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Isomerically Pure *syn*-Anthradithiophenes: Synthesis, Properties, and FET Performance

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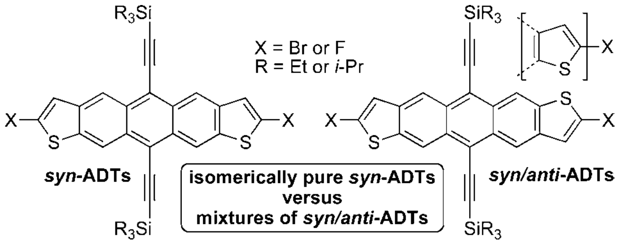
ABSTRACT



The synthesis of isomerically pure *syn*-anthradithiophene derivatives (*syn*-ADTs) is described. X-ray crystallography is used to compare the solid-state arrangement of *syn*-ADT derivatives 2a,b to the analogous mixture of *syn*- and *anti*-ADTs. Single-crystal OFETs based on isomerically pure *syn*-ADTs 2a,b display device performance comparable to those based on a mixture of ADT isomers *syn/anti*-2a,b with mobilities as high as 1 cm^2/(V s).

The synthesis of organic molecules for optoelectronic applications has seen exponential growth in the past decade with intense interest in photovoltaics,[1] OLEDs, and OFETs.[2] Many promising small molecule semiconductors are based on a hydrocarbon skeleton, such as pentacene and its derivatives.[2] The incorporation of heteroatoms into an acene framework, on the other hand, offers an opportunity to vary physical and electronic properties, and toward this goal many thienoacene-based small molecule semiconductors have been recently developed.[3] An important class of thienoacenes are the anthradithiophenes (ADTs, Figure 1), and ADTs with well-designed substitution patterns afford devices with intriguing performance in organic field-effect transistors (OFETs)[4] and organic photovoltaics (OPVs).[4i] In specific cases, functionalization of the ADT skeleton has been exploited, for example, to control solid-state ordering, improve stability, and facilitate thermal vacuum deposition for device fabrication.[5] A common substitution pattern for ADTs features ethynyl groups in the 5- and 11-positions and incorporation of alkyl, halogen, or cyano groups at the 2- and 8-positions.

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An important point of ADTs studied to date, however, is that they are nearly always formed as an inseparable mixture of *syn*- and *anti*-isomers. This is a result of a common synthetic approach in which a regiorandom aldol condensation is used for formation of anthradithiophenequinone precursors. During the course of the studies reported herein, however, two recent examples[6,7] of isomerically pure ADTs have appeared.[8]

We hypothesized that the formation and use of isomerically pure ADT derivatives might improve device performance. To test this hypothesis, we chose fluorinated ADTs **2a** and **2b** because earlier work with the *syn*/*anti* mixtures of these compounds has shown promising hole mobilities in OFETs, especially for ***syn*/*anti*-2a**.[4g,5b] We report here the synthesis of *syn*-ADTs (***syn*-2a**–**d**) and a comparison of performance for single-crystal OFET devices of pure *syn*-isomers versus the *syn*/*anti*-mixture of isomers for **2a** and **2b**.

The synthesis of halogenated *syn*-ADT derivatives (***syn*-2a**–**d**) begins from commercially available 3-thiophenecarboxaldehyde (**3**, Scheme 1). Attempts at regioselective monobromination at the 5-position of **3** proved to be difficult because of a significant amount of dibromination. Thus, thiophene **3** was dibrominated using excess bromine in the presence of $AlCl_3$ to afford **4**.[9] Protection of the aldehyde as an acetal using ethylene glycol provided **5**. The acetal acts as a directing group for the regioselective Li–halogen exchange, and subsequent trapping of aryllithium species with ethyl formate provides the differentially protected dialdehyde **6**. An aldol reaction between **7** and monoprotected thiophenealdehyde **6** (2.1 equiv) then afforded **8** in 89% yield. This reaction also sets the regiochemistry of the sulfur atoms toward forming *syn*-ADTs. The structure of **8** was determined by X-ray crystallography, confirming the desired geometry.[10]

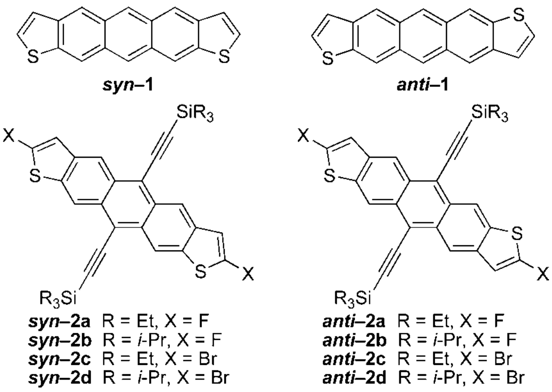

Figure 1. Structures of *syn*- and *anti*-ADTs **1** and **2a**–**d**.

