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Synthesis and Evaluation of 2,5-Linked Alternating Pyridine−Thiophene Oligomers

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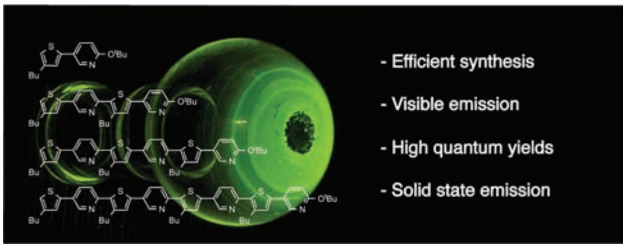
ABSTRACT



The first iterative access to alternating 2,5-linked pyridine−thiophene (Py−Th) oligomers is presented. These oligomers exhibit strong absorption and emission, even in the solid state (picture of the longest oligomer, above). Protonation leads to large red shifts in emission and, unlike most known thiophene-containing oligomers, they are readily reduced but not oxidized. These species represent a promising new class of materials for further study and potential application.

Polythiophenes and oligothiophenes are among the most intensively studied classes of organic electronic materials, having found application in, e.g., light-emitting diodes (LEDs) and solar cells.[1,2] This is in large part the result of their facile synthesis and the ease with which their optical, electronic, and material properties can be tuned by structural modification. Over time, two notable strategic trends have emerged: an increasing emphasis on the synthesis and study of thiophene oligomers of defined structure and the incorporation of electron-deficient aromatic components into the electron-rich oligothiophenes.

The first trend is driven by the need for materials with uniform purity, regiochemistry, and properties. While it is more laborious (and thus costly) relative to polymer synthesis, these objectives can be realized via the controlled synthesis of oligomers. The second trend, the donor−acceptor (D−A) approach to electronic materials,[3] grew out of a desire to reduce the band gap of poly- and oligothiophenes, which is influenced by the donor HOMO and the acceptor LUMO energies. Oligomeric alkylthiophenes are in widespread use, and there are now numerous examples of thiophene-containing D−A oligomers.[4]

Our interests began with the observation that, despite being the archetypal electron-deficient heterocycle, pyridine has been conspicuous in its absence in the development of D−A oligomers.[5–8] We report here the first controlled, iterative

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(1) For recent monographs, see: (a) György, I. *Conducting Polymers*;Springer: Berlin, 2008. (b) Petty, M. C. *Molecular Electronics*; Wiley: Chichester, 2008.

(2) For representative reviews, see:(a) Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev.* **2009**, *109*, 1141–1276. (b) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202–1214. (c) Perepichka, I. F.; Perepichka, D.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281–2305. (d) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; R. Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481–494.

(3) For representative reviews, see: (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173–206. (b) Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mat. Sci. Eng.* **2001**, *32*, 1–40. (c) Meijer, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2482–2506.

(4) For representative examples, see: (a) Karsten, B. P.; Janssen, R. A. J. *Org. Lett.* **2008**, *10*, 3513–3516. (b) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900–3903. (c) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem.−Eur. J.* **1998**, *4*, 1235–1243. See also refs 1–3.

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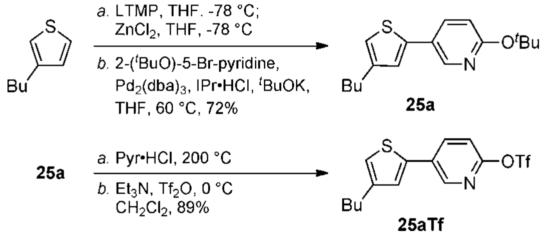
synthesis of 2,5-linked pyridine−thiophene oligomers and show that they have remarkable optical and electrochemical properties which make them a promising new class of electronic materials. Of particular note are long absorption and emission wavelengths, especially in protonated form, solid-state luminescence, and facile electrochemical reduction.

