ORGANIC
LETTERS

2010
Vol. 12, No. 18
4054−4057

N-Acyldithieno[3,2-*b*:2′,3′-*d*]pyrroles: Second Generation Dithieno[3,2-*b*:2′,3′-*d*]pyrrole Building Blocks with Stabilized Energy Levels

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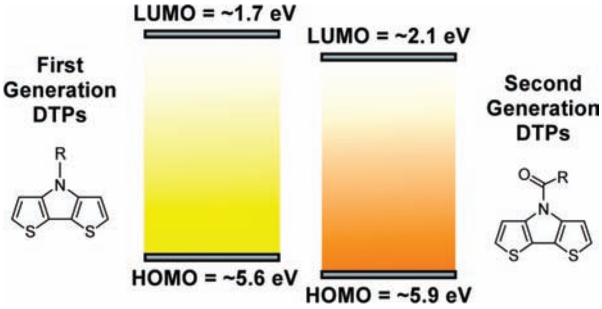
Received July 15, 2010

ABSTRACT



A new class of dithieno[3,2-*b*:2′,3′-*d*]pyrroles (DTPs) incorporating *N*-acyl groups have been prepared from 3-bromothiophene via copper-catalyzed amidation. The utilization of various electron-withdrawing acyl groups has allowed stabilization of the HOMO and LUMO energy levels of these popular building blocks for conjugated materials. The synthesis and characterization of this new class of compounds is described, including electrochemical and photophysical data for all compounds and X-ray structural data for the octanoyl, benzoyl, and cyclohexanoyl functionalized compounds. Initial polymers generated via electropolymerization are also reported.

Conjugated organic materials have received considerable fundamental and technological interest due to their combination of the electronic and optical properties of inorganic semiconductors with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs.[1,2] In addition, one of the key advantages of these materials is the ability to tune the electronic and optical properties at the molecular level via synthetic modification. One approach to such synthetic modification is the introduction of fused aromatic units into the conjugated backbone, resulting in materials exhibiting enhanced carrier mobilities and lowered band gaps. Such fused-ring building blocks that have found recent popularity are the *N*-alkyl- and *N*-aryl-dithieno[3,2-*b*:2′,3′-*d*]pyrroles (DTPs).[3] Since their introduction, these building blocks have been incorporated into various polymeric,[4−14] oligomeric,[15−17] and molecular materials[18−20] to give high carrier mobilities, enhanced

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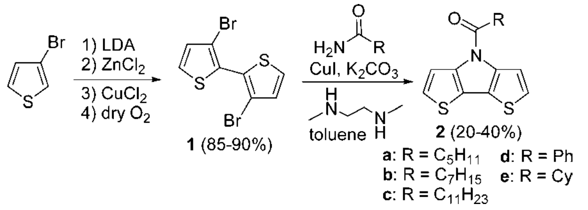
10.1021/ol101647f

solution and solid-state fluorescence, and materials with reduced and low band gaps. As a result, these materials have been applied to organic light-emitting diodes (OLEDs),[9] organic photovoltaic cells (OPVs),[10−14] electrochromics,[13] and field effect transistors (FETs).[7,8,11,13] One limitation of the current DTP building blocks, however, is the high energy of the HOMO, which limits stability and the effective application of DTP-based materials to various devices. As a solution to this limitation, we report herein the successful synthesis of a new class of DTPs that incorporate *N*-acyl groups to significantly stabilize the HOMO and LUMO energy levels.

The new family of *N*-acylDTPs (**2a**−**e**) was prepared via copper-catalyzed amidation[21] of 3,3′-dibromo-2,2′-bithiophene (**1**) as shown in Scheme 1. After our initial introduction of the preparation of DTPs via Pd-catalyzed amination of 3-bromothiophene,[3] other groups reported variant routes utilizing **1** as an intermediate.[22] As **1** is commonly produced in moderate yield (60−75%) via the lithiation and oxidative Cu-coupling of 2,3-dibromothiophene,[23] its use increases the material cost of the resulting DTPs. Thus, to improve the utility of **1**, new synthetic methods for its production were desirable. By utilizing LDA, rather than BuLi, selective deprotonation of the more cost-effective 3-bromothiophene can be used to generate the lithiated intermediate. Transmetalation to the copper species is then facilitated by first reacting with $ZnCl_2$, followed by $CuCl_2$.[24] Oxidative coupling of the copper intermediate is assisted with the addition of dry O_2 to produce **1** in high yield (85−90%) via this one-pot method. It should be acknowledged that during the preparation of this manuscript, a related synthesis of **1** from 3-bromothiophene and LDA was reported.[9] However, without the additional modifications to the oxidative coupling steps, yields were still limited to 73%.

