

Functionalized Tetrathienoanthracene: Enhancing $\pi-\pi$ Interactions Through Expansion of the π -Conjugated Framework

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Supporting Information

ABSTRACT: The functionalization of tetrathienoanthracene (TTA) with bromine and 2-hexylthiophene moieties is described, and their influence at both the molecular and solid-state level has been investigated. Comparative optical and electrochemical studies indicate an increase in conjugation for the thiophene derivative compared to the parent TTA. In the solid state, these materials form slipped π -stack structures with a number of close intermolecular contacts. Comparison of the two structures reveals a more steeply inclined slipped π -stack for the thiophene derivative resulting in a closer interplanar separation. This, coupled with the extended molecular framework, leads to an enhanced number of π - π interactions within the stack. The combination of increased conjugation



at the molecular level, and π -stacked structures with strong intermolecular communication at the solid-state level, augurs well for the use of TTA materials in optoelectronic applications.

INTRODUCTION

Organic semiconductors (OSC), both molecular and polymeric, have seen significant development over the past two decades owing to their potential use in next-generation electronic devices. With regard to polymeric materials, most consist of one-dimensional (1D) chains in which delocalization occurs through the polymer backbone, facilitating efficient movement of charge carriers and excitons along the chain. Unfortunately, polymer films tend to be disordered in the bulk, resulting in a decrease in the effective conjugation due to twisting of the polymer backbone. Since the charge mobility is largely anisotropic in 1D conjugated polymers, this disorder limits the total electronic communication. In the case of molecular materials, a particularly important requirement for the realization of high performance thin film optoelectronic devices is tight π -stacking interactions, which provide a pathway for charge transport. For example, field effect transistors (FETs) based on small molecules (e.g., pentacene)¹ generally attain higher mobilities compared to polymer-based devices owing to the crystallinity and, hence, morphology of the OSC. It is anticipated that expanding the dimensionality of conjugated systems should increase the degree of intermolecular communication and enhance the carrier mobility while diminishing the anisotropy associated with polymeric systems.^{2,3}

The development of "star-shaped" conjugated molecules, where the dimensionality is extended in two or three dimensions through a central core unit, leads to materials with physical properties that can be markedly different from their simple, linearly conjugated analogues.⁴ In recent years, a great deal of effort has been dedicated to the development of two- and three-dimensional (2D and 3D) conjugated molecules where oligothiophenes are covalently linked to a central benzenic core (1, Chart 1).^{5–14}

When the oligothiophene arms are attached to a rigid core (e.g., trithienothiophene, 2), tight π -stacking interactions are observed, and, in thin films, the molecules are oriented parallel to the surface of the substrate, maximizing the absorbance of incident light (sought-after properties for photovoltaic applications).¹⁵ In that regard, tetrathienoanthracene (TTA, 3) represents an ideal structure for a central core unit in star-shaped conjugated materials. Not only does it possess a planar, delocalized π -electron system, it has been shown to form a highly organized 2D thin film network and possesses high thermal stability in air.¹⁶ Herein we report the preparation and characterization of TTA functionalized with halogens (3c) and thiophenes (3d). It is anticipated that extending the conjugation in 2D, through the attachment of thiophene moieties, will favor close π -stacking interactions and, hence, enhance charge transport. Comparative studies with the alkylated parent compound (3b) by cyclic voltammetry, UV-vis, and fluorescence spectroscopy were performed to investigate the effect that "expanding" the conjugation of the TTA core has on the



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optoelectronic properties. The solid-state structures were studied by X-ray crystallography and revealed a number of close $\pi - \pi$ contacts in 3d compared to the brominated derivative 3c.