Global deprotection of the three acetal groups of **8** was successfully achieved using $In(OTf)_3$ in acetone under reflux, and these conditions effected the subsequent aldol condensation to give dibromo-*syn*-anthradithiophenequinone **9**. The synthesis of **9** should be amenable to large scale, as the product precipitates directly from the reaction mixture and can then be collected in analytical pure form via filtration.

Addition of Li–acetylides to **9** afforded diols **10a**,**b** in modest yields. Aromatization of diols **10a**,**b** using $SnCl_2 \cdot 2H_2O$ and aqueous H_2SO_4 afforded functionalized ***syn*-2c**,**d** in near-quantitative yields (92–96%). Lithiation of ***syn*-2c**,**d** via Li–halogen exchange, followed by reaction with *N*-fluorobenzenesulfonimide (NFSI) provided fluorinated *syn*-ADTs ***syn*-2a**,**b**. Yields of ***syn*-2a**,**b** were moderate, and the pure ADTs were isolated from the numerous byproduct via column chromatography.

The thermal characteristics of ***syn*-2a**–**d** as well as ***syn*/*anti*-2a**,**b** have been examined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC, Table 1). Notably, the isomerically pure *syn*-ADT material has a slightly lower melting point (~10 °C) as observed by DSC analyses, whereas decomposition is observed at about the same temperature.

Single crystals of isomerically pure ***syn*-2a**,**b** suitable for X-ray crystallographic analysis were obtained from slow evaporation at 4 °C of dichloromethane solutions layered with acetone or from slow evaporation at −15 °C of *n*-pentane solutions layered with acetone. Analysis of these data revealed that the packing of ***syn*-2a**,**b** is remarkably similar to that reported for *syn*/*anti* mixtures of ***syn*/*anti*-2a**,**b**. In particular, the 2,8-difluoroanthra[2,3-*b*:7,6-*b*′]dithiophene

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(5) See, for example: (a) Facchetti, A.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Adv. Mater.* **2003**, *15*, 33–38. (b) Subramanian, S.; Park, S. K.; Parkin, S. R.; Podzorov, V.; Jackson, T. N.; Anthony, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 2706–2707. (c) Lee, W.-Y.; Oh, J. H.; Suraru, S.-L.; Chen, W.-C.; Würthner, F.; Bao, Z. *Adv. Funct. Mater.* **2011**, *21*, 4173–4181. (d) Gutzler, R.; Ivasenko, O.; Fu, C.; Brusso, J. L.; Rosei, F.; Perepichka, D. F. *Chem. Commun.* **2011**, *47*, 9453–9455.

(6) Geerts and co-workers reported the synthesis of isomerically pure *anti*-ADT derivatives with alkyl groups in the 2- and 8-positions, although to our knowledge no device data have been reported; see: Tylleman, B.; Vande Velde, C. M. L.; Balandier, J.-Y.; Stas, S.; Sergeyev, S.; Geerts, Y. H. *Org. Lett.* **2011**, *13*, 5208–5211.

(7) Anthony and co-workers have showed that amide substitution at the ADT 2- and 8-positions allows for selective crystallization of the *syn*- and *anti*-isomers and that regiochemistry has a significant impact on solar cell performance; see: Li, Z.; Lim, Y.-F.; Kim, J. B.; Parkin, S. R.; Loo, Y.-L.; Malliaras, G. G.; Anthony, J. E. *Chem. Commun.* **2011**, *47*, 7617–7619.

(8) Formation of structurally related *syn*-anthrabisbenzothiophenes has been reported; see: Lehnherr, D.; Hallani, R.; McDonald, R.; Anthony, J. E.; Tykwinski, R. R. *Org. Lett.* **2012**, *14*, 62–65.