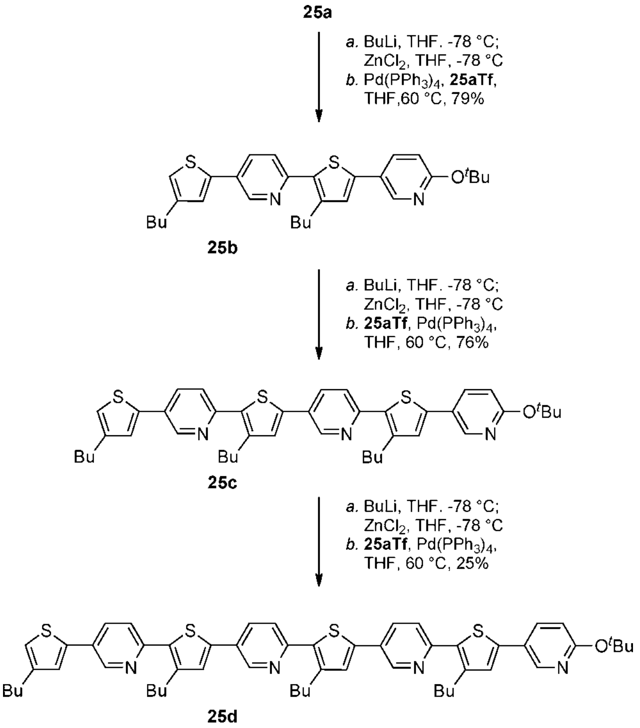
Beginning with 3-butylthiophene, two-ring precursors were synthesized:[9] **25a** was prepared by regioselective lithiation,[10] transmetalation with zinc chloride, and Negishi coupling with 2-*tert*-butoxy-5-bromopyripine (Scheme 1)[11,12] in the presence of an *N*-heterocyclic carbene ligand;[13] deprotection and sulfonylation provided the corresponding triflate **25aTf**.[14] Four-, six- and eight-ring oligomers (**25b**−**d**) were prepared by efficient homologation with **25aTf** via iterative lithiation/Negishi coupling (Scheme 2).

The oligomers show a steady increase in λ_{max} of absorption and emission with chain length (Table 1, Figure 1), accompanied by a rise in quantum yield. The longest, **25d**, is strongly absorbent in the visible region and is more emissive than comparable D−A oligothiophenes of similar length:[5] its quantum yield and extinction coefficient approach those of benchmark fluorophores such as fluorescein or rhodamine 6G.[18]

Scheme 1. Synthesis of Two-Ring Precursors



Scheme 2. Iterative Oligomer Synthesis



An additional attribute of pyridine−thiophene oligomers is that each pyridine provides a well-defined site for postsynthetic modulation of optical properties. Indeed, we find that protonation of the oligomers with trifluoroacetic acid (TFA) leads to significant red shifts in emission (Table 1, Figure 2).[15,16] This bodes well for further manipulating optical and electronic properties by alkylation or Lewis acid coordination.[17]

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(5) Since the inception of this work, there have been reports describing pyridine-thiophene and pyrimidine-thiophene oligomers. See: (a) Fukumoto, H.; Kumagai, A.; Fujiwara, Y.; Koinuma, H.; Yamamoto, T. *Heterocycles* **2006**, *68*, 1349−1357. (b) Kumagai, A.; Fukumoto, H.; Yamamoto, T. *J. Phys. Chem. B* **2007**, *111*, 8020–8026. (c) Yue, W.; Tian, H.; Hu, N.; Geng, Y.; Wang, F. *Cryst. Growth Des.* **2008**, *8*, 2352–2358. (d) Chevallier, F.; Charlot, M.; Katan, C.; Mongin, F.; Blanchard-Desce, M. *Chem. Commun.* **2009**, 692–694. (e) Ortiz, R. P.; Casado, J.; Hernandez, V.; Navarrete, J. T. L.; Letizia, J. A.; Ratner, M. A.; Facchetti, A.; Marks, T. J. *Chem.*−*Eur. J.* **2009**, *15*, 5023–5039.

(6) For conducting and/or electroluminescent polymers containing pyridine groups, see : (a) Zhou, Z.; Maruyama, T.; Kanbara, T.; Ikeda, T.; Ichimura, K.; Yamamoto, T.; Tokuda, K. *Chem. Commun.* **1991**, 1210–1212. (b) Yamamoto, T.; Maruyama, J. T.; Zhou, Z.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubotall, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832–4845. (c) Monkman, A. P.; Halim, M.; Samuel, I. D. W.; Horsburgh, L. E. *J. Chem. Phys.* **1998**, *109*, 10372–10378. (d) Meghdadi, F.; Leising, G.; Wang, Y. Z.; Gebler, D. D.; Swager, T. M.; Epstein, A. I. *Synth. Met.* **1999**, *102*, 1085–1086. (e) Feller, F.; Monkman, A. P. *Synth. Met.* **2001**, *116*, 149–152. (f) Eichen, Y.; Nakhmanovich, G.; Gorelik, V.; Epshtein, O.; Poplawski, J. M.; Ehrenfreund, E. *J. Am. Chem. Soc.* **1998**, *120*, 10463–10470. (g) Wang, C.; Kilitziraki, M.; McBride, J. A. H.; Bryce, M. R.; Horsburgh, L. E.; Sheridan, A. K.; Monkman, A. P.; Samuel, I. D. *Adv. Mater.* **2000**, *12*, 217–222.

