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Journal

ACS Omega, 4(5)

ISSN

2470-1343

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Publication Date

2019-05-31

DOI

10.1021/acsomega.9b01125

Peer reviewed

Synthesis and Optoelectronic Properties of New Methoxy-Substituted Diketopyrrolopyrrole Polymers

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S Supporting Information

ABSTRACT: The introduction of functional groups with varying electron-donating/-withdrawing properties at the β-position of diketopyrrolopyrrole (DPP) has been shown to affect the optoelectronic properties of the polymers. We report the synthesis of a new diketopyrrolopyrrole monomer wherein a strong electron-donating substituent, a methoxy group, was incorporated at the β-position in an effort to modulate polymer properties. Homopolymers and co-polymers of the new β-methoxy DPP and nonderivatized DPP were synthesized, and their properties were measured by cyclic voltammetry and UV−vis−near-infrared. Density functional theory computations also were employed to predict the degree of planarity of β-methoxy oligomers to probe the significance of the newly introduced S−O conformational lock. The combined experimental and computational results showed a reduction in the gap between highest occupied molecular orbital/lowest unoccupied molecular orbital levels, a redshift toward the near-infrared region, and an increased planarity in the β-methoxy polymers.
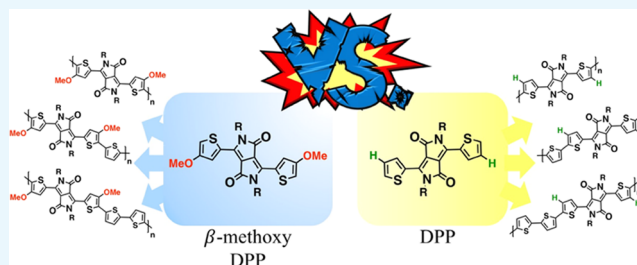
INTRODUCTION

π-Conjugated polymers are widely considered to be low-cost, next generation semiconducting materials because of their excellent optoelectronic properties and their potential application in inexpensive solution processing methods.[1−5] In addition, they have attracted considerable attention as high-performance materials, when compared to silicon-based alternatives, due to examples of charge carrier mobilities in polymer systems of 12 cm²/(V s) in organic field effect transistors devices and power conversion efficiencies in excess of 14%.[6−8] In addition, these materials have found extended application in the biomedical and optical fields as near-infrared (NIR) probes for photoacoustic imaging, photothermal/photodynamic therapy, and organic light-emitting diodes as a result of their unique tunability and photophysical nature.[9−13]

Of these π-conjugated polymers, those that are based on a diketopyrrolopyrrole (DPP) core have garnered considerable attention for the ability with which derivatization allows for the desirable tuning of optoelectronic properties and its ease of combination with a number of donors in donor−acceptor (D−A) based systems.[14−18] Although many DPP derivatives have been synthesized with aryl and heteroaryl groups flanking the DPP core, thiophenes continue to provide an advantage due to their reduced steric component and favorable electronics when compared to larger aryl/heteroaryl groups in solid-state morphology. Thiophenes, thereby, allow for planar configurations with longer effective conjugation and smaller π−π-stacking distances to effectively modulate the electrochemical and optical band-gaps (E_g) of polymers.[17−20] Other strategies include the incorporation of various solubilizing side-chains,[21−23] the modification of polymer backbones,[24,25] favorable D−A co-monomer matching,[18] and donor unit modification.[15] Only recently has the derivatization of the 4-position of the flanking thiophenes of the DPP unit with functional groups of varying electron densities taken hold as an avenue for exploration in polymer systems.[26−31] Of the derivatives synthesized, most involve a σ/π-withdrawing group, including −F, −Cl, −CN, whereas the only other derivative imparts a slightly donating −Me. All of these showed optical and electrochemical E_g changes attributed to the newly imparted functional group.

