ORGANIC
LETTERS

2013
Vol. 15, No. 20
5230–5233

Synthesis of Thiophene 1,1-Dioxides and Tuning Their Optoelectronic Properties

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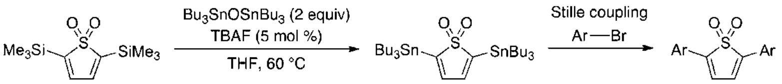
Received August 20, 2013

ABSTRACT



A 2,5-bis(tributylstannyl)thiophene 1,1-dioxide was prepared from 2,5-bis(trimethylsilyl)thiophene 1,1-dioxide, bis(tributyltin) oxide, and tetrabutylammonium fluoride (TBAF). The 2,5-bis(tributylstannyl)thiophene 1,1-dioxide and a 2,5-diiodothiophene 1,1-dioxide were utilized in a series of Stille cross-coupling reactions to afford thiophene 1,1-dioxides with either electron-donating or electron-withdrawing substituents. Electron-withdrawing groups greatly facilitate the reduction of these sulfone heterocycles, and $-C_6H_4$-*p*-NO_2 substituents produce a 510 mV shift as compared to a thiophene 1,1-dioxide with two phenyl groups.

Organic electronics are altering the technology landscape with diverse applications from sensing[1] to mimicking human skin.[2] The solution processability and modular structure of conjugated materials make them attractive for organic photovoltaics (OPVs),[3] organic light-emitting devices (OLEDs),[4] and organic field effect transistors (OFETs).[5]

Organic semiconductors are generally classified as either hole-transport (p-type) or electron-transport (n-type) materials. The n-type systems are not as well developed, particularly in OFETs, due to challenges with stability under ambient conditions and lower charge mobility.[5] In the late 1990s, Barbarella pioneered the unique strategy of converting p-type oligothiophenes into n-type materials by inserting thiophene 1,1-dioxides.[6] Judicious placement of one or more oxidized heterocycles within the conjugated architecture produced materials that exhibit much more facile reductions than their unoxidized analogues.[6c,d] Moreover, some thiophene dioxide oligomers are highly luminescent in the solid state.[6b,7]

Barbarella typically utilized a coupling strategy to connect the thiophene dioxide with other aromatics (e.g., benzene, thiophene).[8] Subsequent work by Rozen and co-workers highlighted HOF·CH_3CN as an oxidant to completely oxidize a variety of different thiophene oligomers and obtain [all]-S,S-dioxides.[9] Additionally, Rozen

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reported oxidations of fused thiophenes and star thiophenes using HOF·CH_3CN.[10] To date, a variety of different small molecules and oligomers bearing oxygenated thiophene rings have been synthesized and characterized.[11] Thiophene dioxide moieties have also been incorporated into conjugated polymer architectures.[12]

These heterocycles have attracted attention for electron transport,[13] but to the best of our knowledge, electron withdrawing groups have not yet been investigated as a method to influence their electronic properties. In other families of n-type materials such as arylene diimides,[14] substitution of the conjugated core with electron-withdrawing groups (e.g., CN) has resulted in stability and high electron mobility.[15] Inspired by the potential of thiophene 1,1-dioxides as n-type materials, we developed a new synthetic scheme for coupling these sulfone heterocycles with electron-withdrawing groups and explored the effects of electronic modulation on their properties.

We sought a thiophene 1,1-dioxide that could be employed in cross-coupling reactions to attach various aryl groups. Compound **1** can be converted to 2,5-dihalo derivatives (**2a** and **2b**) following a published report by Furukawa and co-workers (Scheme 1).[16] Compound **2b** and other substituted thiophene 1,1-dioxides have been successfully employed as coupling partners in palladium-catalyzed Stille reactions.[8,17] However, to take advantage of widely available aryl halides, we also envisioned a novel distannylated thiophene 1,1-dioxide. A previous report by Buchwald and coworkers highlighted the potential of TBAF to convert alkynylsilanes to alkynyl stannanes,[18] and Burton illustrated that a similar method could convert vinylsilanes to vinylstannanes.[19] We found that the combination of compound **1** with bis(tributyltin) oxide in the presence of TBAF produced the desired distannylated precursor **3** (yield: 49%, Scheme 1).

