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Conjugated Polymers from Naphthalene Bisimide

Xugang Guo and Mark D. Watson*

Department of Chemistry, University of Kentucky, Lexington, Kentucky, 40506-0055

mdwatson@uky.edu

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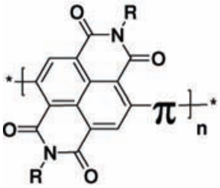
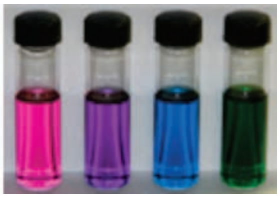
ABSTRACT





Stille coupling of regioisomerically pure dibromonaphthalene bisimides (NBI) with various stannylated thiophene-based monomers yields (very) high molecular weight donor−acceptor conjugated polymers. Electrochemical and optical absorption measurements reveal that LUMO energies are essentially invariant and dictated by the NBI units, while HOMO energies are dictated by the thienyl comonomers. Optical energy gaps ranging from 1.7 to 1.1 eV are thus obtained. The polymers are also characterized by differential scanning calorimetry and fiber WAXD.

Due to their strong electron-withdrawing ability, imide substituents have been employed to impart n-type characteristics to small-molecule organic semiconductors. While there are some noteworthy exceptions, e.g., imide-functionalized anthracenes,[1] the most studied imide-functionalized small molecules for organic n-type materials are based on the rylenes: naphthalene bisimide (NBI) and perylene bisimide (PBI).[2] There are, however, only a few published examples of conjugated polymers with imide-functionalized π-systems entrained such that they can be in conjugation along the backbone. Examples published without device studies include polyanilines[3a] and poly(phenylene ethynylene)s[3b] with backbone phthalimide units and homo- or copolymers of thiophene derivatives with imide groups fused at their 3,4-positions.[3c−e] An imide-functionalized isothianaphthene gave a very low band gap homopolymer, and its copolymers with 3,4-ethylenedioxythiophene (EDOT) have been implicated as promising charge-storage media and evaluated in PVDs.[4] A 2,2′-bithiophene fused at its 3,3′-positions via an imide linkage yielded a homo- and copolymer with electron or hole mobilities ≥0.01 cm^2/V s.[5] However, there is only a single report[6] of a copolymer containing rylene bisimides electronically conjugated along the polymer backbone (PBIs bridged via their "bay" positions by dithienothiophene). This polymer yielded an n-type field-effect transistor and an all-polymer photovoltaic device with average power conversion efficiency slightly over 1%.

We report here a series of copolymers with NBI units electronically conjugated along the backbone. As we show here, relevant intrinsic electronic properties (e.g., LUMO) imparted to polymers by NBI are very similar to those imparted by PBI. However, NBI is an attractive alternative

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Table 1. Yields and properties of polymers

	yield (%)	M_n [PDI]^a (kDa)	$T_m{}^b$ (°C)	soln $\lambda_{max}{}^c$abs (nm)	film $\lambda_{max}{}^d$ abs (nm)	$\Delta\ \lambda_{max}$soln−film	$E_g{}^{opt\ e}$ (eV)	$E_{1/2}{}^1{}_{red}{}^f$ (V)	$E_{1/2}{}^2{}_{red}{}^f$ (V)	LUMO^g (eV)	HOMO^h (eV)
P1	94	23.6 [2.2]	235	568	618	50	1.66	−0.97	−1.40	−3.83	−5.49
P2a	98	252 [2.5]	285	693	707	14	1.48	−1.03	−1.38	−3.77	−5.25
P2b	99	73.0 [1.6]	222	539	626	87	1.56	−1.04	−1.39	−3.76	−5.32
P2c	91	78.7 [1.6]	269	534	588	54	1.65	−1.03	−1.40	−3.77	−5.42
P2d	95	133 [3.5]	252	985	966	−19	1.08	−1.04	−1.40	−3.76	−4.84
NBI				381			3.07	−1.01	−1.47	−3.79	−6.86

