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PAPER

Synthesis and properties of thienopyrrole based heteroacenes – indolodibenzothienopyrrole and dicarbazolodithienopyrrole†

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We report the syntheses and properties of thienopyrrole based unsymmetrical and extended heteroacenes, which are isoelectronic with heptacene (30π) and nonacene (38π), respectively. Optical and electrochemical properties of these seven and nine rings fused systems are studied. The optoelectronic properties of the *syn* and *anti*-isomers of the unsymmetrical heteroacenes are also compared. The influence of the position of the heteroatoms in the fused corona, upon the optical and electrochemical properties, is rationalized based on the contributions from the benzenoid *vs.* quinonoid-type structures of these molecules.

Introduction

Extended π-structures have attracted significant attention from several fields, especially in organic electronics.[1] The reason for the interest stems from the fact that intermolecular frontier orbital overlap in molecular organizations is thought to greatly influence charge transport in these materials.[2] Then, it is reasonable to assume that these desired MO overlaps will be enhanced in flat aromatic systems with a large π-surface area. Thus, extended acenes have become interesting synthetic targets. The relatively limited access to extended acenes has led to the use of heteroacenes.[3] Heteroacenes have the advantage of structural tunability based on the chosen heterocyclic systems.[4] Heteroacenes are also versatile in their structural variations due to the differences in number, nature, and position of heteroatoms in the fused aromatic system which enables the variation of their structures for a targeted property.[5] Several families of heteroacenes bearing heteroatoms such as boron, nitrogen, oxygen, silicon, phosphorous, sulfur or a combination of these heteroatoms have been reported.[6] Among them, thiophene and pyrrole based heteroacenes gained significant attention, due to their prior success as components of materials for organic field effect transistor (OFET) or photovoltaics applications.[7]

Fused systems containing both thiophene and pyrrole units are interesting, because they have the potential to retain the advantages of both pyrrole and thiophene units. The trivalent nature of the nitrogen in the pyrrole units allows for the convenient introduction of functional groups that facilitate solubilization necessary for processibility and to optimize packing in condensed phase for efficient charge transport. Similarly, thiophene units are thought to bring about secondary interactions such as S···S contacts in the condensed phase, which should also influence packing.[8] Therefore, we considered the thienopyrrole core as a promising unit to construct the extended fused structures. In this manuscript, we report on the syntheses and properties of unsymmetrically fused (seven rings) and symmetrically fused (nine rings), thienopyrrole based heteroacenes utilizing Cadogan reductive cyclization. Photophysical and electrochemical properties of the target molecules are also presented. The structures of the synthesized molecules are represented in Fig. 1.

Experimental

General considerations

All chemicals and reagents were purchased from commercial suppliers and used without further purification, unless otherwise mentioned. Solvents used for spectroscopic measurements were spectral grade quality. Tetrahydrofuran (THF) was distilled over sodium. All reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates. Preparative separations were performed using Combiflash Rf-200 automated flash chromatography.

Characterization techniques

All molecules were characterized using ^{1}H NMR, ^{13}C NMR and high resolution mass spectrometry to confirm the molecular structure. ^{1}H NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in

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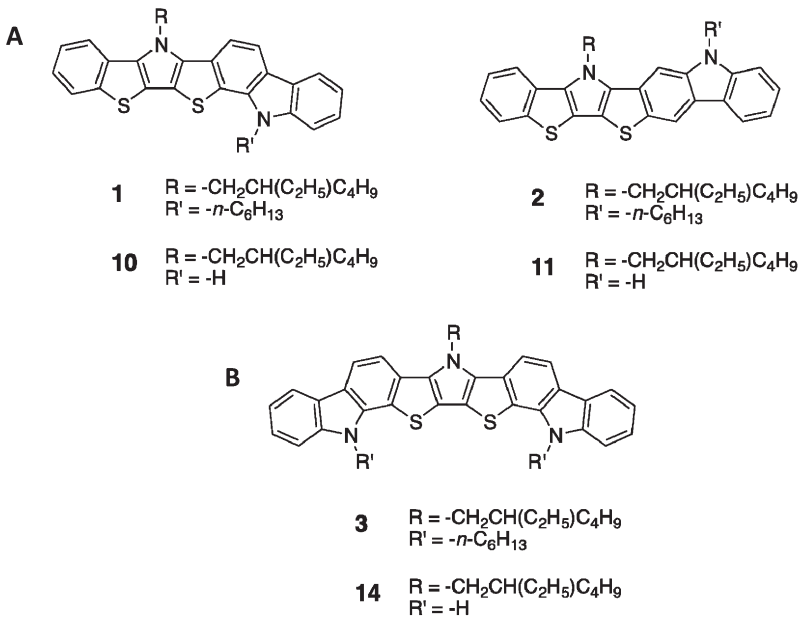


Fig. 1 Structures of synthesized heteroacenes (A) indolodibenzothienopyrrole and (B) dicarbazolodithienopyrrole.

parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet; b, broad. ^{13}C NMR spectra were proton decoupled and recorded on a 100 MHz Bruker spectrometer using the carbon signal of the deuterated solvent as an internal standard. Cyclic voltammetry experiments were carried out at room temperature using BASi C3 cell stand fitted with three electrodes; a platinum disk working electrode, platinum auxiliary electrode and Ag/Ag^+ reference electrode. The voltammograms were recorded in dry dichloromethane (DCM) using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the internal standard under nitrogen atmosphere. The scan rate in all experiments was 100 mV s^{-1}. Theoretical calculations were performed in Gaussian 03[1] at the density functional theory (DFT) level with the B3LYP functional and a 6-311g(d,p) basis set.[9] The HOMO and LUMO surfaces were generated from the optimized geometries. UV-Visible spectra were obtained using a Cary 100 spectrophotometer and fluorescence data were collected using a JASCO FP-6500 spectrofluorimeter. Solution state photoluminescence quantum yields were measured using quinine sulfate (0.1 M H_2SO_4) as the standard.[10] Spectroscopic grade solvent was used to prepare sample solutions and checked for background fluorescence. The solution of each sample and standard at five different concentrations (concentration was chosen such that the absorption of the sample was less than 0.1 at the excitation wavelength) was analyzed. The absorbance and integrated fluorescence intensity values at each concentration was obtained and plotted to get the gradient (m) with intercept = 0. The quantum yield value was calculated using the relation,

$$\Phi_x = \Phi_s[\text{Gra X}/\text{Gra S}][\eta_x^2/\eta_s^2]$$

where S and X denotes the standard and test sample respectively. Φ_s of quinine sulfate in 0.1 M H_2SO_4 = 54%.

X-ray crystallography

The X-ray crystallographic studies were performed using a Nonius KappaCCD diffractometer and graphite monochromated MoKα radiation (λ = 0.71073 Å). Data was collected at 293 K, $\theta_{MoK\alpha} \leq 25°$. All data was included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least squares. Refinements were based on F^2 and computations were performed using SHELXS-86 for solution and SHELXL-97 for refinement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement as isotropic scatterers riding in ideal positions on the bonded atoms. The hydrogens on disordered atoms were not included in the calculations. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$.

Synthesis of compound 7

To a 250 mL round-bottom flask under argon atmosphere, catalyst $Pd_2(dba)_3$ (0.1 mmol), ligand (±)-BINAP (0.1 mmol) and toluene (20 mL) were added and allowed to stir for 5 minutes. The base NaO^tBu (3 mmol) and dibromodibenzo[*b*]thiophene (**6**) (1 mmol) were added followed by the addition of 2-ethylhexylamine (1.2 mmol) and the reaction mixture was allowed to reflux for six hours. Reaction mixture was cooled to room temperature and extracted with ethyl acetate–brine. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude compound was purified by column chromatography with hexane as the eluent to give the desired compound as white solid. **7**: (70% yield). Mp 147–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J = 8 Hz, 2H), 7.86 (d, J = 8 Hz, 2H), 7.41 (m, 2H), 7.29 (m, 2H), 4.67 (m, 2H), 2.18 (m, 1H), 1.48–1.39 (m, 5H), 1.23 (m, 3H), 0.89 (t, J = 7.4 Hz, 3H), 0.82 (t, J = 7.12 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.9, 137.9, 127.7, 124.5, 124.2, 123.1, 119.2, 114.6, 51.8, 40.7, 30.5, 28.6, 23.8, 23.0, 13.9, 11.1. IR (solid)

3048, 2922, 1587, 1406, 742, 724 cm^{-1}. HRMS *m/z* calculated for $C_{24}H_{25}NS_2$: 391.1428, found by EI: 391.1419.

Synthesis of compound 8

Bromine (2 mmol) was added drop wise to a solution of compound **7** (2 mmol) in chloroform (50 mL) over a period of 20 min. The reaction mixture was stirred for 4 hours at room temperature. After completion of the reaction, the reaction mixture was extracted with dichloromethane–water twice and finally with sodium thiosulphate solution. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography to give the monobromo compound as a white solid. **8**: (60% yield). Mp 153–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, J = 1.72 Hz, 1H), 7.87 (d, J = 8.06 Hz, 1H), 7.85 (d, J = 7.96 Hz, 1H), 7.70 (m, 1H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, 1H), 7.41 (m, 1H), 7.31 (m, 1H), 4.66 (m, 2H), 2.10 (m, 1H), 1.46–1.18 (m, 8H), 0.88 (t, J = 7.4 Hz, 3H), 0.82 (t, J = 7.28 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.3, 142.0, 137.1, 127.5, 127.4, 126.8, 126.4, 124.5, 124.3, 123.3, 120.0, 119.9, 119.3, 116.2, 114.8, 114.5, 51.7, 40.7, 30.5, 28.6, 23.9, 23.0, 13.9, 11.0. IR (solid) 3060, 2922, 1587, 1551, 797, 724 cm^{-1}. HRMS *m/z* calculated for $C_{24}H_{24}NBrS_2$: 469.0534, found by EI: 469.0545.

Synthesis of compound 12

Bromine (5 mmol) was added dropwise to a solution of compound **7** (2 mmol) in chloroform (50 mL). The reaction mixture was stirred for 8 hours at room temperature. After completion, the reaction mixture was extracted with dichloromethane–water twice and finally with a sodium thiosulphate solution. The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed under pressure and the crude product was purified by column chromatography to give the dibromo compound **12** as a white solid (80% yield). Mp 175–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J = 1.72 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 7.49 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 2H), 4.54 (m, 2H), 2.05 (m, 1H), 1.47–1.16 (m, 8H), 0.86 (t, J = 7.44 Hz, 3H), 0.81 (t, J = 7.04 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.4, 137.4, 127.5, 126.9, 126.2, 120.0, 116.5, 114.8, 51.8, 40.7, 30.5, 28.6, 23.9, 22.9, 13.9, 11.0. IR (solid) 3072, 2919, 1546, 1499, 1089, 794 cm^{-1}. HRMS *m/z* calculated for $C_{24}H_{23}NBr_2S_2$: 546.9639, found by EI: 546.9603.