A DPP-2T with a stronger electron-donating group, such as a methoxy moiety, has yet to be reported, though evidence suggests that such an analogue could carry many distinct advantages, including significantly modulated optoelectronic effects that are completely different from those imparted by electron-withdrawing group introduction in traditionally "weak donor−strong acceptor" materials.[32] Adding this relatively small electron-donating group could allow for enhancement of planarity in polymer systems by providing a foothold for a sulfur−oxygen conformational lock that can appreciably shrink the dihedral angles between repeating units and further affect optoelectronic properties.[33]

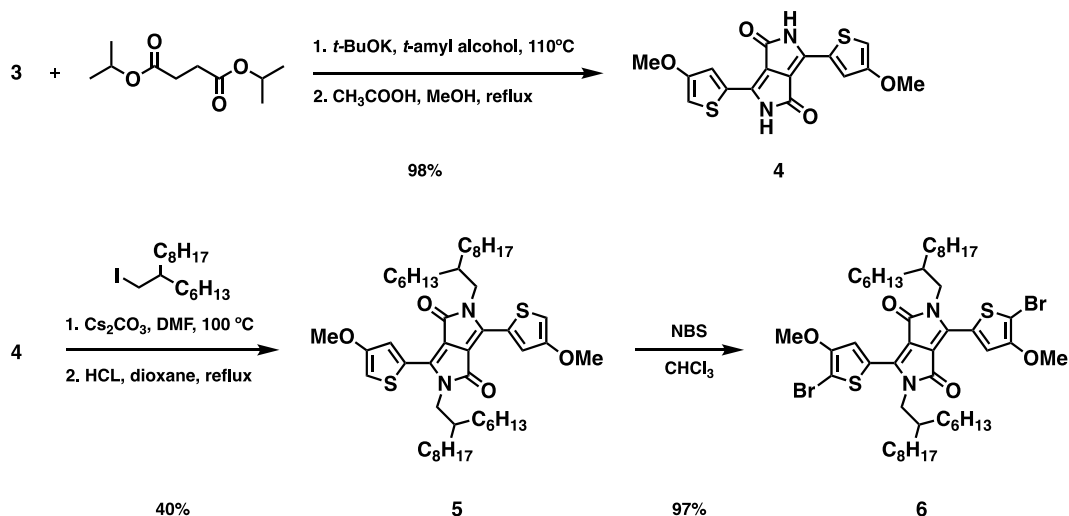**Scheme 1. Synthesis of 4-Methoxythiophene-2-carbonitrile**
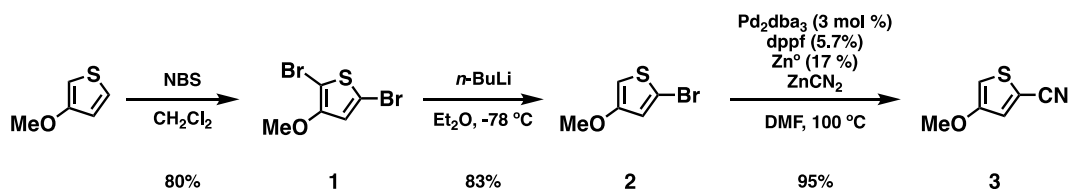
Scheme 2. Synthesis of DPP-2T-OMe

Herein, we report the synthesis of a new methoxy-substituted DPP core (DPP-2T-OMe) and its introduction into thiophene-containing polymer systems. With this new set of methoxylated DPP polymers, we systematically studied the effects of the methoxy functionality on the optical and electrochemical E_g and compared these values to those observed in nonmethoxylated polymer counterparts.

■ RESULTS AND DISCUSSION

Synthesis of Monomer. To make DPP-2T-OMe polymers, 4-methoxythiophene-2-carbonitrile would have to be synthesized prior to DPP formation. Multiple possible routes to derivatize thiophenes were analyzed to assess their applicability to our synthesis.[34,35] An example was the synthesis of 4-fluorothiophene-2-carbonitrile, wherein the fluorine was installed selectively from 2,3-dibromothiophene, whereas the nitrile was installed through an oxime dehydration.[26,27] Another example utilized a methyl group installed on the β-position of DPP-2T prior to subsequent condensation and alkylation.[28−30] Thus, the synthesis of the β-methoxy monomer **6** would be accomplished through a similar derivatization of a thiophene subunit, starting from 3-methoxythiophene (Schemes 1 and 2).