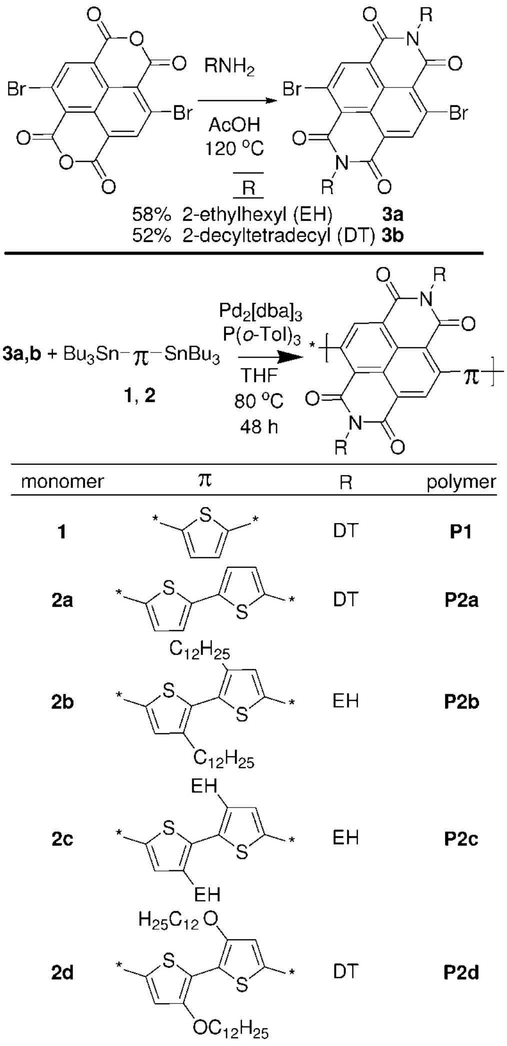
[a] Number-average molecular weight and polydispersity (GPC vs polystyrene standards in THF). [b] Peak melting point, differential scanning calorimetry (10 °C/min) [c] Solution absorption spectra (5×10^{-6} M THF). [d] Thin film absorption spectra (annealed at $T_m - 40$ °C). [e] Optical energy gap estimated from the absorption edge of annealed films except parent NBI measured in solution. [f] CV measurements of thin films except parent NBI measured in solution, vs Fc/Fc$^+$. [g] Estimated from LUMO = $-4.8 - E_{1/2}{}^1{}_{red}$) [h] Estimated from HOMO = LUMO − $E_g{}^{opt}$.

to PBI as the requisite dibromo-monomers are much more readily obtained in regioisomerically pure form, the smaller naphthalene unit will likely generally lead to polymers with greater solubility, and bridging aryl units connected to the 2,6-positions of NBI should allow for a more coplanarized backbone (extended conjugation) than bridging via the sterically congested bay positions of PBI.

The NBI monomers were prepared in regioisomerically pure form by standard procedures in two laboratory steps (Scheme 1 and Supporting Information). It has been reported[7] that commercially available naphthalene bisanhydride (NBA) can be selectively and quantitatively brominated at its 2,6-positions with dibromoisocyanuric acid (DBI) in concentrated sulfuric acid at 130 °C. We could not reproduce these results but found the published[8] adaptation using 1 equiv of DBI in fuming sulfuric acid to be effective. The resulting mixture of products with varying levels of bromination can be enriched in the 2,6-dibromo NBA by recrystallization from various polar aprotic solvents (not shown), but this effort is unnecessary since separation is easily effected after subsequent imidization. The crude mixture of brominated NBAs was thus converted to a mixture of brominated NBIs by reaction with amines in glacial acetic acid. The desired 2,6-dibromo NBIs **3** are easily separated from the coproducts of nucleophilic aromatic substitution in moderate yields after simple flash chromatography and/or recrystallization. Racemic “swallow-tail” side chains were employed to ensure polymer solubility. 2-Ethylhexylamine is commercially available, while 2-decyltetradecylamine was prepared in three steps from 2-decyltetradecanol via Gabriel synthesis[9] (Supporting Information).

All of the thiophene-based monomers were prepared by standard procedures (Supporting Information). The stannylated thiophenes **1** and **2** were characteristically susceptible to protiodestannylation but gave satisfactory $^1H/^{13}C$ NMR spectra and elemental analysis after chromatography using alumina treated with triethylamine. Due to its electron-donating alkoxy substituents, monomer **2d** is particularly unstable but can be stored under inert atmosphere at low temperature.

Scheme 1. Synthesis of Polymers



Polymer molecular weight is an important factor affecting performance of organic FETs and PVDs.[10] The electron-poor NBI monomers **3** are ideal coupling partners for

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electron-rich stannylated thiophenes,[11] leading to high molecular weights and isolated yields indicating excellent conversion in the Stille coupling reaction using the catalyst system of $Pd_2[dba]_3$ and tri(*o*-tolyl)phosphine (Table 1). $Cl_2Pd(PPh_3)_2$ as catalyst (not shown) gave slightly lower molecular weights here, which has been previously attributed[11] to stoichiometric imbalance upon reduction of Pd(II) by stannyl monomers. Typical overestimation of relative molecular weights of semirigid rod polymers by GPC versus polystyrene standards is assumed here, and the exceptionally high relative molecular weight for polymer **P2a** probably further reflects aggregation in solution. All of the polymers are soluble in common organic solvents including THF, toluene, and chloroform. **P2c** is even highly soluble in hexanes due to the branched side chains on its bithiophene units, while **P2a** with unsubstituted bithiophene units requires mild heating in chloroform.