General procedure for Suzuki coupling – synthesis of compounds 9 and 13

To a 250 mL two-neck round-bottom flask, THF (20 mL), monobromo or dibromo compound (**8** or **12**) (2.5 mmol) and 2-nitrophenylboronic acid (3.0 mmol for **9**/6.0 mmol for **13**) were added followed by the addition of catalyst $Pd_2(dba)_3$ (0.25 mmol), P(*o*-Tol)$_3$ (0.25 mmol) and 2 M aqueous potassium carbonate (15 mL). The reaction mixture was heated to 50 °C for 8 hours. The reaction mixture was then allowed to cool to room temperature and extracted with ethyl acetate–brine. The collected organic layer was dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude solid was subjected to column chromatography with ethyl acetate–hexane as eluent to get the pure product.

9: (60% yield). Mp 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 7.92–7.83 (m, 5H), 7.68–7.64 (m, 1H), 7.57–7.49 (m, 2H), 7.44–7.40 (m, 1H), 7.36–7.29 (m, 2H), 4.67 (m, 2H), 2.17 (m, 1H), 1.53–1.21 (m, 8H), 0.90 (t, J = 7.44 Hz, 3H), 0.83 (m, J = 7.18 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 142.3, 142.0, 138.4, 137.5, 136.0, 133.4, 132.3, 132.2, 132.0, 128.1, 127.6, 127.3, 124.5, 124.3, 123.7, 123.3, 119.3, 119.1, 115.6, 114.6, 51.8, 40.8, 30.5, 28.6, 23.9, 23.0, 13.9, 11.1. IR (solid) 3054, 2927, 1648, 1520, 1340, 748, 693 cm^{-1}. HRMS *m/z* calculated for $C_{30}H_{28}N_2O_2S_2$: 512.1592, found by EI: 512.1567.

13: (50% yield). Mp 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95–7.90 (m, 4H), 7.85 (d, J = 1.44 Hz, 2H), 7.68–7.64 (m, 2H), 7.57–7.50 (m, 4H), 7.36 (dd, J_1 = 8.32 Hz, J_2 = 1.60 Hz, 2H), 4.68 (m, 2H), 2.21 (m, 1H), 1.51–1.26 (m, 6H), 1.21–1.18 (m, 2H), 0.92 (t, J = 7.40 Hz, 3H), 0.84 (t, J = 7.16 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.3, 142.5, 138.0, 135.9, 132.4, 132.3, 132.2, 128.2, 127.2, 124.3, 124.2, 123.7, 119.3, 115.6, 51.9, 40.8, 30.6, 28.6, 23.9, 23.0, 13.9, 11.1. IR (solid) 3060, 2922, 1611, 1520, 1346, 748 cm^{-1}. HRMS *m/z* calculated for $C_{36}H_{31}N_3O_4S_2$: 633.1756, found by EI: 633.1754.

General procedure for Cadogan reaction – synthesis of compounds 10, 11, 14 and 4

To a 100 mL two-neck round-bottomed flask under argon atmosphere, the nitro compound (**9**/**13**) (0.5 mmol) was added followed by the addition of triethyl phosphite (5 mL) and 1,2-dichlorobenzene (5 mL). The reaction mixture was heated under reflux for 12 hours. After completion, the reaction mixture was cooled to ambient temperature and concentrated *in vacuo*. The crude product was purified by column chromatography (ethyl acetate–hexane) to result in the desired fused compounds.

10: (50% yield). Mp 205–207 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ: 10.92 (b, 1H), 8.21 (d, J = 8.21 Hz, 1H), 8.16 (d, J = 7.76 Hz, 1H), 8.11 (d, J = 8.04 Hz, 1H), 7.97–7.94 (m, 2H), 7.59 (d, J = 8.08 Hz, 1H), 7.48 (m, 1H), 7.41 (m, 1H), 7.34 (m, 1H), 7.24 (m, 1H), 4.90 (d, J = 7.92 Hz, 2H), 2.25–2.20 (m, 1H), 1.57–1.37 (m, 6H), 1.18–1.13 (m, 2H), 0.92 (t, J = 7.44 Hz, 3H), 0.76 (t, J = 7.26 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ: 141.2, 139.6, 139.5, 137.5, 135.3, 127.5, 125.7, 125.0, 124.2, 124.1, 123.5, 122.9, 119.5, 119.3, 119.3, 118.8, 116.9, 114.0, 113.0, 111.5, 110.9, 110.8, 51.1, 40.6, 30.0, 28.2, 23.5, 22.5, 12.9, 10.2. IR (solid) 3368, 3043, 2923, 1613, 724 cm^{-1}. HRMS *m/z* calculated for $C_{30}H_{28}N_2S_2$: 480.1694, found by EI: 480.1694.

14: (40% yield). Mp > 350 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ: 10.91 (s, 2H), 8.23 (d, J = 8.4 Hz, 2H), 8.17 (d, J = 7.68 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.08 Hz, 2H), 7.41 (m, 2H), 7.25 (m, 2H), 5.03 (d, J = 8.24 Hz, 2H), 2.33 (m, 1H), 1.61–1.53 (m, 4H), 1.21–1.15 (m, 4H), 0.95 (t, J = 7.40 Hz, 3H), 0.77 (t, J = 7.30 Hz, 3H). ^{13}C NMR (100 MHz $CDCl_3$) δ:139.6, 139.3, 125.9, 124.9, 123.59, 123.55, 119.5, 119.3, 118.6, 117.0, 113.1, 111.4, 110.83, 110.78, 51.1, 40.6, 30.1, 23.56, 22.5, 12.9, 10.27. IR (solid) 3397, 3052, 2926, 1609, 724 cm^{-1}. HRMS *m/z* calculated for $C_{36}H_{31}N_3S_2$: 569.1959, found by EI: 569.1955.

