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Conjugated donor-acceptor copolymers from dicyanated naphthalene diimide

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ABSTRACT

A series of donor–acceptor (D–A) alternating copolymers including P(2CNNDI-T), P(2CNNDI-TT), P(2CNNDI-BT), and P(2CNNDI-BDT) based on dicyanated naphthalene diimide (2CN-NDI) in backbones were presented and characterized in this contribution. Their structures were unambiguously identified by NMR spectra. Optical and electrochemical measurements revealed that their LUMO energy levels are substantially lowered at about −4.4 eV by the substitution of electron-deficient cyano groups on the backbone of as-synthesized polymers. And the HOMO levels varied from −6.15 eV to −5.70 eV as a reflection of electron-donating ability of combined thiophene derivatives. The moderate electron-transporting characteristics under ambient conditions based on these dicyanated polymers indicated their promising applications as air-stable electron transporting semiconductors in future electronics.

1. Introduction

In recent years, donor–acceptor (D–A) conjugated copolymers are developing rapidly in view of extensive applications such as organic field-effect transistors (OFETs),[1–3] organic photovoltaics (OPVs),[4–6] and chemosensor[7–9] with low cost, solution-processability, light weight and flexibility. Naphthalene diimide (NDI),[10–14] perylene biimide (PBI),[15–17] diketopyrrolopyrrole,[18–20] isoindigo,[21–23] benzothiadiazole,[24–26] and so on were usually used as electron-accepting units to construct D–A conjugated copolymers. The NDI core is among the most prominent building blocks for polymeric semiconductors mainly due to its high electron affinity and coplanar backbone, and also the readily available and regioisomerically pure of the corresponding dibrominated precursors. Generally, fine-tuning opto-electronic properties and improving processability of these NDI-based polymers can be achieved either by combining varied electron-donating moieties or N-alkylation.[11,27] A series of NDI-based D–A copolymers has been initially investigated by Waston et al. and demonstrated them as promising candidates for applications in either *n*-channel or ambipolar transistors.[10,27] By varying the *N*-alkyl substituents, an NDI-based polymer named P(NDI2OD-T2) showed unprecedented field-effect characteristics with electron mobilities up to 0.85 $cm^2 V^{-1} s^{-1}$ in top-gate/bottom-contact device architecture.[11]

Recently, we are particularly interested in the chemistry and functionalities of NDI derivatives. A new family of laterally π-expanded acene diimides based on NDI including tetracene diimides (TDIs) and heterocyclic acene diimides intergrated with sulfur, nitrogen, or hydronitrogen bridges with unique opto-electronic properties and crystal packing arrangement have been obtained.[28–31] Furthermore, a series of oligo-butadiynylene-NDI arrays up to five units were efficiently synthesized in one pot by oxidative homocoupling of 1,6-di((trimethylsilyl)ethynyl)-NDIs.[32] Direct perfluoroalkylation of the NDI core and intensive investigation of fluoroalkyl substituted NDI derivatives on its anisotropic electron-transporting characteristics have been also focused.[33,34]

Cyano-substitution on the aromatic core has been widely utilized to lower the lowest unoccupied molecular orbital (LUMO) energy levels substantially, which can improve the air-stability and facilitate electron injection and transport.[35–38] The LUMO levels of cyanated NDI molecules reported by Chi group have been efficiently lowered by stepwise cyanation of NDI core. And the dicyanated NDI analogue (2CN2Br-NDI) has been demonstrated its depressed LUMO level of −4.42 eV and thus air-stable electron-transporting features with OFET mobility up to 0.05 $cm^2 V^{-1} s^{-1}$.[39] Our interest herein is to introduce the dicyanated NDI subunit (2CN-NDI) into the polymer backbone alternating with different

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donor moieties of varying electron-donating ability for the first time. The integration of two cyano groups leads to stronger electron-accepting ability of dicyano-NDI monomer, but induces less distortion compared with the cyano-free NDI,[39] which is vital and virtual for achieving effective π–π stacking and ordered polymer packing that would facilitate efficient charge transporting.[40]