EXPERIMENTAL SECTION

General Procedures and Starting Materials. The reagents palladium chloride and triphenylphosphine were obtained commercially and used as received. Compounds 4b and 3b were prepared as outlined in the literature.¹⁶ All reactions were performed under an atmosphere of dry nitrogen. Melting points are uncorrected. ¹H NMR spectra were run in CDCl₃ solutions at 50 °C on a Bruker Avance 500 MHz Wide Bore spectrometer. Infrared spectra were recorded on a Nicolet Avatar FTIR spectrometer at 2 cm⁻¹ resolution using KBr optics and a nujol mull. UV-vis spectra were measured with a Varian Cary-100 spectrophotometer, and the fluorescence spectra were obtained using a Photon Technology International (PTI) spectrofluorimeter. Both UV-vis and fluorescence spectra were measured on dichloromethane solutions with a 1 cm precision quartz cuvette. Sublimation of 3c was carried out on an ATS series 3210 three-zone tube furnace, mounted horizontally, and linked to a series 1400 temperature control system.

Electrochemistry. Cyclic voltammetry was performed using a Princeton Applied Research (PAR) VersaSTAT 3 potentiostat/ galvanostat/frequency response analyzer and V3-Studio electrochemical software (V 1.0.281 (c) 2008 PAR) employing a glass cell fitted with platinum electrodes. The measurements were carried out on dichloromethane solutions (dried by distillation over CaH₂) containing 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich) as supporting electrolyte with a scan rate of 100 mV/s. The experiments were referenced to the Fc/Fc⁺ couple of ferrocene at +0.48 V vs SCE.¹⁷

Crystal Growth. Because of its virtual insolubility in organic solvents, compound **3c** was purified by zone sublimation at 10^{-4} Torr along a temperature gradient of 420-300-260 °C using an ATS series 3210 three-zone tube furnace, mounted horizontally, and linked to a series 1400 temperature control system. The resulting yellow needles were suitable for X-ray analysis. Yellow needles of **3d** suitable for X-ray analysis were grown by slowly cooling a saturated dichloroethane solution. Compound **3d** is soluble in most chlorinated solvents; however, attempts to grow crystals suitable for X-ray analysis were only successful from dichloroethane; other chlorinated solvents provided microcrystal-line material.

Crystallography. Compounds 3c and 3d consistently produced very small crystals. The presented results are the best from a series of data collection attempts. Crystals of 3c were mounted on thin glass fibers using epoxy glue and the data were collected at room temperature (25 °C). A crystal of 3d was mounted on a thin glass fiber with oil and cooled to -73 °C prior to data collection.

Data acquisition was carried out on a Bruker AXS KAPPA single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) and APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.¹⁸ Diffraction data for 3c were collected with a sequence of $0.5^{\circ} \omega$ scans at 0° , 120° , and 240° in ϕ . Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. The significantly weaker diffraction of 3d required a considerable increase in the exposure time as well as the collection of thinner $0.3^{\circ} \omega$ scans at 0° , 90° , 180° , 270° in ϕ . Initial unit cell parameters were determined from 320 data frames of the original data set positioned at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.¹⁹ Systematic absences in the diffraction data set and unit-cell parameters for both 3c and 3d were consistent with monoclinic $P2_1/n$ (alternative setting of $P2_1/c$ No. 14) space group. Solutions in this centrosymmetric space group yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2 . In both crystal structures molecules of the compounds are

situated at the inversion center, and all non-hydrogen atoms were refined anisotropically with satisfactory thermal parameter values. Solution of the structure for 3d revealed the positional disorder for one of the alkyl chains. Disordered fragments are located in general positions and are not related by any symmetry elements. Occupational factors for the disordered fragments were successfully modeled with a 1:1 ratio with stable refinement results. However, in order to obtain satisfactory thermal parameters, and due to the low data to parameter ratio of the collected data set, a set of SIMU restraints was used in the refinement of the disordered moiety. Positions of all hydrogen atoms were obtained from the Fourier map analysis; nonetheless, all hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library with the latest version (v.6.12) being used.²⁰ Crystallographic data and selected data collection parameters are reported in Table S1, Supporting Information.

