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Highly Fluorescent Oligothiophenes through the Incorporation of Central Dithieno[3,2-*b*:2′,3′-*d*]pyrrole Units

Karla R. Radke, Katsu Ogawa, and Seth C. Rasmussen*

Department of Chemistry and Molecular Biology, North Dakota State University, Fargo, North Dakota 58105

seth.rasmussen@ndsu.edu

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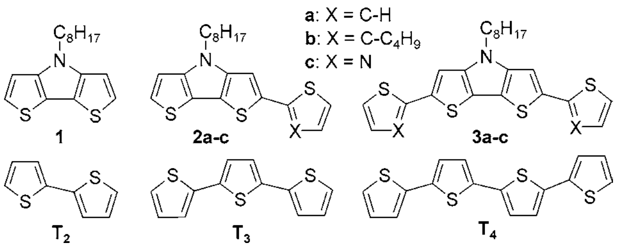
ABSTRACT



Dithieno[3,2-*b*:2′,3′-*d*]pyrrole-based terthiophene (2a–c) and quaterthiophene (3a–c) analogues have been prepared from dithieno[3,2-*b*:2′,3′-*d*]pyrrole (1) via Stille coupling utilizing a one-pot method. In comparison to the parent oligothiophenes (T_n, where $n = 2$–4), the resulting dithieno[3,2-*b*:2′,3′-*d*]pyrrole-based systems exhibit enhanced fluorescence efficiencies in solution (up to 53%). These new oligomeric systems also allow the incorporation of solubilizing side chains without the negative steric interactions that typically reduce backbone planarity.

Conjugated organic materials are of considerable fundamental and technological interest as they combine the electronic and optical properties typical of semiconductors with many of the desirable properties of plastics, including mechanical flexibility, low production costs, and the ability to tune the electronic properties at the molecular level via synthetic modification.[1−5] As a result of their environmental stability and ease of synthetic modification, poly- and oligothiophenes are thought to be one of the most versatile classes of conjugated systems.[1−5] In recent years, particular attention has been paid to oligothiophenes,[5−14] both as model systems for the parent polymers and active materials in devices such as field effect transistors (FETs),[7,8] light emitting diodes (LEDs),[9,10] photovoltaic cells,[11] and spintronics.[12]

One key advantage of the oligomer approach to conjugated materials is their controllable and rigorously defined structure, thus allowing correlation of properties with chain and conjugation length. In addition, oligomers can provide more flexibility in the formation of the thin films needed for most devices. The oligomers' lower molecular weights allow deposition via vacuum sublimation and, providing the oligomers have significant solubility, can also be solvent cast in the same manner as the polymeric analogues.[1,3]

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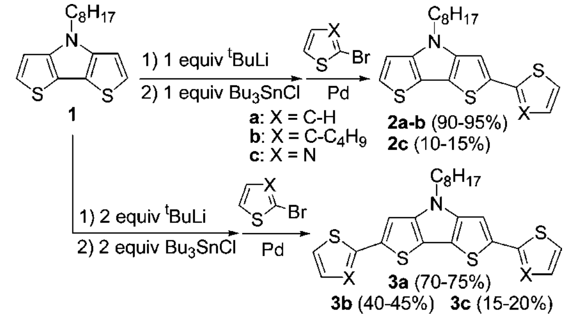
A recent approach to the design of improved oligothiophenes is the combination of the stability of the thiophene ring with the planarity of the linear acenes such as pentacene.[6,14] Such systems should retain the desirable properties of oligothiophenes, while limiting deviations from planarity that disrupt conjugation and potentially affect the band gap in the solid state. Continuing our previous work with dithieno[3,2-*b*:2′,3′-*d*]-pyrroles (DTPs, **1**),[14,15] we prepared a series of terthiophene and quaterthiophene analogues as illustrated in Scheme 1. The incorporation of the fused-ring DTP unit eliminates rotation around the central thiophene−thiophene bond and the *N*-octyl side chain of the pyrrole allows for greater solubility without additional steric interactions that cause deviations from planarity.[4] The combination of these effects leads to oligothiophenes exhibiting significantly enhanced fluorescence.

Scheme 1. Synthesis of Dithieno[3,2-*b*:2′,3′-*d*]pyrrole Oligomers



Pd = $PdCl_2(PPh_3)_2$.

