ChemComm

Cite this: Chem. Commun., 2012, 48, 12174–12176

Neutral tetrathia[22]annulene[2.1.2.1] based field-effect transistors: improved *on/off* ratio defies ring puckering[†]

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Received 27th September 2012, Accepted 1st November 2012 DOI: 10.1039/c2cc37004b

New, neutral, slightly puckered aromatic *meso*-substituted tetrathia[22]annulene[2.1.2.1] macrocyclic architectures display p-type semiconductor behaviour and constitute molecular field-effect transistors with high *on/off* ratios (8.67 × 10⁶) and high mobility (0.23 cm² V⁻¹ s⁻¹) in thin films deposited on octadecyl-trichlorosilane (OTS) modified SiO₂.

Organic field-effect transistors (OFETs), the critical components of future organic electronics, attract much interest because of their attractive applications, such as radio frequency identification tags. flexible displays, and large-area sensors.¹ Considerable effort has been invested in molecular design to synthesize planar, electron rich, stable molecules capable of being easily processed into devices with high hole mobility and switchability. Neutral heteroannulenes are porphyrin like aromatic macrocycles, which display p-type transport properties in vacuum deposited thin films. Among these materials, the meso-p-tolyl substituted tetrathia[22]annulene[2.1.2.1] 1 constituted an efficacious molecular field-effect transistor and displayed reproducible bulk-like hole mobility (as high as $0.63 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in highly crystalline thin films deposited on OTS modified SiO_2 , while the *meso*-phenyl substituted one 2 was a moderate electron donor with a HOMO energy level of -4.88 eV and depicted a hole mobility of 0.29 cm² V⁻¹ s⁻¹ in thin films.² The meso-substituted oxygen bridged tetraoxa[22]annulene[2.1.2.1] 3 depicted both stability as well as a competitive hole mobility of 0.4 cm² V⁻¹ s⁻¹ in thin films.³ Incidentally, these charge mobility values are among the highest of thin film OFETs. Further, these values are much higher than the related and most studied α -oligofurans 4 (mobility: 0.05–0.066 cm² V⁻¹ s⁻¹) and α -oligothiophenes 5 (mobility: 0.09 cm² V⁻¹ s⁻¹).⁴ The superior charge transport of 1-3 is believed to be benefited from the extended π -conjugation, which lowers the reorganization energy and enhances intermolecular π - π overlapping. Recently, we demonstrated⁵ the feasibility of growing crystals of a self-assembled mixed-stack neutral donor-acceptor π - π complex from a solution

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Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China. E-mail: wxu@iccas.ac.cn of **2** and tetracyanoquinodimethane (TCNQ) in a 1 : 1 ratio. Devices based on such highly ordered structure exhibited ambipolar behaviour with a stable balance hole mobility of 0.04 cm² V⁻¹ s⁻¹ and an electron mobility of 0.03 cm² V⁻¹ s⁻¹ in an ambient atmosphere. This "molecular level heterojunction" provided a novel strategy for the construction of ambipolar devices with great potential for light-emitting transistors, lowcost devices and complementary metal oxide semiconductor (CMOS)-like circuits.⁵

A characteristic feature of 1–2 (Fig. 1) is the planarity of these aromatic systems as well as their propensity to lose two electrons to form dicationic antiaromatic species 6 and 7. The devices based on 1 on OTS modified SiO₂ films showed a favourable threshold voltage ($V_{\rm T} = -7.47$ to -12.9 V, $T_{\rm sub}$ 25 °C) but low *on/off* ($I_{\rm on}/I_{\rm off}$) ratios (10² to 10³) while the thin film devices of 3 showed a more positive threshold voltage (*ca.* 20 V) with low *on/off* ratios similar to 1. Thus, given the high mobility values, neutral heteroannulenes based on 1–3 could provide alternative and potentially competitive materials for the next generation of low-cost and flexible portable electronic devices where traditional semiconductors cannot be used. However, the transistor's electrical performance was not impressive owing to the low current *on/off* ratios which is not suitable for switching applications.

Compared with *meso*-unsubstituted tetrathia[22]annulene, the *meso*-substituents (Ph, *p*-MePh) in **1** and **2** altered the molecular stacking pattern and significantly improved the transport properties of the materials based on **1** and **2** in the thin films. We wondered if the presence of strongly electron withdrawing groups on the *meso*-aryl groups of such materials would improve the charge transport properties especially the current *on/off* ratios of the thin film devices. In this communication, we report the synthesis as well as OFET characteristics of new neutral tetrathia[22]annulene[2.1.2.1]s bearing electronegative groups on the *meso*-phenyl substituents.