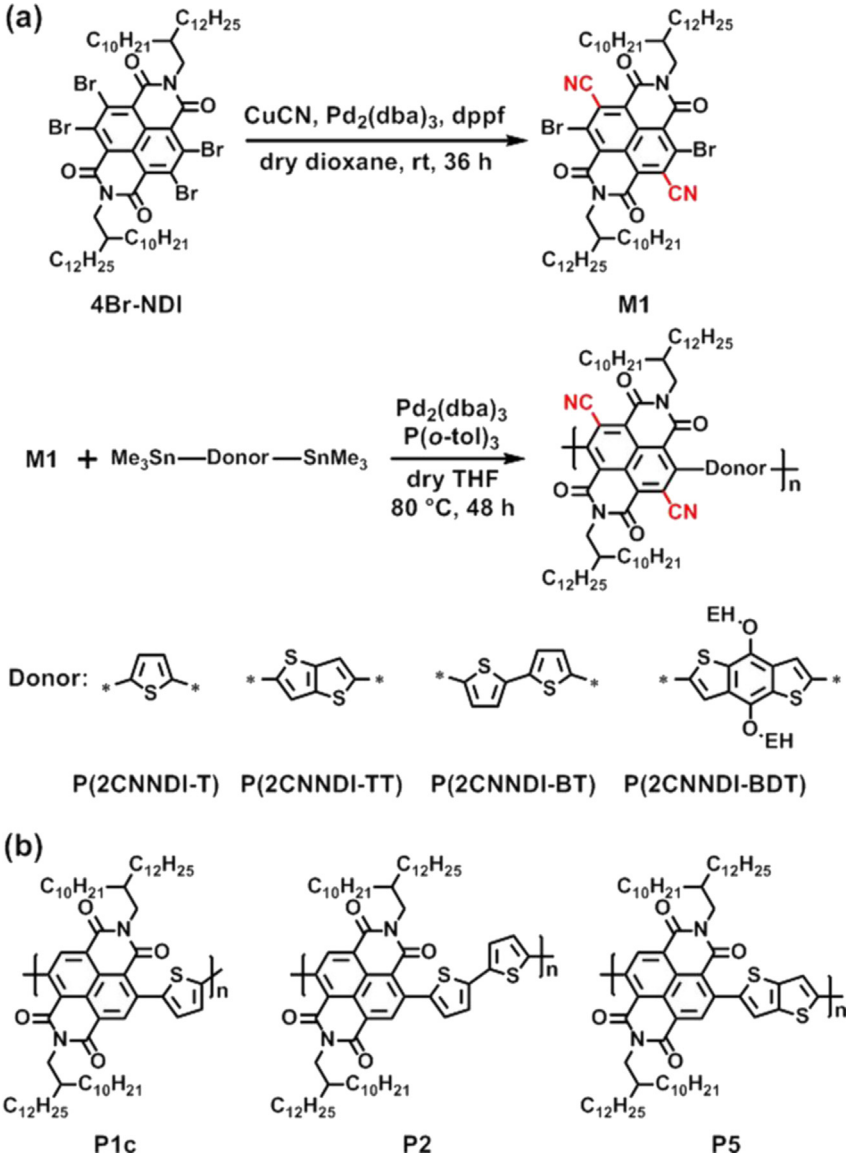
In this contribution, four typical thiophene units serving as electron-donators, including thiophene (T), thieno[3,2-*b*]thiophene (TT), 2,2′-bithiophene (BT), and benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) were combined with dicyano-NDI (2CN-NDI). The resulting 2CN-NDI-based D–A copolymers of P(2CNNDI-T), P(2CNNDI-TT), P(2CNNDI-BT), and P(2CNNDI-BDT) were presented in Scheme 1a. They all exhibited excellent thermal stability and solubility in common organic solvents by the presence of branched alkyl chains in N-positions of NDI subunits. Besides, the significantly lowered LUMO levels at about −4.4 eV were dictated by the more electron-deficient dicyano-NDI units. Employing them in solution-processed OFETs under ambient conditions produced a moderate electron mobility of 2.54×10^{-4} cm^2 V^{-1} s^{-1} in bottom-gate/top-contact device configuration.

2. Experimental section

2.1. General methods and materials

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified. 2,5-Bis(trimethylstannyl)thiophene, 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]thiophene, 5,5′- bis(trimethylstannyl)-2,2′-bithiophene, and 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*']dithiophene were purchased from Solarmer Materials Inc. ^1H and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer. NMR chemical shifts are reported in parts per million (ppm) using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer.