General procedure for alkylation – synthesis of compounds 1, 2 and 3

To a 100 mL round-bottom flask under argon atmosphere, fused compound (**10**/**11**/**14**) (0.1 mmol), dry THF (10 mL) and alkyl bromide (0.3 mmol) were added. To this reaction mixture NaH (60% in mineral oil) (0.25 mmol) was added and refluxed for 6 hours. The reaction mixture was quenched by careful addition of water and extracted with ethyl acetate–water three times. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography to obtain the corresponding alkyl derivative.

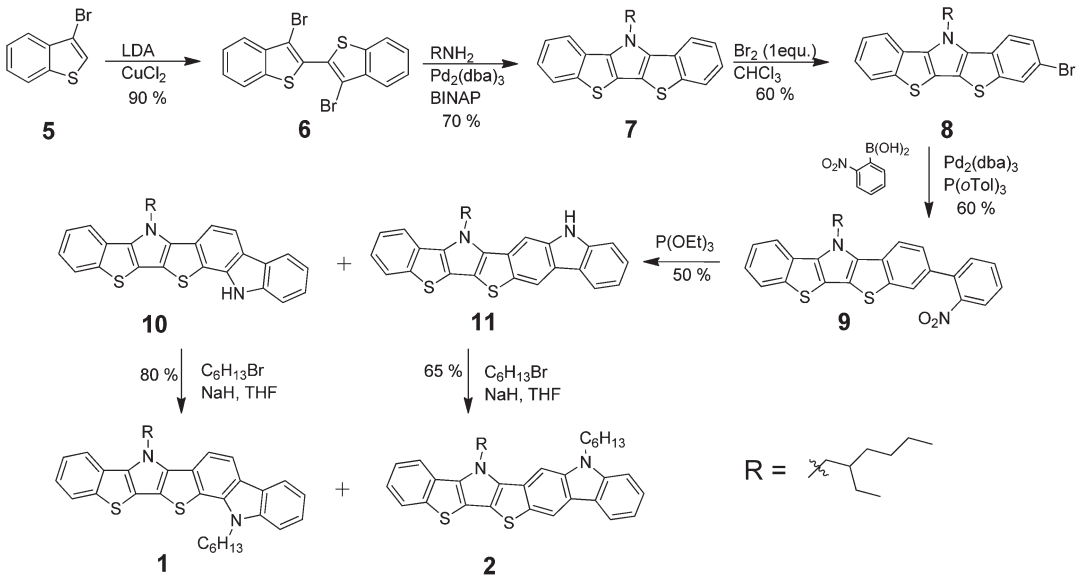
1: (80% yield). Mp 106–108 °C. ^{1}H NMR (400 MHz $CDCl_3$) δ: 8.12 (d, J = 7.72 Hz, 1H), 8.09 (d, J = 8.36 Hz, 1H), 7.87 (d, J = 8.60 Hz, 2H), 7.74 (d, J = 8.36 Hz, 1H), 7.49–7.39 (m, 3H), 7.31–7.27 (m, 2H), 4.64 (m, 2H), 4.55 (t, J = 8.00 Hz, 2H), 2.24–2.20 (m, 1H), 2.01–1.93 (m, 2H), 1.56–1.21 (m, 14H), 0.93–0.81 (m, 9H). ^{13}C NMR (100 MHz $CDCl_3$) δ: 141.7, 140.2, 139.5, 137.9, 136.2, 127.8, 126.4, 125.0, 124.4, 124.2, 123.4, 122.8, 122.4, 119.8, 119.4, 119.2, 118.5, 117.0, 114.3, 113.7, 111.3, 108.9, 51.6, 44.9, 40.7, 31.6, 31.0, 30.5, 28.6. 26.8, 23.8, 23.0, 22.6, 14.1, 13.9, 11.1. IR (solid) 3043, 2923, 1690, 1597, 743, 724 cm^{-1}. HRMS *m*/*z* calculated for $C_{36}H_{40}N_2S_2$: 564.2633, found by EI: 564.2655.

2: (65% yield). Mp 144–146 °C. ^{1}H NMR (400 MHz $CDCl_3$) δ: 8.47 (s, 1H), 8.10 (d, J = 7.68 Hz, 1H), 7.82 (d, J = 8.08 Hz, 2H), 7.66 (s, 1H), 7.46 (m, 1H), 7.36 (m, 2H), 7.27–7.22 (m, 2H), 4.61–4.58 (m, 2H), 4.23 (t, J = 7.28 Hz, 2H), 2.21 (m, 1H), 1.90 (m, 2H), 1.52–1.21 (m, 14H), 0.93–0.81 (m, 9H). ^{13}C NMR (100 MHz $CDCl_3$) δ: 141.9, 141.5, 139.1, 137.9, 137.7, 133.4, 127.6, 126.1, 125.7, 124.4, 124.1, 123.9, 122.1, 120.8, 120.1, 119.1, 118.8, 115.6, 115.1, 114.8, 108.3, 98.2, 51.6, 43.2, 40.8, 31.7, 30.6, 28.8, 28.6, 27.1, 23.8, 23.1, 22.6, 14.0, 13.9, 11.0. IR (solid) 3047, 2920, 1598, 1471, 739, 725 cm^{-1}. HRMS *m*/*z* calculated for $C_{36}H_{40}N_2S_2$: 564.2633, found by EI: 564.2618.