Based on the literature precedent, commercially available 3-methoxythiophene was brominated to form **1** and subsequently reduced using butyllithium to form 2-bromo-4-methoxythiophene (**2**) in good yield.[36] From **2**, a direct transformation from bromine to nitrile via the Rosenmund–von Braun reaction was attempted by treating **2** with copper(II) cyanide in dimethylformamide at elevated temperatures,[37−39] which yielded no product. Consequently, a palladium(II)-catalyzed Negishi-style cyanation was explored using zinc(II) cyanide.[40] After optimization of temperature and

solvent, the reaction provided excellent yields and proved to be a synthetically viable route to **3**.

The subsequent steps of DPP formation were performed according to established literature procedures[41] to give DPP-2T-OMe in similar yields to the analogous nonmethoxylated DPP synthesis (Scheme 2). The condensation reaction of **3** with diisopropyl succinate yielded **4**. The DPP monomer **4** was subjected to N-alkylation with 2-hexyl-1-decyl iodide to yield **5**. Finally, **5** was brominated with N-bromosuccinimide to yield the target monomer **6**.

Synthesis of Polymers. Homopolymers (P1, P2; Scheme 3) were synthesized according to a modified literature procedure initially used by Singh[42] for PDPP2T after Stille and Suzuki reactions failed to provide the expected homopolymer. The target polymers were prepared by combining dibrominated **6** and a Ni(0) catalyst in anhydrous tetrahydrofuran. The resulting product was purified by precipitation in methanol followed by the Soxhlet extraction to remove catalytic impurities and low-molecular-weight oligomers to provide both polymers in excess of 65% yield.

