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Synthesis and Characterization of Unsymmetric Indolodithienopyrrole and Extended Diindolodithienopyrrole

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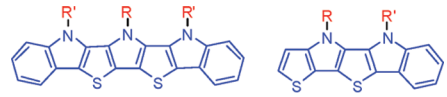
ABSTRACT



R = phenyl, 4-hexylphenyl
R' = H, CH_3

Indole-fused dithieno[3,2-*b*:2′,3′-*d*]pyrrole-based unsymmetrical and extended heteroacenes were synthesized and characterized. Solid-state structures were examined using single-crystal X-ray diffraction to understand their packing behavior. The optical and electrochemical properties of these new heteroacenes are also described in detail.

Ladder-type π-conjugated systems with fused-rigid backbones are actively explored in organic electronic applications.[1] Pentacene and its derivatives have shown a hole mobility of ~3 $cm^2 \cdot V^{-1} \cdot s^{-1}$.[2] Unfortunately, pentacene and higher acenes are unstable and undergo photo-oxidation due to their high-lying HOMO and narrow band gap.[3] Such higher [*n*]acenes also exhibit poor solubility in common solvents, which limits their processability.[4] The incorporation of heteroatoms and solublizing groups has been part of the ongoing efforts to prepare new [*n*]acene analogues with improved device performances.[5] These heteroacenes with low HOMO level offer stability to the fused ring systems.[6] Furthermore, easy functionalization on the heteroatoms (e.g., N, P, Si) allows for facile derivatization[7] and incorporation of substituents designed to tune the molecular organization and solubility.[8] Heteroacenes are expected to possess better organic field effect transistor (OFET) performance[9] due to

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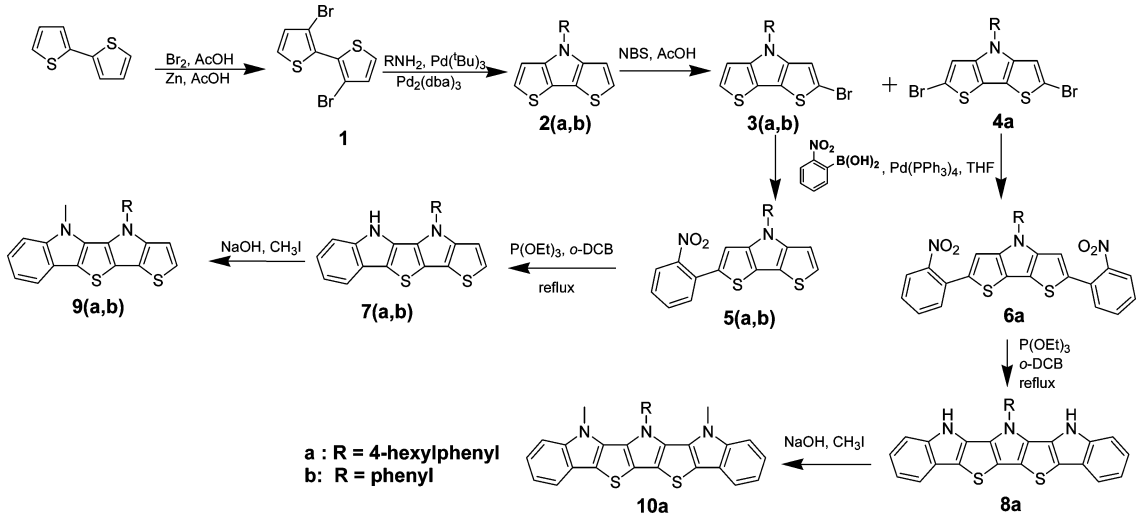
Scheme 1. Synthesis of Unsymmetrical and Extended Heteroacene



secondary interactions such as hydrogen bonding, π-stacking, and sulfur−sulfur (S···S) interactions originating from the high polarizability of sulfur electrons in thiophene rings.[10] Thiophene-based dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) represents a promising class of semiconducting materials because of their fused-rigid backbone and good molecular planarity.[11] Thiophene- and pyrrole-based symmetrical heteroacenes were also successfully tested for OFET applications.[12] Most of the reported heteroacenes (five rings fused) are symmetrical in nature.[13] Only a few unsymmetrical heteroacenes[14] and extended heteroacenes have been reported.[15] In this regard, a series of unsymmetrical indolodithienopyrroles (**7**, **9**) and the extended (seven-fused ring) diindolodithienopyrroles (**8**, **10**) were synthesized. Their photophysical and electrochemical properties along with their molecular organization in the crystal lattice are presented in this study.

