve as the D moiety not only due to their strong electron-donating ability, but also their contributions for reducing charge recombination and dye aggregation [52–55]. The π-linker of a dye for using in SM-OPV may play an important role to ensure low-lying energy of highest occupied molecular orbital (E_{HOMO}) and to maximize photovoltaic properties, such as V_{oc}. Thiophene ring is usually used as the π-linker which could reduce steric hindrance and result in a planar molecular conformation from the π-linker to the A moiety. The A moiety of the electron-donating dye in an SM-OPV can also provide a positive effect on its photovoltaic and photophysical properties [56,57]. Among A moieties used in electron-donating dyes, TII, in which the outer phenyl ring of isoindigo is replaced by a thiophene unit, exhibits good co-planarity *via* S—O interaction and can improve electronic delocalization through quinoidal structure along the backbone. The thiophene ring of TII shows stronger electron-donating ability than that of the benzene ring of isoindigo. Thus, TII-based dyes should exhibit high absorption coefficients, very long absorption wavelengths and high charge carrier mobilities [58,59]. TII-based conjugated polymers have been successfully applied in organic field effect transistors (OFET) with high hole and electron mobilities ($> 0.28\ cm^2V^{-1}s^{-1}$) [58–60]. In recent studies, TII-based organic dyes have also been synthesized for application in SM-OPVs [61–64]. However, the absorption bands of these dyes are mainly located in the visible region. TII-based small molecular dyes whose absorption covers the NIR region are still rare.

Generally, the PCE of an SM-OPV can be determined by V_{oc}, J_{sc}, and fill factor (FF). In order to obtain high PCE for an SM-OPV, one effective method is to improve J_{sc} without the reduction of V_{oc} and FF. There are many ways to enhance J_{sc} in an SM-OPV, such as active layer morphology controlling, thermal annealing, modification of buffer layer, applying anti-reflection coating, and so on [65–73]. However, the direct and fundamental strategy for improving J_{sc} is to design new electron-donating dyes with board absorption region and high light harvesting efficiency (LHE). Additionally, E_{HOMO} of the electron-donating dye and energy of lowest unoccupied molecular orbital (E_{LUMO}) of the electron-withdrawing molecule, such as [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), are also the factors to influence V_{oc} in SM-OPVs [74]. An electron-donating dye with higher E_{HOMO} decreases the energy difference between E_{HOMO} of the electron-donating dye and E_{LUMO} of the electron-withdrawing molecule, resulting in lower V_{oc}. It is necessary to get a balance between V_{oc} and E_{HOMO} by controlling the electron-donating ability of the D moiety in order to obtain high PCE [75,76]. Therefore, different types of D moieties are selected for the purpose of improving the electronic, photovoltaic, and photophysical properties in this study.

In this study, a series of TII-based dyes (**TII 1–4** in Fig. 1), in which di-*p*-tolyamine and 9H-carbazole are adopted as the electron-donating moiety (D), thiophene and benzene as the π-linker and TII as the electron-withdrawing moiety (A) was synthesized. The photophysical, electrochemical, and photovoltaic properties of these dyes were investigated. In order to investigate the relationship between molecular structure and photovoltaic properties, **TII 5–8** (Fig. 1) was also designed and their electron-donating and π-conjugation effects were investigated by using the quantum chemical calculations. As shown in Scheme 1 and Fig. 1, these TII-based dyes include of four types of D moieties, such as di-*p*-tolylamine (D 1), 9H-carbazole (D 2), diethylfluorenylamine (D 3), and bis(9-ethyl-9H-carbazol-2-yl)amine (D 4), and four types of π-linkers, such as thiophene (π-linker 1), benzene (π-linker 2), anthracene (π-linker 3), and 9,9-diethyl-9H-fluorene (π-linker 4). First, the electronic properties (E_{HOMO}, E_{LUMO}, and E_g) and photovoltaic properties (V_{oc} and energy driving force (ΔE)) were studied for these dyes. Second, the time dependent density functional methods (TD-DFT) method with the Polarizable Continuum Model (PCM) was adopted to obtain the theoretical lifetimes of the first excited state (S_1), absorption wavelengths (λ) and oscillator strengths (f), related molecular transitions, and RLHE in the CH_2Cl_2 environment. In this study, we attempted to investigate the relationships between the optimized geometries, electronic properties, photovoltaic and photophysical properties of these TII-based dyes. Factors influencing J_{sc} and V_{oc} were also proposed by performing aforementioned quantum chemical calculations. We believe that these results can provide useful information for further application in SM-OPVs.

2. Experimental and theoretical procedures

2.1. Materials and instruments

All required chemicals were purchased from local suppliers and used as received. The synthesis of (*E*)-2,2′-dibromo-4,4′-bis(2-ethylhexyl)-[6,6′-bithieno[3,2-*b*]pyrroly- lidene]-5,5′(4*H*,4′*H*)-dione (1) can be found in previous literature [77]. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV300 or AV600 spectrometer. Mass spectra (ESI) were recorded on a Bruker, EVOQ Elite mass spectrometer. UV–Vis absorption spectra were obtained on a Thermo Scientific Evolution 60S UV–vis spectrophotometer. Cyclic voltammetry experiments were performed with a CH Instruments Electrochemical analyzer. All measurements were carried out at room temperature with a conventional three electrode configuration consisting of a platinum working electrode, a platinum wire auxiliary electrode, and a nonaqueous Ag/$AgNO_3$ reference electrode. The $E_{1/2}$ values were determined as $(E_{pa} + E_{pc})/2$, in which E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. The potentials are quoted against the ferrocene external standard. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate.

2.2. Synthesis of **TII 1–4**

The detail synthetic procedures and corresponding NMR and MS data were included in the supplementary information.

2.3. Theoretical background and quantum chemical calculations

2.3.1. Short-circuit current density, J_{sc}

The photoelectric conversion efficiency (PCE) of solar cell devices under sunlight irradiation can be determined by J_{sc} and V_{oc}. J_{sc}can be defined as:

$$J_{sc} = \int_{\lambda} LHE(\lambda)\Phi_{inject}\eta_{collect}d\lambda$$

where LHE (λ) is the light harvesting efficiency at a given absorption wavelength (λ); Φ_{inject} and $\eta_{collect}$ are the electron injection efficiency and the charge collection efficiency, respectively. For solar cell systems in which only the electron-donating dyes differ, $\eta_{collect}$ is assumed to be constant. In order to obtain a high J_{sc} value, efficient solar cell electron-donating dyes should exhibit high LHE (λ), which can be expressed as [78]:

$$LHE\ (\lambda) = 1 - 10^{-f\,(\lambda)}$$

where f is the oscillator strength at the given absorption wavelength (λ) of the electron-donating dye molecule. In this study, we discuss the related light harvesting efficiencies (RLHEs) based on the maximum absorption wavelength (λ_{max}) of TII-based dyes.

2.3.2. Open-circuit voltage, V_{oc}

Based on the results of Scharber et al., V_{oc} can be approximately estimated based on the relationship of molecular orbital energy of the electron-donating dye with that of the electron-withdrawing molecule