UV–vis spectra were measured with Hitachi (Model U-3010) UV–vis spectrophotometer in a 1-cm quartz cell. Cyclic voltammograms (CVs) were recorded an a Zahner IM6e electrochemical workstation at a scan rate of 100 mV/s, with using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/



Scheme 1. (a) The synthetic route to monomer (**M1**) and copolymers P(2CNNDI-T), P(2CNNDI-TT), P(2CNNDI-BT), and P(2CNNDI-BDT); (b) structures of NDI-based copolymers **P1c**, **P2**, and **P5**.[27]

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AgCl electrode as the reference electrode at a scanning rate of 100 mV/s in film, and ferrocene/ferrocenium (Fc/Fc^+) as an external potential marker for the calibration of potential. 0.1 M tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) dissolved in acetonitrile (HPLC grade) was employed as the supporting electrolyte. TGA measurements were performed on a PE TGA-7 instrument under a dry nitrogen flow, heating from room temperature to 550 °C, at a heating rate of 10 °C/min. Molecular weight of polymers was measured by GPC method, using polystyrene as the standard with THF as an eluent. Atomic force microscopy (AFM) images of films were obtained an a Nanoscope IIIa Dimension 3100 operating in the tapping mode.

The OFET characteristics were measured in air at room temperature by Keithley 4200 SCS semiconductor parameter analyzer. In the spin-coating procedure, the rotation speed is at 3000 rpm. For the device fabrication, a layer of single-molecular semiconductor film (~40 nm) was deposited on the octadecyltrichlorosilane (OTS) modified SiO_2/Si substrates by gate voltage.

2.2. Synthesis and characterization of 2CN2Br-NDI (M1)

To a dry round bottom flask were added tetrabromonaphthalene diimide (4Br-NDI)[41] (500 mg, 0.398 mmol), $Pd_2(dba)_3$ (37 mg, 0.040 mmol), 1,1′-bis(diphenylphosphino)ferrocene (dppf) (33 mg, 0.060 mmol), CuCN (1.433 g, 15.92 mmol), and dry dioxane (40 ml). The solution was stirred at room temperature about 36 h. The mixture was then filtered and washed with CH_2Cl_2. The solvent in the collected solution was removed by rotary evaporation and the residue was diluted with CH_2Cl_2 and washed with brine for three times. The collected organic potion was dried and the crude product was subjected to flash column chromatography (hexane/CH_2Cl_2=1:1) to afford a yellow solid **M1** (251 mg, yield: 56.1%). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ=4.21 (d, J=8.0 Hz, 4H), 2.00 (m, 2H), 1.23–1.37 (m, 80H), 0.85–0.89 (t, J=8.0 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=159.35, 158.61, 132.98, 129.41, 127.81, 126.09, 123.93, 114.63, 46.81, 36.75, 32.24, 31.80, 30.36, 29.97, 29.92, 29.68, 26.56, 23.01, 14.43. Elemental Anal. Calcd for ($C_{64}H_{98}Br_2N_4O_4$): C, 67.00; H, 8.61; N, 4.88. Found: C, 67.14; H, 8.58; N, 4.89.

2.3. General procedure for the Stille coupling polymerization

M1 (229 mg, 0.2 mmol), ditin reagent (0.21 mmol), $Pd_2(dba)_3$ (4 mg, 2 mol %), P(o-tol)$_3$ (11 mg, 17.6%), and 5 ml of anhydrous, degassed THF were added to a Schlenk tube. The tube was charge with argon through a freeze–pump–thaw cycle for three times. The mixture was stirred for 48 h at 80 °C. After cooling to room temperature, the deeply colored reaction mixture was dripped into 200 ml vigorously stirred methanol (containing 5 ml 12 M hydrochloride acid). After stirring for 4 h, the precipitated solid was filtered through a nylon filter. The solid polymer was redissolved in chloroform and reprecipitated into methanol. After filtration and dried under reduced pressure, the polymer was purified via Soxhlet extraction for 8 h with methanol, 8 h with n-hexane, and finally was collected with chloroform. The chloroform solution was then concentrated by evaporation and precipitated into methanol (200 ml) and filtered off to afford the desired 2CN-NDI-based copolymers.