The DTP-containing oligothiophenes were prepared via Stille coupling[16] as shown in Scheme 1. To produce the desired thienyllithium intermediates, it was necessary to use ^{t}BuLi in the initial step. Previous attempts to deprotonate using ^{n}BuLi or ^{n}BuLi/TMEDA were unsuccessful and illustrate that the acidity of the DTP α-hydrogens is reduced in comparison to typical thiophenes.[17] Even when using ^{t}BuLi, it was found that the second deprotonation is highly concentration-dependent as a result of the decreased solubility of the DTP anions in ether solvents. As such, it was found that lower concentrations near 0.01 M were required to obtain high conversion to the dianion.

Reaction of the thienyllithium intermediates with Bu_3SnCl successfully produced the desired stannyl compounds, but attempts to isolate and purify these intermediates failed because of their instability. However, direct use of the freshly prepared mono- or distannyl-DTP solution via a one-pot Pd-catalyzed aryl−aryl coupling allowed the production of the desired oligothiophenes in good yield.[18]

Representative UV−vis spectra of **2a** and **3a** are shown in Figure 1, and complete photophysical data for all DTP-based oligothiophenes are given in Table 1. As seen in previous oligothiophenes, increasing conjugation length (i.e., **1** to **2a** to **3a**) results in red-shifts of the transitions and increased extinction coefficients.[19] The spectra also broaden and lose vibrational structure with increasing length. This is expected, as with the addition of each thiophene unit, the oligothiophene becomes more conformationally flexible, thus producing a more diffuse spectrum.[20]

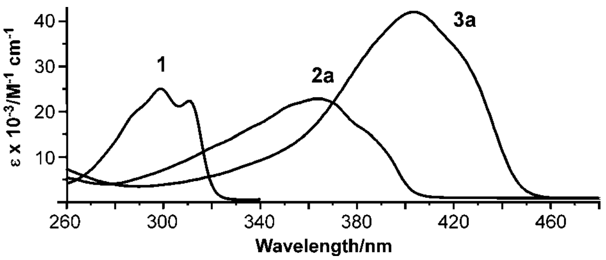


Figure 1. Solution UV−vis spectra of DTP oligothiophenes **1**, **2a**, and **3a**.

Table 1. Photophysical Data for Various Oligothiophenes

oligothiophene	λ_{max} (abs, nm)[a]	ϵ (M^{-1} cm^{-1})	λ_{max} (em, nm)[b]	Φ_F[b]
bithiophene[c]	303	12400	362	0.017
1[d]	310	26100	324	0.0011
	298	29300		
	289 (sh)	24200		
terthiophene[c]	354	22100	407	0.066
			426	
2a	383 (sh)	16700	408 (sh)	0.29
	364	23400	421	
			452 (sh)	
2b	341	19200	407 (sh)	0.089
			420	
			451 (sh)	
2c	390 (sh)	25600	418	0.55
	378	28800		
quaterthiophene[c]	392	31600	437	0.18
			478	
3a	405	44000	444	0.49
			470	
			506 (sh)	
3b	382	35000	446	0.36
			472	
			508 (sh)	
3c	433	48800	451	0.54
	413	50800	478	

[a] In CH_2Cl_2, sh = shoulder. [b] In cyclohexane. [c] In dioxane.[19] [d] Reference 14.

The extinction coefficients for the DTP oligothiophene transitions are roughly 1.9−2.4 × 10^4 M^{-1} cm^{-1} for

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oligomers **2a**−**c** and 3.5−5.1 × 10^4 M^{-1} cm^{-1} for oligomers **3a**−**c**. Such values all correspond to strongly allowed transitions, and with the exception of **2b**, all DTP oligomers exhibit coefficients larger than those of the corresponding parent oligothiophenes. As the nitrogen lone pair is involved in the π-bonding of the DTP pyrrole ring, nitrogen-based n $\rightarrow \pi^*$ transitions would not be expected, and sulfur-based n $\rightarrow \pi^*$ transitions have not been identified for thiophenes.[21] Thus, the observed DTP oligomer absorptions should all correspond to simple $\pi \rightarrow \pi^*$ transitions.

The DTP quaterthiophene analogues **3a**−**c** exhibit a single transition ranging from a low of 382 nm for **3b** and a high of 413 nm for **3c**, which also exhibits a second lower energy peak at 433 nm. The parent quaterthiophene $\mathbf{T_4}$ is in the center of this range at 392 nm.[19] Oligomers **3a** and **3c** are red-shifted in comparison to $\mathbf{T_4}$ presumably as a result of increased planarity due to the central DTP unit. This is further supported by the narrowing of the absorption spectra and the increase in extinction coefficients as expected from a more planar ground state.[20] The nitrogens of the thiazole rings in **3c** could result in further lowering of the transition by either additional electron donation or by reducing steric interactions to allow a more planar conformation in solution. The two additional butyl side chains of oligomer **3b**, however, add significant alkyl-sulfur interactions[4] causing increased torsional strain and a reduction in conjugation. The observed blue shift for **3b** indicates that the loss of conjugation from these interactions is greater than any benefit from the increased planarity of the central DTP unit. The DTP terthiophene analogues **2a**−**c** exhibit transitions between 341 and 390 nm and follow similar trends as the quaterthiophene analogues.

