Macromolecules

Conjugated NDI–Donor Polymers: Exploration of Donor Size and Electrostatic Complementarity

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Supporting Information

ABSTRACT: Conjugated donor-acceptor copolymers comprised of electron-deficient 1,4,5,8-naphthalenetetracarboxylic diimide (NDI) linked to a series of relatively electron-rich aromatics via ethynyl spacers were synthesized and characterized. While LUMO levels remained constant at -3.75 eV, HOMO levels were sensitive to the relatively electron-rich aromatic donors and systematically tuned from -5.68 to -5.17eV. Regardless of the electron-rich comonomer, fluorescence



and X-ray diffraction data were consistent with the polymer chains being assembled through the stacking of NDI moieties in an offset face-to-face fashion rather than alternating donor-acceptor stacks.

INTRODUCTION

The unique electronic properties of conjugated polymers have rendered them desirable materials for applications that range from photovoltaic (PV) cells¹ to field effect transistors² and electrochromic devices.³ Conjugation along the polymer backbone allows for extended π -delocalization that can result in a relatively high HOMO level, a relatively low LUMO level, or a small HOMO–LUMO band gap. As a result, certain electronic characteristics are attainable such as p-type or n-type behaviors, high charge carrier mobilities, and, for photovoltaic purposes, a broad visible absorption spectrum.^{1–3}

As a practical material, semiconducting polymers should have tunable electronic and photovoltaic properties. One method to fine-tune the electronic properties of these materials has been to synthesize conjugated aromatic donor (electron rich)– acceptor (electron poor) (D–A) polymers.^{1,4} Energy levels can be tuned through careful selections of monomer units, as D–A polymer HOMO–LUMO levels are well-approximated by the individual monomeric donor HOMO and acceptor LUMO orbitals.⁵ Hence, progress in this area has focused on developing new monomers and implementing appropriate combinations of these donor and acceptor moieties.⁶

1,4,5,8-Naphthalenetetracarboxylic diimide (NDI) has emerged as a popular acceptor moiety due to its electrondeficient aromatic core, high electron carrier mobility,⁷ and lowlying LUMO.⁸ Recent synthetic advances have not only allowed for substitution through the imide positions, but direct substitution on the NDI aromatic core is now readily accessible.⁹ In addition, solubility limitations have been addressed and the construction of large polymers with NDI is now possible.^{7,10} Numerous donor monomers have been copolymerized with NDI in a conjugated fashion to alter polymer electronic and photovoltaic properties. These groups have included thiophene-based,^{7,10,11} thiazole-based,¹² and fluorene-based¹³ donors.

Previously, our group has exploited the complementary size and electrostatics of the relatively electron-deficient NDI with electron-rich 1,5-dialkoxynaphthalene (DAN) to affect the macromolecular assembly of aqueous foldamers,¹⁴ self-assembling polymers,¹⁵ and tunable liquid crystals.¹⁶ Although DAN polymers have been reported,¹⁷ to the best of our knowledge there has been no report of a conjugated, alternating polymer incorporating both DAN and NDI. We reasoned that the complementary nature of the DAN and NDI donor-acceptor units could facilitate interchain assembly, thereby leading to useful bulk properties. Alternatively, there are now theoretical arguments asserting that electrostatic complementarity between highly polarized groups on the periphery of aromatics, rather than overall aromatic electron density, can provide the dominant interactions between stacked aromatics.¹⁸ Such considerations and a number of recent experimental examples suggest that NDI units themselves may dominate the interchain assembly of NDI-containing polymers, favoring an offset facecentered stacking mode in which the strong NDI carbonyl dipole moments complement each other from one unit to the next.¹⁹ Herein, we report the synthesis and characterization of a series of conjugated alternating NDI-based aromatic D-A polymers linked by single alkynyl units and present evidence that NDI self-stacking dominates the intermolecular polymer chain assembly.

EXPERIMENTAL SECTION

Reagents. 1,4-Bis(ethynyl)benzene (1) was purchased from Aldrich, and 2,6-dibromonaphthalene (3) was purchased from Alfa Aesar. $Pd(PPh_3)_2Cl_2$, $Pd(Ph_3)_4$, and CuI were purchased from STREM. Dry toluene and TEA were obtained by distillation over CaH. Dry NMP was purchased from Fisher Scientific and stored over

Received:November 13, 2012Revised:January 18, 2013Published:February 4, 2013

molecular sieves prior to use. All other chemicals were acquired from Aldrich and used without further purification. All reactions were carried out under argon.