Polymers incorporating thiophene donors of different lengths were prepared in high yield through Stille polymerization, which utilized the brominated DPP (**6, 6a**) in combination with the stannylated donor comonomers (M1, M2) in the presence of a Pd$_2$dba$_3$/P(o-tol)$_3$ catalytic system. The resulting mixture was then heated in a nonpolar solvent system, end capped, and extracted via Soxhlet extractions. The chloroform fraction was concentrated to give the product. The DPP polymers (P3, P5) and their methoxylated derivatives (P4, P6) were obtained in good yield as dark green/blue solids. All polymers exhibited solubility in chloroform, although the methoxy analogues were significantly more soluble in chloroform at room temperature than the non-methoxylated polymers, which proved only to be soluble in
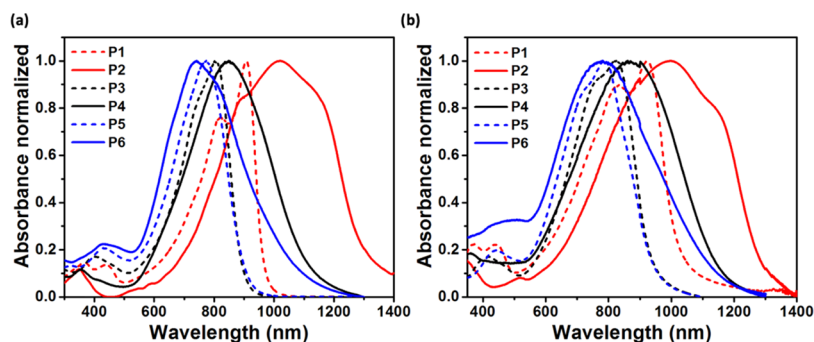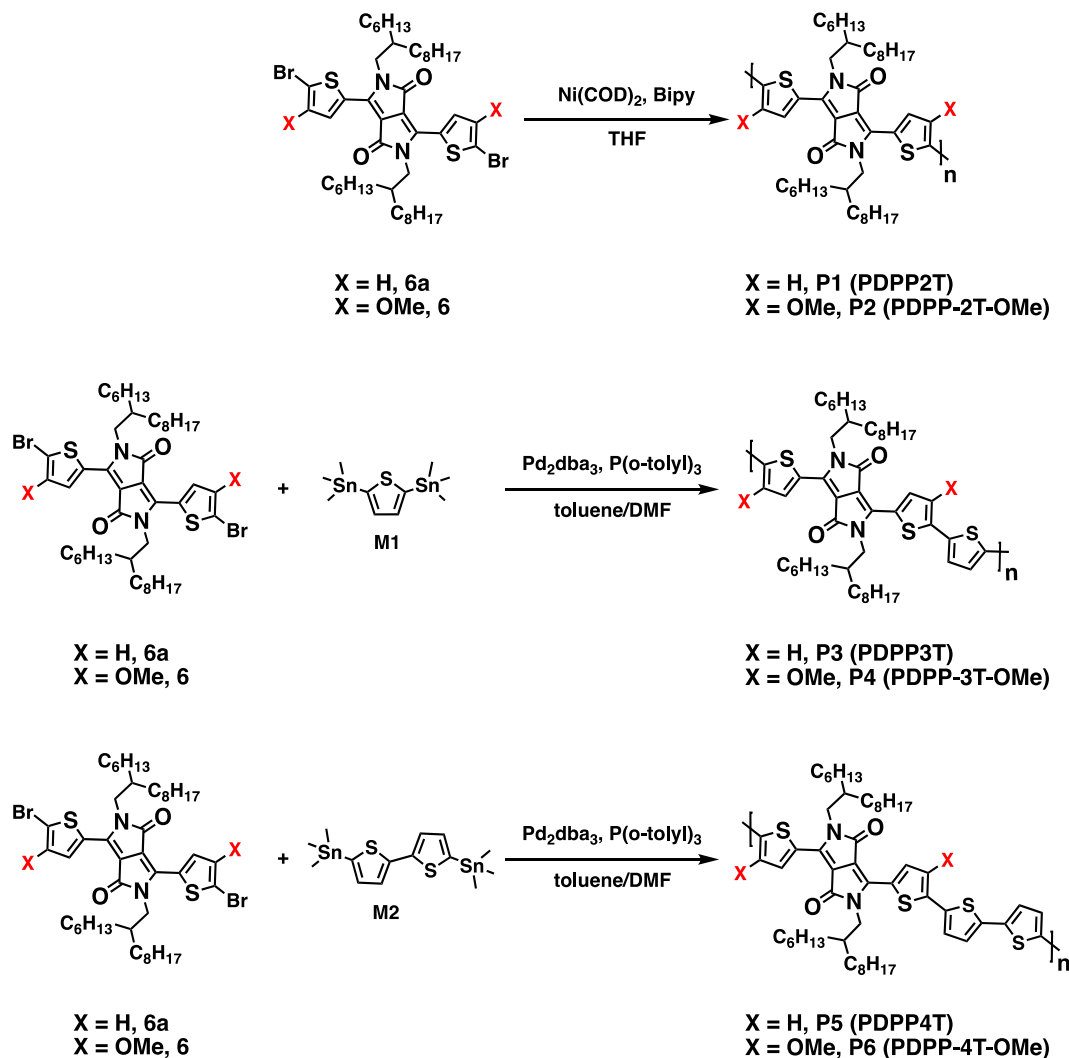
Scheme 3. Polymerizations of P1−P6

X = H, 6a
X = OMe, 6

X = H, P1 (PDPP2T)
X = OMe, P2 (PDPP-2T-OMe)

X = H, 6a
X = OMe, 6

X = H, P3 (PDPP3T)
X = OMe, P4 (PDPP-3T-OMe)

X = H, 6a
X = OMe, 6

X = H, P5 (PDPP4T)
X = OMe, P6 (PDPP-4T-OMe)

Figure 1. UV−vis−NIR absorption spectra of polymers in dilute CHCl$_3$ solution (a) and thin film (b).

chloroform at elevated temperatures. This solubility difference may be attributed to less $\pi-\pi$-stacking due to the added degree of rotation and steric influence from the bulk of the methoxy group, which also affected the resulting number molecular weight (M_n) and polydispersity index of each polymer (as calculated by gel permeation chromatography (GPC)) utilizing chloroform at 50 °C as the eluent (see Supporting Information (SI)).

Optical and Electrochemical Properties. The optical and electrochemical properties of all polymers were inves-

tigated by UV−vis−NIR absorption spectroscopy (Figure 1) and cyclic voltammetry (CV, Figure 2). The UV−vis−NIR absorption spectra of all polymers were measured in both dilute chloroform solution and thin films.