3: (85% yield). Mp 226–228 °C. ^{1}H NMR (400 MHz $CDCl_3$) δ: 8.12 (d, J = 7.60 Hz, 2H), 8.05 (d, J = 8.36 Hz, 2H), 7.68 (d, J = 7.4 Hz, 2H), 7.46 (m, 2H), 7.40 (d, J = 8.04 Hz, 2H), 7.29 (m, 2H), 4.60–4.56 (m, 2H), 4.51 (t, J = 7.8 Hz, 4H), 2.19 (m, 1H), 1.98 (m, 4H), 1.58 (m, 5H), 1.39 (m, 12H), 1.20 (m, 3H), 0.93 (t, J = 7.00 Hz, 6H), 0.86–0.80 (m, 6H). ^{13}C NMR (100 MHz $CDCl_3$) δ: 140.2, 139.2, 136.2, 126.5, 124.9, 123.4, 122.1, 119.7, 119.3, 118.4, 117.0, 113.3, 111.3, 108.8, 51.3, 44.8, 40.7, 31.6, 31.0, 30.5, 28.6, 26.8, 23.8, 23.0, 22.7, 14.1, 14.0, 11.1. IR (solid) 3050, 2925, 1591, 721 cm^{-1}. HRMS *m*/*z* calculated for $C_{48}H_{55}N_3S_2$: 737.3837, found by EI: 737.3876.

Results and discussion

The synthetic route towards the seven-ring fused heteroacenes is shown in Scheme 1. Commercially available 3-bromobenzo[*b*]thiophene (**5**) was deprotonated at the 2-position with lithium diisopropylamide (LDA) followed by oxidative coupling with $CuCl_2$ to obtain 3,3′-dibromo-2,2′-dibenzo[*b*]thiophene (**6**) in 90% yield.[11] Buchwald–Hartwig amination of compound **6** with alkyl amines using $Pd_2(dba)_3$/(±)-BINAP as the catalyst resulted in dibenzodithienopyrrole **7** in a moderate yield of 70%. Controlled bromination of dibenzodithienopyrrole with one equivalent of Br_2 in $CHCl_3$ for 2 hours resulted in the mono-bromo product (**8**). The regioselectivity in bromination is influenced by the directing effect of the pyrrole and possibly by the steric effect of the *N*-alkyl chains which favors substitution at the 2- and 8-positions. The monobromo compound (**8**), upon Suzuki coupling with 2-nitrophenylboronic acid in the presence of $Pd_2(dba)_3$ as the catalyst and P(*o*-Tol)$_3$ as the ligand resulted in the nitroarene molecule **9**. The heteroacene skeleton was achieved by a Cadogan reductive ring-closure reaction.[12] The compound **9** was refluxed with triethyl phosphite in 1,2-dichlorobenzene for 12 hours to achieve the seven-ring fused heteroacene. The Cadogan ring-closure reaction was non-regioselective to result in a mixture of two regioisomeric heteroacenes **10** (*anti*)



Scheme 1 Synthesis of thienopyrrole based seven-ring fused unsymmetrical heteroacenes.

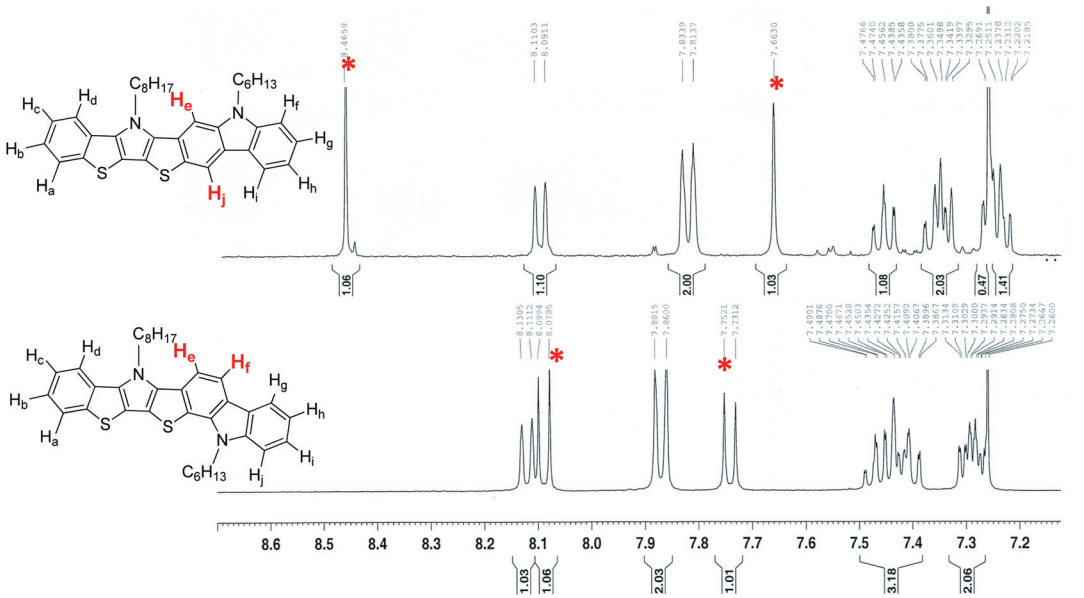
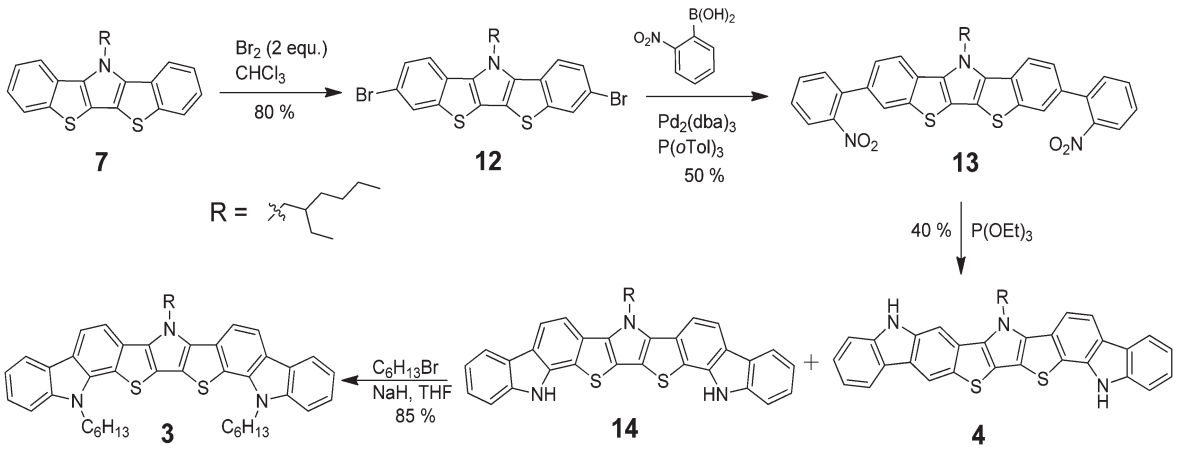