Fig. 1 π -Conjugated OFET materials 1–5 and dications 6 and 7.

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[†] Electronic supplementary information (ESI) available: Details of experimental procedures and full characterization. CCDC 900288. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc37004b



Scheme 1 Synthesis of 11a,b: (a) *n*-BuLi (2.24 mmol)/DMF (2.2 mmol); (b) Zn (21 mmol)/TiCl₄ (11.0 mmol)/pyridine (20 mmol)/THF, reflux; (c) DDQ (3.0 mmol)/hydrazine; (d) conc. H_2SO_4 .



Fig. 2 X-ray crystal structure and stacking pattern of **11a** (view along the *a*-axis).

The bis(thien-2yl)methane derivatives **8a–b** could be conveniently di-formylated following a dilithiation–formylation sequence (Scheme 1). The reductive McMurry coupling of the dialdehydes **9a–b** gave the corresponding dihydrotetrathiaannulene derivatives **10a–b** in high yield. The dehydrogenation of **10a–b** by DDQ occurred immediately in toluene solution to give insoluble black complexes which were readily reduced by hydrazine to obtain the crystalline tetrathia-[22]annulene[2.1.2.1] derivatives **11a–b** (S2–S5, ESI†).

Thermogravimetric analysis (TGA) indicated good thermal stability (Fig. S42 and S43, ESI[†]), with sublimation occurring prior to decomposition (>355 °C, **11a** and >380 °C, **11b**). Further, **11a** and **11b** showed exceptional stability in air and did not require any inert atmosphere conditions for handling.

Crystals of 11a suitable for X-ray structure determination were obtained from a methylene chloride-toluene solution of the purified product. The compound crystallizes in an orthorhombic unit cell and belongs to the Fdd2 space group with unit cell parameters $a = 60.299, b = 19.5214, c = 9.5973 \text{ Å}, \alpha = \beta =$ $\gamma = 90^{\circ}$. Unlike, *meso*-phenyltetrathia[22]annulene[2.1.2.1],² the four sulfur atoms of the macrocycle are not in the same plane (Fig. 2), as are the thiophene rings, like the [18]annulene analogue in which the three thiophene units are totally out of plane. Two sulphur atoms linked through the meso-bridge are below the plane of the twisted macrocyclic ring, while the other set intercepted by a four-carbon bridge is well above the mean plane of the macrocyclic ring. Out of the four sulfur atoms, the ones intercepted by four-carbon atoms are 3.092 and 3.118 Å apart, while the neighbouring sulfur atoms separated by a three-carbon bridge are 3.038 and 3.044 Å apart. These

2.5 4.00E-06 2 2.00E-06 1.5 0.00F+00 I/A А 1 -2.00F-06 0.5 -4.00E-06 -6.00E-06 0 235 335 435 535 635 735 835 1.5 0.5 0 E/V λ / nm (b)

Fig. 3 (a) UV-vis spectra of 10a (DCM), 11a (DCM) and 12a (H_2SO_4) ; (b) CV for 11a.

distances are marginally shorter than twice the van der Waals radius of sulfur (3.60 Å). The distances between the two sets of the opposite sulphur atoms are 4.317 and 4.373 Å. Like most of the aromatic porphyrinoids, 11a is purple but is not as planar as the other meso-aryltetrathia[22]annulene[2.1.2.1]s. This is also indicated by the torsion angles between all sulphur atoms (Table S5, ESI[†]). Electron delocalization was expected and is attested by the carbon-carbon distances in the thiophene rings as well as the macrocycle. The thiophene units show the bond length relation $C\alpha$ – $C\beta$ > $C\beta$ – $C\beta$ in concurrence with electron delocalized systems such as porphyrins. It is worth mentioning that the centrosymmetric tetrathiaporphyrin dication with four thiophene rings tilted up and down from the mean molecular plane by 22.8° and 3.7°, respectively, showing⁶ the above bond length relationship very clearly. Further, we have found that the m-substituted meso-substituents around the annulene core induced slight ring puckering of the molecule but did not affect aromaticity. The molecules of 11a stacked in a shifted face-to-face pattern into a layer structure along the bc plane (Fig. 2). The intermolecular π - π interactions could be observed as the interplanar distance between the adjacent molecules in one stack is in the range of 3.4–3.6 Å. Such π – π overlapping will provide the path for electron transport. As can be seen the individual molecules in the stacking figure are somewhat curved rather than fully planar, still showing perfect transistor behaviour.