Preparation of 3c. Compound 3c was prepared as outlined in the literature.¹⁶ Purification of the crude yellow-green powder involved washes with 10% aq. HCl, saturated aq. sodium bicarbonate solution, and MeOH followed by fractional sublimation at 10^{-4} Torr along a temperature gradient of 420-300-260 °C. The resulting yellow needles were suitable for X-ray analysis; mp > 350 °C. IR: 1546.11 (m), 1482.93 (s), 1457.41 (s), 1429.82 (w), 1406.58 (w), 1392.24 (w), 1377.11 (m), 1304.20 (w), 1297.96 (m), 1262.48 (w), 1185.63 (w), 1128.94 (w), 978.63 (w), 971.77 (w), 960.91 (m), 913.36 (s), 860.06 (s), 816.64 (m), 800.24 (s), 722.01 (w), 697.16 (w), 655.41 (w), 613.36 (m), 559.32 (m), 494.10 (s), 434.07 (s) cm⁻¹. Anal. Calcd for C₂₂H₆S₄Br₄: C, 36.79; H, 0.84. Found: C, 36.75; H, 1.00. Given the low solubility of this compound, ¹H and ¹³C NMR spectroscopy was not possible. The identity of this compound was confirmed by elemental analysis and X-ray crystallography.

Preparation of 3d. 4b (0.764 g, 1.67 mmol) was added to a slurry of **3c** (0.200 g, 0.278 mmol), PdCl₂ (10 mg, 0.0564 mmol), and PPh₃ (30 mg, 0.114 mmol) in degassed DMF (0.45 mL) and the reaction mixture was set to heat at 130 °C under N₂. After 16 h, hexanes were added to the reaction flask and the crude product was filtered off and washed with hexanes, crude yield 0.218 g (0.204 mmol, 73%). The crude material was washed with hot EtOAc and recrystallized from DCE to afford yellow needles (0.155 g, 0.145 mmol, 71%); dec > 200 °C. ¹H NMR (δ, CDCl₃, 50 °C): 7.88 (2H, s), 7.16 (4H, s), 7.00 (4H, d, *J* = 3.2 Hz), 6.65 (4H, d, *J* = 3.4 Hz), 2.82 (8H, t, *J* = 7.5 Hz), 1.76 (8H, m, *J* = 7.6 Hz), 1.52–1.33 (24H, m), 0.96 (12H, t, *J* = 7.1 Hz). Anal. Calcd for C₆₂H₆₆S₈: C, 69.74; H, 6.23. Found: C, 69.54; H, 6.04. Given the low solubility of this compound was confirmed by ¹H NMR spectroscopy, elemental analysis, and X-ray crystallography.

RESULTS AND DISCUSSION

Synthesis. Our first attempts to prepare 3d were focused on 4-fold Stille coupling of tetrabromobenzene with 5-hexyl-5'tributylstannyl-2,2'-bithiophene followed by oxidative cyclodehydrogenation with FeCl₃, analogous to the synthesis of the parent compound 3b.^{16,21} Unfortunately, an uncharacterizable solid was isolated, which may be attributed to side reactions of the β -thienyl positions generating a complicated mixture of materials.²² To circumvent these challenges, focus shifted to preparation of the TTA core prior to functionalization. Following the route outlined in Scheme 1, 5a was prepared via Stille coupling of 4a with tetrabromobenzene. Subsequent treatment with NBS followed by oxidative cyclization with FeCl₃ afforded the brominated derivative 3c.²³ Although 3c is essentially insoluble, coupling reactions with solubilizing alkylthiophenes is possible, as 4-fold Stille coupling of 3c with 4b proved successful, providing a general procedure to the functionalization of TTA. We are currently exploring the versatility of this route via the attachment of longer oligothiophenes. Using this approach, the peripheral substituent may be easily altered, and

Scheme 1. Synthesis of Functionalized Thienoanthracenes^a



^aReagents and Conditions: (a) 1,2,4,5-tetrabromobenzene, PdCl₂(PPh₃)₂, DMF, 130 °C; (b) NBS, THF, RT; (c) FeCl₃, MeNO₂/chlorobenzene, RT; (d) **4b**, PdCl₂(PPh₃)₂, DMF, 130 °C.