The identity and purity of the polymers is supported by elemental analysis and solution NMR measurements (Supporting Information). Resolved ^1H NMR spectra of higher molecular weight polymers **P2a** and **P2d** could only be obtained at elevated temperatures (130 °C) due to aggregation. No ^{13}C signals arising from their polymer backbones could be observed even after collection for 12 h at this elevated temperature.

Reaction mixtures of the most electron-rich thienyl monomer **2d** and NBI **3b** exhibited a green color upon dissolution in THF, suggesting a charge-transfer (CT) complex. Swager and Iverson reported CT complexes between NBIs and 1,5-dialkoxynaphthalenes leading to alternating donor−acceptor columnar mesophases with substantial thermal stability.[12] Combination of nonstannylated 3,3′-dialkoxy-2,2′-bithiohene (absorption $\lambda_{max} = 326$ nm) and nonbrominated *N*,*N*′-2-decyltetradecylnaphthalene bisiimide (absorption $\lambda_{max} = 381$ nm) gives a blue solution with a CT absorption band at $\lambda_{max} = 588$ nm (Figure 1). It is possible that inter- and intramolecular CT states contribute to the particularly low optical energy gap for polymer **P2d** described below.

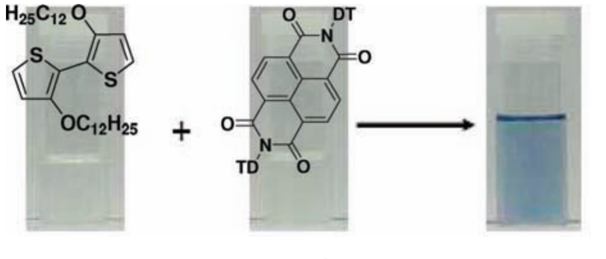

Figure 1. Charge-transfer complex ($\lambda_{max} = 588$ nm, 0.01 M toluene) from 3,3′-dialkoxybithiophene and NBI.

Thin film electrochemical measurements reveal two reversible reduction waves for each polymer (Table 1 and Supporting Information). The $E_{1/2}$ values for the first reduction waves are invariably near −1 V versus the ferrocene/ferrocenium redox couple (Fc/Fc^+) regardless of the comonomer. This is essentially the same value for the parent NBI measured by us and reported[13] by others (after using a standard conversion factor[14] to convert from SCE to Fc/Fc^+). In fact, this is within 0.1 V of the value for the PBI copolymer reported[6] by Marder, the parent PBI, and even the higher rylenes: terrylene bisimide and quaterylene bisimide.[15] The LUMO levels of our polymers (∼−3.8 eV) are dictated entirely by the rylene and may be similar for all thienyl copolymers of the rylene bisimides. No oxidation waves were observed within our experimentally accessible window (± 2 V), regardless of scan rate.

Room-temperature solution and thin film absorption spectra of all new polymers are shown in Figure 2, and relevant data are collected in Table 1. Absorption λ_{max} and optical energy gaps (E_g^{opt}), estimated from the low-energy absorption edge, vary across the visible spectrum into the near IR. Changing from thiophene to bithiophene comonomer (**P1** vs **P2a**) causes a red-shift of 125 nm in solution and 89 nm in annealed thin films. However, alkylation of the bithiophene units (**P2b**,**c** vs **P2a**) leads to a solution blue-shift of 154−159 nm, while alkoxylation (**P2d** vs **P2a**) leads to a very large red shift of nearly 300 nm.

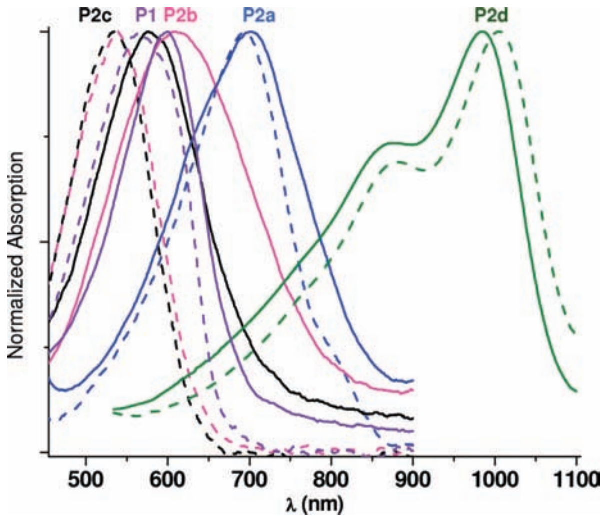

Figure 2. Absorption spectra of polymers in solution (dashed lines, 5×10^{-6} M THF) and thin film (solid lines).