Instrumentation. NMR spectra were taken on a Varian Unity 400 spectrometer. Melting points were detected using a MEL-TEMP apparatus. GPC analyses were performed on polymer solutions in THF using a Waters Model 510 HPLC pump, two fluorinated polystyrene columns (IMBHW-3078 and I-MBLMW-03078) arranged in series, and a Waters 486 tunable absorbance detector (λ = 450 nm). Calibration was based on polystyrene standards in THF. Absorption spectra were obtained on an Agilent 8453 UV-vis spectrometer. Fluorescence measurements were made on a PTI fluorimeter (4 nm slits) with an 814 photomultiplier detection system using a 75 W xenon short arc lamp. IR spectra were obtained using polymer solids on a PerkinElmer Spectrum 100 FT-IR equipped with a universal ATR (UATR) accessory. Electrochemical cyclic voltammetry was performed under a nitrogen atmosphere. The cell was equipped with platinum working, tungsten counter, and silver electrodes. Thin films were measured in a 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) MeCN solution at a scan rate of 50 mV s⁻¹ and referenced to Fc/Fc^+ by shifting $(Fc^*)^{0/+}$ to 0.0 V.²⁰ X-ray powder diffraction (XRD) patterns were obtained with a Scintag X1 theta-theta diffractometer equipped with a Cu X-ray tube and a solid-state X-ray detector set to count Cu K α radiation. Samples were prepared by smearing a small amount of polymer onto a zero background quartz plate sample holder. Suitable samples were obtained by methanol precipitation or slow evaporation from CH₂Cl₂ to yield a powder and film, respectively. Both methods gave the same XRD pattern.

2,6-Dibromo-1,5-bis(methoxy)naphthalene (6).²¹ To a solution of 2,6-dibromonaphthalene-1,5-diol²² (5.90 g, 19.0 mmol) in dry, degassed NMP (85 mL) at 0 °C was added NaH (60% mineral oil dispersion, 1.70 g, 42.0 mmol). After allowing the solution to stir at 0 °C for 5 min, MeI (6.20 g, 44.0 mmol) was added and the solution warmed to room temperature while stirring overnight. The solution was poured onto ice (400 g), extracted with diethyl ether, and the organic fractions were poured through a short neutral alumina plug. The solvent was removed by rotary evaporation and the crude material was purified by recrystallization from acetone to yield a light brown solid (5.24 g, 15.0 mmol, 79% yield); mp 149–156 °C. ¹³C NMR (400 MHz, CDCl₃) δ : 153.68, 131.32, 129.87, 119.68, 113.83, 61.76 ppm. ¹H NMR (400 MHz, CDCl₃) δ : 7.78 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 3.99 (s, 6H) ppm. CI-HRMS (positive ion) calculated for C₁₂H₁₀Br₂O₂, 343.9048; found, 343.9048.

2,6-Diethynylnaphthalene (4). 3 (0.3258 g, 1.14 mmol) was dissolved in 11 mL of a 50/50 toluene/TEA solution. The solution was degassed with argon. $Pd(PPh_3)_2Cl_2$ (0.1145 g, 15 mol %), CuI (0.0105 g, 5 mol %), and (tert-butyldimethylsilyl)acetylene (0.3229 g, 2.30 mmol) were subsequently added, and the solution was heated at reflux for 24 h. The solvent was removed by rotary evaporation, and the material was passed through a short silica column (column 1: Hex) to yield a mixture of the disubstituted and monosubstituted protected alkyne intermediates. This mixture was taken up in 11 mL of THF with TBAF (2.3 mL of 1.0 M in THF, 2.3 mmol) and stirred at room temperature for 1 h. The solvent was removed by rotary evaporation, and the crude material was purified by column chromatography (column 2: Hex) to afford the desired product as a white solid (0.1508 g, 0.86 mmol, 75% yield); mp 144-148 °C. ¹³C NMR (400 MHz, CDCl₃) δ: 132.37, 132.03, 129.33, 127.86, 120.45, 83.67, 78.23 ppm. ¹H NMR (400 MHz, CDCl₃) δ : 7.99 (s, 2H), 7.74 (d, J = 12.0 Hz, 2H), 7.54 (dd, J = 1.3 Hz, J = 8.0 Hz, 2H), 3.18 (s, 2H) ppm. CI-HRMS (positive ion) calculated for C₁₄H₈, 176.0626; found, 176.0626. IR: 678, 706, 819, 884, 1255, 1364, 1494, 1597, 3268 cm⁻¹