Scheme 1. Synthesis of Thiophene 1,1-Dioxide Precursors

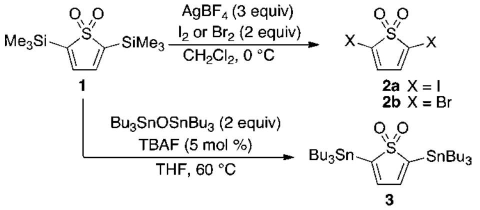
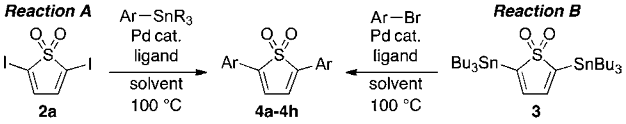
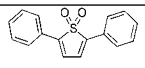
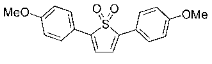
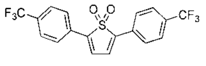
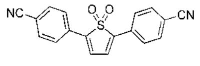
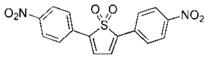
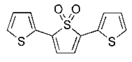
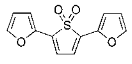
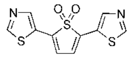


Table 1. Synthesis of 2,5-Bis(aryl)thiophene 1,1-Dioxides



compd	rxn	cat./ ligand	solvent/ yield	product
4a	*A*	$Pd_2(dba)_3$ $AsPh_3$	dioxane 10%	
4b	*A*	$Pd(PPh_3)_4$ none	toluene 27%	
4c	*B*	$Pd_2(dba)_3$ $AsPh_3$	dioxane 28%	
4d	*B*	$Pd_2(dba)_3$ $AsPh_3$	dioxane 44%	
4e	*B*	$Pd_2(dba)_3$ $AsPh_3$	dioxane 58%	
4f	*A*	$Pd_2(dba)_3$ $AsPh_3$	dioxane 31%	
4g	*A*	$Pd_2(dba)_3$ $AsPh_3$	dioxane 52%	
4h	*B*	$Pd_2(dba)_3$ $AsPh_3$	dioxane 20%	

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Compounds **2a** and **3** were utilized in a series of Stille cross-coupling reactions to afford compounds **4a**−**h** (Table 1). The diiodo precursor (**2a**) was employed to couple more electron-rich substituents (Ph, $-C_6H_4$-*p*-OMe, 2-thienyl, 2-furyl) to the central sulfone ring (reaction A, Table 1). Electron-withdrawing substituents were connected to the dioxide moiety by coupling compound **3** with the appropriate aryl bromide (reaction B, Table 1). All compounds except **4b** were synthesized using Pd_2dba_3 and $AsPh_3$, similar to a previous report by Barbarella and co-workers.[8]

Though compounds **4a**[6b] and **4f**[8] have been prepared previously, no cyclic voltammetry was reported. Here, all synthesized thiophene 1,1-dioxides were probed electrochemically to investigate redox properties and frontier orbitals. The oxidation signal observed for **4a** (1.85 V, Table 2) is similar to the oxidations reported previously for **5** and **6** (1.88 and 1.85 V, respectively, Figure 1).[6b] The first reduction of **4a** (−1.16 V, Table 2) is easier than the first reductions of **5** and **6**, which are likely inhibited by electron donation from the additional R groups (**5**, E_{red} = −1.30 V and **6**, E_{red} = −1.57 V).[6b]

Compound **4b**, with the electron-donating $-C_6H_4$-*p*-OMe groups, exhibits a lower oxidation (1.39 V) and more negative reduction (−1.30 V) when compared to **4a** (Table 2). In direct contrast, substitution of the thiophene 1,1-dioxide core with electron-withdrawing groups has the opposite effect. Compounds **4c** and **4d** ($-C_6H_4$-*p*-CF_3 and $-C_6H_4$-*p*-CN groups) exhibit no oxidation within the solvent window, and both are more easily reduced than **4a** (−0.90 for **4c** and −0.77 for **4d**). Reduction is most positively shifted for **4e** giving an impressive first reduction potential of −0.65 V (Figure 2). This reveals strong electron accepting ability and may stem from significant LUMO delocalization over **4e**'s $-C_6H_4$-*p*-NO_2 groups observed via DFT computation (Supporting Information). The reduction of **4e** is also fully reversible which is unique as compared to the other phenyl substituted derivatives (**4a**−**d**).