When the spectra for the nonmethoxylated **P1**, **P3**, and **P5** to the methoxylated **P2**, **P4**, and **P6** were compared, significant variances due to the introduction of the methoxy substituents were apparent. As expected in solution, **P1**, **P3**, and **P5** showed similar absorption spectra compared to literature standards. Bathochromic shifts were observed at maximum absorption,
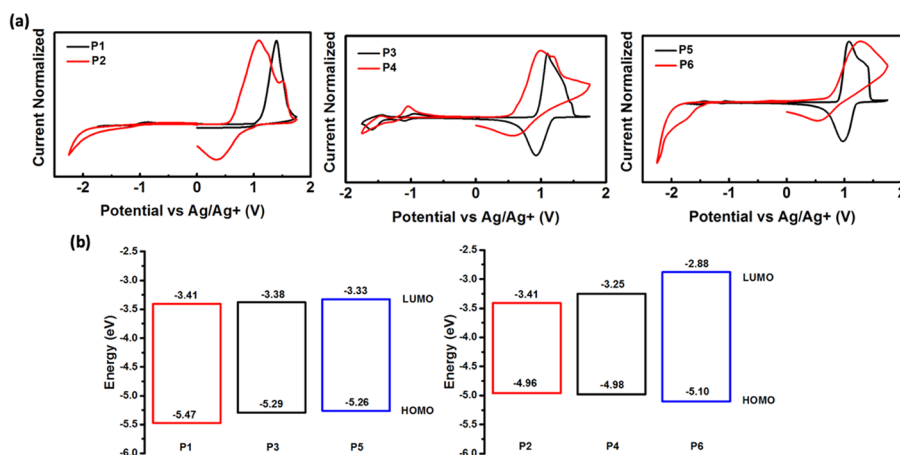
Figure 2. (a) Cyclic voltammetry curves of **P1**−**P6** films drop-cast on a platinum electrode. (b) Corresponding highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) levels of **P1**, **P3**, **P5** and **P2**, **P4**, **P6**.

most likely arising from the combination of the increased electron deficiency and the decreased number of thiophene units in the repeating polymer structure. A similar trend is visible with **P2**, **P4**, and **P6**. The maximum absorption was observed to have decreased with increasing numbers of thiophenes. However, the range for **P2**, **P4**, and **P6** occurred over roughly 280 nm as opposed to 134 nm for **P1**, **P3**, and **P5**. In thin film, this same trend was observed with the exception of **P2**, wherein the maximum absorption was blue shifted. When comparing the solution to thin film spectra, **P1**, **P3**, and **P5** showed enhanced vibrational peaks, whereas **P2**, **P4**, and **P6** showed slightly diminished vibrational peaks in thin films. Diminished peaks could indicate that the steric environment of the methoxy group had a large influence on solid-state packing.

When investigating the optical energy, E_g, similar trends between methoxylated and nonmethoxylated polymers were observed. In both cases, **P1** and **P2** showed a much higher absorption onset than their thiophene or bithiophene containing analogues **P3**, **P4** and **P5**, **P6**. This observation may result from torsional constraints related to the incorporation of more thiophene units in the polymer backbone. These methoxylated polymers showed a significantly smaller bandgap than their counterparts.

All polymers were investigated by CV to gain information on the energies of the HOMO and LUMO. Figure 2 depicts the overlaid CV spectra, wherein the methoxy polymer derivatives were observed to have a heavy shift in the onset of oxidation. **P2** and **P4** showed this onset after 0.5 V and **P6** following not far behind. They each showed very limited reduction peaks compared to their overwhelming oxidation peaks. **P2**, **P4**, and **P6** show a lag in the re-reduction peak when compared to the easily reversible oxidation of **P1**, **P3**, and **P5**. Polymers with these properties are expected to be primarily p-type (hole transporting), due to their electron-rich nature.

