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Thiadiazole Fused Indolo[2,3-*a*]carbazole Based Oligomers and Polymer

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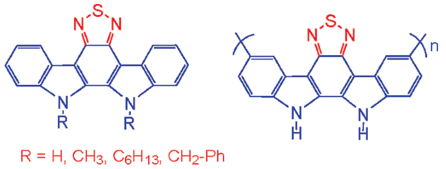
ABSTRACT



Indolo[2,3-*a*]carbazole-based heteroacenes containing thiadiazole units were synthesized. Compounds showed a sandwich herringbone packing in solid state with improved stability. The change in photophysical and electrochemical properties upon incorporation of an acceptor moiety (benzothiadazole) in a fused ring system was studied. The unsubstituted compound was electropolymerized to yield a stable polymer.

Over the years, development of conjugated materials for the applications in organic electronics involves several common groups such as oligothiophenes,[1] oligofluorenes,[2] polycyclic aromatic compounds,[3] and fused heterocyclic aromatic compounds.[4] In particular, fused-ring aromatic compounds exhibit good π-stacking and highly ordered molecular structure, which are beneficial for the efficient charge transport. Among the reported fused-ring aromatic systems, mobilities of ~3 cm^2 V^{-1} s^{-1} were obtained for pentacene.[5] However, pentacene is vulnerable to photooxidation due to a high-lying HOMO and a narrow band gap.[6] In addition, higher [*n*]acenes exhibit poor solubility in most of the common solvents which limits the processability of such materials.[7] Hence, for electronic applications, molecules of high planarity with optimum band gap, close packing, and good solubility are desired. Among the conjugated systems, fused heterocyclic aromatic compounds (heteroacenes) containing nitrogen atom showed a diverse range of applications, for example, in biological applications, fabrication of new electronic devices, and anion sensing.[8] In electronic applications, heteroacenes demonstrated improved properties of the highly ordered acene molecules.[9] Among the five indolocarbazole isomers,[8] indolo[3,2-*b*]carbazole has been explored extensively for electronic applications.[10] Extensive studies

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on indolo[2,3-*a*]carbazole-based compounds are illustrated in biological applications such as protein kinase inhibitor,[11] antimicrobial agents,[12] and as a ligand for aromatic hydrocarbon receptors (AhR).[13] Indolo[2,3-*a*]carbazole and its derivatives are also efficient sensors for anionic guest species, such as F^-, Cl^-, $PhCO_2^-$, $H_2PO_4^-$, and HSO_4^-.[14] However, the material aspects of this isomer of indolocarbazole are poorly explored. In this regard, thiadazole (acceptor moiety)-fused indolo[2,3-*a*]carbazole (donor moiety)-based new heteroacenes were synthesized. Their photophysical and electrochemical properties along with their packing in the crystal lattice were studied. Structures of the synthesized compounds are depicted in Figure 1.

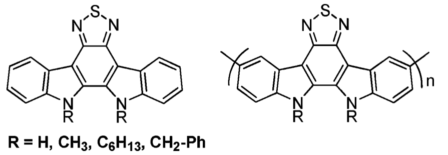
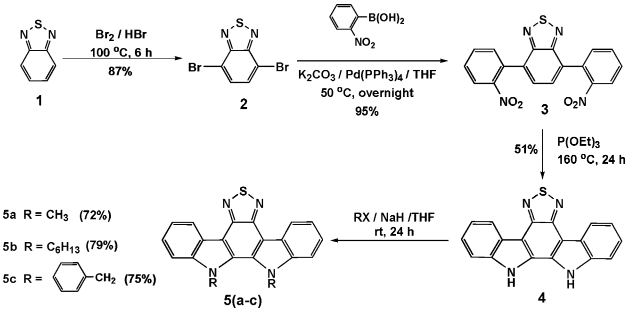


Figure 1. Structure of synthesized thiadiazole-fused indolocarbazole-based molecules.