As a quantitative probe of aromaticity, we have calculated Nucleus-Independent Chemical Shift, NICS(1), values using *ab initio* quantum mechanical DFT calculations at the B3LYP/6-311G(d) level using the Gauge Independent Atomic Orbitals (GIAO) method.⁷ The large negative NICS(1) values of **11a** (-13.33 ppm) and **11b** (-13.32 ppm), calculated at centre of the molecules, indicate a marginally greater degree of aromaticity compared to similarly substituted oxa annulenes (*ca.* -13.17 ppm), reflecting the enhanced ring current effects. The shapes of the plots of the chemical shifts as a function of distance of the NICS probe (bq) from the molecular plane gave a clear indication of occurrence of diamagnetic ring currents (Fig. S30 and S33, ESI[†]).

The aromaticity of **11a** was further evidenced by its ¹H NMR and UV-visible absorbance spectra. In the ¹H NMR (Fig. S23, ESI[†]) spectrum, a singlet is observed at 11.09 ppm, corresponding to the protons on the ethene carbons, and an AB system corresponding to the thiophene protons at 10.40 and 9.99 ppm. The aromatic protons appeared at 8.46 (2H), 8.35 (2H) and 7.95 (4H) ppm. In contrast, no protons of the dihydro compound **10a** appeared above 7.25 ppm (for NMR data of **11b**, see Fig. S26, ESI[†]). The LCMS spectrum of **11a** showed a strong molecular ion peak and minimal fragmentation.

UV-visible absorption spectra recorded in DCM showed a sharp and strong absorption maximum for **11a** at 430 nm (ε = 271 514 dm³ mol⁻¹ cm⁻¹), compared to **10a** (Fig. 3a), and several weaker absorptions at wavelengths [384, 470, 513, 552, 598 and 774 nm (ε = 36 585, 3571, 4285, 15 428, 70 942, 2157 dm³ mol⁻¹ cm⁻¹, respectively)]. The unsplit Soret band at 430 nm of the **11a** is analogous to the split Soret band at 415 and 433 nm of the low (C_2) symmetry **3** while the Q-type bands appeared to be slightly red shifted than porphycenes.⁸ In analogy with **3**,³ the 22 π annulenes **11a** and **11b** were found to dissolve in sulfuric acid to give a reddish-orange solution, indicative of formation of the dication **12a** and **12b**, respectively



Fig. 4 AFM images $(2 \ \mu m \times 2 \ \mu m)$ of 50 nm thick films of **11a**: (a) deposited on the OTS/SiO₂/Si substrate, $T_s = 20 \ ^{\circ}$ C; (b) deposited on the OTS/SiO₂/Si substrate, $T_s = 60 \ ^{\circ}$ C; (c) deposited on the OTS/SiO₂/Si substrate, $T_s = 100 \ ^{\circ}$ C; AFM images (5 $\ \mu m \times 5 \ \mu m$) of 50 nm thick films of **11b**: (d) deposited on the OTS/SiO₂/Si substrate, $T_s = 20 \ ^{\circ}$ C; (e) deposited on the OTS/SiO₂/Si substrate, $T_s = 20 \ ^{\circ}$ C; (f) deposited on the OTS/SiO₂/Si substrate, $T_s = 60 \ ^{\circ}$ C; (f) deposited on the OTS/SiO₂/Si substrate, $T_s = 100 \ ^{\circ}$ C.

(disappearance of sharp Soret bands and appearance of broadened absorption bands). Also **12b** depicted a considerably positive (10.65 ppm) NICS(1) value [Fig. S36, ESI[†]]. The UV-vis data of thin films (Fig. S40a and b, ESI[†]) showed good correlation with the solution absorption spectra. Cyclic voltammogram (CV) of **11a** (Fig. 3b) in CH₂Cl₂ shows two reversible oxidation peaks at $E_{0x}^0 = 642$ and 1097 mV vs. SCE (calibrated using Fc/Fc⁺ = 0.40 V vs. SCE) indicating the formation of 20 π dicationic species, while **11b** showed oxidation peaks at $E_{0x}^0 = 581$ and 983 mV vs. SCE (Fig. S41, ESI[†]). This data corresponds to HOMO energies of -5.04 eV ($-4.4 - E_{0x}^0$ vs. SCE) for **11a** and -4.98 eV for **11b**. Compared with that of **2**, the reduced electron donating ability of **11a** and **11b** is due to the presence of electron withdrawing Cl and F atoms on the *meso*-phenyl group.