2,6-Diethynyl-1,5-bis(methoxy)naphthalene (7). Monomer 7 was synthesized in the same manner as that given for 4, but with 6 as starting material. Column 1: 5% DCM/Hex; column 2: 30% DCM/ Hex; collected as an off-white solid (0.1936 g, 0.82 mmol, 72% yield); mp 142–147 °C. ¹³C NMR (400 MHz, CDCl₃) δ : 159.04, 130.27, 129.14, 117.85, 111.77, 83.18, 80.31, 61.94 ppm. ¹H NMR (400 MHz, CDCl₃) δ : 7.86 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 4.13 (s, 6H), 3.45 (s, 2H) ppm. CI-HRMS (positive ion) calculated for

 $C_{16}H_{12}O_2,\ 236.0837;\ found,\ 236.0834.$ IR: 739, 831, 858, 963, 1041, 1174, 1203, 1229, 1332, 1376, 1449, 1484, 1590, 3284 $cm^{-1}.$

9,10-Diethynylanthracene (10). Monomer 10 was synthesized in the same manner as that given for 4, but with 9 as starting material with some modification explained below. Column 1: 100% Hex (further purified by recrystallization from ethanol to afford disubstituted material); purified product was stored as the silylprotected intermediate. Because of the instability of 10, this material was deprotected and immediately stannylated and polymerized. The material was protected from light during deprotection, and after a reaction period of 1 h, the reaction mixture was quickly passed through a silica plug. The solvent was removed by rotary evaporation, and 10 was collected as a yellow solid (0.1571 g, 0.69 mmol, 61% yield) and immediately used in the next step. ¹³C NMR (400 MHz, CDCl₃) δ : 132.90, 127.49, 127.46, 118.23, 90.34, 80.64 ppm. ¹H NMR (400 MHz, CDCl₃) δ: 8.61 (m, 4H), 7.62 (m, 4H), 4.07 (s, 2H) ppm. IR: 663, 776, 859, 980, 1029, 1170, 1167, 1222, 1370, 1435, 1623, 3280 cm^{-1} .

Polymer P2. A solution of 1 (0.0216 g, 0.17 mmol) and n-BuLi (0.43 mL of 1.6 M in Hex, 0.69 mmol) was allowed to stir in 2 mL of dry THF at -78 °C for 0.5 h. To this solution was added tributyltin iodide (0.19 mL, 0.66 mmol), and the mixture temperature was allowed to reach room temperature while stirring for 2 h. The solution was poured over water and extracted with DCM. The DCM extracts were combined, dried over NaSO₄, and the solvent was removed by rotary evaporation. Proton NMR showed satisfactory conversion to 2, and this material was dissolved with 12 (0.1675 g, 0.17 mmol) in 2 mL of dry toluene. The mixture was subjected to three freeze, pump, and thaw cycles. $Pd(PPh_3)_4~(0.0100$ g, 5 mol %) was added, and the solution was heated at 90 °C. The polymerization progress was monitored by UV-vis spectroscopy. Once the solution absorbance bathochromically shifted to its absorbance maximum, iodobenzene (0.19 mL, 1.7 mmol) was added to the solution, and the reaction proceeded for an additional 2 h. The toluene was concentrated to a minimal volume by rotary evaporation, and the crude material was precipitated with MeOH/2N aqueous HCl (10/1 (v/v)). The solid was purified with a Soxhlet extraction apparatus using methanol, acetone, and DCM in succession. The polymers were collected from the DCM fraction and concentrated to a minimum volume by rotary evaporation. The polymers were precipitated two more times in MeOH/2N aqueous HCl (10/1 (v/v)) to yield a bright red solid (0.1037 g, 0.11 mmol, 64% yield). IR: 724, 767, 793, 839, 930, 1020, 1199, 1226, 1316, 1393, 1395, 1447, 1513, 1578, 1666, 1708, 2206, 2856, 2927, 2960 cm⁻¹. GPC: M_n 18.7, M_w 60.9, PDI 3.3.