(9) The synthesis of compound **4** has been previously reported using alternate procedures; see: (a) Clarke, J. A.; Meth-Cohn, O. *Tetrahedron Lett.* **1975**, *16*, 4705–4708. (b) Fourani, P.; Guilard, R.; Person, M. *Bull. Soc. Chim. Fr.* **1967**, 4115–4120. (c) van Beek, R.; Zoombelt, A. P.; Jenneskens, L. W.; van Walree, C. A.; de Mello Donegá, C.; Veldman, D.; Janssen, R. A. J. *Chem.—Eur. J.* **2006**, *12*, 8075–8083.

(10) See the Supporting Information for details.

Scheme 1. Synthesis of *syn*-Anthradithiophenes (***syn*-2a–d**)

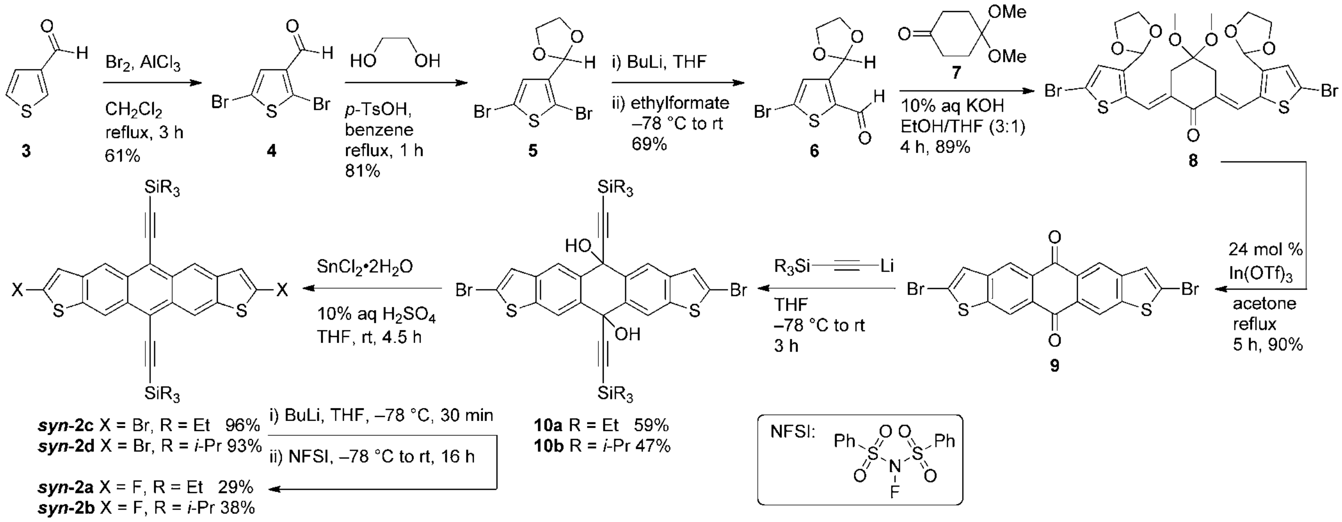

Table 1. Thermal Properties of ADTs ***syn*-2a–d** and ***syn/anti*-2a,b**[a]

			DSC decomposition	
compd	TGA T_d/°C	DSC mp/°C	onset/°C	peak/°C
***syn*-2a**	267	190	291	320
***syn/anti*-2a**	222	200	267	321
***syn*-2b**	296	239	341	370
***syn/anti*-2b**	278	247	345	369
***syn*-2c**	295	273	298	313
***syn*-2d**	315	315	350	NA

[a] Measured under nitrogen atmosphere.

group is disordered about the crystallographic inversion center (0, 1/2, 1/2), and the two inversion-related orientations of the molecule are present in equal abundance (both orientations are shown in Figure 2). The *i*-Pr$_3$Si derivatives also have disorder in the position of the alkyl carbons, whereas the Et$_3$Si derivatives do not.[10] Isomerically pure ***syn*-2a,b** pack with 2-D π-stacking, and there are two types of cofacial interactions with interplanar spacing of 3.30 Å and 3.41 Å for ***syn*-2a**, and 3.30 Å and 3.35 Å for ***syn*-2b** (Figure 2).[11] These values are nearly identical to those found for the solid-structure of ***syn/anti*-2a,b**, which are determined as 3.29 Å and 3.35 Å (***syn/anti*-2a**) and 3.29 Å and 3.34 Å (***syn/anti*-2b**).[12] Thus, isomeric purity has little effect on solid-state packing, as has been noted by others.[7]