2.3.1. P(2CNNDI-T). Dark violet solids (yield: 209 mg, 98.5%). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ=7.36 (s, 2H), 4.16–4.18 (br, 4H), 2.01 (br, 2H), 1.18–1.24 (br, 80H), 0.82–0.89 (br, 12H). Elemental Anal. Calcd for ($C_{70}H_{106}N_4O_4S$)$_n$: C, 76.45; H, 9.72; N, 5.09. Found: C, 74.81; H, 9.41; N, 5.12.

2.3.2. P(2CNNDI-TT). Dark green solids (yield: 205 mg, 95.3%). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ=7.54 (s, 2H), 4.13 (br, 4H), 2.02 (br, 2H), 1.24–1.36 (br, 80H), 0.85–0.88 (br, 12H). Elemental Anal. Calcd for ($C_{72}H_{106}N_4O_4S_2$)$_n$: C, 74.82; H, 9.24; N, 4.85, Found: C, 74.84; H, 9.29; N, 4.62.

2.3.3. P(2CNNDI-BT). Dark green solids (yield: 203 mg, 88.4%). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ=7.42 (s, 2H), 7.16–7.18 (br, 2H), 4.13–4.24 (br, 4H), 2.00–2.10 (br, 2H), 1.23 (br, 80H), 0.84–0.87 (br, 12H). Elemental Anal. Calcd for ($C_{74}H_{108}N_4O_4S_2$)$_n$: C, 75.21; H, 9.21; N, 4.74. Found: C, 73.34; H, 8.91; N, 4.80.

2.3.4. P(2CNNDI-BDT). Dark green solids (yield: 284 mg, 99.1%). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ=7.62 (s, 2H), 4.23–4.32 (br, 4H), 4.10–4.18 (br, 4H), 1.99 (br, 2H), 1.82 (br, 2H), 1.23–1.34 (br, 96H), 0.95–1.00 (br, 12H), 0.86–0.88 (br, 12H). Elemental Anal. Calcd for ($C_{92}H_{140}N_4O_6S_2$)$_n$: C, 75.57; H, 9.65; N, 3.83. Found: C, 73.75; H, 9.17; N, 3.75.

3. Results and discussion

3.1. Design and synthesis

The synthetic routes to of **M1** (2CN2Br-NDI) and its corresponding copolymers are shown in Scheme 1a. Methods for the synthesis of **M1** are based on stepwise cyanation of tetrabrominated NDI according to similar procedures reported in the literature.[39] Herein, 'swallow-tail' branched chains (2-decyltetradecyl) were introduced into NDI imide positions to ensure solubility of target polymers. To investigated the potential of dicyano-NDI unit in a conjugated polymer, four typical thiophene-based building blocks including thiophene (T), thieno[3,2-*b*]thiophene (TT), 2,2′-bithiophene (BT), and benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) were chosen as the electron-donating part to allow for direct copolymerization via $Pd_2(dba)_3$-catalyzed *Stille* copolymerization of **M1** and distannylated thiophenes, respectively. After polymerization, the crude polymers were purified by extracting sequentially with methanol, n-hexane, and chloroform in a Soxhlet extractor for 8 h, respectively. The molecular weight of the polymers was measured by GPC with calibration using polystyrene standards and THF as the eluent. The number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), and polydispersity index (PDI) of polymers are summarized in Table 1.

Table 1
The yields and molecular weights of 2CN-NDI-based D–A copolymers

Polymers	Yields (%)	M_n [kDa][a]	M_w [kDa][b]	PDI[c]
P(2CNNDI-T)	98.5	6	12	2.0
P(2CNNDI-TT)	95.3	26	29	1.1
P(2CNNDI-BT)	88.4	14	20	1.4
P(2CNNDI-BDT)	99.1	9	21	2.3

[a] The number-average molecular weight, determined from GPC using PS standards and THF as eluent.
[b] The weight-average molecular weight.
[c] Polydispersity index of the polymers.

The as-synthesized polymers are soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, dichloromethane, and toluene. Thermogravimetric analysis (TGA) demonstrated that all of the polymers possessed excellent thermal stability with 5% weight-loss temperature over 390 °C shown in Table 2, with the exception of P(2CNNDI-BDT) of 342 °C (Fig. S1).