Table 1. Theoretical,^{*a*} Electrochemical,^{*b*} and Photophysical^{*c*} Properties for 3b and 3d

3b	3d
-5.21	-5.12
3.35	2.95
1.15	0.94
-5.33	-5.11
431	475
440	493
2.83	2.52
435	490
0.03	0.08
	3b -5.21 3.35 1.15 -5.33 431 440 2.83 435 0.03

^{*a*}DFT/B3LYP/6-311G(d,p) level of theory where R = Me. ^{*b*}In DCM, 0.1 M *n*Bu₄NPF₆ as supporting electrolyte, referenced to the Fc/Fc⁺ couple of ferrocene at +0.48 V vs SCE.¹⁷ ^{*c*}Measurements performed in DCM. ^{*d*}Derived using expression from ref 25. ^{*e*}Calculated from λ_{edge} . ^{*f*}In DCM, upon excitation at 320 nm for **3b** and 380 nm for **3d**.

thus the electronic characteristics and solid-state properties of target molecules can be tuned.

Electrochemical and Spectroscopic Studies. To investigate the influence additional thiophene moieties have on the optoelectronic properties of TTA, electrochemical and optical spectroscopy studies were performed on dichloromethane solutions of 3b and 3d; the results are summarized in Table 1.²⁴ Cyclic voltammetry (CV) of 3d revealed a single quasi-reversible redox process corresponding to the formation of the radical cation (Supporting Information Figure S2). Unlike the behavior of the parent compound 3b, 3d does not exhibit a second oxidation process under the conditions used. The oxidation potential of 3d is shifted in the cathodic direction by 0.21 V with respect to 3b resulting from the increase in conjugation length, which has been observed in other star-shaped conjugated molecules with extended oligothiophene arms.¹⁵ This behavior is supported by DFT calculations on the R = Me derivatives of **3b** and **3d** at the B3LYP/6-311G(d,p) level. Comparison of the two molecules demonstrates that the energy of the HOMO of 3d (R = Me) is raised by 0.09 eV due to the extension of conjugation into 2D (Table 1).

Optical spectroscopy provides further evidence of increased effective π -conjugation through the attachment of thiophene units to the TTA core. A bathochromic shift of ~55 nm is observed in the absorption and emission spectra for 3d with respect to 3b (see Table 1 and Figure 1). On the basis of the onset of UV–vis absorption, the addition of thiophene moieties leads to a decrease in the optical band gap of 0.31 eV (3b \rightarrow 3d). Furthermore, the absorption and emission profiles for 3d



Figure 1. Absorption (solid line) and emission spectra (dotted line) of 3b (green) and 3d (blue).

are similar to that of **3b**; however, a much less defined vibronic structure is observed. This may be attributed to a less rigid structure due to the flexibility of the periphery thiophene moieties.²² Comparison of the Stokes shifts reveals a slightly larger energy for **3d** and may also be explained by molecular flexibility; however, the difference is minimal and, when compared to fused thienoacenes (e.g., 0.28 eV for pentathienoacene),²⁶ is indicative of little structural distortion upon excitation. This also strongly suggests that the reorganization energy of the charge carrier (polaron or radical cation), which limits the intrinsic mobility of OSCs, will be low.

X-ray Crystallography. Long-range molecular ordering is of paramount importance to obtain high charge carrier mobilities in OSCs.²⁷ In particular, the degree of π -orbital overlap is expected to strongly influence the mobility, as has been illustrated in structurally related pentacene derivatives.²⁸ To shed light on supramolecular organization and the effect of "widening" the π -conjugated core, single crystals of **3c** and **3d**