(7) For polymers containing both pyridine and thiophene rings, see: (a) Yamamoto, T.; Zhou, Z.; Kanbara, T.; Kizu, K.; Tsukasa Maruyama, T.; Yoshiyuki Nakamura, Y.; Lee, B.-L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389–10399. (b) Irvin, D. J.; DuBois, C. J., Jr.; Reynolds, J. R. *Synth. Met.* **2001**, *119*, 321–322. (c) DuBois, C. J., Jr.; Larmat, F.; Irvin, D. J.; Reynolds, J. R. *Synth. Met.* **2001**, *119*, 321. (d) DuBois, C. J.; Reynolds, J. R. *Adv. Mater.* **2002**, *14*, 1844–1846. (e) Jenkins, I. H.; Salzner, U.; Pickup, P. G. *Chem. Mater.* **1996**, *8*, 2444–2450.

(8) We have found 2,6-biarylpyridines to be useful fluorophores in the context of chemosensor development. See: (a) Mello, J. V.; Finney, N. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1536–1538. (b) Fang, A. G.; Mello, J. V.; Finney, N. S. *Org. Lett.* **2003**, *5*, 967–970. (c) Fang, A. G.; Mello, J. V.; Finney, N. S. *Tetrahedron* **2004**, *60*, 11075–11087. (d) Mello, J. V.; Finney, N. S. *J. Am. Chem. Soc.* **2005**, *127*, 10124–10125.

(9) See the Supporting Informationfor complete experimental and spectroscopic details.

(10) For preparation of 3-butylthiophene, see: McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904–912. For regioselective lithiation, see: Smith, K.; Barratt, M. L. *J. Org. Chem.* **2007**, *72*, 1031–1034.

(11) Negishi, E.; Zeng, X.; Tan, Z.; Qian, M.; Hu, Q.; Huang, Z. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; De Meijere, A., Diederich, F., Eds.; Weinheim: Wiley-VCH, 2004; pp 815−889.

(12) Wang, P.-S.; Liang, C.-K.; Leung, M. *Tetrahedron* **2005**, *61*, 2931–2939.

(13) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organomet. Chem.* **2000**, *606*, 49–54.

(14) For aryl methyl ether cleavage with Py•HCl, see: Loren, J. C.; Gantzel, P.; Linden, A.; Siegel, J. S. *Org. Biomol. Chem.* **2005**, *3*, 3105–3116.

(15) We have previously seen similar protonation effects in 2,6-biarylpyridines. See ref 8.

(16) The red-shift in emission is accompanied by a ca. 3-fold decrease in emission intensity. The emission response to added TFA is instantaneous. However, ^{1}H NMR studies show conversion of protonated oligomers to the corresponding pyridols (via loss of the *tert*-butyl group) over the course of several hours.

Table 1. Optical Properties of **25a−d**[a]

	$\varepsilon/10^5$ M^{-1} cm^{-1} [b]	λ_{max}(abs)/ nm −/+ TFA[c]	λ_{max}(em)/ nm −/+ TFA[c,d]	ϕ[c,d]
25a		290/295	360/441	0.05
25b		363/390	438/500	0.60
25c	4.1	394/407	483/528	0.69
25d	7.0	410/422	501/560	0.74

[a] Values for longest wavelength λ_{max}. [b] In $CHCl_3$. [c] In CH_3CN. [d] Quantum yields for neutral species relative to PPO ($\phi = 0.94$ in cyclohexane) for **25a**, DPA ($\phi = 1$, in cyclohexane) for **25b−d**. PPO = 2,5-diphenyloxazole, 9,10-diphenylanthracene.