The synthetic route leading to the unsymmetrical and extended heteroacenes is presented in Scheme 1. The palladium-catalyzed ($Pd_2(dba)_3$/P^tBu_3) amination of 3,3′-dibromo-2,2′-bithiophene **1** with excess (1.4 equiv) aniline/4-hexyl aniline afforded DTP in 60% yield. Only aryl substituents were incorporated as the alkyl-substituted bromo-DTPs were unstable.[16] It was postulated that the presence of the CH group α to N in the *N*-alkyl derivatives plays a role in the decomposition of the brominated product. The dibromination of DTP was carried out by following a reported procedure.[16] Monobromination of DTP was achieved by the addition of 1.2 equiv of *N*-bromosuccinimide (NBS) under nitrogen atmosphere. Reactions under normal conditions led to decomposed products as indicated by the presence of black insoluble particles. By applying an inert nitrogen atmosphere throughout the reaction, decomposition was avoided, and compound **3** was obtained in a reasonable yield (45%). The dibrominated product **4** was also isolated (20%) during the reaction along with the unreacted starting material **2**. Suzuki coupling of **3a**, **3b**, and **4a** was carried out with 2-nitrophenyl boronic acid (NBA) to obtain compounds **5a**, **5b**, and **6a**, respectively. Suzuki coupling of 2,6-dibromo-*N*-phenyldithieno[3,2-*b*:2′,3′-*d*]pyrrole resulted in an insoluble product. Hence the synthesis of **8b** and **10b** becomes unfeasible. The thienopyrrole-based heteroacenes were prepared by reductive Cadogan cyclization.[17] Refluxing the compounds **5** and **6** with excess of triethyl phosphite and 1,2-dichlorobenzene for 24 h resulted in the target compounds **7** and **8**, respectively, in around 35% yield. *N*-Methyl products, **9** and **10**, were obtained by reacting **7** and **8** with

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iodomethane. Structures of the synthesized compounds were confirmed by ^{1}H NMR, ^{13}C NMR spectroscopy, and high-resolution mass spectrometry. These heteroacenes are highly soluble in organic solvents which is a useful property for thin film processing. Single crystals of **9b** and **10a** suitable for single-crystal X-ray analysis were obtained by slow evaporation from a mixture of hexane and dichloromethane at room temperature. The detailed crystallographic information of **9b** and **10a** are given in the Supporting Information.

The unsymmetrical heteroacene **9b** is not planar, as it deviates 12° from planarity (Figure 1A and 1B). The phenyl

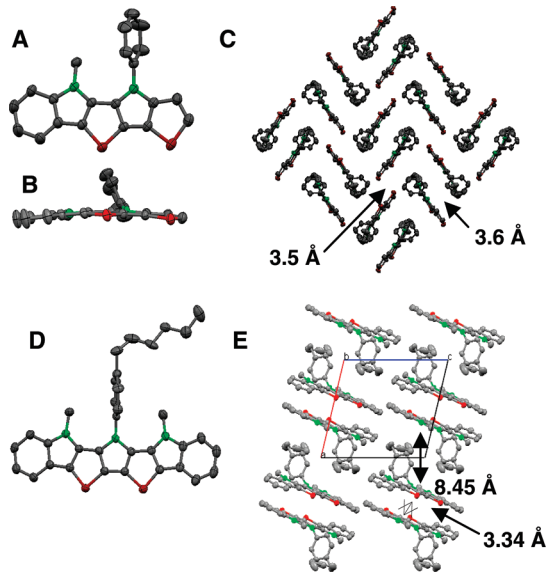

Figure 1. Thermal ellipsoid plot of **9b** (A), lateral view of **9b** (B), crystal packing of **9b** (C), thermal ellipsoid plots of **10a** (D), crystal packing of **10a** (E). Hydrogen atoms are removed for clarity.

