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COMMUNICATION

Development of naphtho[1,2-*b*:5,6-*b*′]dithiophene based novel small molecules for efficient bulk-heterojunction organic solar cells†

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Two new small molecules with a rigid planar naphtho[1,2-*b*:5,6-*b*′]dithiophene (NDT) unit were designed and synthesized. Solution processed bulk-hetereojunction organic solar cells based on blends of the small molecules and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) exhibited promising photovoltaic device performance with a maximum power conversion efficiency up to 2.20% under the illumination of AM 1.5G, 100 mW cm^{-2}.

Over the past decade, conjugated polymers with alternating donor–acceptor (D–A) structures have been extensively investigated as donor materials for bulk-heterojunction (BHJ) polymer solar cells to meet the growing demand for inexpensive renewable energy sources. After a prolonged effort, impressive progress has recently been achieved leading very close to large scale commercialization for plastic solar cells with a power conversion efficiency (PCE) of over 7.7%.[1,2]

Recently, the interest of solution processable π-conjugated D–A organic small molecules has been accelerating for organic solar cell (OSC) applications. These are emerging as promising substitutes for conjugated polymers with substantial potential for generating low cost solar cells owing to the advantages of simple synthesis, high purity, low processing cost, and reproducible photovoltaic performance. So far, using small molecules, the best photovoltaic performance was obtained with diketopyrrolopyrrole units with benzofuran substituents giving rise to a PCE of conventional BHJ OSCs of 4.4%.[3] A variety of other small molecules based on triphenylamine, isoindigo, merocyanine, or squaraine derivatives with either linear, dendritic, X- or star shaped architectures have also been investigated recently in solution-processed OSCs.[4,5] Despite the appreciable recent advances, the device efficiencies obtained for these small molecules are relatively low as compared to the PCEs of polymer solar cells. Obviously, to realize small molecules for commercial applications, at least for generating low cost solar cell devices, their efficiency needs to be increased. New D–A organic small molecules are urgently needed which require new design concepts and novel building blocks to maximize the solar cell parameters.

To address this need, we have designed new solution processable small molecules based on a π-conjugated, rigidly fused, symmetrical, and planar building block, naphtho[1,2-*b*:5,6-*b*′]-dithiophene (**NDT**), which is a potential semiconductor for organic field effect transistors (OFETs).[6a] Semiconducting polymers incorporating **NDT** into a polythiophene backbone exhibited field-effect mobilities as high as 0.5 $cm^2\ V^{-1}\ s^{-1}$ and maximum current on/off ratios (I_{on}/I_{off}) of up to 10^8 in OFET devices, which are believed to be amongst the best values of field-effect mobilities reported thus far.[6b] Taking its symmetrical planar structure and higher mobility into consideration, we envisioned that incorporating an alternating D–A conjugated unit into the **NDT** unit could efficiently reduce the band gap and enhance π–π stacking, thus improving both charge generation and charge transport for photovoltaic applications. However, it is worth mentioning that, despite all of these promising features, this **NDT** unit has not yet been explored in OSCs.

In this communication, we report the syntheses, and photovoltaic performances of first **NDT**-containing π-conjugated D–A organic small molecules. The small molecules, **BNB** and **TBNBT** were synthesized with thiophene-bridged **NDT** as the central donor unit and benzothiadiazole or triphenylamine-capped benzothiadiazole as arms (see Fig. 1 for structures). Benzothiadiazole was selected as an acceptor as it has been established as one of the most efficient acceptors used in low band gap materials for polymer solar cell applications.[7] Motivation for the introduction of a triphenyl amine donor unit at

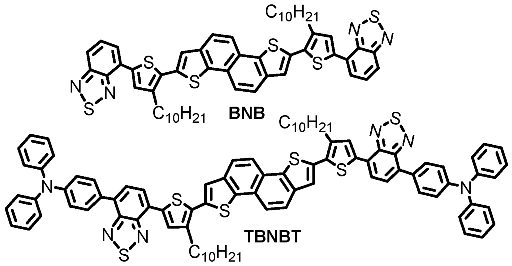

Fig. 1 Molecular structures of the small molecules.

