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Naphthalenediimides Fused with 2-(1,3-Dithiol-2-ylidene)acetonitrile: Strong Electron-Deficient Building Blocks for High-Performance n-Type Polymeric Semiconductors

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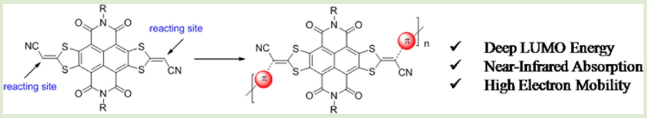
Ⓢ *Supporting Information*

ABSTRACT: Naphthalenediimides (NDI) fused with two 2-(1,3-dithiol-2-ylidene)acetonitrile moieties (NDI-DTYA2), a novel strong electron-deficient monomer, was designed and readily synthesized by aromatic nucleophilic substitution to develop n-type polymers. Two NDI-DTYA2 based donor−acceptor (D−A) polymers P(NDI-DTYA2−1T) and P(NDI-DTYA2−2T) have been prepared (1T = thiophene, 2T = 2,2′-bithiophene) and showed low-lying LUMO energies (<−4.2 eV) and near-infrared optical absorptions (optical band gap <1.3 eV). Although the film feature of these polymers is amorphous, pure electron transport with high mobility of up to 0.38 cm^2 V^{-1} s^{-1} could be achieved for their bottom gate organic thin film transistors, which was among the highest performances for unipolar n-type polymers. The results demonstrate that NDI-DTYA2 derivatives are promising building blocks for developing electron transport π-functional materials.



The π-conjugated semiconducting polymers, including p-type (hole-transporting) and n-type (electron-transporting), are promising candidates in fabricating large-area, low-cost, lightweight, and flexible electronic devices due to their solution processability, mechanical robustness, and compatibility with plastic substrates.[1] So far, some p-type polymers have shown high hole mobility over 10 cm^2 V^{-1} s^{-1} with good device ambient stability.[2] Several ambipolar polymers have also achieved hole mobility of up to 8.8 cm^2 V^{-1} s^{-1} and electron mobility of up to 6.3 cm^2 V^{-1} s^{-1},[3] while for most ambipolar polymers, the very unbalanced hole and electron transport performance indexes including mobility, current on/off ratio, and threshold voltage limit their real application in organic complementary circuits.[3,4] In comparison with the burgeoning p-type and ambipolar polymers, the development of unipolar n-type polymers was outmatched, with much lower electron mobility and unsatisfied device stability.[4−6] Furthermore, the better device performance and stability of unipolar n-type polymers highly depend on the device structure, for example, the top-gate thin film transistors where the polymers were protected in a sandwich structure.[5a−c] However, for the bottom-gate transistors where the polymers were exposed to the environment, there are only a few unipolar n-type polymers that exhibit electron mobility >0.1 cm^2 V^{-1} s^{-1}.[5b,c,6] Since n-type and p-type polymers are equally important in the fabrication of low power complementary circuits and all-polymer bulk-heterojunction organic photovoltaics (BHJ OPVs),[5−7] the exploration of high performance solution processable n-type polymeric semiconductors, especially the unipolar n-type ones with excellent tolerance to different device structures, is a crucial issue in organic electronics.

The construction of donor−acceptor (D−A) polymers has been proven to be a successful strategy in achieving high performance p-type polymers.[2] Recently, this strategy is demonstrated to be also effective in preparing high performance n-type polymers.[5−7] Copolymers P(PDI-DTT)[7a] and P(NDI2OD-T2)[5a] are representative n-type D−A polymers that inspired the extensive research on rylene diimides based D−A polymers.[7,8] To prepare n-type D−A polymers, a primary and crucial challenge is the design and synthesis of electron acceptor units with low-lying LUMO energies. Ideal electron-accepting units should be easy to synthesis and could efficiently decrease the LUMO energies of the D−A polymers to achieve facile and ambient-stable electron injection and transport.[4] However, up to now, the most frequently used accepting units in constructing n-type D−A polymer are still limited to a few old organic dyes/pigments.[4] The innovative acceptors that could effectively decrease the LUMO energies of D−A polymers (<−4.0 eV) and increase the polymers' interchain interactions are very scarce and highly desirable.