Polymer P5. P5 was synthesized using the same procedure and scale as that given for P2, but with 4 and 12 as starting materials. P5 was collected as a red solid (0.1376 g, 0.14 mmol, 82% yield). IR: 693, 725, 776, 836, 931, 1201, 1222, 1316, 1382, 1447, 1514, 1577, 1666, 1709, 2207, 2855, 2925, 2963 cm⁻¹. GPC: M_n 8.2, M_w 23.0, PDI 2.8.

Polymer P8. P8 was synthesized using the same procedure and scale as that given for P2, but with 7 and 12 as starting materials. P8 was collected as a purple solid (0.1619 g, 0.15 mmol, 88% yield). IR: 693, 725, 775, 822, 926, 1062, 1200, 1222, 1314, 1352, 1381, 1451, 1573, 1666, 1709, 2191, 2856, 2926, 2960 cm⁻¹. GPC: M_n 14.9, M_w 58.4, PDI 3.9.

Polymer P11. P11 was synthesized using the same procedure and scale as that given for **P2**, but with **10** and **12** as starting materials. **P11** was collected as a purple solid (0.0698 g, 0.07 mmol, 41% yield). IR: 694, 725, 775, 923, 1212, 1221, 1252, 1312, 1380, 1451, 1575, 1661, 1709, 2179, 2856, 2926, 2961 cm⁻¹. GPC: M_p 3.3, M_w 10.0, PDI 3.0.

RESULTS

Design. DAN, benzene, naphthalene, and anthracene were selected to explore how the physical size and donating properties influence the properties of conjugated NDI–donor polymers. DAN and NDI are known to stack in an alternating fashion^{14a,16a} due to electrostatic complementarity that drives desolvation effects in polar media.²³ Similar self-assembly has also been observed in a 1:1 complex of an anthracene-based



Figure 1. Electrostatic potential maps of the individual monomers (top) and the monomers connected by alkyne linkages (bottom). Models were generated with the same electrostatic potential color scale in Spartan using the DFT B3LYP G-31* method.

host and NDI guest.²⁴ On the contrary, benzene and naphthalene are not expected to stack as well with NDI due to a lesser degree of size and electrostatic complementarity, respectively. Although the differences are small, electrostatic potential maps (Figure 1) show that the area of electron density on the aromatic cores follows the following trend: anthracene > DAN > naphthalene > benzene. The electrostatic potential maps also show that the oxygen atoms on DAN strongly contribute to the increased electron density on the aromatic core when compared to naphthalene which lacks these oxygen atoms. In general, acene-based molecules form polycrystalline assemblies in which the aromatics exhibit some sort of stacked geometry facilitated by the rigid and planar acene structure. Several such derivatives have found use in devices such as OFETs.²⁵ Note the strong local electron density on the DAN oxygen atoms. It is likely that these areas of localized high electron density on the DAN periphery can interact with the relative lack of electron density around the carbon atoms of the NDI carbonyl groups, an interaction that is not possible with the other donors.

Instead of directly connecting together the aromatic cores of NDI and the donors, an alkynyl linkage was selected to serve as

the mode of conjugation in order to alleviate steric hindrance that would otherwise prevent coplanarity of aromatic donor and acceptor units. Thus, we anticipate that all of the aromatic units in the polymers **P2**, **P5**, **P8**, and **P11** (Scheme 1) can adopt a highly conjugated and coplanar conformation. The planar structure is expected to facilitate interchain assembly through some type of stacked arrangement. The minimized structures in Figure 1 indicate that, consistent with our design criteria, the donor moieties should be able to adopt a relatively planar arrangement when connected to two NDI moieties through alkynyl linkages. The alkynyl linkages and subsequent conjugation are expected to result in strong delocalization and diminished electrostatic separation between the donor moieties and NDI, although some level of donor and acceptor properties should remain with the acene and NDI units, respectively.