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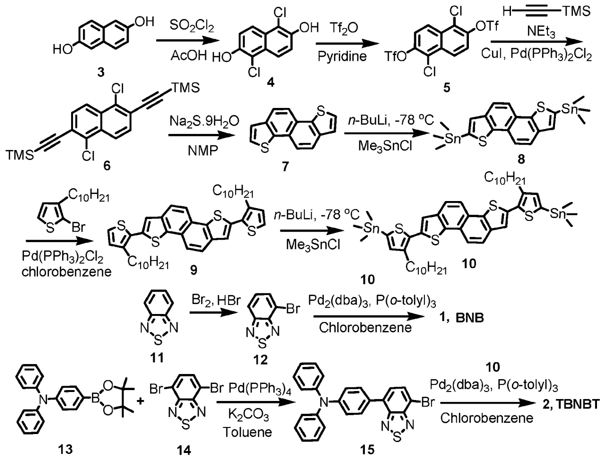

Scheme 1 Synthetic route to the small molecules.

the terminal position in the **TBNBT** molecule was to extend conjugation, enhance absorption and improve the charge transfer capability of the small molecules.[8]

Synthetic approaches for the small molecules are shown in Scheme 1. Starting from commercially available 2,6-dihydroxynaphthalene (**3**), the **NDT** (**7**) molecule was synthesized in four steps following procedures described in the literature.[6a] The pristine **NDT** molecule lacks alkyl chains in its core and thus has limited solubility in organic solvents. In order to improve its solubility and processability, we introduced decanyl thiophene units at the 2- and 7-position of the **NDT** core by a Pd-catalyzed stille coupling reaction between **8** and 2-bromo-3-decylthiophene. 4-Bromobenzo[*c*]-[1,2,5]thiadiazole (**12**) was synthesized by selective bromination of benzothiadiazole (**11**) in a 21% yield. Stille coupling reactions of **12** and **10** were carried out using $Pd_2dba_3/P(o\text{-tolyl})_3$ as a catalyst in anhydrous chlorobenzene resulting in a red solid, **BNB**, in a 68% yield. Compound **15** was obtained in a 54% yield by a $Pd(PPh_3)_4$-assisted Suzuki coupling reaction between **13** and **14**. Finally, similar to **BNB**, a stille coupling reaction of **10** and **15** afforded a desired dark brown solid, **TBNBT** (**2**) in a 72% yield. Detailed synthetic procedures and characterizations can be found in the ESI.†

The UV-vis absorption spectra of the small molecules in the chlorobenzene solutions and in films are shown in Fig. 2(a). The corresponding absorption data are summarized in Table 1. The **BNB** in the chlorobenzene solution exhibited a narrow absorption band covering the wavelength range from 300 to 500 nm with a molar absorptivity of 24 880 L M^{-1} cm^{-1} at 426 nm. The absorption spectra broadened and extended to 600 nm in the solution with a molar absorptivity of 70 445 L M^{-1} cm^{-1} at 499 nm for **TBNBT**, due to its terminal triphenyl amine units. In comparison with their absorption spectra in solution, the absorption spectra for both **BNB** and **TBNBT** in thin films were red-shifted, exhibiting absorption onsets at 572 and 632 nm, corresponding to the optical band gap (E_g^{opt}) of 2.16 and 1.96 eV, respectively, and thus indicating a strong intermolecular interaction in the solid state. The PL spectra of **BNB** and **TBNBT** showed strong emission bands with emission maxima at 631 nm and 671 nm, respectively (see Fig. S4 in ESI†). Upon addition of PCBM, the emission bands of both the small molecules were found to be significantly quenched, indicating an effective charge transfer process between the small molecules and PCBM, which is desired for potential solar cell applications.

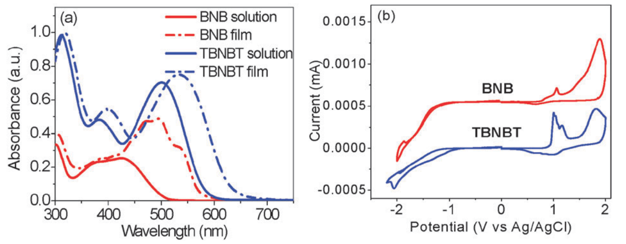

Fig. 2 (a) UV-vis absorption spectra of **BNB** and **TBNBT** in chloroform solutions (1×10^{-5} M) and in thin films. (b) Cyclic voltammograms of **BNB** and **TBNBT** films in a 0.1 mol L^{-1} Bu_4NPF_6/CH_3CN solution.