Scheme 1 displays the synthesis route towards the newly synthesized indolocarbazole derivatives. Benzothiadiazole (**1**) was treated with 2.4-fold excess of bromine under acidic conditions to give 4,7-dibromo-2,1,3-benzothiadiazole (**2**) in good yield, 87%.[15] Suzuki coupling of compound **2** was carried out with 2-nitrophenylboronic acid (2-NBA) to get the compound **3**. Purification of the product was accomplished by washing the crude solid with hexane to achieve quantitative yield of compound **3**. Compound **4** was obtained via the reported procedure of reductive Cadogan ring-closure reaction,[16] where compound **3** in 1,2-dichlorobenzene was refluxed with triethyl phosphite for 24 h. Target molecule **4** in 51% yield was isolated after purification by column chromatography. A few derivatives of compound **4** with various N-alkyl substituents (i.e., CH_3, C_6H_{13}, and CH_2Ph) were prepared by alkylation with the corresponding alkyl halides (**5a**−**c**).

Longer alkyl chain increased the solubility of these indolocarbazoles in common organic solvents such as ethyl acetate, chloroform, dichloromethane, THF, and acetone. The synthesized compounds were characterized using ^1H and ^{13}C NMR and high-resolution mass spectrometry (see the Supporting Information). Among the synthesized molecules, **5a** was analyzed by single-crystal X-ray diffraction techniques. A solution containing **5a** in ethyl acetate was evaporated slowly at room temperature to yield single crystals of **5a** (Figure 2).

Scheme 1. Synthesis of Thiadiazole-Fused Indolocarbazole Derivatives



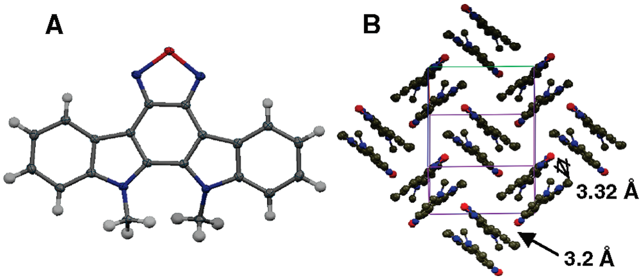


Figure 2. Thermal ellipsoid plot of **5a** (A). Packing diagram of **5a** along *a*-axis. Hydrogen atoms removed for clarity (B).

Compound **5a** exhibits sandwiched herringbone type packing with molecules existing as anti cofacial dimers with a herringbone angle of 89°. This arrangement facilitates two-dimensional electronic transport, which is advantageous for better charge carrier mobility.[17] In addition, a short intermolecular distance of 3.32 Å in the dimer indicates strong $\pi-\pi$ interactions. Such close contact is good as compared to the intermolecular distance (3.45 Å) reported for planar indolo[3,2-*b*]carbazole derivatives.[18] Short N−S contact of 3.2 Å was observed between the edge-to-face interacting **5a** molecules, leading to a close packed structure.

The UV−vis absorption and emission spectra of the oligomers in solution (tetrahydrofuran) are shown in Figure 3. All spectra display multiple maxima in the UV region, featuring typical fused-ring systems with more defined

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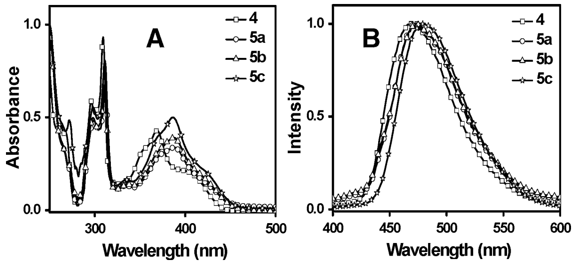
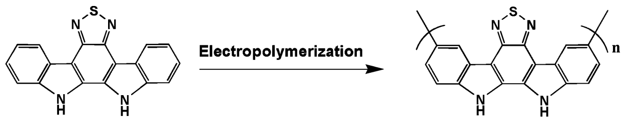


Figure 3. Normalized absorption spectra (A) and emission spectra (B) of thiadiazole fused indolocarbazole derivatives in THF.