group attached to the pyrrole ring is twisted by an angle of 64° with respect to the acene core. In **9b**, molecules pack in an edge-to-face manner leading to a sandwiched herringbone packing with a herringbone angle of 60° along the *a*-axis. Such a packing mode favors two-dimensional electronic interactions in the solid which is advantageous for better charge carrier mobility.[7a] The molecule **9b** forms dimers with an antiparallel, slipped cofacial arrangement, presumably to minimize the dipolar interactions and the steric effect imposed by the pendant phenyl ring. Within each dimer, the molecules are held together by short C−H···π contacts of 2.76 Å between the pendant phenyl ring and the acene core (Figure S1, Supporting Information). The molecules in these dimers are 3.6 Å apart at the shortest intermolecular distance. The S···S interactions of 3.5 Å between the molecules from adjacent columns are also dominant (shown in Figure 1C).

Similar to **9b**, compound **10a** was also not strictly planar, with a deviaton of 13.4° from planarity (Figure 1D). The phenyl group attached to the pyrrole ring is twisted by an angle of 84.6° with respect to the acene core. This pendant phenyl group is tilted from the plane of the molecule due to the steric hindrance imposed by the adjacent methyl groups (Figure S2, Supporting Information). In the crystal lattice, **10a** form π-stacked dimers which are rotated 180° to each other. The distance between these dimers was found to be around 3.34 Å, which equals the sum of van der Waals radii of carbon atoms (Figure 1E). The existence of C−H···π interactions between the hydrogen atoms of the methyl group with a π cloud of the adjacent molecule also accounts for the close interactions in these dimers (2.84 Å, Figure S3, Supporting Information). These dimers interact with other dimers in the lattice through C−H···S interactions between the pendant phenyl group of one dimer with the π-backbone of another dimer (2.89 Å). As a consequence of this interaction, the fused π-backbones (dimer) are well separated from other dimers by a distance of 8.45 Å. Though there exists short S···S contacts (3.34 Å) between the molecules of adjacent columns, a less densely packed structure of **10a** was obtained.

Absorption and emission spectra of heteroacenes are shown in Figure 2, and the spectral characteristics are

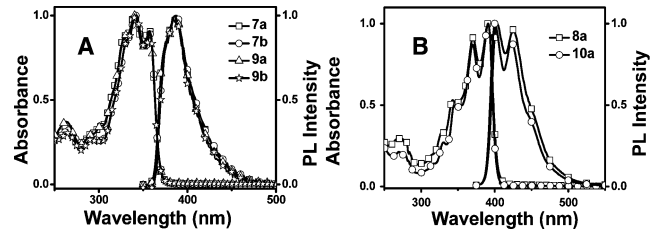

Figure 2. Normalized UV−vis absorption and emission spectra of unsymmetric indolodithienopyrrole (A) and extended diindolodithienopyrrole (B) recorded in THF.

summarized in Table 1. All unsymmetrical heteroacenes showed similar absorption properties with λ_{max} around 340 nm and absorption onset at 370 nm (Figure 2A). Absorption spectra of extended heteroacenes **8a** and **10a** show similar spectral characteristics (Figure 2B) illustrating the insignificant influence of the alkyl substituent on the electronic states of these compounds. It is noteworthy that the absorption spectra of the compounds are featured with several vibronic peaks, characteristic of fused-ring systems with well-defined electronic states. The HOMO−LUMO gap estimated from the onset of UV−vis absorption is identical for both **8a** and **10a** (i.e., ca. 3.02 eV). Interestingly, **8a** and **10a** possess a larger HOMO−LUMO gap compared to diindolocarbazole (2.73 eV).[16] An identical energy level gap of 3.35 eV was obtained for all unsymmetrical heteroacenes. The fluorescence spectra are virtually the mirror images of absorption spectra, indicating the rigid nature of the system.[18] The fluorescence quantum yield (Φ_F) of all compounds was measured in THF using quinine sulfate in 0.1 M sulfuric acid as standard. The solution state quantum yields of around 5% and 18% are observed for unsymmetric and extended heteroacenes, respectively.