The energy levels of the small molecules were investigated by cyclic voltammetry (CV) (Fig. 2b). CV was carried out for **BNB** and **TBNBT** films with a Pt counter electrode and an Ag/Ag^+ reference electrode in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in acetonitrile with a scan rate of 50 mV s^{-1}. The highest occupied molecular orbital (HOMO) energy levels of **BNB** and **TBNBT** were determined to be −5.16 and −5.34 eV, respectively, using the ferrocene reference value of −4.41 eV below the vacuum level.[9] The LUMO levels of **BNB** and **TBNBT** were determined to be −3.18 and −3.34 eV, respectively. The related electrochemical data are listed in Table 1. The estimated energy levels of both **BNB** and **TBNBT** indicate that these molecules are suitable for use as donor materials blended with PCBM as an acceptor in OSCs. Since the V_{oc} of the OSC device is related to the difference between the HOMO of the donor and the LUMO of the acceptor, the low-lying HOMO levels of **BNB** and **TBNBT** further ensure an increase in V_{oc} on construction of the solar cell devices.

To determine the charge carrier mobilities of the small molecules, OFET devices were fabricated with a bottom-contact device configuration built on an n-doped octyltrichlorosilane (OTS-8)-treated silicon wafer as described in the ESI.† Unfortunately, despite our repeated attempts, the solution processed **BNB** devices were unable to exhibit any field effect mobility because of the poor quality of the films on Si/SiO_2 substrates. However, benefiting from the terminal triphenylamine units, the **TBNBT**-based devices showed homogeneous thin films with p-channel FET responses. A field-effect hole mobility of 6.0×10^{-5} cm^2 V^{-1} s^{-1} and a I_{on}/I_{off} ratio of 10^2 were observed in **TBNBT** FETs (Fig. S5, ESI†) under the same experimental conditions.

Photovoltaic performances of the small molecules were investigated by fabricating BHJ devices in a conventional device configuration of ITO/PEDOT : PSS (40 nm)/**BNB** or **TBNBT** : $PC_{71}BM$ (1 : 1 to 1 : 4 w/w)/LiF (0.5 nm)/Al (120 nm). $PC_{71}BM$ was selected as the acceptor due to its stronger light absorption in the visible region compared to $PC_{61}BM$.[10] The detailed device fabrication process is described in the ESI.† In the preliminary device investigations, chlorobenzene (CB) was chosen as a processing solvent because it is believed to be a better solvent in high-performance bulk-heterojunction organic solar cells.[8,11] The active layers were spin-coated from CB at different **BNB**/**TBNBT** and $PC_{71}BM$ blending ratios

Table 1 The optical and electrochemical properties of **BNB** and **TBNBT** and the photovoltaic characteristics of BHJ solar cell devices at 1 : 4 (w/w) small molecule/$PC_{71}BM$ compositions blended in chlorobenzene

Small molecule	$\lambda_{max}{}^{a}$/nm	$\lambda_{max}{}^{b}$/nm	E_g^{optc} (film^b)	HOMO^d/eV	LUMO^e/eV	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	PCE (%)
BNB	426	494	2.16	−5.16	−3.18	3.79	0.93	0.28	0.98
TBNBT	499	533	1.96	−5.34	−3.34	6.18	0.95	0.37	2.20

[a] Measured in chlorobenzene solution. [b] Spin-coated film from chlorobenzene solution. [c] $E_g^{opt} = 1240/\lambda_{onset}$. [d] HOMO $= -(4.4 + E_{onset}^{ox})$ (eV). [e] LUMO $= -(4.4 + E_{onset}^{red})$.