electronic states.[19] The absorption maximum of alkyl-substituted derivatives (**5a**−**c**) is red-shifted as compared to the parent molecule **4**. Leclerc et al. reported similar phenomena in their work on carbazole-based ladder compounds.[19] Emission maximum of all derivatives are in the blue-green region with $\lambda_{\max}$ centered around 475 nm. Interestingly all derivatives exhibit large Stoke′s shifts which are unexpected for fused ring systems (Table 1). The wavelength of emission also showed a strong dependence on solvent (Figure S1, Supporting Information). Such a large Stoke's shift and solvent-dependent emission indicates the effective intramolecular charge transfer (ICT) in the excited state between the thiadiazole unit and indolocarbazole unit.[20] It is observed that the substituents on the N-atom have a marginal effect on the optical properties of these compounds. The fluorescene quantum yield of heteroacenes was recorded in THF with quinine sulfate in 0.1 M H_2SO_4 as standard. The fluorescence quantum yields (Φ_F) of all compounds are relatively low. Such low Φ_F values relative to indolo[3,2-*b*]carbazole may be due to an increase in the nonradiative intersystem crossing caused by the heavy atom (sulfur). The optical band gap estimated from the onset of UV−vis absorption for these derivatives are within the range of ca. 2.7−2.8 eV. Some of the reported indolo[3,2-*b*]carbazole-based molecules show optical band gaps between ca. 2.86 and 2.95 eV.[21]

Cyclic voltammetry (CV) was performed to investigate the redox properties of the new ladder molecules in dry dichloromethane (Figure S2, Supporting Information). Oxidation peaks of **4**, **5a**, **5b**, and **5c** were found to be 1.25, 1.3, 1.34, and 1.35 V. All alkyl-substituted derivatives showed higher oxidation potential than the parent compound **4**. HOMO energy levels of ladder compounds are estimated by the oxidation onset using the relationship $E_{\mathrm{HOMO}} = -(E^{\mathrm{ox}}_{\mathrm{onset}} + 4.38)$ eV.[22] HOMO levels of −5.39, −5.49, −5.53, and −5.57 below vacuum level were estimated for the compounds **4**, **5a**, **5b**, and **5c**, respectively (Table 1). It can be noted that the synthesized compounds have low-lying HOMO as compared to pentacene ($E_{\mathrm{HOMO}} = -4.6$ eV)[6] and indolo[3,2-*b*]carbazoles ($E_{\mathrm{HOMO}} = -5.12$ eV).[4c]

Scheme 2. Synthesis of Thiadiazole-Fused Indolocarbazole Polymer



4

poly 4

Electropolymerization of compound **4** was carried out in acetonitrile containing 0.1 M $TBAPF_6$ as supporting electrolyte at a scan rate of 100 mV/s. Polymer was synthesized electrochemically over the ITO surface (Scheme 2) by repetitive scanning of anodic potential in the range of 0.2 to 1.5 V. The growth of polymer is indicated by a gradual increase in current during the potential cycles (Figure 4A). The polymerization occurred smoothly and resulted in a yellow-brown colored, uniform deposit of polymer on the working electrode. The deposited polymer film was dedoped electrochemically and washed with acetonitrile to remove monomer and supporting electrolyte. To the best of our knowledge, compound **4** is the first indolocarbazole-based material that undergoes electropolymerization.

The IR spectrum (KBr disk) of the polymer showed a strong peak at 3433 cm^{-1} corresponding to N−H stretching vibration (Figure S3, Supporting Information). The other peaks at 2915 cm^{-1} and 1630 cm^{-1} corresponds to aromatic C−H stretching and aromatic C═C stretching, respectively. The possible structure of the polymer is represented in Scheme 2. The absorption spectrum (Figure S4, Supporting Information) of the polymer film showed a broad absorption peak characteristic of a polymeric system with an optical band gap of 2.4 eV, which is less than the corresponding monomer **4** (2.8 eV).