Fig. 2 ^{1}H NMR spectra of *anti* (**1**) and *syn* (**2**) isomer recorded in $CDCl_3$.



Scheme 2 Synthesis of dicarbazolodithienopyrrole.

and **11** (*syn*) (90 : 10). We were successful in isolating the pure form of the major isomer **10** by column chromatography. The minor *syn*-isomer was always contaminated with *anti*-isomer, and owing to its smaller percentage in the mixture, our attempts to achieve a pure form of **11** was unfruitful. Alkylation of these fused cores with hexylbromide in the presence of NaH resulted in the target compounds **1** and **2**. Pure *syn* isomer **2** free of *anti*-isomer was obtained upon alkylation of the mixture of *anti* and *syn* isomers. These isomers are conveniently distinguished by ^{1}H NMR spectroscopy. The *syn* isomer showed the characteristic singlet at 8.47 and 7.67 ppm corresponding to H_e and H_j protons, whereas the *anti* isomer showed the characteristic doublet at 8.09 and 7.74 ppm for H_e and H_f protons (Fig. 2). All synthesised compounds were characterized by ^{1}H NMR, ^{13}C NMR and high resolution mass spectrometric (HRMS) investigation.

The synthetic route towards nine rings fused heteroacene is outlined in Scheme 2. Bromination of **7**, when carried out with excess bromine (2.5 equivalents) for 6 hours, afforded the dibromo product **12**. Suzuki coupling with the nitroarylboronic acid afforded the dinitro arene compound **13** in 50% yield. Cadogan ring-closure of **13** is expected to result in three regio-isomers out of which two isomers were observed. Only the major isomer **14** was isolated, and the other isomer **4** was always contaminated with the major isomer. A similar orientation pattern (substitution *ortho*- to heteroatom) was reported for Cadogan reactions involving carbazole to synthesize diindolocarbazole and the orientation was attributed to the strong *ortho*-directing nature of the hetero atoms.[13] It is noteworthy that the current synthetic scheme allows for the orthogonal substitution on pyrrole nitrogens which provides an additional path to influence their properties. All molecules **1–3** are stable under ambient conditions and soluble in common organic solvents such as THF, $CHCl_3$ and toluene.

Among the compounds synthesized, crystals of **14** were obtained by slow evaporation from ethyl acetate. The molecule

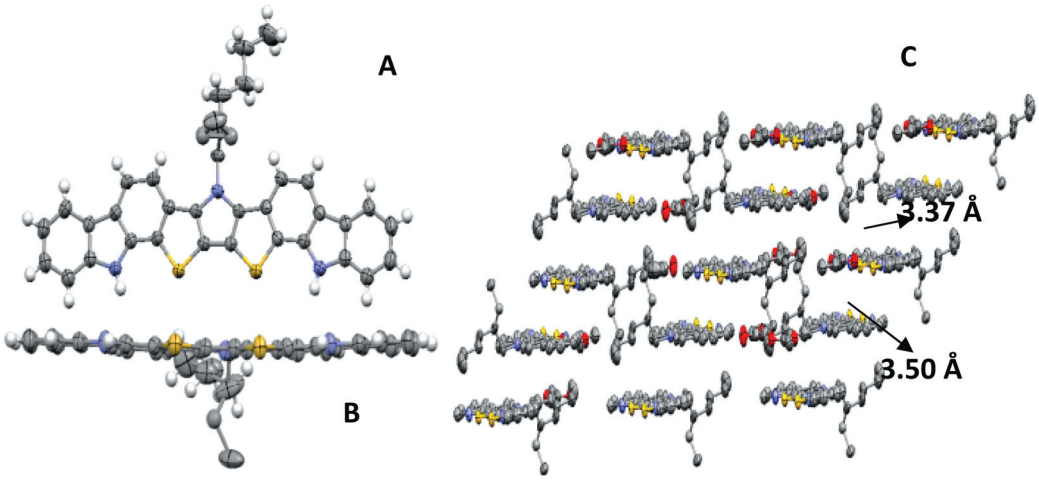


Fig. 3 Thermal ellipsoid plot of **14** (**A**), lateral view (**B**), and packing of **14** in solid state (solvent molecules and hydrogen atoms removed for clarity) (**C**).

