



Development of low band gap molecular donors with phthalimide terminal groups for use in solution processed organic solar cells



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ABSTRACT

The synthesis and characterization of two novel narrow bandgap 'donor' small molecule semiconductors are reported. The new compounds are based upon the popular DTS(FBT-Th₂-Hexyl)₂ donor molecule which has a D2-A-D1-A-D2 architecture with D1 = dithienosilole (DTS), A = 2-fluorobenzothiadiazole (FBT), and D2 = hexyl-bithiophene (Th₂-Hexyl). We have replaced the D2 hexyl-bithiophene unit with electron withdrawing phthalimide units. The new materials were characterized using a combination of theoretical calculations, UV-visible spectroscopy, cyclic voltammetry, and thermal analysis. The phthalimide substitution resulted in an overall stabilization of the highest occupied molecular orbital energy levels, and an increase in both dipole moment and organic solvent solubility. When paired with PC₆₁BM, organic solar cells gave surprisingly low power conversion efficiencies. Investigation of the active layer morphologies revealed large phase segregated domains indicating that phthalimide substitution renders the donor molecule immiscible with fullerene acceptors.

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1. Introduction

Organic photovoltaics (OPV) based on solution-processed small molecules have emerged as a promising energy conversion technology [1–3]. Significant effort focusing on blends of soluble small molecular donors with fullerene based acceptors have led to dramatic increase in device efficiency over the last several years [4–6]. Innovations increases materials design [7–10], active layer processing [11–14], and device engineering [15–17] have led to power conversion efficiencies (PCE) reaching beyond 7%. Of particular importance is the design of new donor architectures that are highly modular and allow for subtle structural modifications to tailor optical, electrochemical and thermal properties as well as self-assembly tendencies [18]. Fine control of such properties can lead to significant improvements in both device performance and stability [14,19]. Some of the most widely studied and best performing small molecule architectures are comprised of electron-rich donor

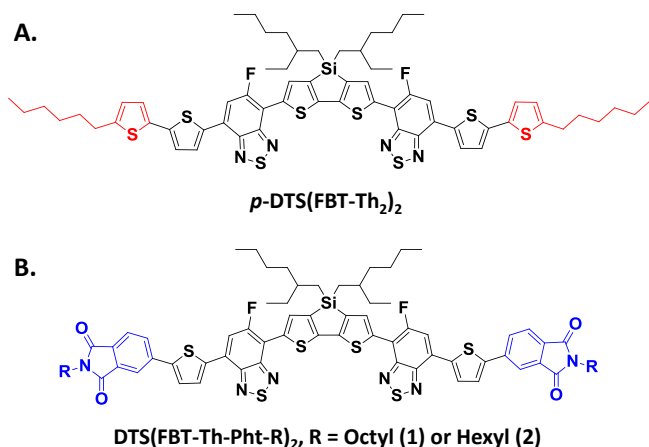
(D) and electron-poor acceptor (A) organic building blocks. The research groups of Chen [20] and Bazan [21] have independently developed two related but different D-A type architectures that have yielded the best performing small molecule based OPV devices to date.

One of the most successful small molecular donor materials reported so far is one consisting of a dithienosilole (DTS) core molecule flanked with 2-fluorobenzothiadiazole (FBT) units and capped with hexyl-bithiophene (Th₂-Hexyl) end-groups (DTS(FBT-Th₂-Hexyl)₂), Scheme 1A [7,17,22–25]. This molecule possess a central electron-rich DTS core (D1), electron-poor FBT acceptor moieties (A), and π-conjugated bithiophene donor units (D2), giving the D2-A-D1-A-D2 architectural structure. When blended with [6,6]-Phenyl C₇₁ butyric acid methyl ester (PC₇₁BM), a PCE of 9% has been achieved [15]. It has been reported that structural modifications to the DTS(FBTTh₂)₂ molecular structure has had a tremendous impact on the material properties and device performance. For example, replacing FBT with thiadiazolo pyridine (PT) moiety increased the material solubility and shifted its optical absorption to lower wavelengths [26,27]. The pyridine based compound had poor device performance when poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was used as an anode interlayer due to the susceptibility of the pyridyl

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Scheme 1. Chemical structures of: A. Previously reported *p*-DTS(FBT-Th₂-Hexyl)₂. B. DTS(FBT-Th-Pht-R)₂. Compounds **1** and **2** bearing octyl and hexyl substituted phthalimide end-capping units, respectively.