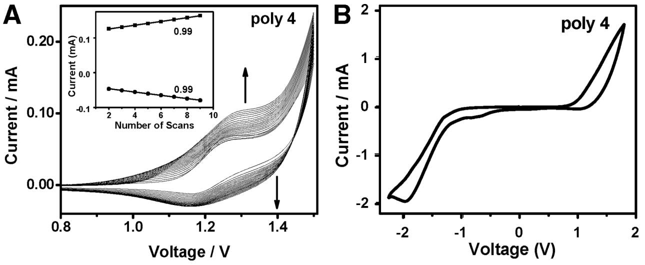


Figure 4. Electropolymerization of **4** from acetonitrile solution at a scan rate of 100 mV/s. Inset picture: Linear relationship of increase in current with number scans (A). Cyclic voltammogram of **poly4** (B).

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Table 1. Photophysical and Electrochemical Properties of Thiadiazole-Fused Indolocarbazoles

compd	λ_{abs} (nm)	λ_{em}[a] (nm)	Stoke's shift (nm)	Φ_F	E_g[b] (eV)	E^c_{oxid} (V)	HOMO[d] (eV)	LUMO[e] (eV)
4	368, 309, 296, 247	469	101	8	2.8	1.25	−5.39	−2.59
5a	387, 311, 298, 249	472	85	10	2.75	1.3	−5.49	−2.74
5b	387, 311, 298, 249	473	86	10	2.74	1.34	−5.33	−2.79
5c	386, 311, 298, 250	481	95	9	2.72	1.35	−5.57	−2.85
poly4					2.4		−5.29	−3.14[f]

[a] The sample was excited at its respective absorption maximum. [b] Optical band gaps estimated from the onset position of absorption spectra. [c] Versus Ag/AgCl electrode in 0.1 M Bu_4NPF_6 in acetonitrile, Pt as working electrode with a scan rate of 100 mV s^{-1}. [d] Calculated using the relationship $E_{HOMO} = -(E_{oxi}^{onset} + 4.38)$. [e] Derived from optical band gap and HOMO. [f] Derived from onset of reduction potential.

The cyclic voltammogram of the polymer showed sharp oxidation peak with the oxidation onset potentials at 1.05 V (Figure 4B). Upon scanning in negative potential, the quasireversible reduction peak is observed at −2 V. The small reduction peaks around −0.7 V may correspond to the reduction of charged species created by irreversible oxidation process. The electrochemical band gap of the polymer is found to be 2.2 eV, which corresponds well with the optical band gap (2.4 eV). The lower oxidation potential of polymers compared to monomer **4** (1.25 V) and reduction in band gap are consistent with extended π-conjugation in the polymer. The electrochemical properties of the polymer are also summarized in Table 1.

The surface morphology of the **poly4** was studied using atomic force microscopy (AFM). AFM image showed a uniform deposition of polymer over ITO surface with rms roughness of ∼10−20 nm (Figure 5). AFM images of visually smooth polymer film reveal the globular feature of 100−200 nm diameter, which are regular in shape and size. The morphology is similar to those of other reported electrodeposited polymers.[23]

In conclusion, thiadiazole-incorporated indolo[2,3-*a*]carbazole derivatives are synthesized and characterized. Thiadiazole fusion leads to a close packing of indolocarbazole systems in the crystal lattice and also decrease of both the HOMO and LUMO energy levels of the system. The decrease in HOMO energy leads to the oxidative stability; therefore, the strategy of thiadiazole fusion can be utilized to stabilize unstable fused ring systems. The unsubstituted compound was electropolymerized to give the first electropolymerized polyindolocarbazole. The device fabrication and characterization of these compounds for opto-electronic application is currently in progress in our laboratory.

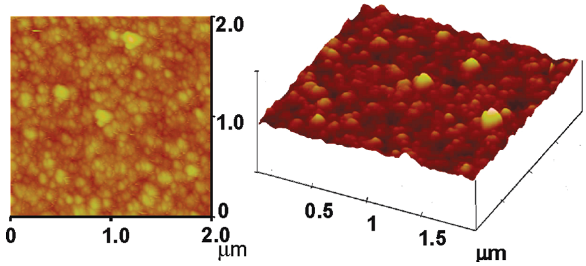

Figure 5. Tapping mode AFM image of electrodeposited polymer film.

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Supporting Information Available: Experimental procedures, spectroscopic data, ^1H and ^{13}C NMR spectra, cyclic voltammograms of all compounds and crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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