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Table 1. Photophysical and Electrochemical Properties of Indolo- and Diindolodithienopyrrole

compd	λ_{Abs} (nm)	λ_{Em}[a] (nm)	Φ_F[b] (%)	HOMO−LUMO gap[c] (eV)	E_{oxid}[d] (V)	HOMO[e]	LUMO[f]
7a	357, 341, 264	386	6	3.35	0.81	−5.04	−1.69
7b	357, 340, 264	386	4	3.35	0.78	−5.01	−1.66
9a	358, 342, 291, 265	387	6	3.35	0.79	−5.01	−1.66
9b	357, 342, 290, 265	388	4	3.35	0.79	−5.01	−1.66
8a	391, 370, 343, 329, 273	425, 403	18	3.02	0.59, 1.23	−4.84	−1.82
10a	391, 370, 345, 330, 270	423, 400	18	3.02	0.56, 1.14	−4.82	−1.8
2a[g]	310, 300, 293, 261[h]	325	0.28	–	0.65, 1.1	–	–

[a] The samples were excited at the absorption maximum. [b] Solution state quantum yield in THF calculated with quinine sulfate as standard. [c] Estimated from the onset of absorption. [d] Potentials (vs Ag/AgCl) calculated from cyclic voltammetry: 0.1 M Bu_4NPF_6 in acetonitrile, Pt as working electrode under the scan rate of 100 $mV{\cdot}s^{-1}$. The potentials are calibrated with ferrocene as the internal standard. [e] Calculated using the relationship $E_{HOMO} = -(E^{ox}{}_{onset} + 4.38)$. [f] Derived from HOMO−LUMO gap and HOMO. [g] From ref 11c. [h] In CH_2Cl_2.

Electrochemical properties of the compounds were investigated with cyclic voltammetry performed using Ag/Ag^+ as the reference electrode (Figure S4, Supporting Information). Electrochemical data and energy levels are summarized in Table 1. Unsymmetrical heteroacenes **7a**, **7b**, **9a**, and **9b** showed an irreversible oxidation peak around 0.8 V. Oxidation potential gradually shifted to lower potential with an increase in peak current during repeated anodic scans (Figure S5, Supporting Information). This can be attributed to the presence of an unblocked electroactive unit (thiophene end) which can undergo oxidative coupling under electrochemical conditions. Unlike the unsymmetrical heteroacenes, the oxidation process in an extended compound was found to be quasi-reversible. The cyclic voltammograms of **8a** and **10a** showed two oxidation peaks around 0.6 and 1.2 V. The HOMO energy level was calculated from the oxidation onset potential using the empirical formula $E_{HOMO} = -(E_{ox}{}^{onset} + 4.38)$ eV.[19] As we were unable to observe any reduction within our scan range, LUMO energy level was empirically calculated from the HOMO energy level and optical data (absorption edges in UV−vis spectra). All unsymmetrical compounds showed an oxidation onset potential around 0.7 V, which corresponds to HOMO energy levels of −5.01 eV. The smaller band gaps for extended ring compounds (**8a** and **10a**) compared to the unsymmetrical systems are consistent with the extension of π-conjugation. The HOMO energy level of these compounds is significantly lower than that reported for pentacene (ca. −4.4 eV).[20] The low-lying HOMO and relatively large band gap afford environmental stability to these molecules.

In summary, we report a simple synthesis of new heteroacenes (unsymmetrical and extended) containing thiophene and pyrrole units. These acenes are stable at ambient conditions and soluble in common organic solvents. Unsymmetrical heteroacene packs in sandwich herringbone manner leading to densely packed structures. Incorporation of these compounds in OFET application is currently in progress in our laboratory.

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Supporting Information Available: Details on experimental procedures, spectroscopic data, ^1H and ^{13}C NMR spectra, cyclic voltammograms of all heteroacenes, and crystal data in CIF format of **10a** and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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