Scheme 1. Synthesis of *N*-Acyldithieno[3,2-*b*:2′,3′-*d*]pyrroles



With good access to **1**, the production of *N*-acylDTPs was then investigated utilizing Cu-catalyzed tandem C−N bond formation methods developed by Buchwald.[21b] These methods had previously been successful in the production of the isomeric dithieno[2,3-*b*:3′,2′-*d*]pyrrole and thus looked promising for the production of DTPs. The initial application of the previously reported conditions successfully produced the desired DTP **2b** but only in 19% yield. While a variety of reaction conditions were investigated (Supporting Information, Table S1), the only condition that enhanced product yield was the increase of catalyst loading to 10 mol %, resulting in isolated yields of ca. 40%. Further increases in the amount of catalyst did not improve product yields, and at this time, it is not clear what is limiting product formation. No significant side products are observed, and all unreacted **1** can be completely recovered. However, further production of **2a** stops at ca. 40%, even with the addition of further fresh catalyst, leading us to suspect that the product itself is inhibiting the catalyst. In fact, the addition of *N*-acylDTP product to the initial reactant/catalyst mixture results in little to no product under the standard conditions discussed above. Similar inhibition has been previously observed in the Cu-catalyzed amination of bromothiophenes.[25] Attempts to apply alternate Pd-catalyzed methods have not been successful.

The structures of three *N*-acylDTPs were examined via X-ray crystallography and selected bond lengths are given

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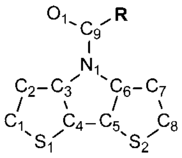
Table 1. Selected Bond Lengths for Various DTPs



bond	*N*-octylDTP[a]	**2b**	**2d**	**2e**
S1-C1	1.719(3)	1.720(2)	1.724(2)	1.728(2)
S1-C4	1.716(3)	1.709(2)	1.710(2)	1.714(2)
C1-C2	1.349(6)	1.341(3)	1.356(3)	1.355(2)
C2-C3	1.416(5)	1.422(3)	1.423(2)	1.419(2)
C3-C4	1.384(4)	1.369(3)	1.374(2)	1.386(2)
N1-C3	1.379(5)	1.402(2)	1.411(2)	1.406(2)
C4-C5	1.420(4)	1.431(2)	1.428(2)	1.425(2)
N1-C9	1.451(4)	1.392(2)	1.394(2)	1.407(2)
C9-O1	-	1.214(2)	1.212(2)	1.208(2)

[a] Reference 3.

in Table 1. Data for the previously reported *N*-octylDTP are included for comparison.[3] As can be seen, the overall structures of the *N*-acylDTPs agree well with *N*-octylDTP and the only significant differences are a shortening of the N−C bond between the pyrrole and the acyl group and an elongation of the two internal N−C bonds of the pyrrole. These deviations are indicative of additional conjugation between the acyl C═O and the fused-ring DTP unit and is consistent with differences previously observed for *N*-arylDTPs,[3] although to a greater extent. For **2b** and **2d**, the C═O unit is nearly coplanar with the DTP backbone, with a dihedral angle of 7.8 and 2.3°, respectively. In contrast, the bulkier *N*-cyclohexanoyl group of **2e** resulted in a larger angle of 18.4°.

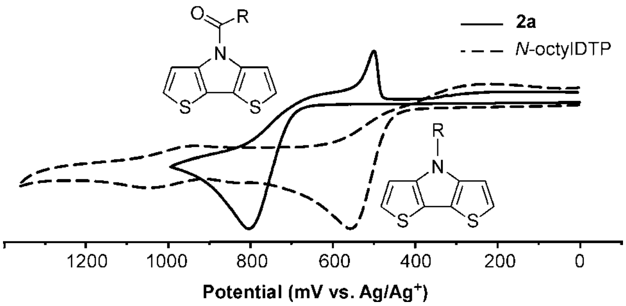


Figure 1. Cyclic voltammograms of *N*-alkyl- and *N*-acylDTPs.