In the case of **P1** and **P2**, a significant difference between HOMO levels was present, with the energy of the **P2** HOMO being ∼0.5 eV higher than that of **P1**. LUMO levels remained constant, indicating that the electron modulating groups of derivatized DPP homopolymers can have a large effect on their electrochemistry. The HOMO level is altered because donor thiophenes are different electronically, whereas the LUMO remains constant, because it is localized to the DPP core. Smaller differences are observed for **P3** and **P4**. However, with

P5 and **P6**, a drastic difference in LUMO energies is observed. The LUMO level of **P6** is observed to be ∼0.5 eV higher in energy than that of **P5**, though their HOMO energies differ by only 0.16 eV. In this case, the donor bithiophene remains consistent between polymers, explaining the consistent HOMO, whereas the LUMO is highly elevated suggesting the localization to the entire DPP-2T-OMe monomer. Of note, **P6** shows similar electrochemical properties to the popular poly(3-hexylthiophene) (P3HT) polymer.[43] In addition, the E_g significantly increases (Table 1) with the addition of thiophene

Table 1. Optical and Electrochemical Properties of Polymers

polymer	λ_{max} (nm)		E_g^{opt} (eV)[a]	E_g^{CV} (eV)[b]	E_{HOMO}^{CV} (eV)[c]	E_{LUMO}^{CV} (eV)[d]
	solution	film				
P1	907	920	1.20	2.06	−5.47	−3.41
P2	1019	998	0.96	1.55	−4.96	−3.41
P3	801	824	1.32	1.91	−5.29	−3.38
P4	848	870	1.11	1.73	−4.98	−3.25
P5	773	786	1.29	1.93	−5.26	−3.33
P6	741	780	1.08	2.22	−5.10	−2.88

[a]Optical E_g estimated from the onset of film absorption. [b]Energy E_g calculation ($E_{HOMO}^{CV} - E_{LUMO}^{CV}$). [c]Electrochemically determined vs Fc/Fc$^+$, $E_{HOMO}^{CV} = -(E_{ox}^{onset} - E_{Fc/Fc^+}^{onset} + 4.8)$. [d]Electrochemically determined vs Fc/Fc$^+$, $E_{LUMO}^{CV} = (E_{ox}^{onset} - E_{red}^{onset} + E_{HOMO}^{CV})$.

units; a trend that is supported by the results of density functional theory (DFT) computations. Selected molecular orbitals are shown in Figure 3, and additional details are provided in the SI. In nonmethoxylated polymers, both HOMO/LUMO levels increase with the addition of thiophenes, and the bandgap remains relatively consistent.

Theoretical Calculations. Density functional theory (DFT) computations were carried out on monomers and oligomers to obtain structural and energetic parameters for comparison with experimental data (see SI for details). As done previously for closely related polymers, the B97X-D/6-31G(d,p) level of theory was used.[44]

First, relaxed scans for rotation around the central bond of bis-thiophenes were examined (Figure 4, top). These scans indicated that mono- and di-methoxy systems prefer conformations in which the thiophene rings are coplanar and
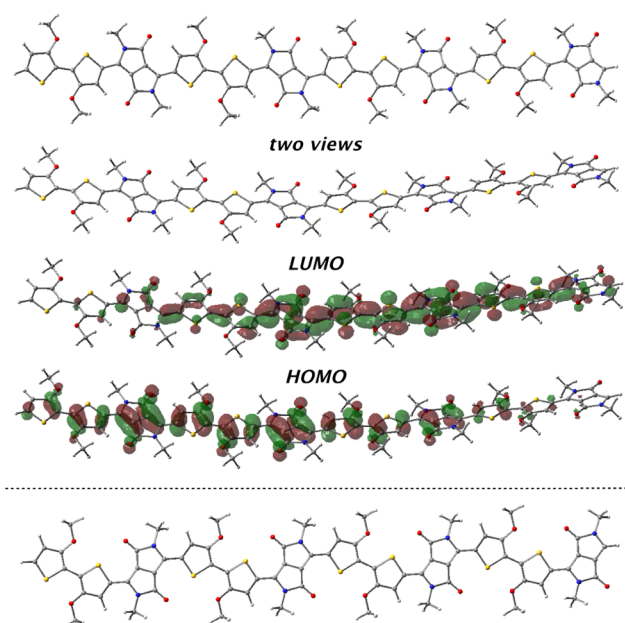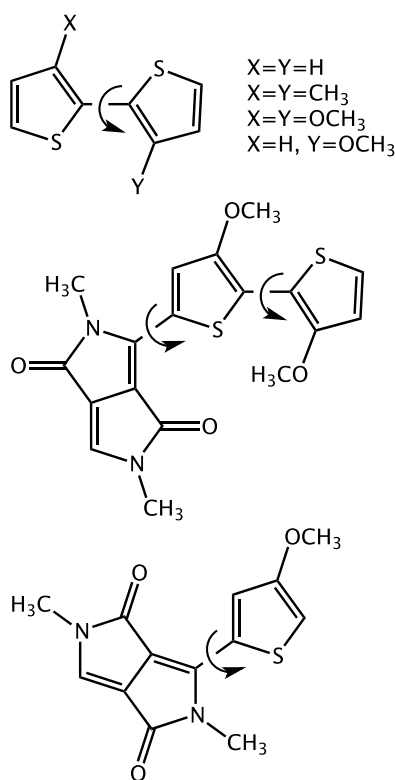
Figure 3. Oligomer structures.