With LUMO levels constant, variation in E_g^{opt} is essentially entirely a function of the nature of the thienyl comonomers.

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Such dependence of LUMO on the acceptor and HOMO on the donor monomer is not unusual for donor−acceptor copolymers.[16] A decrease in E_g^{opt} on changing from thiophene to bithiophene (and further to terthiophene) was also reported for copolymers with fluorene.[17a] The HOMOs of oligothiophenes are destabilized asymptotically with increasing oligomer length;[17b] i.e., bithiophene is a "stronger donor" than thiophene. The longer footprint of bithiophene bridges may also diminish intramolecular steric interaction of NBI side chains in solution and afford more commensurate space-filling in the solid state.

We have shown[18] that 3,3′-dialkylbithiophene (head-to-head, HH) linkages do not preclude backbone planarity in alternating donor−acceptor perfluorobenzene-bithiophene copolymers. However, 2-ethylhexyl side chains proved too bulky in that case and led to amorphous twisted backbones in the solid state. Here, the large solution blue-shift upon alkylation of the bithiophene units is due to a greater barrier to rotation/planarization of the polymer backbones. **P2b** with less sterically encumbering *n*-dodecyl chains undergoes a larger red-shift (87 nm) on going from solution to the solid state compared to **P2c** carrying 2-ethylhexyl chains (54 nm). Increasing E_g^{opt} along the series **P2a** → **P2b** → **P2c** points to attenuated conjugation (stabilize HOMO) and/or π-stacking as a function of side-chain steric bulk.

Electrostatic attraction between ether oxygens and thienyl sulfur atoms[19] of **P2d** likely enhance planarization, while mesomeric effects from pendant ether oxygens destabilize the HOMO, together causing the lowest E_g^{opt}. Fine structure even in the solution spectrum of **P2d** is attributed to greater backbone rigidity. The absorption profiles for all the other polymers undergo small red-shifts (5−17 nm) upon thermal annealing at 40 °C below their peak melting temperatures. The thin-film absorption profile for **P2a** develops fine structure upon annealing, indicating an increase in backbone rigidification and order (Supporting Information). Although highly fluorescent NBI derivatives have been reported,[20] polymers **1** and **2** barely visibly emit under illumination with UV/Vis light.

Two-dimensional wide-angle X-ray diffraction patterns were collected with an area detector from extruded fibers (Supporting Information). Series of equatorial intensity maxima out to the fourth order show that polymers **P1**, **P2a**, and **P2d** assemble to ordered lamella. Meridianal reflections out to the third order also indicate relatively long-range correlation of repeating elements along the backbone. Their *d*-spacings reasonably agree with the repeating unit lengths (**P1**: 9.9 Å, **P2d**: 13.1 Å). π-Stacking distances of 4.0, 3.8, and 4.0 Å, respectively, were estimated from additional equatorial reflections. It must be understood that these values are upper limits, exceeding the actual π-stacking distance if the polymer backbone rings tilt away from normal to the π-stacking axes. This is equivalent to slipped π-stacks[21] formed by most large π-systems. **P2b** forms an ordered superstructure but gives no clear diffractions attributable to π-stacking. Either these diffractions are extinguished or the red-shift (87 nm) of **P2b** upon going from solution to annealed solid film should be attributed to backbone planarization alone. Polymer **P2c** bearing bulky head-to-head 2-ethylhexyl chains borders on amorphous.

In summary, brominated NBIs are excellent coupling partners for Stille polymerization with electron-rich stannylated monomers, leading to high-molecular-weight donor−acceptor conjugated polymers. Optical energy gaps of the polymers are easily tuned across the visible spectrum and into the near IR by variation of comonomers. The polymers are readily soluble and therefore can be solution processed for device fabrication. The polymers reported here, as well as related ones from comonomers based on fused thiophenes, are currently being evaluated in transistors and as both the donor and acceptor component in PVDs. We have so far observed FETs with ambipolar transport characteristics in ambient atmosphere, which will be reported in due course.

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Supporting Information Available: Synthesis and characterization details, abs spectra, and fiber WAXD diffractograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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