3.2. Optical properties

The UV–vis absorption spectra of the polymers P(2CNNDI-T), P(2CNNDI-TT), P(2CNNDI-BT), and P(2CNNDI-BDT) in the chloroform solution and in film are shown in Fig. 1. All of the polymers showed weak intermolecular charge transfer (ICT) peaks from ca. 500 to 800 nm both in solution and film state. And the bands from

Table 2
Optical electrochemical and thermal properties of 2CN-NDI-based D–A copolymers

Polymers	λ_{max}^{soln} [a] [nm]	λ_{max}^{film} [b] [nm]	λ_{onset}^{film} [nm]	E_{onset} [c]	E_{LUMO} [d]	E_{HOMO} [e]	E_g [f]	T_{deg} [°C] [g]
P(2CNNDI-T)	518	527	704	−0.41	−4.39	−6.15	1.76	392
P(2CNNDI-TT)	612	615	798	−0.34	−4.46	−6.01	1.55	392
P(2CNNDI-BT)	647	648	888	−0.36	−4.44	−5.83	1.39	393
P(2CNNDI-BDT)	753	756	968	−0.38	−4.42	5.70	1.28	342

[a] Measured in dilute chloroform solution (1.0×10^{-5} M).
[b] Spin-coated from 5 mg/ml chloroform solution.
[c] The onset reduction potentials in acetonitrile solution versus Fc/Fc^{+}.
[d] LUMO (eV) estimated by the onset of reduction peaks and calculated according to $E_{LUMO}=-(4.8+E_{onset})$ eV.
[e] Calculated according to $E_{HOMO}=(E_{LUMO}-E_g)$ eV.
[f] Calculated by the onset of absorption in $CHCl_3$ solution according to E_g (eV)$=(1240/\lambda_{onset}^{film})$.
[g] Decomposition temperature determined by TGA corresponding to 5% weight-loss at 10 °C/min under nitrogen flow.

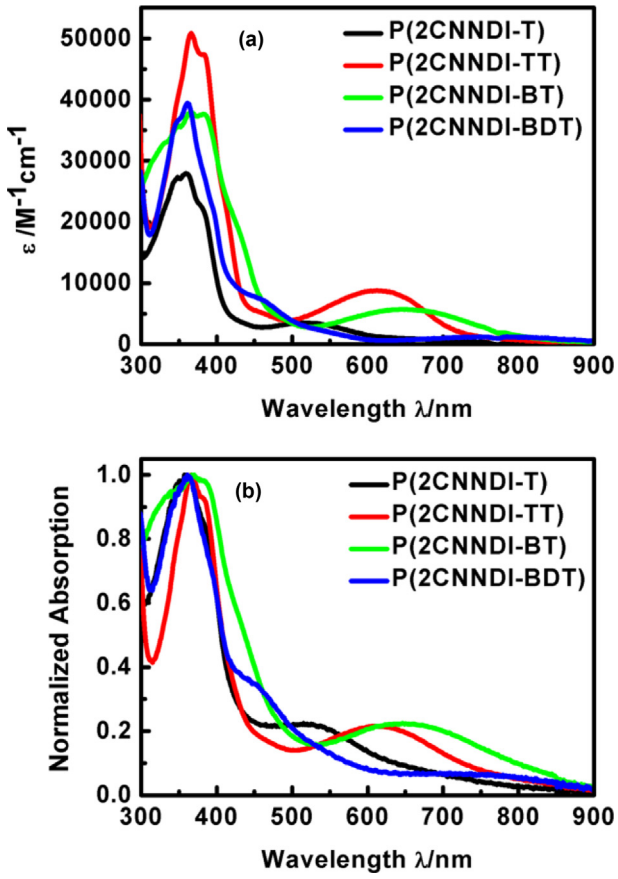

Fig. 1. UV–vis absorption spectra in dilute chloroform solution (a) and in spin-coated films from chloroform solutions (b).

300 to 500 nm are attributed to the strong electron-withdrawing unit of 2CN-NDI. The absorption maxima were shifted from 527 nm for P(2CNNDI-T), to 615 nm for P(2CNNDI-TT), to 648 nm for P(2CNNDI-BT), to 756 nm for P(2CNNDI-BDT) in the film states; the absorption in solution also followed the same trend as the electron-donating strength of the thiophene unit increases. All of their absorption spectra in film exhibited a few nanometers red-shifts relative to those in solution. According the literature,[27] those cyano-free NDI analogues displayed stronger ICT peaks with absorption maxima of 600 nm for **P1c**, 661 nm for **P2**, and 703 nm for **P5**, respectively (Scheme 1b), indicating significantly red-shifted of about 40–80 nm than those of the 2CN-NDI-based polymers. The results can be attributed to the relatively weak ICT process between the enhanced electron-accepting moieties by incorporating two cyano groups in NDI core and thiophene donators. Optical band gaps (E_g^{opt}), estimated from the absorption onset of polymer films, are listed in Table 2 as follows: 1.76 eV for P(2CNNDI-T), 1.55 for P(2CNNDI-TT), 1.39 eV for P(2CNNDI-BT), and 1.28 eV for P(2CNNDI-BDT).