Synthesis and Characterization. NDI monomer $12^{10b,12}$ (Scheme 1) was prepared from dibrominated 1,4,5,8-naphthalenetetracarboxylic dianhydride^{9b} and 2-octyldodecylamine²⁶ using literature procedures. Synthesis of the donor monomers 2, 5, 8, and 11 is shown in Scheme 2. Dibrominated naphthalene derivative 6 was synthesized by the deprotonation of 2,6-dibromonaphthalene-1,5-diol and its reaction with

Scheme 1. Copolymerization of NDI 12 with Donor Monomers



Scheme 2. General Synthesis of Monomers 2, 5, 8, and 11



methyl iodide. Naphthalene **3** was commercially available, and **9** was prepared by the direct bromination of anthracene according to literature procedures.²⁷

Next, (*tert*-butyldimethylsilyl)acetylene (TBDMSA) moieties were appended onto the aromatic cores of **3**, **6**, and **9** using standard Sonogashira conditions, followed by TBAF deprotection to afford terminal alkynes **4**, **7**, and **10** (Scheme 2). These intermediates, along with commercially available **1**, were subsequently stannylated with tributyltin iodide to yield suitable electron-rich coupling partners (**2**, **5**, **8**, and **11**). Because of its instability,²⁸ **10** was stannylated immediately after deprotection and polymerized before significant decomposition

occurred. To prevent loss of the stannyl groups on the silica column, 2, 5, 8, and 11 were used without purification prior to polymerization.

D–A polymers (P2, P5, P8, and P11) were synthesized through the copolymerization of dibrominated NDI 12 with diethynyl donor monomers 2, 5, 8, and 11 using the Stille protocol²⁹ (Scheme 1). An advantage of this route is that it permits precise control over polymer architecture. An analogous Sonogashira approach was successfully utilized by Guo and Watson to copolymerize substituted diethynyl benzene monomers with pyromellitic diimide (PMDI).³⁰

The polymerization progress was monitored by UV-vis spectroscopy, and reactions were stopped upon reaching the maximum bathochromic shift to provide solubility in common organic solvents such as tetrahydrofuran, methylene chloride, chloroform, and toluene. Excess iodobenzene was added to the reaction mixture to cap the polymers. The reaction proceeded another 2 h before the solvent was removed, and crude polymers were collected by precipitation from methanol. Purification was achieved by successive Soxhlet extractions with methanol, acetone, and methylene chloride. The filtrate collected from the extraction with methylene chloride was then concentrated, and the polymers were isolated following two more precipitations from methanol. Reactions resulted in satisfactory yields with the exception of P11, which was isolated in 41% yield. Even with the short reaction period, a significant amount of insoluble material remained in the Soxhlet thimble. Therefore, the reported yields only represent the readily soluble fraction of each sample.

Number-average (M_n) and weight-average (M_w) molecular weights were determined by gel permeation chromatography (GPC). M_n values that ranged from 3.3 to 18.7 kDa were observed with polydispersity indices (PDI) between 2.8 and 3.9. These values may be overestimated in analogy to previously reported GPC data for other rigid-rod polymers.³¹

The presence of aggregated polymers was supported by ¹H NMR spectroscopy, as resolved spectra of these polymers were unattainable even at 130 °C. Similar characterization problems were encountered with the conjugated PMDI–benzene polymers.³⁰ In light of these NMR characterization complications, infrared spectroscopy (IR) was used to structurally characterize the polymers as shown in Figure 2 for **P2**, **12**, and **1**. The IR spectrum of **12** exhibits strong signals from 2828 to



Figure 2. IR spectrum of 12 (green), 1 (pink), and P2 (black). Red arrows indicate the presence of an internal alkyne signal at 2207 cm⁻¹ and absence of a terminal alkyne signal at 3262 cm⁻¹ for P2.

3000 cm⁻¹ (C–H stretching vibrations of the alkyl chains) and signals at 1656 and 1710 cm⁻¹ (carbonyl stretching vibrations) while the spectrum of 1 shows a signal at 3262 cm⁻¹ (C–H stretching vibrations of the terminal alkyne). The IR spectrum of **P2** maintains both the alkyl C–H and carbonyl stretching signals of 12 and lacks the C–H stretching vibration of a terminal alkyne as seen in 1. The asymmetric, internal alkynes of **P2** result in a new stretching vibration at 2207 cm⁻¹.

Optical and Electrochemical Properties. The absorption spectra for all polymers in chloroform and as a thin film are shown in Figure 3. The polymer absorption maximum (λ_{max})



Figure 3. Normalized absorption spectra in chloroform (top) and as a thin film (bottom) of P2 (black), P5 (red), P8 (purple), and P11 (teal). The inset picture of the polymers dissolved in chloroform shows the bright red color of P2 and P5 and the purple and teal color of P8 and P11, respectively.

and the corresponding optical band gap (E_g^{opt}) energies are listed in Table 1. Absorption maxima in solution were 558, 534, 576, and 678 nm for **P2**, **P5**, **P8**, and **P11**, respectively, and little change from these numbers was observed in the thin film measurements. In the thin films, peak broadening was clearly visible for **P11**, and **P5** appears to develop a shoulder much like the one present in **P2**. The maximum shift (blue or red) observed between the solution and thin film absorption maxima was only 7 nm, suggesting that the polymers adopt a similar structure in both solution and solid state.