Table 2. Crystal Data for 3c and 3d

	3c	3d
formula	$C_{22}H_6Br_4S_4$	$C_{31}H_{33}S_4$
fw	718.15	533.81
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	13.9674(6)	5.9663(6)
b (Å)	3.9096(2)	25.007(3)
c (Å)	19.9845(9)	18.1843(15)
β (deg)	106.906(3)	95.154(3)
V (Å ³)	1044.13(8)	2702.1(4)
Ζ	2	4
$D_{\rm calc}~({\rm mg}/{\rm m}^3)$	2.284	1.312
T (K)	298	200
$\mu \text{ (mm}^{-1})$	8.119	0.371
$2\theta_{\max}$ (deg)	56.62	37.70
no. of total reflections	10037	13041
no. of unique reflections	2536	2119
R _{int}	0.0306	0.0540
R_1 , wR_2 (on F^2)	0.0474, 0.1270	0.0494, 0.1217
$\tau \; (\deg)^a$	65.48(2)	34.34(2)
δ (Å) ^b	3.557(1)	3.365(2)

" τ is the tilt angle between the mean molecular plane and the stacking axis. ^b δ is the mean interplanar separation between molecules along the π -stack.

have been analyzed by X-ray diffraction (Table 2). Similar to the protonated parent compound 3a,¹⁶ crystals of 3c and 3d



Figure 2. Unit cell (top) and slipped π -stack (bottom) drawings of 3c (left) and 3d (right). In the π -stacked structure of 3d the hexyl chains are omitted for clarity. For 3c (left), close intermolecular contacts between stacks are shown; Br---Br' contacts are shown in brown; Br---S' are in purple; S---S' are in red.

belong to the monoclinic space group $P2_1/n$ and consist of slipped π -stacks (along y and x) which are aligned in herringbone arrays running along the z- and y-directions, respectively. Two views of the crystal structures, showing the unitcell packing and the slipped π -stacked structure, are provided in Figure 2. These molecules are essentially planar as the core atoms show minimal displacement from the mean plane (0.0211 Å and 0.0213 Å for 3c and 3d, respectively) formed by the 26-atom TTA core. In the case of the brominated derivative 3c, close S---S' (3.669(2) Å), Br---Br' (3.676(1) Å), and S---Br' (3.660(1) Å) contacts exist laterally between the herringbone ribbons, as shown in Figure 2. Such Br---Br' and S---Br interactions have been observed in other bromo-substituted π -conjugated organic molecules.²⁹⁻³³ Their influence on the packing arrangement of these types of materials is difficult to assess as the solid-state structure results from a balance between $\pi - \pi$ and dipole-dipole interactions, among other factors.^{32,34} Similar interactions were also observed in 2D arrays of 3c when measured at the liquid/solid interface, although when confined to a graphite surface the monolayers form a more tightly packed structure (i.e., shorter contacts).³⁵ Additional S---C' interactions also exist along the slipped π -stacks (see Figure 3).

Interestingly, although the replacement of bromine substituents with hexylthiophene moieties introduces the potential for distortion through the flexibility of the C-C bond between the TTA core and the substituents, only a slight propeller-like distortion with dihedral angles of $4.3(4)^{\circ}$ and $7.8(3)^{\circ}$ from the mean plane for the two unique thiophene moieties is observed in the crystal structure of 3d. Furthermore, as is apparent from Figure 2, the hexyl substituents in 3d form an interdigitated network along the herringbone array, and, consequently, the degree of lateral communication is diminished in 3d compared to 3c. A similar motif was observed in thin films of the parent compound 3b where the molecules formed monolayers consisting of a highly oriented 2D structure held together by interactions between the interdigitated hexyl chains.¹⁶ Interdigitation or alkyl-alkyl interactions are commonly observed in the solid state for alkyllated π -conjugated molecules;^{36–38} however, whether the packing arrangement is dominated by the alkyl-alkyl or $\pi - \pi$ interactions is very difficult to determine and is dependent on many factors (e.g., the size and shape of the conjugated core, length and number of alkyl substituents, etc). For example, Wang et al. attributed the packing arrangement of a dodecyl functionalized pyrazinoquinoxaline to the alkyl–alkyl interactions rather than the stacking of π -planes due to the lack of $\pi - \pi$ interactions between the conjugated cores and the completely parallel and overlapped dodecyl chains which maximizes the alkyl-alkyl interactions.³⁷ Conversely, a "layer-by-layer" structure with alternating alkyl chains and arene cores was observed with strong intermolecular $\pi - \pi$ inter-