3.3. Electrochemical properties

The electrochemical redox properties of 2CN-NDI-based polymers were investigated by cyclic voltammetry (CV). Fig. 2showed the cyclic voltammogram traces of all the polymers, and the associated results were summarized in Table 2. All polymers showed two reversible or quasireversible reduction waves corresponded to the formation of the monoanion and dianion of polymers. The p-doping of these D–A copolymers appeared weak but not negligible peaks.

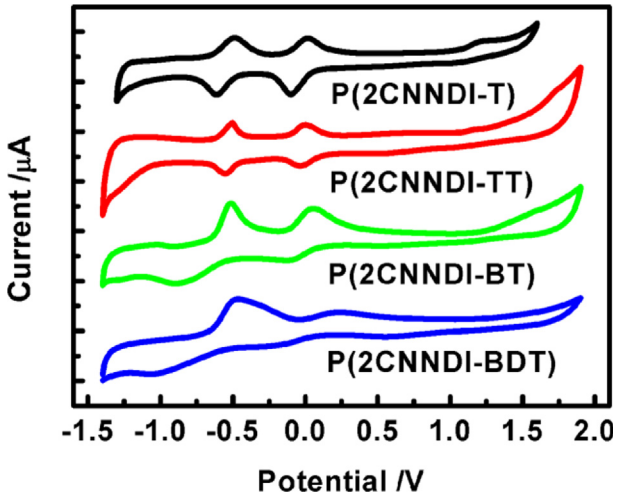

Fig. 2. Cyclic voltammogram of copolymers P(2CNNDI-T), P(2CNNDI-TT), P(2CNNDI-BT) and P(2CNNDI-BDT) in thin-film drop-coated on a glassy carbon electrode and tested in n-Bu_4NPF_6/CH_3CN solution (scan rate: 100 mV s^{-1}).

Their LUMO energy levels calculated from the onset reduction potentials (E_{onset}^{red}) are −4.39, −4.46, −4.44, and −4.42 eV from P(2CNNDI-T) to P(2CNNDI-BDT), respectively (Table 2), which are almost invariant and dictated by the dicyano-substituted NDI units (−4.42 eV).[39] And their HOMO levels calculated from $E_{HOMO} = E_{LUMO} - E_g^{opt}$ varied from −6.15 to −5.70 eV as a reflection of electron-donating ability and coplanarity of polymer. It is noteworthy that, in contrast to LUMO levels of about −3.8 eV of polymers **P1c**, **P2**, and **P5**, these four polymers expressed lowered LUMO levels by ~0.6 eV. In consideration of the devices of NDI-based polymers fabricated or tested in inert gas atmosphere, these low-lying LUMO levels of 2CN-NDI-based polymers suggested higher electron affinity to facilitate electron injection and transportation, thus promising candidates for air-stable n-channel OFETs.

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3.4. OFET characteristics

To identify the air-stability of this series of polymer, a bottom-gate top-contact device configuration was afforded to investigate their OFETs properties. Films of the polymers were spin-coated from chloroform solution (10 mg/ml, 3000 r/min, 40–60 nm) onto SiO_2/Si substrates treated with octadecyltrichlorosilane (OTS). Gold source/drain electrodes with width/length of 240 μm/80 μm were deposited on the polymer films through a shadow mask. All the devices were tested and stored in ambient conditions. Among them, the unannealed thin-film devices of P(2CNNDI-TT) and P(2CNNDI-BT) showed relatively low electron mobilities of 8.17×10^{-7} and 1.05×10^{-6} cm^2 V^{-1} s^{-1}, respectively. Higher electron mobilities of about 1.30×10^{-4} cm^2 V^{-1} s^{-1} and 2.54×10^{-4} cm^2 V^{-1} s^{-1} were achieved after annealing at 240 °C with a threshold voltage of 11.7 and 18.1 V, an on/off ratio of 4.31×10^3 and 4.89×10^3, respectively (Fig. 3). The highest electron mobility is still lower than reported for cyano-free polymers tested in glove box, and the morphology of these polymer films annealed at different temperatures did not induce significant change of crystallinity (Figs. S2 and S3), which hints that there is a lot of room for morphology improvement by structural modification via selecting electron-donator and proper side chains on the 2CN-NDI imide positions.