A representative cyclic voltammogram (CV) of **2a** is shown in Figure 1, and the combined electrochemical data for the series are given in Table 2. As with most oligothiophenes, *N*-acylDTPs exhibit a well-defined, irreversible oxidation, corresponding to a removal of an electron from the monomer π-system and the formation of the radical cation. However, unlike previous DTPs, the *N*-acylDTPs exhibit a well-defined reduction coupled to the initial oxidation. This would indicate some partial rereduction of the radical cation formed and suggests the acyl group helps stabilize the radical cation intermediate.

Table 2. Electronic and Optical Data of *N*-AcylDTPs[a]

molecule	E_{pa} (V)	E_{HOMO} (eV)	λ_{max} (nm)	ε (M^{-1} cm^{-1})	E_{LUMO} (eV)
N-alkylDTP[b]	0.56	5.61	310	26100	1.61
			298	29300	
N-arylDTP[c]	0.65	5.70	310	42400	1.70
			300	46700	
2a	0.80	5.85	305	14800	2.13
			289	26300	
2b	0.78	5.83	305	15400	2.10
			289	27600	
2c	0.77	5.82	305	13100	2.10
			289	23500	
2d	0.82	5.87	320	11000	2.25
			290	27000	
2e	0.80	5.85	305	14500	2.13
			289	27200	

[a] In CH_3CN. Potentials vs Ag/Ag^+ in 0.1 M $TBAPF_6$. E_{HOMO} values were determined in reference to ferrocene (5.1 eV vs vacuum).[26] $E_{LUMO} = E_{HOMO} - \lambda_{onset}$. [b] $R = C_8H_{17}$.[3] [c] $R = Ph-C_6H_{13}$.[3]

As previously reported, the larger π system of the DTP attenuates the effect of N-functional groups in comparison to pyrrole.[3] However, the addition of the *N*-acyl group still has a significant effect and shifts the peak potentials of the *N*-acylDTP oxidations to ∼0.78 V (vs Ag/Ag^+), approximately 220 mV more positive than the previous *N*-alkylDTPs. Calculations show that the addition of the N-acyl group does not change the nature of the DTP HOMO and the functional group still resides at a node (Supporting Information, Figure S14). As a result, the observed stabilization of the HOMO energy level is the result of an inductive effect, rather than a direct contribution to the HOMO.

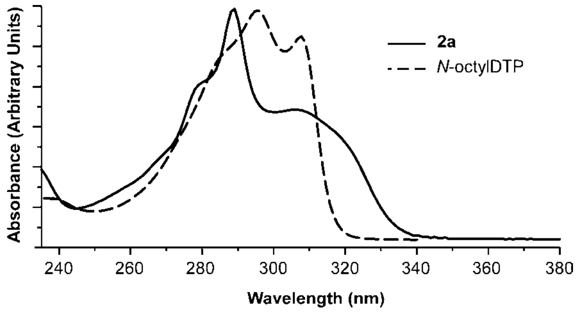


Figure 2. UV−visible spectra of *N*-alkyl- and *N*-acylDTPs.

A representative UV−visible spectrum of **2a** is shown in Figure 2, and the combined spectroscopic data for the series are given in Table 2. All of the *N*-acylDTPs exhibit two primary transitions, a sharp transition at 289 and a broader transition at 305 nm. A prominent shoulder is also observed for all species at ∼280 nm.

While all of the transitions of the previous *N*-alkylDTPs were assigned as various vibrational components of the same electronic transition, it seems that the *N*-acylDTPs exhibit two separate electronic transitions, with the high energy

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transition consisting of a simple $\pi-\pi^*$ transition and the lower energy transition exhibiting some charge-transfer (CT) character. The CT assignment is consistent with the broad nature and lower extinction coefficients (~11−15 × 10^3 M^{-1} cm^{-1}) of this transition. In addition, calculations indicate that while the acyl group does not contribute to the DTP HOMO, it does contribute significantly to the LUMO and LUMO+1. Thus, HOMO−LUMO excitation would result in charge-transfer from the localized DTP unit out onto the acyl group. Calculations indicate that the lowest energy transition arises from excitation between the HOMO and a combination of the LUMO and LUMO+1, supporting the CT nature of this transition. The contribution of the acyl group to the DTP LUMO also results in greater stabilization of the LUMO in comparison to the HOMO, producing a red-shift in the onset of absorption of the *N*-acylDTPs in comparison to the previous *N*-alkylDTPs as shown in Figure 2.

