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Synthesis and Structures of Novel Luminescent Bent Acenedithiophenes

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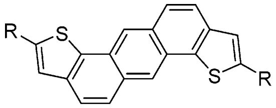
ABSTRACT



BADTs

R = H, CH_3, C_6H_{13}, $C_{12}H_{25}$

1,4-Dithienyl-2,5-divinylbenzenes are readily available compounds that undergo oxidative photocyclization to afford bent anthradithiophenes (BADTs). The new parent and didodecyl-functionalized derivatives have been structurally characterized, and their absorption and emission spectra are reported.

Acenes have optical and electronic properties that are desirable for application in organic-based electronic devices such as organic field-effect transistors (OFETs) and light-emitting diodes (OLEDs).[1] Incorporating heteroarenes such as thiophene into these frameworks has been part of an ongoing effort to prepare new materials with improved device performances.[2]

Linear anthradithiophenes (LADTs, Figure 1) have been prepared for use as semiconductors in OFETs.[3] LADTs are of particular interest because they possess a rigid conjugated framework that is structurally analogous to pentacene, an organic semiconductor.[4] These heteroacenes are prepared as a mixture of *syn* and *anti* isomers that form highly ordered polycrystalline films by vacuum evaporation. Hole mobilities of LADTs approach that of pentacene while showing improved oxidative stability. In addition, theoretical studies have suggested that increasing the cofacial interactions between adjacent LADT molecules could lead to improved device performances.[5] Anthony and co-workers have prepared a series of silylethynyl-functionalized LADTs that have improved solubilities and favorable solid-state packing motifs.[6] More importantly, thin films of these compounds are processable from solution and exhibit good hole mobilities that can be further improved by annealing the films with solvent vapor.[7]

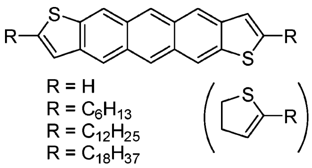


Figure 1. LADTs.

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(1) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028.

(2) (a) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224. (b) Wex, B.; Kaafarani, B. R.; Schroeder, R.; Majewski, L. A.; Burckel, P.; Grell, M.; Neckers, D. C. *J. Mater. Chem.* **2006**, *16*, 1121. (c) Cicoira, F.; Santato, C.; Melucci, M.; Favaretto, L.; Gazzano, M.; Muccini, M.; Barbarella, G. *Adv. Mater.* **2006**, *18*, 169. (d) Xiao, K.; Liu, Y.; Qi, T.; Zhang, W.; Wang, F.; Gao, J.; Qiu, W.; Ma, Y.; Cui, G.; Chen, S.; Zhan, X.; Yu, G.; Qin, J.; Hu, W.; Zhu, D. *J. Am. Chem. Soc.* **2005**, *127*, 13281. (e) Takimiya, K.; Kunugi, Y.; Konda, Y.; Niihara, N.; Otsubo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5084. (f) Iosip, M. D.; Destri, S.; Pasini, M.; Porzio, W.; Pernstich, K. P.; Batlogg, B. *Synth. Met.* **2004**, *146*, 251. (g) Li, X.-C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 2206. (h) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Adv. Mater.* **1997**, *9*, 36.

(3) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664.

(4) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Chem. Mater.* **1996**, *8*, 2542.

(5) Kwon, O.; Coropceanu, V.; Gruhn, N. E.; Durivage, J. C.; Laquindanum, J. G.; Katz, H. E.; Cornil, J.; Brédas, J. L. *J. Chem. Phys.* **2004**, *120*, 8186.