For all phenyl derivatives, the observed oxidation and first reduction processes are consistently reproduced in multiple potential sweeps. Compounds **4f** and **4g** do not show the same electrochemical stability. The redox processes of **4f** are altered by scanning to high potentials (~2 V), while all of **4g**'s redox processes diminish following oxidation. In both cases, slight deposition was visually observed on the surface of the working electrode and may signify either degradation or electro-polymerization. Several substituted analogues of **4f** (Figure 1, Compounds **7** and **8**) have been characterized electrochemically, and **8** was polymerized in MeCN by repeated cyclic voltammetry scans.[6b,c]

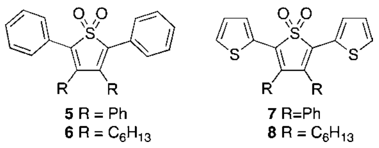

Figure 1. Previously prepared thiophene 1,1-dioxides that have been probed electrochemically.

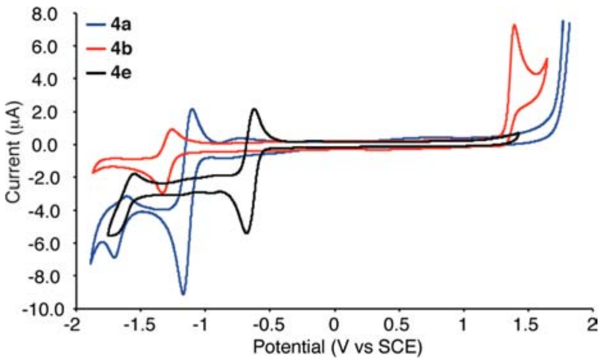

Figure 2. Cyclic voltammograms of **4a** (blue), **4b** (red), and **4e** (black). All voltammograms were collected in 0.10 M N(*n*-Bu)$_4$PF$_6$ (MeCN) solution.

Negative scan polarity was used to delay scanning highly positive potentials in **4f** and **4g**, and the resulting cyclic voltammograms resemble that of **4a**. Notably, oxidation is easier in **4f** and **4g** than in **4a**, while reduction occurs at a similar potential. Compound **4h** meanwhile exhibits the most complex electrochemical behavior showing three reductions within the solvent window (Supporting Information).

In previous studies on oligothiophenes with a central thiophene dioxide, reduction potentials were not tuned by increasing the number of thiophenes. Computations attributed this to concentration of the LUMO on the dioxide.[6c] Here, calculations of the LUMOs for **4a**−**h** still show strong contributions from the dioxide rationalizing the similarity of reduction in **4a**, **4f**, and **4g**. However, the LUMOs also extend to the substituents, particularly with para substituted phenyl groups which explains the exciting reduction modulation achieved in **4a**−**e**.

Poor correlation is observed when comparing the LUMO energies (DFT) to the reduction potentials of **4a**−**h**. The radical anion SOMO energies from DFT also exhibited poor correlation to the reduction potentials. However, the SCF energy difference between the calculated radical anion and the calculated neutral molecule reveals a strong correlation with the first reductions of **4a**−**h** (Figure 3). Consequently, DFT calculations should be helpful in identifying other thiophene 1,1-dioxides as good candidates for n-type charge transport.

The λ_{abs} for the synthesized family of heterocyclic sulfones ranges from 373 to 423 nm, and the absorption has been assigned as a $\pi-\pi^*$ transition using time dependent DFT calculations. All derivatives except **4g** luminesce in acetonitrile solution upon excitation at 390 nm

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Table 2. Electrochemical and Photophysical Properties of 2,5-Bis(aryl)thiophene 1,1-Dioxides

compd	λ_{abs}[b] (nm) (ε M^{-1} cm^{-1})	λ_{em}[b]	ϕ[b] (%)	E_{ox}[c] (V vs SCE)	$E_{1/2\ red\ 1}$ (V vs SCE)	ΔE (mV)	$E_{red\ 2}$ (V vs SCE)	ΔE (mV)
4a	378 (11700)	483	3.9	1.85	−1.16[e]	66.7	−1.73[g]	
4b	407 (13200)	452	8.7	1.39	−1.30[e]	66.9		
4c	373 (16200)	471	7.6		−0.90[e]	63.8	−1.41[e]	157.3
4d	383 (17300)	477	15.2		−0.77[e]	60.3	−1.16[f]	82.4
4e[a]	392 (18800)	479	15.3		−0.65[f]	58.9	−1.65[e,h]	189.2
4f[a]	421 (17300)	476	1.3	1.46	−1.10[f]	70.8	−1.64[c]	
4g[a]	423 (18600)			1.42[d]	−1.11[e]	72.4	−1.76[g,h]	
4h[i]	397 (11300)	460	4.5		−0.92[e]	71.9	−1.47[c]	

[a] Negative scan polarity. [b] Spectra were collected in MeCN. Emission was measured versus quinine sulfate. [c] Irreversible. [d] Process seems to cause reaction or degradation. [e] Quasi-reversible. [f] Fully reversible. [g] Irreversible process with lower intensity than 1st reduction. [h] Cannot be cycled. [i] Compound **4h** also has a third quasi-reversible reduction at −1.85 (ΔE = 117.8), and none of its processes can be cycled if the anodic scans exceed ~1.6 V.