A class of high performance naphthalene diimides (NDIs) fused with 2-(1,3-dithiol-2-ylidene)malononitrile moieties (NDI-DTYM2) have been developed by Gao and co-workers.[9] The long, planar π-conjugated backbone, the low-lying LUMO

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energy level as well as the excellent electron transport property of NDI-DTYM2 derivatives indicate that the modification of π-backbone of NDI-DTYM2 might afford promising electron-accepting building blocks for constructing n-type copolymers. Herein, NDI fused with 2-(1,3-dithiol-2-ylidene)acetonitrile moieties (NDI-DTYA2, Figure 1), a novel strong electron-deficient building block, is designed and synthesized for developing n-type polymers. The advantages of NDI-DTYA2 building block include: (i) the ease of synthesis; (ii) a low-lying LUMO energy (−4.0 eV),[10] which could effectively decrease the LUMO energies of copolymers, thus, in favor of facile and ambient-stable electron injection and transport; (iii) rigid and coplanar π-backbone, which could promote effective intermolecular π–π overlap in solid state and favor charge transport; (iv) two additional reacting sites that could be further halogenated, enabling the synthesis of various NDI-DTYA2-based π-functional materials including small molecules, oligomers, and polymers. Two thiophene-based donor moieties, thiophene (T) and 2,2′-bithiophene (2T), are copolymerized with NDI2DT-DTYA2 (2DT: 2-decyltetradecyl), affording the D–A polymers P(NDI2DT-DTYA2–1T) and P(NDI2DT-DTYA2–2T) (Scheme 1). Both of the polymers exhibit near-infrared (NIR) optical absorptions with optical band gaps <1.3 eV and low-lying LUMO energies <−4.2 eV, which make them great potential for multifunctional electron-transporting opto-electronic materials.[11] Semiconducting properties of these polymers were evaluated by organic thin film transistor (OTFT) measurements. Although these polymers have amorphous film morphology, their bottom-gate OTFT devices showed high mobilities of up to 0.38 $cm^2\ V^{-1}\ s^{-1}$ with pure electron transport characteristic and very low threshold voltages.

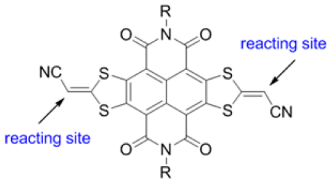
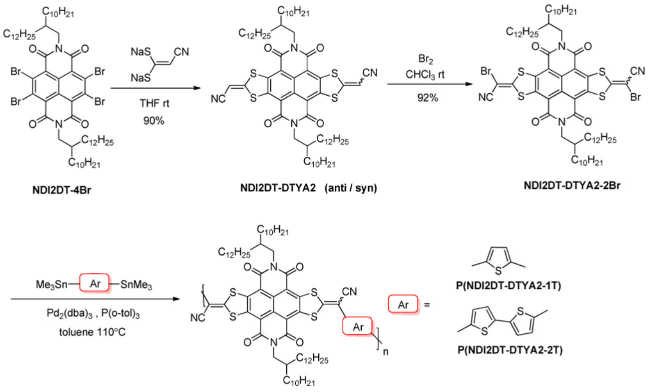


Figure 1. Chemical structure of NDI-DTYA2 building block.

Scheme 1. Synthetic Route to NDI2DT-DTYA2 and Its Based Donor–Acceptor Polymers



As shown in Scheme 1, NDI2DT-DTYA2 was prepared by the aromatic nucleophilic substitution (S_NAr) of sodium 2-cyanoethene-1,1-bis(thiolate)[12] and NDI2DT-4Br in 90% yield.

It is worthy to note that the resulting NDI2DT-DTYA2 product is a mixture of anti/syn isomers due to the nonselectivity of the S_NAr reaction between NDI2DT-4Br and sodium 2-cyanoethene-1,1-bis(thiolate), and the ratio of anti/syn isomers is close to 1/1, which was demonstrated by NMR and high performance liquid chromatography (HPLC; Figure S1). NDI2DT-DTYA2 can be efficiently brominated by bromine in chloroform, affording NDI2DT-DTYA2-2Br in a yield of 92%. The copolymers P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) were synthesized by palladium catalyzed Stille cross-coupling polymerization of NDI2DT-DTYA2-2Br with 2,5-di(trimethyltin)-thiophene and 5,5′-di(trimethyltin)-2,2′-bithiophene, respectively (Scheme 1).

Molecular weights and polydispersity indices (PDI, M_w/M_n) of P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) are determined by high temperature gel permeation chromatography (GPC) using polystyrene standards as calibrants (Figures S2 and S3). P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) showed number-average molecular weight (M_n) of 33.2 and 29.3 kDa, with PDI values of 7.0 and 4.5, respectively. The relative higher PDI values of the polymers could probably be ascribed to their poor solubility, which would increase the viscosity of the reaction mixture and make the heating and mixing of the reactants uneven, leading to a much broader distribution of molecular weight in the final polymer.[13] Both polymers exhibit good thermal stability with decomposition temperatures of 437 and 443 °C, respectively (Figures S4 and S5). As shown in Figures S6 and S7, differential scanning calorimetry (DSC) scans indicated that no endotherm or exotherm transitions were observed for both of the polymers from the entire scanning range of rt to 350 °C.

