



# 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.

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## 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),<sup>1–3</sup> organic photovoltaics (OPVs),<sup>4–6</sup> and chemosensor<sup>7–9</sup> with low cost, solution-processability, light weight and flexibility. Naphthalene diimide (NDI),<sup>10–14</sup> perylene biimide (PBI),<sup>15–17</sup> diketopyrrolopyrrole,<sup>18–20</sup> isoindigo,<sup>21–23</sup> benzothiadiazole,<sup>24–26</sup> 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.<sup>11,27</sup> A series of NDI-based D-A copolymers has been initially investigated by Weston et al. and demonstrated them as promising candidates for applications in either *n*-channel or ambipolar transistors.<sup>10,27</sup> By varying the *N*-alkyl substituents, an NDI-based polymer named P(NDI2OD-T2) showed unprecedented

field-effect characteristics with electron mobilities up to  $0.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in top-gate/bottom-contact device architecture.<sup>11</sup>

Recently, we are particularly interested in the chemistry and functionalities of NDI derivatives. A new family of laterally  $\pi$ -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.<sup>28–31</sup> 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.<sup>32</sup> Direct perfluoroalkylation of the NDI core and intensive investigation of fluoroalkyl substituted NDI derivatives on its anisotropic electron-transporting characteristics have been also focused.<sup>33,34</sup>

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.<sup>35–38</sup> 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  $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>39</sup> 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,<sup>39</sup> which is vital and virtual for achieving effective  $\pi$ - $\pi$  stacking and ordered polymer packing that would facilitate efficient charge transporting.<sup>40</sup>

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  $2.54 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in bottom-gate/top-contact device configuration.

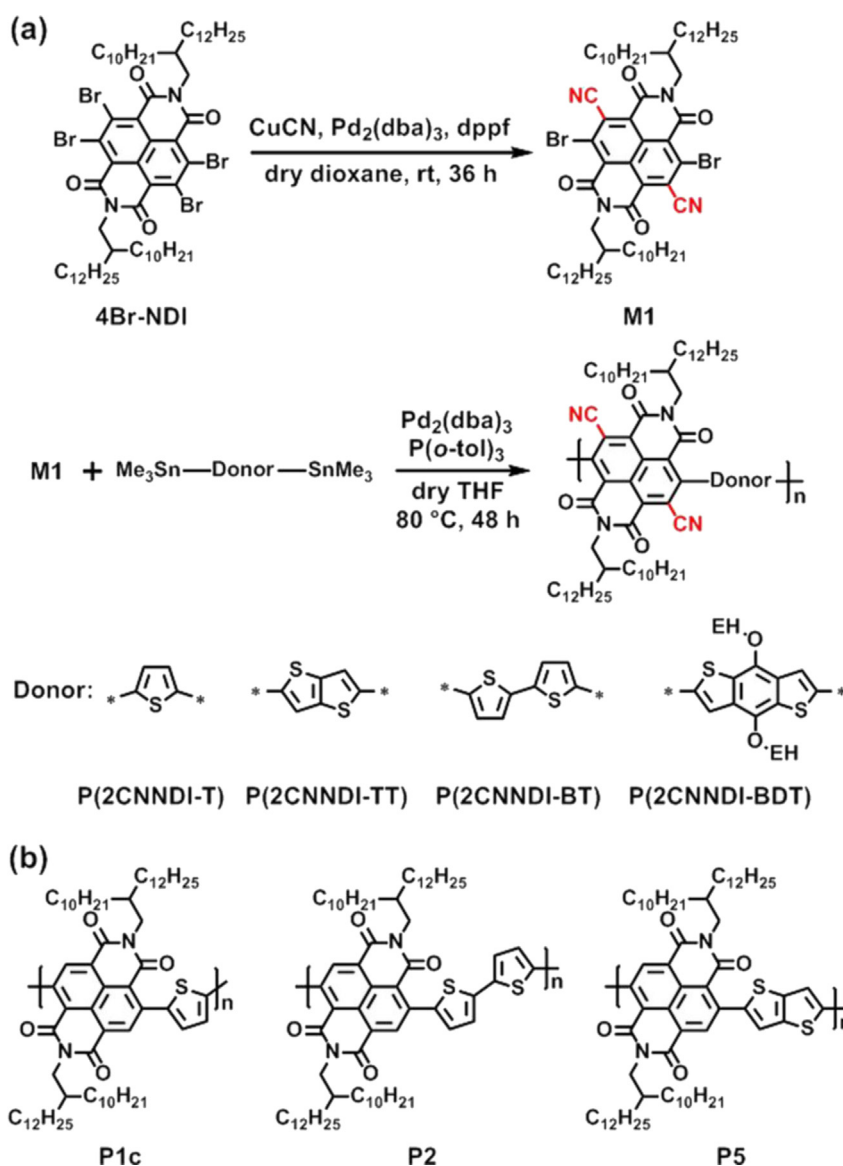
## 2. Experimental section

### 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. <sup>1</sup>H and <sup>13</sup>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 on 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.<sup>27</sup>

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