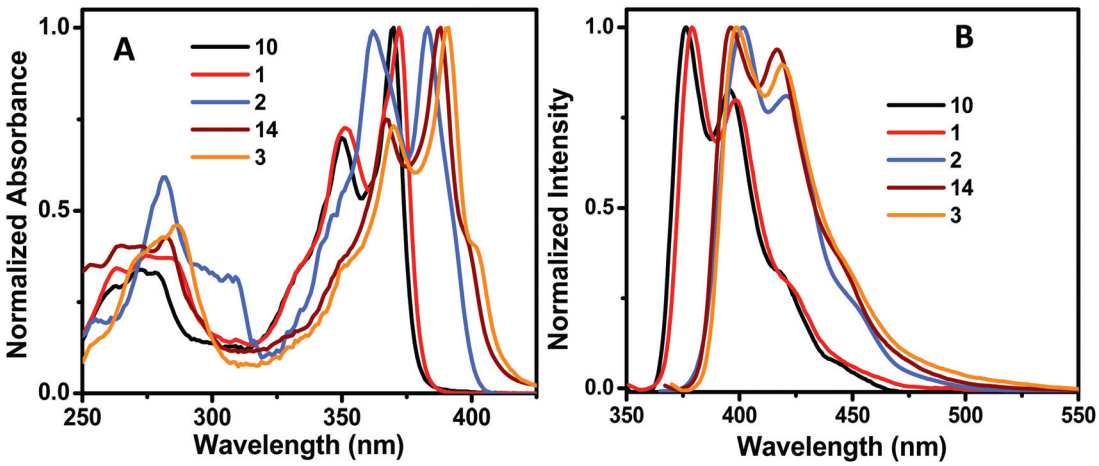


Fig. 4 Normalized absorption spectra (A) and emission spectra (B) of heteroacenes in THF.

Table 1 Optoelectronic properties of heteroacenes

Compd	λ_{max} [a] (nm)	log ε (L mol^{-1} cm^{-1})	$\lambda_{emi\ (nm)}$	ϕ_F [b] (%)	HOMO–LUMO gap[c] (eV)	E_{pa} [d](V)	HOMO[e](eV)	LUMO[f](eV)
10	370, 350, 273	2.08	396, 377	36	3.28	0.51, 1.27	−5.15	−1.87
1	372, 351, 274	1.98	397, 378	35	3.26	0.60, 1.30	−5.18	−1.92
2	383, 362, 282	2.17	421, 404	30	3.09	0.42, 1.06	−5.08	−1.99
14	388, 367, 283	2.39	416, 396	31	3.03	0.30, 1.04	−4.98	−1.95
3	390, 370, 286	2.36	419, 399	30	3.01	0.37, 1.04	−5.00	−1.99

[a] Solvent: tetrahydrofuran. [b] Solution state quantum yield calculated with quinine sulfate as standard. [c] Estimated from the onset of absorption spectra 1240/λ. [d] Oxidation peak potential *versus* Fc/Fc+. [e] Calculated from the empirical relationship $E_{HOMO} = -(E_{oxid}^{onset} + 4.8)$ eV. [f] Calculated LUMO from the relationship $E_{LUMO} = E_{HOMO} - E_g$(optical).

co-crystallizes with two molecules of ethyl acetate which are hydrogen bonded with the pyrrole hydrogen. The thermal ellipsoid plot at 50% probability and crystal packing in solid state are represented in Fig. 3. The crystal structure reveals that the conjugated backbone is highly planar with a deviation of less than 3° from planarity. In solid state, these molecules form a slip-stacked structure of alternate C–H···π interactions of 3.37 Å and close contact of 3.50 Å. No significant π overlap is apparent from the packing along these stacks. These stacked layers are insulated from the other layers by solvent molecule and also by bulky 2-ethylhexyl chains.

Absorption and emission spectra of the fused systems were recorded in THF (Fig. 4) and the values are summarized in Table 1. All fused systems show multiple absorption peaks with the absorption maxima around 370–390 nm. The seven-rings fused *anti*-isomer (**10**) showed absorption maxima at 370 nm.

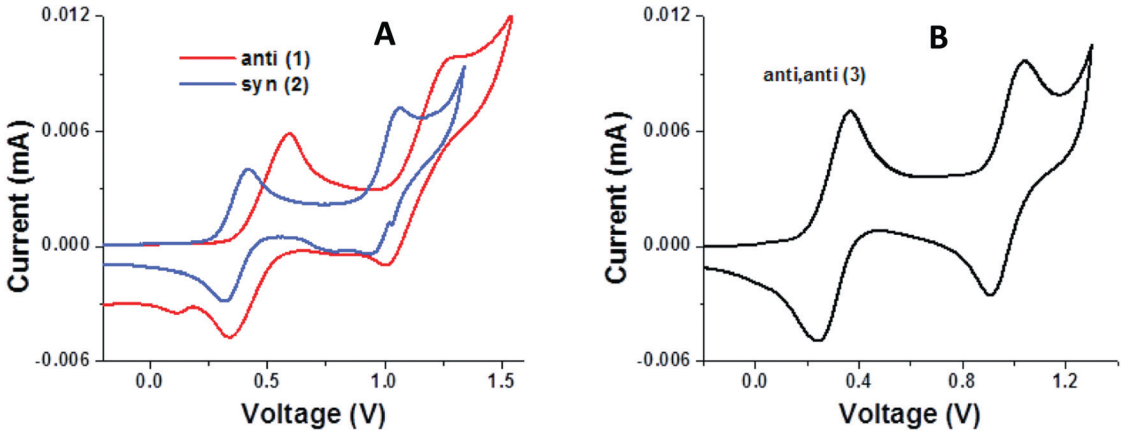


Fig. 5 Cyclic voltammogram of seven-ring (A) and nine-ring fused systems (B) recorded at the scan rate of 100 mV s^{-1}. Potentials are calibrated with respect to ferrocene–ferrocenium couple.