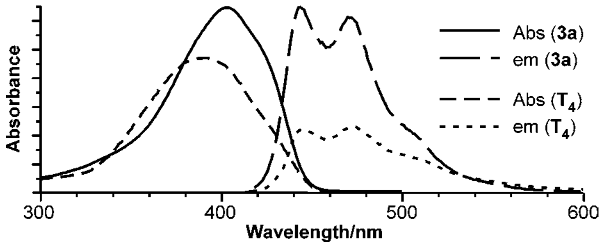

Figure 2. UV−vis and emission spectra of oligothiophene **3a** and quaterthiophene ($\mathbf{T_4}$).[19]

As shown in Figure 2 and Table 1, the DTP-based quaterthiophenes give a blue emission that is similar in both energy and structure to that of the parent $\mathbf{T_4}$. The vibrational spacing of the DTP analogues is ~1200−1500 cm^{-1}, corresponding well with the ring breathing modes of thiophene and pyrrole.[21] The structured emission spectra are characteristic of a planar excited state, which is consistent with the planar quinoid-like structure proposed for the singlet excited state of oligothiophenes.[22]

The frontier orbitals of **3a** were determined by ab initio (HF STO-3G) methods and, as seen in Figure 3, the LUMO exhibits significant quinoid character. Thus it would be expected that population of the LUMO during excitation would contribute to a planar excited state. As illustrated by the absorbance data above, the ring fusion of the DTP unit results in a more planar conformation in contrast to the typically twisted ground state thought to be adopted by oligothiophenes in solution.[23] As a result, the ground-state geometry of the DTP analogues would better match the predicted quinoid-like excited-state geometry, thus requiring less conformational reorganization and producing a smaller Stokes shift as seen in Figure 2.[6,20,23]

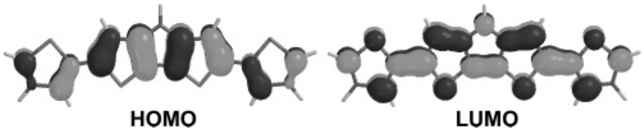

Figure 3. Calculated HOMO and LUMO of oligothiophene **3a**.

The fluorescence intensities of the DTP-based oligomers **3a**−**c** are significantly enhanced in comparison to $\mathbf{T_4}$, with solution quantum efficiencies (Φ_F) of 36−54%. This was initially unexpected, as monomeric DTPs exhibit significantly less detectable fluorescence ($\Phi_F = \sim 10^{-3}$)[14] than bithiophene ($\Phi_F = 0.017$).[19] The often weak fluorescence of thiophene-based chromophores has been attributed to significant spin−orbit coupling due to the heavy atom effect of the sulfur,[5,10] which is possibly also mediated by charge transfer mixing.[19] The spin−orbit coupling thus results in high triplet quantum yields (0.99 for bithiophene),[19] and highly efficient nonradiative processes between the triplet and ground states usually lead to relaxation from the triplet state without emission. However, as the length of the oligothiophene is increased, the triplet quantum yields typically decrease and Φ_F increases.[19]

Structural factors such as backbone rigidity can also have significant effects on the fluorescence efficiencies of oligo- and polythiophenes. It is believed that the primary source for nonradiative deactivation in oligothiophenes is low frequency, interannular torsional modes, which are dominant for twisted configurations. Such torsional vibrations are expected in the twisted form of oligothiophenes in solution, thus resulting in decreased fluorescence.[24] By incorporating fused-ring units such as DTP, a more planar conformation is favored and these torsional modes are decreased, resulting in increased fluorescence.

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The effect of planarization via ring fusions has been previously investigated through the study of quaterthiophene analogues incorporating 4*H*-cyclopenta[2,1-*b*;3,4-*b*′]bithiophene units (Figure 4).[25,26] The absorption energy ($\lambda_{max} = 407$ nm) and profile of **4** are almost identical to those of the DTP oligomer **3a**. Its reported flourescence is slightly lower in energy ($\lambda = 457$ nm) but was measured in the more polar THF solvent. By comparing the energies of **4** and **3a** in relation to $\mathbf{T_4}$ in the two different solvents, the same 7 nm red-shift is found for both fused analogues. The quantum efficiencies of the two analogues, however, are significantly different. Oligomer **4** exhibits a value of 24%, only slightly greater than that of quaterthiophene (18%) and significantly lower than **3a** (49%).