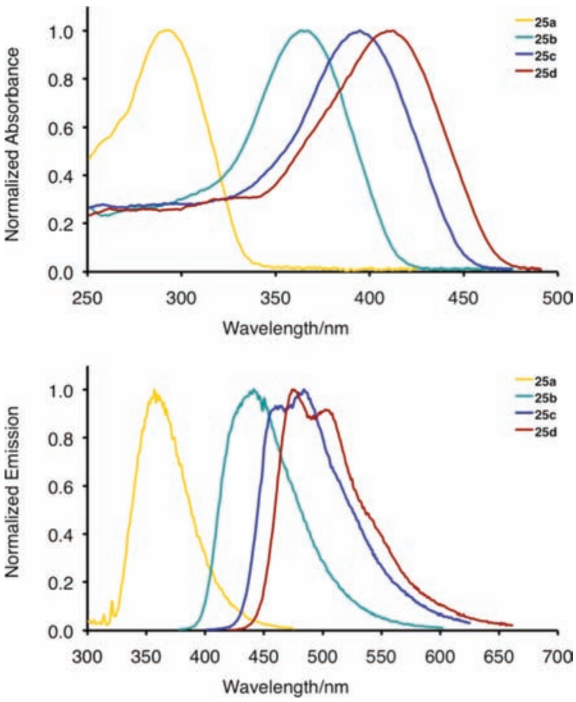

Figure 1. Absorbance and emission of **25a−d**.

Plots of absorption and emission energy vs 1/*n* are linear (*n* = number of PyTh units, Figure 3)[9,19] for both neutral and protonated forms of the oligomers. This indicates that the maximum conjugation length has not yet been reached, and longer oligomers are expected to have even longer wavelength absorption and emission maxima. (For example, the 16-ring compound is extrapolated to emit at 560/590 nm in neutral/protonated form.)

Beyond strong solution-phase emission, **25b−d** are visibly luminescent in the solid state, which distinguishes them from typical oligothiophenes and the few known pyridine−thiophene conjugates.[2] They are waxy solids and are readily soluble in most organic solvents, allowing them to be spin-coated onto inorganic substrates such as glass. We observe red-shifts in emission for **25c** ($\lambda_{max} = 500$ nm) and **25d** ($\lambda_{max} = 535$ nm) in thin films on glass (Figure 4),[9] consistent with aggregation or increased planarization in the solid state. The absence of self-quenching makes these and related oligomers attractive candidates for incorporation into light-emitting devices.

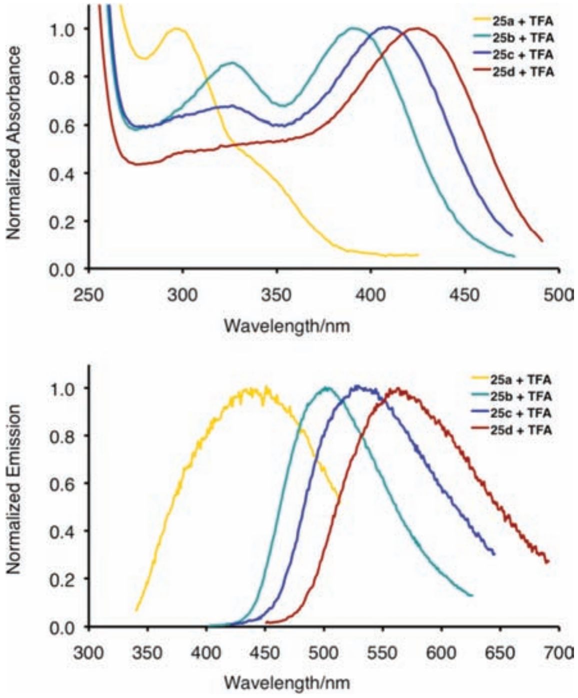

Figure 2. Absorbance and emission of **25a−d** with added TFA.

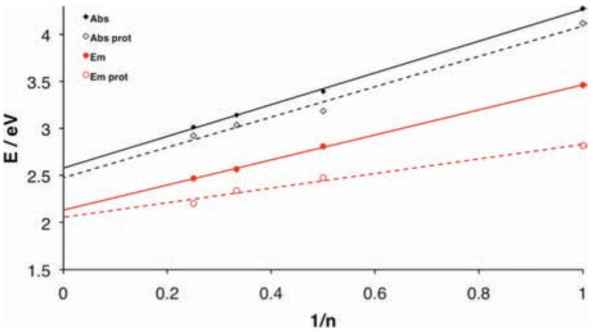

Figure 3. Plot of 1/*n* vs absorption or emission energy for **25a−d** (*n* = no. of Py−Th units).