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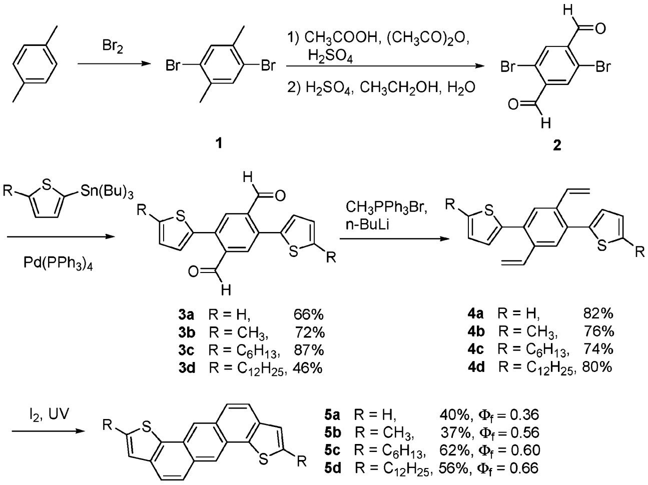
In this work, we were motivated by the hypothesis that bent anthradithiophenes (BADTs), structurally analogous to dibenz[*a*,*h*]anthracene, a structural isomer of pentacene, may also be of interest for organic electronics applications. BADTs are virtually unexplored[8] and there is no reported route to the parent unsubstituted compound. Swager and coworkers have developed aryl-functionalized derivatives using a chemical cyclization strategy; however, this is limited in scope.[9]

Here we report a new route to luminescent BADTs using an oxidative photocyclization-based synthetic strategy. This route also enables access to dialkyl-functionalized BADTs, with the alkyl groups modifying both the solubility and structural organization of the rigid BADT framework.

The synthetic route to 1,4-di(2-thienyl)-2,5-divinylbenzene **4a** and its alkylated derivatives **4b−d** is outlined in Scheme 1. Compounds **3a−d** were prepared via a Pd(0)-catalyzed Stille cross-coupling reaction between **2** and the appropriate 2-(tributylstannyl)thiophene. Wittig olefination of the dialdehyde species with methyltriphenylphosphonium bromide offered compounds **4a−d** in good yield. The BADTs **5a−d** were prepared by irradiating dilute benzene solutions of **4a−d** with UV light. Unlike the parent LADT and its alkylated derivatives, compounds **5a−d** are formed as single isomers and are readily soluble in common organic solvents at room temperature, thus enabling purification by column chromatography.

Scheme 1



Crystals of **5a** suitable for single-crystal X-ray diffraction (XRD) studies were grown from cold dichloromethane. The parent BADT is planar and shows a small extent of cofacial overlap between adjacent molecules (Figure 2). An interplanar distance of 3.46 Å indicates the presence of $\pi-\pi$ interactions along the intermolecular stacking axis. For comparison, dibenz[*a*,*h*]anthracene crystallizes into a herringbone arrangement ($P2_1$ or P_{cab}) with no intermolecular cofacial interactions.[10] Thus, the incorporation of thienyl groups appears to enhance π-stacking in the crystal lattice.

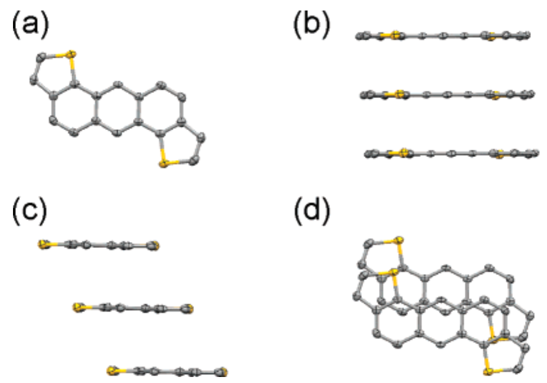


Figure 2. (a) Thermal ellipsoid plot of **5a**. (b) View down the short molecular axis of **5a**; the stacking axis is vertical. (c) View down the long molecular axis of **5a**; the stacking axis is vertical. (d) View down the stacking axis of two cofacial molecules of **5a**.

The XRD pattern of a thin film of **5a** prepared by vacuum evaporation (Figure 3a) exhibits two strong reflections corresponding to the (1,0,−1) and (2,0,−2) planes assigned from the diffraction pattern calculated from the single-crystal XRD data. The thin film is highly crystalline, with reflections indicating that the molecules in the thin film are oriented with their long molecular axes nearly perpendicular to the substrate surface, a phenomenon seen in oligothiophenes as well as in LADTs.[3,11]

Single crystals of **5d** were grown from cold chloroform and the structure was determined by XRD (Figure 4a). Functionalizing the thienyl α-positions with dodecyl chains imparts a larger degree of cofacial slipping along both the short and long molecular axes (Figure 4b). The interplanar stacking distance of 3.49 Å is indicative of $\pi-\pi$ interactions along the stacking axis.