N-atom for protonation [28]. Bazan and coworkers [29] replaced the DTS core with a less electron-rich donor, namely silaindacenodithiophene (SIDT), which resulted in lowering the highest occupied molecular orbital (HOMO) of the donor molecule and subsequently increased the open circuit voltage (V_{OC}) of the small molecular donor-fullerene bulk heterojunction (BHJ) solar cells. Increasing the conjugation length along the molecular backbone by adding additional (A-D2) units shifted the optical absorption of the compound into the near-infrared region and increased the material and device thermal stability [30]. Changing the topology of the small molecule through incorporating additional FBT units diminished the materials propensity for crystallization, which negatively impacted solar devices leading to poor performance [31]. In all cases, modifications were made to the internal building blocks, while keeping hexyl-bithiophene moiety as the end capping units. We envisioned that replacing the terminal thiophene moiety with a slightly electron-poor group, *viz.* phthalimide (Pth), would increase the electron affinity across the π -conjugated backbone and stabilize the frontier molecular orbitals, subsequently increasing V_{OC} of the fabricated devices [32–34]. Over the past few years, small molecules containing phthalimide building blocks have shown potential utility for organic electronic applications [35,36]. Key advantages include one-step synthesis with a range of choices for tethering the *N*-alkyl group and the straightforward coupling using direct heteroarylation conditions [37,38]. Our recent work has shown that phthalimide-end capped small molecules exhibited high charge carrier mobility and can tailor optical and physical properties [33,39]. Additionally, bis-imide functional groups are known to direct self-assembly [40–42].

In this work, we report on the design and synthesis of a new DTS-FBT based small donor molecule with phthalimide end-capping unit tethered with octyl (C₈H₁₇) and hexyl (C₆H₁₃) groups. The molecular structure of the phthalimide end-capped molecule (DTS(FBT-Th-Pht-R)₂) is depicted in Scheme 1B. Octyl and hexyl side chains were chosen to promote the solubility of the donor molecules in common solvents used for solution processable devices such as chlorobenzene and chloroform. The potential utility of DTS(FBT-Th-Pht-R)₂ as an electron donor for solar cell application has been investigated by studying its opto-electronic and thermal properties. Moreover, its photovoltaic performance in BHJ blends using fullerene as an electron acceptor was examined and compared with DTS(FBT-Th₂-Hexyl)₂-fullerene blends reported in the literature.

2. Materials and methods

2.1. Chemicals

Unless otherwise stated, all chemicals were used without further purification. 4-bromophthalic anhydride and *N,N*-dimethylacetamide were purchased from TCI Chemicals. *n*-octylamine, *n*-hexylamine, 2-(tributylstannyl)thiophene, anhydrous toluene, pivalic acid and K₂CO₃ were purchased from Sigma-Aldrich. Pd(OAc)₂ and Pd(PPh₃)₄ were purchased from Strem Chemicals. 3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene was stannylated with trimethylstannyl chloride in our labs following standard procedures.

2.2. Methods

UV-vis spectroscopy and differential scanning calorimetry (DSC) measurements were carried out as reported previously [43]. The detailed materials synthesis and characterization are presented in the [Supplementary Information \(SI\)](#).

2.2.1. Nuclear magnetic resonance (NMR)

NMR spectroscopic data were obtained on a Bruker Avance 300 MHz or Avance 500 MHz spectrometer at room temperature. Chemical shifts are reported in parts per million (ppm). ¹⁹F NMR spectra were referenced to CCl₃F ($\delta = 0$ ppm). ¹H NMR spectra were referenced to residual proton peaks of CDCl₃ ($\delta = 7.27$ ppm). ¹³C NMR spectra were referenced to carbon peaks of CDCl₃ ($\delta = 77.0$ ppm).

2.2.2. Cyclic Voltammetry (CV)

CV measurements were performed using a BASi Cell Stand instrument and BASi Epsilon EC software. Measurements were performed in a three-electrode, one compartment configuration equipped with silver/silver chloride electrode, platinum wire, and glassy carbon electrode (3 mm diameter) as a pseudo reference, counter electrode, and working electrode, respectively. The glassy carbon electrodes were polished with alumina. The measurements were performed using 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in an anhydrous dichloromethane as a supporting electrolyte. All solutions were purged with nitrogen and then scanned at varying rates (50–200 mV/s) as-is and at 100 mV/s after the addition of a ferrocene (Fc) standard. The resulting voltammograms were referenced to the oxidation potential of Fc/Fc⁺. The values of the HOMO levels (relative to vacuum) were obtained by comparing the onset of oxidation to the standard hydrogen electrode (SHE), assuming that the HOMO of Fc/Fc⁺ is 4.80 eV below the vacuum level.

2.2.3. Device fabrication

Standard organic solar cell devices were made following literature precedence but with slight modifications [9]. The devices were prepared on cleaned, UV/ozone-treated Corning glass patterned with ITO, upon which the conductive polymer PEDOT:PSS was spin cast at 5000 rpm for 60 s. The active layers were prepared from solutions of **1** or **2** and PC₆₁BM at a weight ratio of 6:4 in chlorobenzene at an overall concentration of 35 mg mL⁻¹. Solution preparation follows that reported by Bazan and coworkers [22] and was used for a direct comparison. The solutions were heated for several hours and residual solids were quickly filtered prior to casting at 80 °C under inert atmosphere (1750 rpm for 60 s). Cathodes were deposited by sequential thermal evaporation of 7.5 nm Ca followed by 100 nm Al. Device characteristics were measured under illumination by a simulated 100 mW cm⁻² light

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