The normalized and non-normalized fluorescence spectra of the polymers in chloroform are shown in Figure 4. There was a dramatic decrease in fluorescence in **P8** and **P11**, amounting to approximately a 10-fold and 50-fold decrease of emission intensity in chloroform, respectively, when compared to that of **P2**. Two possible explanations could account for such a dramatic decrease in fluorescence. Since DAN and anthracene can stack with NDI, it is reasonable to assume that at least some



Figure 4. Normalized (top) and non-normalized (bottom) polymer fluorescence spectra in chloroform $(4 \times 10^{-6} \text{ M})$ of P2 (black), P5 (red), P8 (purple), and P11 (teal). Concentration is based on the molecular weight of the polymer repeat unit.

of the dramatic fluorescence decrease seen with P8 and P11 could be due to interchain assembly through intermolecular donor-acceptor interactions. Alternatively, increased intra-molecular charge transfer could be playing a significant role in the fluorescence quenching of P8 and P11.

Electrochemical data were collected by thin film cyclic voltammetry (CV) using a standard three-electrode cell with platinum working, tungsten counter, and silver reference electrodes. No oxidation peaks were observed within the solvent operating window during the anodic sweep, but two clear reduction peaks were observed for each polymer during the cathodic sweep (Table 1), results that are characteristic of n-type materials. Cyclic voltammograms can be found in the Supporting Information.

LUMO energy levels (Table 1) were determined from the $E_{1/2}$ values of the first reduction potentials. As previously reported, ^{10a} the $E_{1/2}$ from the first reduction potentials are around -1.0 V and resemble that of the parent NDI monomer⁸ (see Supporting Information). LUMO levels are relatively consistent among the four polymers with values between -3.73and -3.79 eV, reflecting the dominant NDI contribution to the overall polymer LUMO energy level. A likely explanation is that the LUMO is predominately localized on the NDI units, even in the conjugated systems. The HOMO energy levels were estimated from the calculated LUMO energies and the E_{σ}^{opt} . As expected, the HOMO energies exhibited a strong dependence on the donor monomer used. P2 and P5, possessing comparable visible absorbance onsets, have calculated HOMO levels of -5.68 and -5.65 eV, respectively. The acene units, which were expected to be stronger donor monomers, exhibited an increase of the HOMO level; the

Table 1. A Summary of Optical and Electrochemical Properties

	soln abs λ_{\max} (nm)	film abs λ_{\max} (nm)	soln flu λ_{\max} (nm)	$E_{\rm g}^{\rm opt}$ (eV)	$E_{1/2}$ red1 ^{<i>a</i>} (V)	$E_{1/2} \operatorname{red2}^{a} (V)$	$LUMO^{b}$ (eV)	$HOMO^{c}$ (eV)
P2	558	561	646	1.89	-1.01	-1.31	-3.79	-5.68
P5	534	527	579	1.90	-1.05	-1.34	-3.75	-5.65
P8	576	583	677	1.82	-1.06	-1.42	-3.74	-5.56
P11	678	673	791	1.44	-1.07	-1.31	-3.73	-5.17

^{*a*}Values were estimated using the vacuum ferrocene reference value of -4.8 eV at 0.0 V. ^{*b*}LUMO = $-(E_{1/2} \text{ red1} + 4.8) \text{ eV}$. ^{*c*}HOMO = LUMO - E_g^{opt} .

DAN-containing **P8** exhibited a HOMO of -5.56 eV, a 0.09 eV increase over the HOMO of **P5**. Incorporation of anthracene resulted in the highest HOMO energy level, as **P11** exhibited a HOMO energy of -5.17 eV.

Using the maximum thin film absorption edge for each polymer, the E_g^{opt} values for **P2**, **P5**, and **P8** were calculated to be 1.89, 1.90, and 1.82 eV, respectively. The additional electron donation from the oxygen atoms on the naphthalene rings in **P8** resulted in a minimum band gap change (0.08 eV) when compared to **P5**, which lacks oxygen atoms on the naphthalene rings. Replacing naphthalene with anthracene, however, resulted in a significant lowering of the band gap; **P11** exhibited the lowest band gap of 1.44 eV.