The absorption spectra of P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) in *o*-dichlorobenzene (ODCB) solutions and in thin films are shown in Figures 2a and S8, respectively. The corresponding data are listed in Table 1. As shown in Figure 2a, both of the polymers show two main

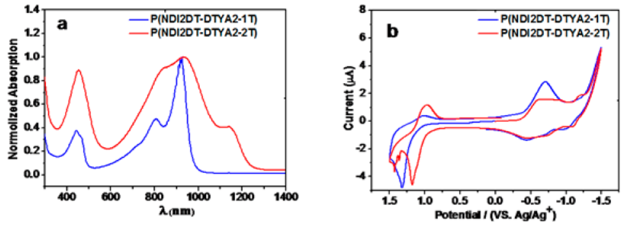


Figure 2. (a) Absorption spectra of P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) in *o*-dichlorobenzene solution. (b) Cyclic voltammograms of thin films of P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at 100 mV/s.

Table 1. Optical Properties and Energy Levels of the P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T)

polymers^a	λ_{max} (nm) soln	λ_{max} (nm) film	E_g (eV) opt^b/cv^c	HOMO^d (eV)	LUMO^e (eV)
P1	920	918	1.25/1.57	−5.82	−4.25
P2	931	935	1.15/1.34	−5.63	−4.29

^{a}**P1** = P(NDI2DT-DTYA2-1T) and **P2** = P(NDI2DT-DTYA2-2T). $^b E_g^{opt}$ was calculated from the onset absorption of the thin films. $^c E_g^{cv}$ = LUMO − HOMO. ^{d}HOMO = $-(E_{ox}^{onset} - E_{1/2}(Fc/Fc^+) + 4.8)$ eV. ^{e}LUMO = $-(E_{red}^{onset} - E_{1/2}(Fc/Fc^+) + 4.8)$ eV.

absorptions that cover the visible region and extend to NIR region, where the former bands centered at about 450 nm can be assigned to $\pi-\pi^*$ transitions of the conjugated backbones, and the low energy bands centered at about 920–930 nm are intramolecular charge transfer (ICT) absorption of the polymeric backbone. In comparison with P(NDI2DT-DTYA2-1T), P(NDI2DT-DTYA2-2T) shows a red-shifted absorption maxima and absorption edge due to the π-extension of donor unit (2T vs 1T). From solution to thin film, the main absorptions of these polymers show no obvious change (Table 1), suggesting that these polymers probably formed some preaggregation in dilute ODCB solution due to strong interchain interactions.[14] In addition, thermal annealing did not influence the absorptions of thin films of these polymers (Figure S9), indicating that the films of these polymers are insensitive to thermal treatments, a phenomenon that has been observed in some amorphous polymers.[8e] P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) showed narrow optical band gaps of 1.25 and 1.15 eV, respectively, which makes these polymers attractive candidates for near-infrared optoelectronic applications.[11]

The cyclic voltammetry (CV) measurements of these polymers were implemented to evaluate their electrochemical properties and electronic structures (Figure 2b), giving HOMO/LUMO energy levels of −5.82/−4.25 eV and −5.63/−4.29 eV for P(NDI2DT-DTYA2-1T) and P-(NDI2DT-DTYA2-2T), respectively. Both of the polymers exhibited lower LUMO energies (close to −4.30 eV) than most previously reported D–A polymers.[5−8] The low-lying LUMO energies of these polymers suggested their great potential for excellent n-type polymeric semiconductors.

Figures 3a–d and S10 show atomic force microscopy (AFM) images of the as-spun and annealed films of polymers P(ND2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T), respectively. Both of the polymers exhibit smooth and uniform film morphology without obvious changes upon annealing. X-ray diffraction (XRD) was performed to investigate the crystallinity and molecular organization of P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) in the solid state. As shown in Figures 3e and S11a, the films of these two polymers showed no appreciable diffraction peaks even annealed at different temperatures, implying that films of the polymers were disordered, which was consistent with the invariability of their absorption spectra upon annealing (Figure S9). To further ensure the amorphism of these polymers, two-dimensional grazing-incidence X-ray diffraction (2D–GIXD) was carried out on the films of these polymers and no obvious diffraction features were observed (Figures 3f and S11b), demonstrating that the films of these polymers were in the amorphous state. The amorphous state of these polymers might be correlated with the anti/syn isomeric structures of the NDI-DTYA2 unit, which will hinder polymers to form linear and regular molecular backbones, leading to the disordered molecular arrangement.