Solution-state UV–vis absorption data (CH$_2$Cl$_2$, Figure 3) show that the lowest energy absorption maximum (λ_{max}) is located at 543 nm for Br derivatives ***syn*-2c,d**, while F derivatives ***syn*-2a,b** are hypsochromically shifted to 525 and 526 nm, respectively. The identity of silyl group has a more profound effect on the λ_{max} values of thin film samples of ***syn*-2a,b** cast from CH$_2$Cl$_2$.[10] In each case, λ_{max} values of thin films of Et$_3$Si derivatives [543 nm (***syn*-2a**) and 561 nm (***syn*-2c**)] are more red-shifted in comparison to the *i*-Pr$_3$Si derivatives [530 nm (***syn*-2b**) and 555 nm (***syn*-2d**)], which is, in principle, consistent with solid-state packing observed in the crystallographic analysis. Overall, however, solution- and solid-state absorption properties of ***syn*-2a,b** are not significantly affected by the isomeric purity of the material in comparison to ***syn/anti*-2a,b**.[13,14]

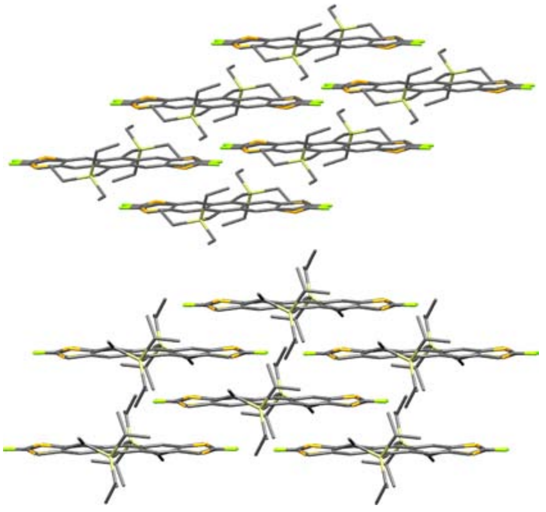

Figure 2. Crystal packing of ***syn*-2a** (top) and ***syn*-2b** (bottom).

Single crystals of isomerically pure ***syn*-2a** and ***syn*-2b** and of isomers ***syn/anti*-2a** and ***syn/anti*-2b** were grown by physical vapor transport,[15] and their electrical properties were compared using field-effect transistor (FET) measurements. Figure 4 shows the evolution of the drain

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(11) Interplanar distances were calculated as the distance between planes generated from the atoms of each anthradithiophene moiety. Because of the positional disorder in the thiophenes, this results in 26 atoms for each plane instead of 20 atoms found in the anthradithiophene moiety.

(12) Calculated using CIFs of ref 5b.

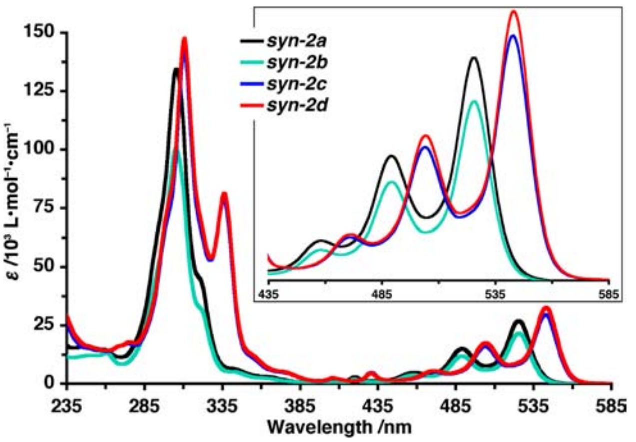

Figure 3. UV−vis absorption spectra of ***syn*-2a**−**d** in CH_2Cl_2.