In the solid state, the molecules are organized into a lamellar packing arrangement with the rigid central motif separated by dodecyl chains (Figure 4c). The XRD pattern of a thin film of **5d** prepared by vacuum evaporation exhibits six strong reflections that correspond to the (0,0,1) through (0,0,6) planes. The molecules are oriented with the long molecular axes inclined approximately 45° with respect to

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(6) (a) Payne, M. M.; Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 3325. (b) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986.

(7) Dickey, K. C.; Anthony, J. E.; Loo, Y.-L. *Adv. Mater.* **2006**, *18*, 1721.

(8) A different isomer than described here has been prepared; see: Shen, H.-C.; Tang, J.-M.; Chang, H.-K.; Yang, C.-W.; Liu, R.-S. *J. Org. Chem.* **2005**, *70*, 10113.

(9) (a) Tovar, J. D.; Swager, T. M. *J. Organomet. Chem.* **2002**, *653*, 215. (b) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578.

(10) (a) Iball, J.; Morgan, C. H.; Zacharias, D. E. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1271. (b) Iball, J. *Nature* **1936**, *137*, 361. (c) Krishnan, K. S.; Banerjee, S. *Z. Kristallogr.* **1935**, *91*, 173. (d) Robertson, J. M.; White, J. G. *J. Chem. Soc.* **1947**, 1001. (e) Robertson, J. M.; White, J. G. *J. Chem. Soc.* **1956**, 925.

(11) (a) Lovinger, A. J.; Davis, D. D.; Ruel, R.; Torsi, L.; Dodabalapur, A.; Katz, H. E. *J. Mater. Res.* **1995**, *10*, 2958. (b) Servet, B.; Horowitz, G.; Ries, S.; Lagorsse, O.; Alnot, P.; Yassar, A.; Deloffre, F.; Srivastava, P.; Hajlaoui, R.; Lang, P.; Garnier, F. *Chem. Mater.* **1994**, *6*, 1809.

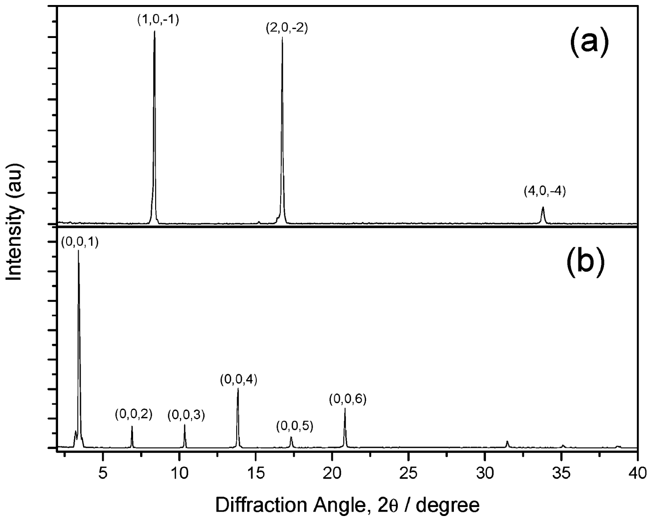

Figure 3. X-ray diffractograms of films of (a) **5a** and (b) **5d** on glass substrates deposited by vacuum evaporation.

the (0,0,1) plane that is parallel to the substrate surface. These reflections are consistent with those observed in films prepared from the didodecyl derivative of LADT,[3] suggesting that this compound packs into a similar arrangement as **5d**.