Finally, cyclic voltammetry reveals that while these oligomers cannot be oxidized (in THF), they are electron acceptors. The two-ring compound, **25a**, shows a single reduction at $E_c = -3.4$ V vs Fc/Fc^+ (−2.9 V vs Ag/AgCl).[9] The number of electrons accepted by the oligomers increases with chain length, and **25d** can accept up to five electrons

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(17) For a recent example in which Lewis acid coordination to a nitrogen atom significantly alters the band gap of a D-A oligomer, see: Welch, G. C.; Coffin, R.; Peet, J.; Bazan, G. C. *J. Am. Chem. Soc.* **2009**, *131*, 10802–10803.

(18) Fluorescein in EtOH: $\varepsilon = 95000$ M^{-1} cm^{-1}; $\phi = 1.0$. Rhodamine 6G in EtOH: $\varepsilon = 116000$ M^{-1} cm^{-1}; $\phi = 0.95$. Data obtained from the PhotochemCAD database. See : Du, H.; Fuh, R. A.; Li, J.; Corkan, A.; Lindsey, J. S. *Photochem. Photobiol.* **1998**, *68*, 141–142.

(19) Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.* **1997**, *48*, 379.

over the range −2.1 to −3.3 V (Figure 5). Compounds **25b** and **25c** show intermediate behavior.

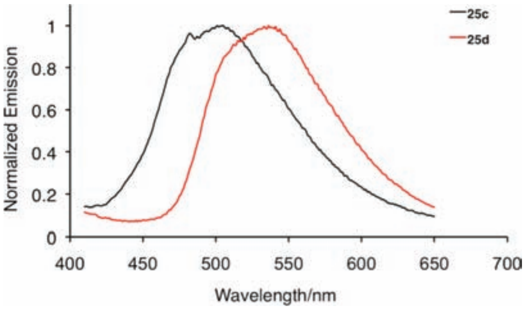

Figure 4. Solid-state emission of **25c**,**d**.

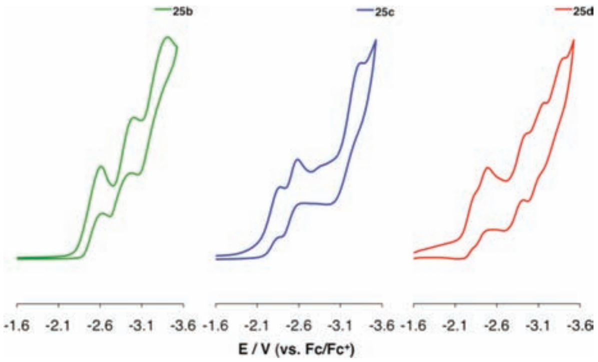

Figure 5. Reductive portion of cyclic voltammograms for **25b**−**d**. (1 mM in THF, 0.1 M Bu_4NClO_4, scan rate 50 mV s^{-1}, glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl reference electrode, ferrocene (Fc) internal reference.)

While the CV measurements were conducted in freshly distilled, anhydrous THF, the reductions of **25c** and **25d** are not fully reversible. Potential complicating factors include the possibility of protonation by residual H_2O and loss of *tert*-butyl radical from highly reduced intermediates, and this issue will need to be addressed by the preparation of oligomers with nonlabile terminating groups. However, this electrochemical behavior still differentiates these oligomers from the majority of reported D−A oligomers, including those containing pyridine and thiophene rings, which are readily oxidized but not reduced.[5a−c,20]

In conclusion, we have reported the concise iterative synthesis of a new class of D−A oligomers based on thiophene and pyridine units. The longer oligomers show strong absorption and emission, which can be tuned by protonation of the pyridine units. In addition, they remain emissive in the solid state, and undergo ready electrochemical reductions. These oligomers thus have a range of potential applications, such as use as electron-transporting or electroluminescent materials. Ongoing work includes further solid-state characterization of **25d** and its analogues, synthesis of longer oligomers, and evaluation of electroluminescence, as well as computational modeling.

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Supporting Information Available: Experimental procedures; characterization of all new compounds; cyclic voltammetry details. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Oligothiophenes capped on both ends by fluoroalkyl, fluorocarbonyl, or fluorobenzene groups are representative exceptions. For examples, see: Yoon, M.-H.; DiBenedetto, S. A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 1348–1349. (b) Yoon, M.-H.; DiBenedetto, S. A.; Russell, M. T.; Facchetti, A.; Marks, T. J. *Chem. Mater.* **2007**, *19*, 4864–4881. For a pyrimidine−thiophene conjugate that can undergo two-electron reduction, see ref 5e.