Structural and Organization Properties. The aggregation properties of the different polymers were investigated to probe the nature of interchain interactions. In particular, the dramatic loss of fluorescence seen with P8 and P11 could in part be the result of aromatic D–A stacking interactions between chains. Unfortunately, the strong absorbance associated with intramolecular charge transfer deterred detection of possible intermolecular donor–acceptor interactions with UV–vis spectroscopy. Serial dilution fluorescence was instead conducted to investigate the interchain stacking behavior of the polymers (Figure 5). Although each polymer



Figure 5. Normalized serial dilution fluorescence pattern of P2 (black), P5 (red), P8 (purple), and P11 (teal) in chloroform. Concentration is based on the molecular weight of the polymer repeat unit. The solutions were 2-fold diluted in serial fashion, and each point represents the maximum fluorescence at that particular concentration.

exhibited different fluorescence intensities (Figure 4), their serial dilution plots are presented as a normalized series to compare the overall fluorescence behavior of the polymers at various concentrations.

All of the polymers exhibited a similar dramatic decrease in fluorescence at high concentrations in chloroform. The fluorescence intensity for each polymer increased with decreasing concentration, and a maximum signal was attained in the range of $125-62 \ \mu$ M before the fluorescence intensity again decreased with decreasing concentration.

XRD and Modeling. Bulk polymers collected from methanol precipitation (slow evaporation from dichloromethane to form a film gave analogous results) were analyzed by X-ray diffraction (XRD) to determine the actual stacking mode of the polymer chains. Four peaks were consistent in all of the XRD patterns (Figure 6). These peaks corresponded to *d*-spacings of 23, 12–13, 4.6, and 3.5 Å. In addition, the variation among peak intensities at $2\theta \approx 3.8^{\circ}$ indicates that P8 and P11 possess a higher relative crystallinity than P2 and P5.

The *d*-spacing of 23 Å is representative of a lamellar structure with interdigitated side chains^{11b} as this distance is shorter than the extended length of the NDI moiety (\sim 35 Å). A scale model of P2 and the proposed packing mode (representative of P5, P8, and P11 as well) is shown in Figure 7. The viewpoint of a single layer (Figure 7B) along the Y-X axis shows the 23 Å distance between two parallel polymer chains. The distance of 3.5 Å matches the characteristic distance between stacked aromatic units seen in numerous XRD studies of NDI-based or other aromatic systems.^{19a-c} The polymer chains were then separated by a distance of 3.5 Å along the Z-axis (Figure 7C) in the scale model. Importantly, the observed *d*-spacing of 4.6 Å closely resembles the reported centroid-to-centroid distance between adjacent NDI moieties stacked in an offset face-to-face fashion,^{19d} and the polymer chains were adjusted as such in the model. It was then possible to draw parallel planes along the Yaxis that matched the 4.6 Å *d*-spacing (Figure 7C). In addition, another set of parallel planes could be drawn along the Y-axis that have a distance of ~12.5 Å (Figure 7D) which resembles the *d*-spacing of 13.3 Å. The difference may be due to the error associated with a broad XRD peak. It also seems plausible that the distance (12.5 Å) between these particular parallel planes would be sensitive to the donor size and could explain the small difference among the polymers at $2\theta \approx 7^{\circ}$ (11.7, 12.2, 13.3, and 13.5 Å).

For the sake of completeness, two other models were generated: one that set the centroid-to-centroid distance between NDI and benzene at 4.6 Å and another one that assumed a complete alternating donor-acceptor assembly along the Z-axis. Neither of these models accounted for all of the XRD peaks (see Supporting Information).