The band gap of **11a** and **11b** was estimated to be 1.57 eV from the absorption onsets. The HOMO levels of **11a** and **11b** were estimated to be -5.04 and -4.98 eV, respectively, by CV measurements which are comparable to the HOMO level of gold (-4.9 eV) suggesting an effective hole mobility between the electrode and the semiconductor leading to improved device performance. Visualization of the HOMOs and LUMOs of **11a** and **11b** revealed π -delocalization over the annulene rings of both **11a** and **11b** supporting the observed aromatic character and greater contribution of sulphur atoms to HOMOs compared to LUMOs (Fig. S38 and S39, ESI⁺).

Morphologies of the thin (50 nm) film of the heteroannulenes 11a and 11b vacuum deposited on OTS treated SiO₂/Si wafers were studied by atomic force microscopy (AFM) (Fig. 4). The organic semiconductors (top contact bottom gate) were deposited on the substrate by thermal evaporation under a pressure of $8 \times$ 10^{-4} Pa at a deposition rate gradually increased from 0.1 Å s⁻¹ to 0.4 Å s⁻¹ up to the first 20 nm and then maintained 0.5 Å s⁻¹ until the thickness of the film was 50 nm. When the substrate was at ambient temperature (20 °C), the film deposited on the OTS-treated SiO₂/Si substrate essentially consisted of small grains. At elevated temperature (60 °C), the grains became bigger in size and resulted in more ordered film on the OTS/ SiO₂/Si substrate. When the substrate temperature was further increased to 100 °C, the film cracked and lamellar crystalline grains were observed. However, no obvious diffraction peaks could be observed in the XRD patterns, which indicated the amorphous character of the thin films. In fact, small molecule based amorphous thin films with a relatively high mobility are

Table 1 Detailed performance of OFETs based on 11a, 11b thin films

Compound	$T_{\rm s}/^{\circ}{\rm C}$	$\mu/{\rm cm}^{-2}~{\rm V}^{-1}~{\rm s}^{-1}$	$I_{\rm on}/I_{\rm off}$	$V_{\mathrm{T}}/\mathrm{V}$
11a	20	2.73×10^{-2}	2.82×10^{5}	-17.5
	60	7.17×10^{-2}	8.67×10^{6}	-23.4
	100	$0.20 (0.23)^a$	5.27×10^{5}	-17.7
11b	20	1.42×10^{-4}	1.83×10^{5}	-21.3
	60	1.83×10^{-3}	1.28×10^{5}	-42.6
	100	9.60×10^{-3}	2.42×10^{5}	-56.1
		$(0.012)^a$		

^{*a*} The maximum values of mobility are presented in the brackets besides the average values.

still rare. Since, the extended π -conjugation contributes to efficient intermolecular coupling in these solids lacking molecular structural ordering, further modification of the structure may lead to high performance solution processable materials.

The performance of the OFETs is summarized in Table 1. The mobilities (μ) were calculated in the saturation regime by the equation: $I_{\rm D} = \mu C_{\rm i} (W/2L) (V_{\rm G} - V_{\rm T})^2$, where $I_{\rm D}$ is the drain current, μ is the field-effect mobility, $C_{\rm i}$ is the gate dielectric capacitance, W and L are the channel width and length, respectively, $V_{\rm T}$ is the threshold voltage. **11a** deposited at 100 °C exhibited the best OFET performance (0.23 cm² V⁻¹ s⁻¹) with a much improved *on/off* ratio of 5 × 10⁵. The FET characteristics of **11a** and **11b** are shown in Fig. S44, ESI.† Further, mobility of these devices did not change significantly, upon exposure to air for ten days, although the *on/off* ratio decreased by one order of magnitude.

In summary, a facile, high yielding synthesis of new *meso* substituted tetrathia[22]annulene[2.1.2.1]s has been described.

Compared to the previously reported neutral annulenes these materials depicted much improved *on/off* ratios. Their charge mobility is much superior to analogous α -oligothiophenes. This difference serves to highlight the role that neutral tetrathiaannulenes can play in the development of potentially useful OFETs.

KS and TSV thank DST, New Delhi, for the Research grant SR/S1/OC-27/2009 and UGC, New Delhi, for the SAP grant and the Sophisticated Instruments Centre at IIT Indore for X-ray structure determination.

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