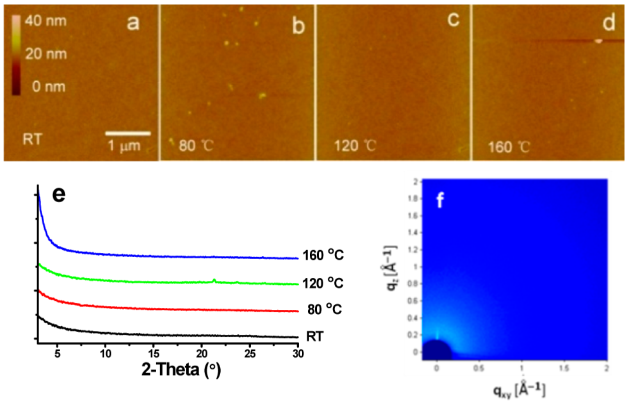


Figure 3. AFM (a–d) and XRD (e) images of as-spun and annealed thin films of P(NDI2DT-DTYA2-1T). 2D-GIXD (f) patterns of the annealed thin films of P(NDI2DT-DTYA2-1T) at 120 °C.

To investigate the charge transport properties of these polymers, we fabricated their bottom-gate/bottom-contact (BG/BC) thin film transistors and evaluated the device performance in nitrogen. Both of the polymers exhibit typical n-channel charge transport characteristics (Figures 4 and S12), indicating the efficiency of NDI-DTYA2 units in constructing n-type polymers. When annealed at 120 °C, P(NDI2DT-DTYA2-1T) showed unipolar n-channel charge transport with an optimized electron mobility of 0.38 $cm^2\ V^{-1}\ s^{-1}$ and a current on/off ratio of 10^6, as well as a low threshold voltage of −4.32 V. In addition, the as-spun and annealed (from 80 to 160 °C) thin films showed comparable average electron mobility (0.22–0.29 $cm^2\ V^{-1}\ s^{-1}$, see Table S1 for details). To the best of our knowledge, currently reported pure electron transport polymers generally showed mobilities ≤0.3 $cm^2\ V^{-1}\ s^{-1}$ for their bottom gate OTFT devices,[5,6,7a,8a−d] thus, P(NDI2DT-DTYA2-1T) are among the best unipolar n-type polymers. OTFTs based on P(NDI2DT-DTYA2-2T) also displayed unipolar n-channel charge transport within an annealing temperature range of 80–200 °C (see Table S1 for details). The average electron mobilities of P(NDI2DT-DTYA2-2T) were about 10^{-2} $cm^2\ V^{-1}\ s^{-1}$ with threshold voltage as low as −2 ∼ −5 V, the optimized electron mobility is about 0.08 $cm^2\ V^{-1}\ s^{-1}$ (Table S1). The lower molecular weight of P(NDI2DT-DTYA2-2T) relative to P(NDI2DT-DTYA2-1T) may be one of the reasons for the lower mobility.[15] For both of the polymers, the change of annealing temperature has little impact on device performance due to their amorphous thin film morphology. This amorphous feature makes copolymers P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) advantageous in reducing device processing effort, which is appealing for real application of organic devices.[16]

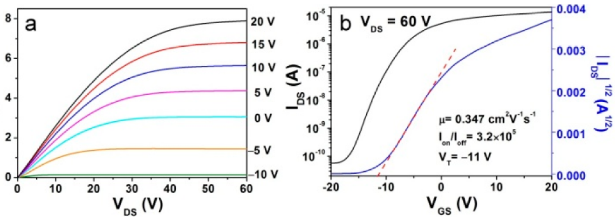


Figure 4. Output (a) and transfer (b) characteristics of OTFTs based on P(NDI2DT-DTYA2-1T).

In summary, a novel strong electron-deficient NDI-DTYA2 building block has been designed and facilely synthesized to develop n-type copolymers. Two D–A polymers P(NDI2DT-DTYA2-1T) and P(NDI2DT-DTYA2-2T) were synthesized, and showed low-lying LUMO energies and near-infrared optical absorptions. In spite of the disordered film feature, bottom-gate OTFTs of P(NDI2DT-DTYA2-1T) showed a high electron mobility of up to 0.38 $cm^2\ V^{-1}\ s^{-1}$, which makes P(NDI2DT-DTYA2-1T) one of the best unipolar n-type polymers and demonstrates the great potential of NDI-

DTYA2 for constructing electron transport polymers. Side chain engineering and other effort to improving the device performance of more NDI-DTYA2 based copolymers are currently underway in our lab. We believe that NDI-DTYA2 building blocks will play an important role in developing novel electron-deficient π-functional materials.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, synthesis, characterization data, tables, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Cyclic voltammetry and UV−vis spectra for NDI2DT-DTYA2 have been shown in Figures S13 and S14. LUMO energy of NDI2DT-DTYA2 estimated from the half-wave reduction potential was −4.0 eV.

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