However, *syn*-isomer **2** showed a red shifted absorption with the absorption maximum at 383 nm. This difference in absorption maxima in *anti* and *syn* isomers can be attributed to the difference in conjugation (*vide infra*). Alkylation of the pyrrole unit in compound **10** did not have any effect on the absorption spectrum. Similarly, the absorption spectra of the nine rings fused compound is red-shifted compared to the seven-ring fused systems, with absorption maxima around 390 nm due to an extension in conjugation. The HOMO–LUMO energy gap calculated from absorption onset was estimated to be 3.26, 3.09, and 3.01 eV for compounds **1**, **2** and **3** respectively.

All heteroacenes are blue emissive in solution state with compounds **1**, **2** and **3** showing the emission maximum at 378, 401 and 399 nm respectively with a quantum yield of around 30%. The absorption and emission spectra of these fused systems hold a mirror image relationship with a small Stokes shift, characteristic of rigid conjugated systems with well-defined electronic states.[14]

The redox properties of these compounds were studied using cyclic voltammetry (Fig. 5). All compounds showed two quasi-reversible oxidation peaks; the anodic peak potentials, E_{pa} *vs.* Fc/Fc^{+}, are tabulated in Table 1. They showed two oxidation peaks attributed to the successive oxidation of the pyrrole nitrogens. Alkylation of **10** resulted in a 90 mV positive shift of the first oxidation potential and a 30 mV shift in the second oxidation potential, suggesting that the first oxidation peak can be ascribed to the indole nitrogen. Peak separation between consecutive redox events in a molecule can be used as a tool for the characterization of coupling strength.[15] The *anti*-isomer **1** showed a greater peak separation (700 mV) compared to the *syn*-isomer (640 mV) **2** indicating a slightly better communication between the redox centers in the *anti*-isomer, which can be understood from the canonical structures of these molecules shown below.

The HOMO energy levels were calculated from the oxidation onset potentials using the empirical relationship $E_{HOMO} = (E_{oxid}^{onset} + 4.8)$ eV.[16] The HOMO levels of −5.18, −5.08 and −5.00 eV were estimated for compounds **1**, **2** and **3** respectively. It is interesting to note that all compounds have a low-lying HOMO as compared to heptacene (−4.8 eV)[17] and nonacene (−4.69 eV).[18] The low lying HOMO imparts stability and

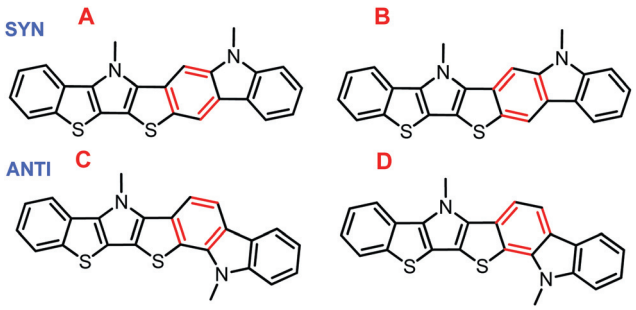


Fig. 6 Canonical structures for *syn* and *anti* isomers.

renders these molecules as viable candidates for components of electronic materials.

In order to understand the difference in optoelectronic properties of *syn* and *anti*-isomers, their canonical structures were compared. A number of canonical structures are possible for both *syn* and *anti*-isomers, of which we consider the one involving the central benzene ring (point of fusion). From Fig. 6, it can be noted that in case of the *syn*-isomer either one of the heterocycles fused to the central benzene ring [pyrrole (**A**) or thiophene (**B**)], resides in a partial quinoidal state, whereas, in case of the *anti*-isomer, canonical structure **C**, with all fused rings in the benzenoid state, will be favored over the canonical structure **D**, with both pyrrole and thiophene in a partial quinoid state. This explains the better conjugation in the *syn*-isomer over the *anti*-isomer which is reflected in their energy gap, absorption maxima and oxidation potential (Table 1). To obtain further support for this, we also calculated HOMO energy levels of the *syn*- and *anti*-isomers of the seven-ring system using DFT calculations. As shown in Fig. 7, *anti* and *syn* isomers showed subtle differences in the distribution of HOMO energy levels. The difference in HOMO energy levels is more pronounced along the central benzene ring, consistent with the canonical structure analysis provided above.

In summary, we report a new family of seven and nine rings fused heteroacenes which are isoelectronic with heptacene and nonacene. The handiness of using thienopyrrole core to construct highly stable and soluble fused aromatic systems is demonstrated. The current synthetic routes also allow for the orthogonal

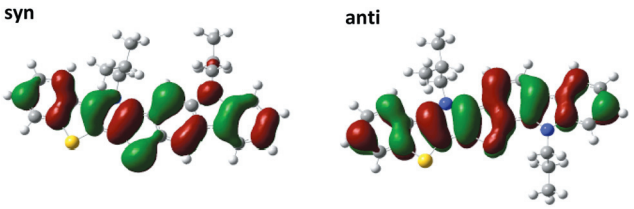


Fig. 7 HOMO energy calculated by density functional theory (DFT) at the B3LYP/6-311g (d,p) level.

substitution on the pyrrole rings. Utilizing the non-regioselective nature of Cadogan cyclization, both *syn* and *anti* isomers are synthesized in one pot. The synthesized heteroacenes are highly stable and are soluble in common organic solvents. The photophysical and electrochemical properties of the *syn*- and *anti*-isomers were studied, both of which indicate that the positions of heteroatoms has a significant influence on the physiochemical properties of these molecules. Investigation of charge transport behavior and incorporation of these fused heterocycles into a semiconducting polymeric backbone is under progress in our laboratory.

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