DISCUSSION

Four new conjugated aromatic D-A polymers incorporating NDI as the acceptor moiety were synthesized and characterized. A Stille coupling reaction between diethynyl aryl monomers and dibromo NDI yielded high molecular weight polymers that were readily soluble in organic solvents. As with previously reported conjugated NDI polymers, the NDI-aryl polymers reported herein also exhibited interesting electrochemical properties. LUMO levels remained around -3.75 eV for all polymers examined, a higher value than that of the commonly used PV acceptor PCBM (-4.3 eV), while the HOMO levels were sensitive to the aromatic donor groups and resembled those of commonly employed thiophene or fluorene-based monomers (HOMO approximately -5.8 to -4.8 eV). Most notably, polymer P11 possesses one of the smallest conjugated NDI-donor polymer band gaps to date as well as HOMO/LUMO levels that may be suitable for use in PV devices.³²

All of the polymers experienced a dramatically quenched fluorescence at high concentrations which is characteristic of an aggregated material. In addition, polymers **P8** and **P11** displayed dramatically quenched fluorescence at all concen-



Figure 6. XRD patterns of P2 (black), P5 (red), P8 (purple), and P11 (teal). Peaks are labeled with their corresponding *d*-spacing value, and the inset plots represent an enlarged portion of the pattern.



Figure 7. Scale representation (A) of P2 and the proposed stacking (B-D) to account for the *d*-spacing values obtained by XRD. NDI = blue and benzene = red. Side chains were removed for clarity (C, D) and marked by a black dot on the blue NDI.

trations examined compared to P2 and P5. NDI is known to quench fluorescence when stacked with a fluorophore.^{33,19c} A noticeable difference was expected in the fluorescence behavior of P2, P5, P8, and P11 during the dilution experiments if interchain assembly was driven by intermolecular D–A interactions because these units, representing a range of different sizes and donor capabilities, are expected to display different levels of interaction with NDI. In contrast to this expectation, the strong similarity among the concentration dependencies of the fluorescence patterns in Figure 5 can most easily be interpreted to indicate that all four polymers aggregate in a similar fashion. In other words, aggregation is apparently not dependent on the nature of the donor monomer, ruling out D–A interactions as the primary driving force for aggregation. A reasonable explanation is that interchain aggregation and, by inference, the concentration-dependent fluorescence quenching, is the result of interactions between the NDI units common to all the polymers. To the extent that this is true, the diminished fluorescence of **P8** and **P11** is most likely the result of intramolecular charge transfer and not interchain aromatic D-A interactions.

The XRD data were strikingly similar among all four polymers and combined with models to further refine the mode of interchain aggregation. The only model that was able to explain the observed XRD data for all of the polymers contained interdigitated side chains with the NDI moieties stacked in an offset face-to-face fashion (Figure 7). Although DAN and anthracene are known to form aromatic D-Ainteractions with NDI, none of the aromatic donor units investigated in this study were able to interrupt NDI self-

Article

stacking in these conjugated polymer chains. NDI is wellknown to have a propensity for self-association in an offset facecentered stacking mode, presumably because such a stacking geometry provides for maximum complementary electrostatic interactions between the carbon and oxygen atoms of the highly polarized NDI carbonyl groups on adjacent NDI units. Taken together, our results are therefore consistent with more recent discussions of aromatic stacking dominated by interactions between highly polarized groups on the periphery of aromatic units rather than overall polarization of the aromatic ring itself (i.e., D–A interactions). Interestingly, the XRD patterns additionally suggest that **P8** and **P11** have a higher degree of crystallinity than **P2** or **P5**, possibly the result of larger acene donor moieties.

It is worth pointing out that the branched side chains, which are necessary to solubilize the polymers, might also drive the observed polymer assembly geometry as evidenced by an interdigitated side chain arrangement. We have previously shown that side chains can have a great impact on the solid-state packing of donor-acceptor assemblies,^{16b} and this influence should not be ruled out.

CONCLUSION

The electronic properties of conjugated D–A polymers containing NDI have been thoroughly investigated over the past few years. A common feature of these systems is the ability to tune the HOMO/LUMO energy levels, making these polymers popular candidates for electronic materials investigations. However, a thorough understanding of the polymer chain organization is necessary to take these systems past the investigation level and on to application. The ideal material will exhibit both suitable electronic properties and predictable self-assembly into well-organized architectures. The results reported here have shed considerable light on the interchain stacking behavior of a set of NDI D–A polymer systems and have brought into sharp focus the apparent dominance of NDI–NDI interactions. We are currently developing next-generation polymers based on these findings.

ASSOCIATED CONTENT

S Supporting Information

NMR spectra, IR spectra, cyclic voltammograms, GPC traces, and additional models. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Robert A. Welch Foundation, grant F1188 to B.L.I. We thank Eric Anslyn and his group for use of their fluorometer. We also thank Steve Swinnea for collecting the XRD patterns.

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