Figure 4. Structures for which torsional profiles were computed (see SI for details).

the S−C−C−S dihedral angle is 180°, whereas systems with −H or −CH$_3$ groups prefer nonplanar conformations. In the coplanar conformation, the oxygen of each methoxy group is near to the sulfur of the thiophene ring to which it is not directly attached. Relaxed scans for structures bearing diketopyrrolopyrrole groups were then carried out (Figure 4, middle and bottom). Scanning rotation around the thiophene−thiophene bond in the middle structure again demonstrated a preference (here ~4 kcal/mol) for the

coplanar structure. Scanning rotation around the C−C bond connecting the diketopyrrolopyrrole group to a thiophene, for either the middle or bottom structures in Figure 4, demonstrated a preference (again ~4 kcal/mol) for not having a close contact between sulfur and the ketone oxygen. In short, the methoxy groups prefer to be near sulfur, but the keto groups do not.

Structures of oligomers were also computed. These supported the conclusions about conformational preferences discussed above. Figure 3 shows two conformations of a P2 model containing four diketopyrrolopyrrole groups and four bis-methoxythiophene groups. The top conformation is favored over the bottom conformation by ~23 kcal/mol in free energy (~29 kcal/mol in electronic energy, i.e., ~4 kcal/mol per carbonyl-thiophene contact). The preferred conformation has a slight overall twist, but the O−C−C−O dihedral angles are all 178−180°.

■ CONCLUSIONS

We have successfully introduced methoxy groups onto the thiophene groups of DPP by creating a derivatized 4-methoxythiophene-2-carbonitrile precursor. A series of homo- and co-polymers using the new methoxylated DPP acceptor unit were then synthesized to investigate the effects of the new electron-rich β-functionality on material characteristics. DFT calculations showed that this motif created a nearly planar confirmation between adjacent thiophenes, consistent with favorable S−O interactions. Using optical and electrochemical analysis, methoxy- and nonmethoxy-substituted polymers were directly compared to reveal that the new methoxy DPP unit markedly reduced or enlarged the E_g by varying the number of accompanying thiophene units. Our studies emphasize, for the first time, the tuning effects of strongly electron-donating groups on DPP-based polymers in comparison to the previously described fluoro-, cyano-, chloro-, and methyl-substituted counterparts. According to the absorption and electrochemical characteristics, the newly synthesized methoxy-substituted polymers may be viable candidates for a number of functional applications including p-type semiconductors and photoacoustic probes.

■ EXPERIMENTAL SECTION

The electrochemical properties of the co-polymers were investigated as thin films in deoxygenated anhydrous acetonitrile under nitrogen using 0.1 M tetrakis(n-butyl)-ammonium hexafluorophosphate $[(n\text{-Bu})_4\text{N} + \text{PF}_6^-]$ as the supporting electrolyte. Pt electrodes were used as both the working and counter electrodes and with Ag/Ag$^+$ (sat. NaCl) as the pseudoreference electrode. Co-polymer films were generally drop-cast onto the Pt working electrode from a 5 mg/mL of CHCl$_3$ solution. Monomers and building blocks were characterized by ^{1}H NMR and ^{13}C NMR, and polymers were characterized by high-temperature ^{1}H NMR. Full details and synthetic procedures are provided in the Supporting Information.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsome-ga.9b01125.

Experimental procedures; small molecule and polymer characterization (^{1}H,^{13}C NMR, GPC, VT-NMR); details on computational results (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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