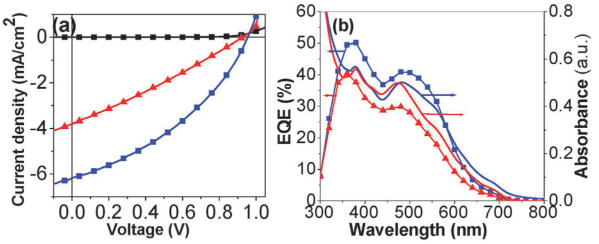

Fig. 3 (a) *J–V* curves of BHJ solar cell devices based on the **BNB** : $PC_{71}BM$ (red line) and **TBNBT** : $PC_{71}BM$ (blue line) at a 1 : 4 w/w ratio in CB under an illumination of AM 1.5G, 100 mW cm^{-2}. (b) EQE and absorption spectra of the corresponding devices.

(1 : 1 to 1 : 4 w/w) with active layer thicknesses ranging from 55 to 75 nm. Optimal fabrication conditions were achieved with a small molecule/$PC_{71}BM$ ratio of 1 : 4 (w/w) at a 65 nm active layer thickness. Fig. 3(a) shows the current density–voltage (*J–V*) curves of the OSCs in the dark and under illumination of AM 1.5G (100 mW cm^{-2}). The corresponding photovoltaic properties of the devices are summarized in Table 1. The device with a 1 : 4 weight ratio of **BNB** to $PC_{71}BM$ provided a V_{oc} of 0.93 V, a J_{sc} of 3.79 mA cm^{-2}, and a fill factor (FF) of 0.28, resulting in an estimated PCE of 0.98%. In contrast, the device based on **TBNBT** and $PC_{71}BM$ with the same weight ratio delivered a superior performance with a V_{oc} of 0.95 V, a J_{sc} of 6.18 mA cm^{-2}, and an FF of 0.37, yielding a PCE of 2.20%. The higher V_{oc} values are consistent with the deep lying HOMO values of both **BNB** and **TBNBT**. However, the slightly larger band gap and smaller absorption coefficient of **BNB** translated into a lower J_{sc} in the **BNB**/$PC_{71}BM$ solar cell devices.

External quantum efficiencies (EQE) of the devices (1 : 4 w/w) measured under the illumination of monochromatic light are presented in Fig. 3(b) together with their composite film absorptions. Both BHJ devices exhibited significant photon-to-current responses in the range of 300–700 nm, similar to their absorption spectra in the composite films. The **BNB** : $PC_{71}BM$ device exhibited a maximum EQE of 40% at 360 nm. In comparison, the **TBNBT** : $PC_{71}BM$-based device showed even better spectral response with its maximum EQE being approximately 50% at 370 nm. The broad and relatively high coverage of EQE for the **TBNBT** : $PC_{71}BM$ devices also contributed to a considerable increase in the J_{sc} value.

The film morphologies of the active layers were observed by atomic force microscopy (AFM) measurements. The surface topography of **BNB** : $PC_{71}BM$ and **TBNBT** : $PC_{71}BM$ blend films at a 1 : 4 w/w blend ratio is shown in Fig. S7 (ESI†). Smooth surfaces lacking large phase separation were observed for both the **BNB** : $PC_{71}BM$ and **TBNBT** : $PC_{71}BM$ films. However, the **TBNBT** : $PC_{71}BM$ blend film (rms = 0.245 nm) showed better miscibility with low PCBM grain aggregation compared with the **BNB** : $PC_{71}BM$ blend film (rms = 0.41 nm), which could explain the relatively higher FF of the **TBNBT** : $PC_{71}BM$ cell.[12]

In conclusion, a new π-conjugated rigidly fused, symmetrical, and planar building block naphtho[1,2-*b*:5,6-*b*′]dithiophene (**NDT**) was employed for the first time to develop novel conjugated small molecules for OSCs. As an outcome of our sequential structural design, solution-processed BHJ OSCs based on one of the small molecules, **TBNBT**, reached a PCE of 2.20% with a noticeably high V_{oc} of 0.95 V under preliminary device characterizations. This work shows for the first time that a naphtho[1,2-*b*:5,6-*b*′]dithiophene moiety bridged with a thiophene as a conjugated spacer is a quite promising, simple, and useful building block for designing efficient photoactive materials.

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