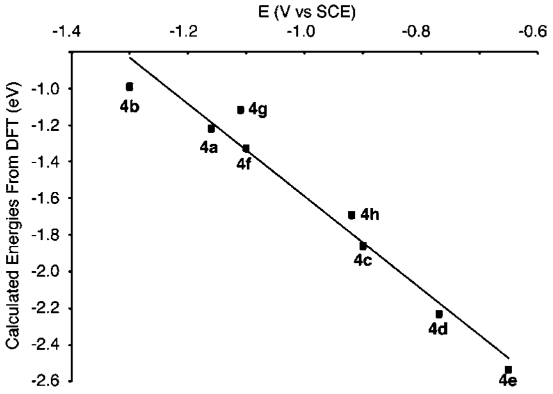

Figure 3. Calculated SCF energy difference (B3LYP/6-31G(d, p)) between the radical anion and neutral thiophene 1,1-dioxides correlated to the first reduction potentials.

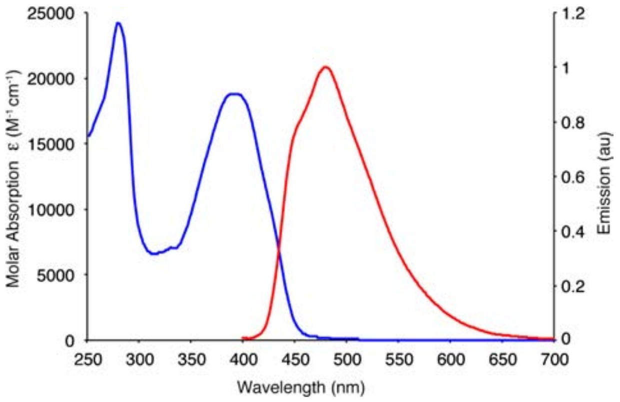

Figure 4. Absorption spectrum (blue) and luminescence spectrum (red) of **4e** collected for a 10 μM MeCN solution. Luminescence was measured following excitation at 390 nm.

(Table 2). Emission from most phenyl-substituted derivatives (**4b**−**e**) is red-shifted as the substituent becomes more electron withdrawing and lowers the LUMO, but **4a** breaks this pattern. Emission quantum yields vary widely among the dioxides. In the phenyl-substituted derivatives (**4a**−**e**), functionalization enhances quantum yield (Table 2). Notably, compound **4e** (Figure 4) demonstrates the best emission efficiency (15.3%) despite its nitro groups which normally accept electron density during excitation of π systems to create nonluminescent charge-transfer excited states.[20] For **4e**, computations show that the excitation has π−π* character rather than charge transfer character because the LUMO delocalizes over both the electron deficient thiophene dioxide and nitrophenyl substituent (Supporting Information).

In conclusion, we have prepared a 2,5-bis(tributylstannyl)thiophene 1,1-dioxide using TBAF and bis(tributyltin)oxide. The distannylated thiophene 1,1-dioxide and a diiodo precursor were utilized to prepare a family of 2,5-bis(aryl)thiophene 1,1-dioxides. The electrochemical and photophysical properties of these molecules were evaluated using cyclic voltammetry and fluorescence spectroscopy. Several molecules show significant quantum yields including the compound with nitro groups. Reduction and oxidation potentials are readily tuned using electron-donating and -withdrawing substituents. The nitro substituent $-C_6H_4$-p-NO_2 most dramatically faciliates reduction enhancing the possibility for n-type behavior.

Acknowledgment. We are grateful to Carnegie Mellon for financial support of this work and to Prof. Roberto Gil (CMU) for help with NMR assignments. Financial support from the NSF is gratefully acknowledged (CHE-0130903, CHE-1039870, CHE-1055547, and DMR-0819860). D.N. C. gratefully acknowledges the support of the U.S. DOE Office of Science Graduate Research Fellowship.

Supporting Information Available. NMR spectra, cyclic voltammograms, absorption and emission spectra, calculated energies, coordinates, and orbital images. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.