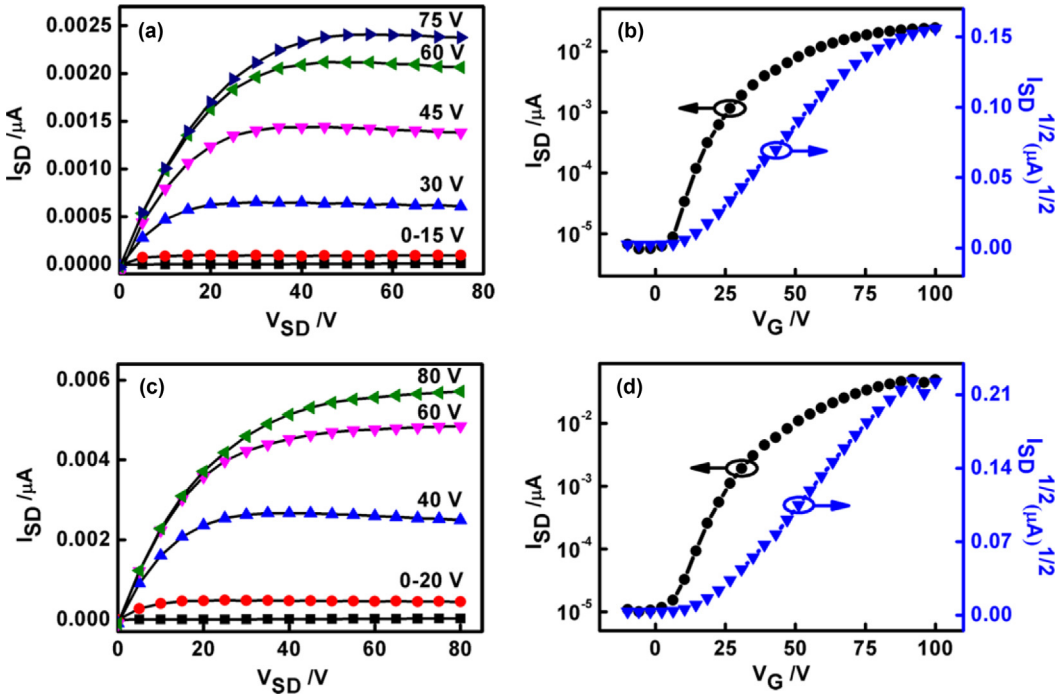

Fig. 3. Representative output and transfer characteristics for copolymers P(2CNNDI-TT) (a, b) and P(2CNNDI-BT) (c, d).

4. Conclusions

We have successfully synthesized a series of D–A copolymers alternated between dicyano-NDI (2CN-NDI) and thiophene derivatives, named P(2CNNDI-T), P(2CNNDI-TT), P(2CNNDI-BT), and P(2CNNDI-BDT) via *Stille* copolymerization. Detailed investigation of their photophysical and thermal properties was carried out by absorption spectroscopy, cyclic voltammetry, and TGA analysis. With the introduction of the electron-deficient group cyano into core of NDI, the LUMO energy levels of polymers are significantly lowered in the range from −4.39 to −4.46 eV dictated by the dicyano-substituted NDI units, indicating sufficient air-stability. And their HOMO levels varied from −6.15 to −5.70 eV by the electron-donating moieties as a reflection of electron-donating ability. Employing them in bottom-gate top-contact devices, P(2CNNDI-TT) and P(2CNNDI-BT) exhibited the highest electron mobilities of 1.30×10^{-4} and 2.54×10^{-4} cm^2 V^{-1} s^{-1}, respectively. These preliminary results indicated that a new and stronger electron-accepting building block for constructing n-channel polymeric materials with high electronic performances were developed, and still spurred us to further optimize the polymer structures in view of molecular weight, alkyl side chains and electron-donating units.

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Supplementary data

Characterization data of new compounds, photophysical properties including TGA, AFM, and NMR data. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.04.002.

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