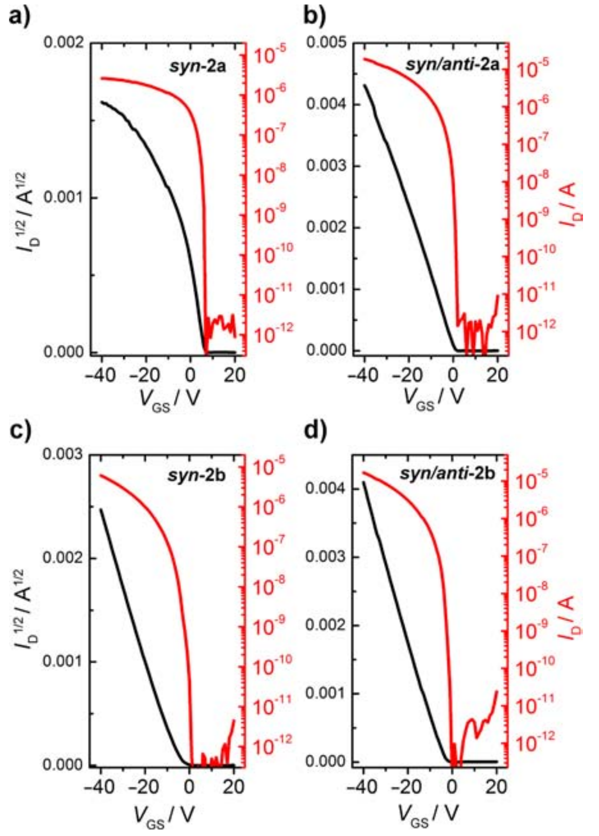

Figure 4. Drain current (I_D) versus gate-to-source voltage (V_{GS}) in the saturation regime for a representative single crystal FET fabricated with (a) ***syn*-2a** (L/W = 100/102), (b) ***syn*/*anti*-2a** (L/W = 100/140), (c) ***syn*-2b** (L/W = 100/210), and (d) ***syn*/*anti*-2b** (L/W = 100/350) in red. The slope of square root of I_D (black) was used to estimate mobility.[10]

current (I_D) with the gate-to-source voltage (V_{GS}) in the saturation regime (drain-to-source voltage V_{DS} = −40 V) for compounds **2a** and **2b**, respectively. All devices investigated here presented excellent electrical characteristics,[10] with a very sharp turn on and current on/off ratios greater than 10^6. We could not detect any significant difference in performance between devices based on isomerically pure *syn*-material compared to mixtures of *syn*/*anti*-isomers. The charge-carrier mobilities determined for the devices presented in Figure 4 are as follows: 1.07 cm^2/(V s) for ***syn*-2a**, 1.01 cm^2/(V s) for ***syn*/*anti*-2a**, 0.30 cm^2/(V s) for ***syn*-2b**, and 0.41 cm^2/(V s) for ***syn*/*anti*-2b**. These mobility values are typical for each compound and agree well with previous reports on single crystals of *syn*/*anti*-isomers.[4g] The improved device performance of the Et_3Si versus *i*-Pr_3Si-ADT devices (***syn*-2a** versus ***syn*-2b**, respectively) is due to the improved π-stacking overlap, as observed in the X-ray data.

In summary, the synthesis of isomerically pure *syn*-anthradithiophenes has been developed. The bromide moieties of ***syn*-2c**,**d** ADTs allow for further synthetic derivatization to give fluorinated ***syn*-2a**,**b**, and additional modes of functionalization for ***syn*-2c**,**d** are easily foreseen through metal-catalyzed coupling reactions. Initial comparisons of physical properties of ***syn*-2a**,**b** versus those of ***syn*/*anti*-2a**,**b** show that the physical properties of the two classes are remarkably similar, as established by X-ray crystallography, UV−vis spectroscopy, and thermal analysis. The performance of ***syn*-2a**,**b** and ***syn*/*anti*-2a**,**b** in single-crystal OFET devices is comparable, showing mobility values of ca. 1 cm^2/(V s) for **2a** and ca. 0.4 cm^2/(V s) for **2b**. The lack of difference between devices based on isomerically pure *syn*-ADTs and *syn*/*anti*-ADTs is likely attributed to the fact that both materials suffer from similar positional disorder of the thiophene moieties in the solid state.

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Supporting Information Available. Experimental procedures, spectroscopic data, ^1H and ^{13}C NMR spectra for all new compounds, FET device characteristics; summary of crystallographic data and CIF file for compounds ***syn*-2a**,**b** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) UV−vis data of ***syn*/*anti*-2a**,**b**, see refs 4g and 5b.

(14) The synthesis of ***syn*/*anti*-2c**,**d** has been reported for use as a polymeric building block; see: Okamoto, T.; Jiang, Y.; Qu, F; Mayer, A. C.; Parmer, J. E.; McGehee, M. D.; Bao, Z. *Macromolecules* **2008**, *41*, 6977–6980. No UV−vis data are reported.

(15) For additional details on the crystal growth technique, see ref 4g.