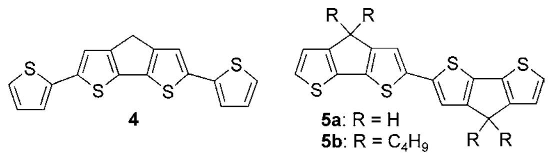

Figure 4. 4*H*-Cyclopenta[2,1-*b*;3,4-*b*′]bithiophene oligomers.

The doubly fused compounds **5a** and **5b** exhibit even lower efficiencies of 14% and 9%, respectively.[26] The lower values of these systems were determined to be due to photochemical decomposition resulting from both bond scission and oxidation, as evidenced by the presence of epoxide, hydroxyl, and carbonyl groups after photolysis.[26a] Such photochemical pathways would act as alternate methods of excited-state deactivation, thus lowering Φ_F. Although such photochemistry was not reported for **4**, it is likely that this reactivity is a limit of the 4*H*-cyclopenta[2,1-*b*;3,4-*b*′]bithiophene unit and the photophysics of **4** would be similarly complicated. In contrast, the DTP analogues are photochemically stable, and no decomposition was observed over the time frame of the photophysical measurements. As a result, the DTP-based oligomers provide a better example of the benefits of backbone rigidification for enhancing Φ_F. While electrochemical measurements indicate that the pyrrole nitrogen raises the HOMO,[14] the spectral properties seem to suggest that both the HOMO and LUMO are equally affected.

The addition of alkyl side chains can also affect the fluorescence efficiencies of oligo- and polythiophenes. Alkyl side chains are often used to increase solubility, but such alkyl groups can also introduce steric interactions that reduce backbone planarity and result in decreased fluorescence.[24] In addition, the alkyl groups add high-frequency modes that increase with the number of side chain methylene units. This increase in high-frequency modes results in a greater number of additional deactivation pathways via internal conversion and an overall decrease in Φ_F.[9,20] A good example of the negative effect of side chains is oligothiophene **3b** that contains butyl groups on the two external thiophenes. As illustrated with the absorbance data, these side chains cause increased torsional strain and a reduction in conjugation. As a result, Φ_F is also reduced in comparison to the other DTP analogues. What is interesting, however, is that while the absorbance of **3b** is blue-shifted in comparison to that of $\mathbf{T_4}$, its Φ_F is still twice that of $\mathbf{T_4}$. This shows the ring fusion still plays an important role in reducing torsional vibrations and mediating the formation of the planar excited state.

The *N*-octyl side chain on all of the DTP-based oligomers does not contribute any steric interactions to reduce planarity and thus the only negative effects from its presence would be the additional high-frequency modes that could promote internal conversion. However, any negative contribution seems minor compared to the positive effect of the planarization as a result of the fused-ring DTP unit as evidenced by the enhanced emission in all DTP-based oligomers. As such, it may be possible to tune the physical properties (solubility, solid-state packing, etc.) of such oligomers by varying this side chain without large negative effects on Φ_F.

In conclusion, the incorporation of DTP units in oligothiophenes allows the inclusion of solubilizing side chains without the negative steric interactions that typically reduce backbone planarity. In addition, the DTP unit's fused-ring nature significantly increases the solution fluorescence efficiency. As far as we are aware, the fluoresence efficiencies reported here for **2c** (55%) and **3c** (54%) are the highest reported for a terthiophene and quaterthiophene analogue, respectively. Both values constitute two of the highest reported for any oligothiophene (Bäuerle and co-workers[10b] have reported 62% for a quinquethiophene analogue). It is understood that the additional quenching common in thin films (Φ_F of thin films are typically $10-10^3$ times lower than solution)[19] may be promoted by the increased planarization of the DTP-based oligothiophenes, which would promote aggregate formation via closepacked structures.[24,27] However, it is hoped that the solid-state packing can be tuned through the use of the N-functionalization of the DTP unit to produce thin flims with improved photo- and electroluminescence. Continued study of the DTP oligothiophene systems is underway, including investigation of solid-state properties and the influence of various types of N-functionalization on both the photophysics and crystal packing.

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Supporting Information Available: Experimental details for **2a**−**c** and **3a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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