Figure 3. Crystal structure of (a) **3c** and (b) **3d** showing atom numbering and close intermolecular contacts along the π -stacks. S---S' contacts are shown in red; S---C' are in green; C---C' are in blue. Hexyl chains omitted for clarity in (b).

actions when *n*-propyl substituents were attached to a fused thienoacene core.³⁶ In the case of **3d**, the packing arrangement appears to result from a delicate balance between the alkyl– alkyl interactions coupled with $\pi - \pi$ orbital overlap (vide infra).

The inclusion of hexylthiophene moieties at the periphery of the TTA core results in more steeply inclined π -stacks compared to the brominated derivative (Table 2; Figures S3 and S4). The larger degree of inclination, quantified in terms of the slippage angle τ — a smaller angle value of τ indicates a higher degree of slippage — leads to a decrease in the interplanar separation between molecules ($\delta_{3c} > \delta_{3d}$). Recently, a report on seven-ring-fused dibenzothienotetrathiophenes functionalized with ethyl and hexyl substituents found a similar observation of a greater degree of slippage and decrease in interplanar separation with increase in alkyl chain length.³⁹

The diminishing of the interplanar separation, coupled with the larger molecular framework, results in an increase in the number of close contacts within the slipped π -stacks for 3d which are within or nominally larger than the van der Waals separation, as shown in Figure 3.⁴⁰ Interestingly, 3d, the compound with the flexible substituents, has a slippage angle and interplanar distance that is more comparable to the parent compound 3a than the brominated derivative 3c (δ_{3a} = 3.354(3) Å, $\tau_{3a} = 41.79(1)^{\circ}$).¹⁶ The observation of a number of $\pi - \pi$ contacts in 3d, even though the molecules are more steeply inclined than 3a and 3c, may be attributed to the extended π -conjugated core; that is, the potential for $\pi - \pi$ interactions is increased due to the larger molecular framework. Similar results were observed by He et al. when they compared the crystal packing arrangement of decyl substituted linearly fused tetrathienoacene and pentathienoacene.³⁸ In both structures the alkyl-alkyl interactions dominate the crystal packing motif; however, the larger conjugated framework of pentathienoacene afforded $\pi - \pi$ interactions, whereas very little π -orbital overlap was reported for tetrathienoacene.

CONCLUSIONS

To summarize, a general route for the synthesis of thiophene functionalized tetrathienoanthracenes has been developed. The effect of "widening" the conjugation of the thienoacene core on the optoelectronic properties and solid-state structure was investigated by cyclic voltammetry, UV-vis and fluorescence spectroscopy, and X-ray crystallography. On the basis of these studies, we can conclude that attachment of thiophene moieties to the periphery of TTA leads to an increase in the effective conjugation as evidenced by the bathochromic shift in the absorption profile and reduced oxidation potential compared to the alkylated derivative 3b, and is supported by DFT calculations. Along with the relatively small Stokes shift, which implies that little structural reorganization occurs upon excitation, these results augur well for enhanced charge transport. X-ray crystallography reveals a less superimposed π -stack for 3d compared to 3c, and an interplanar separation between molecules less than the sum of van der Waals radii of carbon (3.4 Å). Since the planar molecular framework of 3d is extended out to the peripheral thiophene moieties, a number of close contacts within the π -stacks exist. The favorable intermolecular interactions observed in the solid state, coupled with the extended π -conjugation, bode well for the use of this material in device applications. To that end, further studies are needed to investigate the thin film morphology of the thiophene functionalized TTA, and implementation into FET devices is required to determine the hole mobility; such investigations are currently being pursued.

ASSOCIATED CONTENT

S Supporting Information

¹H NMR spectrum of 3d; CVs and DFT archival files for 3b and 3d; CIF files and illustrations of τ and δ for 3c and 3d. This material is available free of charge via the Internet at http://pubs.acs.org.

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