To illustrate the effect of the stabilized *N*-acylDTPs on their respective conjugated materials, the homopolymer of DTP **2b** was generated via electropolymerization.[27] The resulted CV of the poly(**2b**) film is shown in Figure 3 and compared to the analogous poly(*N*-octylDTP). As expected, the polymer of **2b** exhibits an oxidative onset significantly more positive (~400 mV) than the previous *N*-alkylDTP polymers. In addition, the *N*-acylDTP polymers exhibit two well-defined redox waves in comparison to the single broad response observed for the previous *N*-alkylDTP polymers.[5]

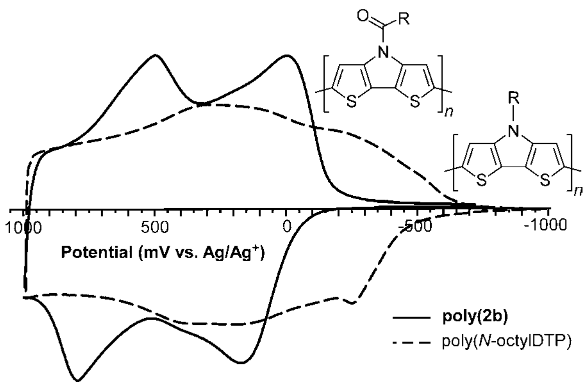

Figure 3. Cyclic voltammograms of electropolymerized films of *N*-acyl- and *N*-alkylDTP homopolymers.

To further characterize the overall effect of the new *N*-acylDTPs, polymer films were grown on ITO to measure the resulting solid-state absorption spectra, and illustrative visible spectra are given in Figure 4. While the λ_{max} of poly(**2b**) is similar to that of the *N*-octylDTP polymer, the *N*-acylDTP polymer exhibits a low energy shoulder consistent with the previously discussed monomeric *N*-acylDTP absorption spectra. As a result, the absorption onset of poly(**2b**) is red-shifted by ~55 nm, giving a polymeric band gap of 1.60 eV. This results in an ~0.1 eV reduction in band gap in comparison to the previously reported poly(*N*-alkylDTPs).[5]

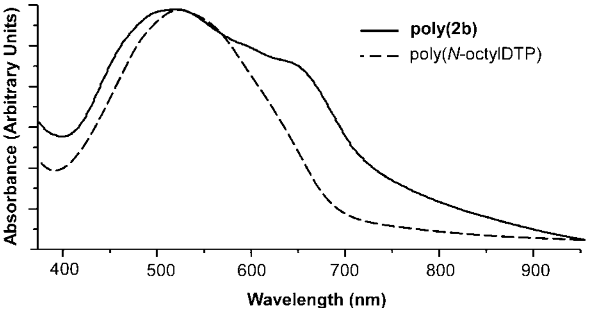

Figure 4. Solid-state absorption spectra of electropolymerized films of *N*-acyl- and *N*-alkylDTP homopolymers.

In conclusion, a new class of dithieno[3,2-*b*:2′,3′-*d*]-pyrroles incorporating *N*-acyl groups has been prepared via copper-catalyzed amidation. Electrochemical and optical characterization of the resulting *N*-acylDTPs shows that both the HOMO and LUMO energy levels are significantly stabilized in comparison to previous *N*-alkylDTPs, thus demonstrating how the electronic properties of DTPs can be tuned through N-functionalization. In addition, initial polymeric materials prepared by electropolymerization of the monomeric *N*-acylDTPs confirm that their application to conjugated materials results in both deeper HOMO levels and reduced band gaps.

Acknowledgment. We thank the ND EPSCoR Flexible Electronics program (EPS-0814442) for support of this research. We would also like to thank Dr. Angel Ugrinov (NDSU) for the collection of the X-ray crystal data and Dr. Christopher L. Heth (NDSU) for assistance with the calculations.

Supporting Information Available: Experimental and synthetic details for compounds **1** and **2a**−**e**. Full UV−vis data for **2a**−**e**, X-ray data for **2b**, **2d**, and **2e**, and calculations for *N*-acetylDTP. This material is available free of charge via the Internet at http://pubs.acs.org.

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