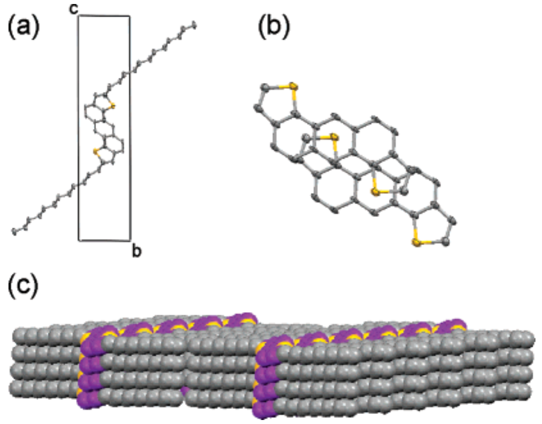

Figure 4. (a) Thermal ellipsoid plot of **5d**. View down the *a*-axis. (b) View down the "stacking axis" of two cofacial molecules of **5d** with dodecyl chains omitted. (c) Space-filling diagram of **5d** illustrating packing structure. Sulfur atoms are yellow, sp^3-hybridized carbon atoms are gray, and sp^2-hybridized carbons atoms are purple.

The solution-phase UV/vis absorption spectra of compounds **5a**−**d** (see Supporting Information) exhibit nearly identical features (λ_{max} between 304 and 311 nm), and are similar to the absorption spectrum of dibenz[*a*,*h*]anthracene,[12] although slightly red-shifted. Compounds **5a**−**d** exhibit blue luminescence in solution with emission maxima between 408 and 427 nm, and quantum yields (Φ_f) of 0.36−0.66 (see Scheme 1).

The higher energy peaks in the solid-state emission spectrum of the thin film of **5a** are similar to those found in the solution-phase spectrum of this compound (Figure 5a). At longer wavelengths, however, the emission intensity from the thin film is greater and a new peak is present at 486 nm. The emission spectrum of **5d** (thin film) is also red-shifted relative to solution. The broad red-shifted emission features are attributed to intermolecular interactions in the microcrystalline film,[13] and are possibly related to the $\pi-\pi$ stacking observed in the solid-state structures.

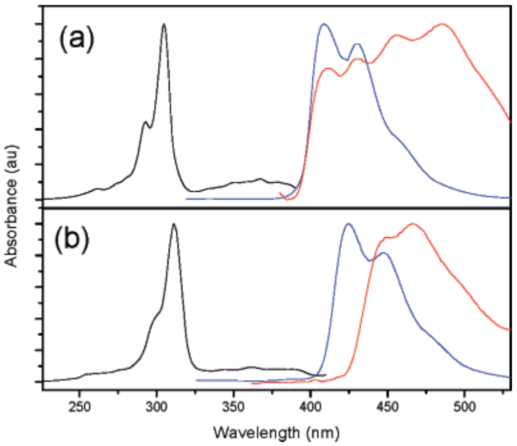

Figure 5. (a) Excitation spectrum of **5a** in solution (black). Emission spectrum of **5a** in solution (blue) and as a thin film (red). (b) Excitation spectrum of **5d** in solution (black). Emission spectrum of **5d** in solution (blue) and as a thin film (red).

In summary, we report here a new family of acenedithiophenes, the dithienyl[*a*,*h*]anthracenes, prepared via double oxidative photocyclization of precursors **4a**−**d**. Single-crystal and powder XRD studies demonstrate that films prepared via vacuum evaporation are highly crystalline with a preferred specific orientation relative to the substrate surface. Compounds **5a** and **5d** adopt packing motifs in the crystalline phase displaying different degrees of cofacial $\pi-\pi$ interactions, and show red-shifted emission spectra in the thin films relative to solution. The incorporation of these luminescent compounds into OLEDs and OFETs is being investigated.

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Supporting Information Available: Experimental procedures, spectroscopic data, and ^{1}H and ^{13}C spectra for all new compounds, as well as crystallographic data presented in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OL071387E

(12) Karcher, W.; Fordham, R. J.; Dubois, J. J.; Glaude, P. G. J. M.; Ligthart, J. A. M. *Spectral Atlas of Polycyclic Aromatic Compounds*; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1985.

(13) Dabestani, R.; Ivanov, I. N. *Photochem. Photobiol.* **1999**, *70*, 10.