# New sulfur bridged neutral annulenes. Structure, physical properties and applications in organic field-effect transistors†

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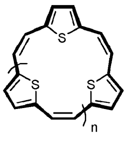
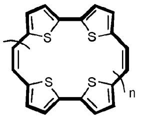
**New, neutral, *meso*-substituted tetrathia[22]annulene[2,1,2,1] aromatic macrocyclic architectures display p-type semiconductor behaviour and constitute efficacious molecular field-effect transistors with reproducible bulk-like carrier mobility (as high as $0.63\ cm^2\ V^{-1}\ S^{-1}$) on highly crystalline thin films deposited on octadecyltrichlorosilane modified $SiO_2$.**

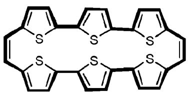
Aromaticity of cyclic conjugated chemical entities in terms of cyclic delocalization of mobile electrons is a distinctive feature implicated in the understanding of structural, electronic as well as magnetic properties.[1] The neutral alkene linked thiaannulenes, **1** and **2** represent 18π- and 24π-electron systems which deviate from planarity and are devoid of any ring current and are thus neither aromatic nor antiaromatic.[2] The conjugation in these apparently conjugated ring systems is restricted to the thiophene rings only. On the other hand tetrathiaporphycene **3** is found to be a distorted non-planar 20π system, which in spite of being strained, depicts remarkable stability.[3] Whereas the UV data ($\lambda_{max}$ 336, 274, 229, 210 nm) of **3** depicts modest conjugation, the NMR data does not show any obvious ring current. The $(4n + 2)\pi$ tetrathia[22]-annulene[2,1,2,1] **4**, which ought to be a planar and aromatic 22π system, depicts NMR data similar to **3** ($4n\pi$) *i.e.* without an obvious ring current. Further, corroborated by the X-ray evidence, the UV data suggests non-planarity and it shows a tendency to get reduced electrochemically to the diatropic 22π dianion.[3] The six-thiophene system **5** possesses only partial conjugation (UV data: $\lambda_{max}$ 431, 394, 381, 272, 222 nm). This 28π system in its cyclic voltamogram shows two reversible oxidation peaks (0.51 and 0.78 eV), indicating the formation of 26π dicationic $(4n + 2)\pi$ species. In its $^1H$ NMR spectrum (11.28 and 12.10 ppm), recorded in 98% $D_2SO_4$, strong ring currents were observed and the UV data (98% $H_2SO_4$) depicted bathochromic shifts in comparison to the original spectrum, showing peaks at 885, 858, 521 nm. The only neutral tetrathiaannulene possessing alternate methine and ethene links reported thus far is **6**.[3] The peripheral aromaticity of **6** was evidenced by its $^1H$ NMR [two singlets at $\delta$ 12.34 (methine H), 11.36 (ethene H) ppm] and UV-Vis absorption spectra (417, 503, 540, 579, 771 nm). These cyclic conjugated chemical entities have gained significance in biomedicine,[4] micro-electronic devices[5] as well as for the development of advanced materials (*e.g.*, conducting polymers,[6] organic field effect transistors, OFETs)[7] *etc.*, and are thus challenging synthetic targets. Appending substituents on **6** at methine carbons (*meso*-positions) appeared particularly attractive to us as it would provide experimental probes for expanding the scope to understand features related to structure and aromaticity, and would allow access to the hitherto under-appreciated evaluation of *meso*-elaborated cyclic conjugated architectures **10** as active materials for organic field-effect devices. In that light, while the McMurry strategy introduced by Vogel[8] remains the method of choice for constructing the annulene ring **6**, the synthesis of *meso*-aryl substituted building block **7**, however, was conveniently achieved through the known aldehyde–thiophene condensation route.



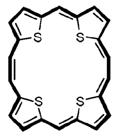
**1** n = 1
**2** n = 2



**3** n = 1
**4** n = 2



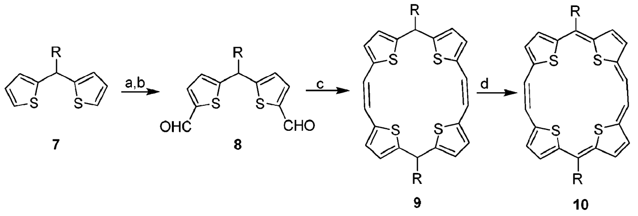
**5**



**6**

The bis(thien-2yl)methane derivatives **7a–d** could be conveniently di-formylated following a dilithiation–formylation sequence (Scheme 1).[9] The reductive McMurry coupling of the dialdehydes **8a–c** gave the corresponding dihydro-tetrathiaannulene derivatives **9a–c** in high yield. The dehydrogenation of **9a–c** 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 **10a–c** (see ESI† for experimental details).

Being a 22π macrocycle, annulene **10a** may be expected to be capable of losing two electrons (Scheme 2) to form a 20π dication. The cyclic voltammogram (Fig. 1) of **10a** shows two reversible oxidation peaks at 552.6 and 968.2 mV (*vs.* SCE), respectively, indicating that a 20π dication **11** is formed.



**a**, R = $C_6H_5$; **b**, R = $p$-$MeC_6H_4$; **c**, R = $p$-$ClC_6H_4$

**Scheme 1** Synthesis of **10a–c**; *n*-BuLi (4.1 mmol)/THF, 20 °C; (b) DMF (9.7 mmol); (c) Zn (54 mmol)/$TiCl_4$ (27 mmol), pyridine (45 mmol), THF, reflux; (d) DDQ (1.05 mmol), hydrazine.

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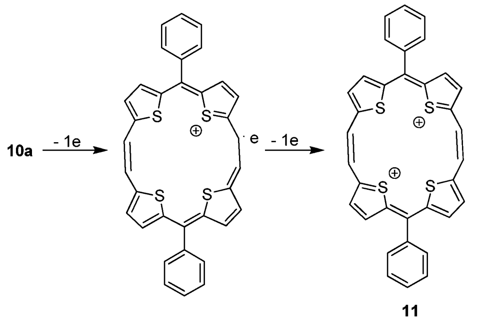

**Scheme 2** Electrochemical oxidation of **10a** to dicationic **11**.

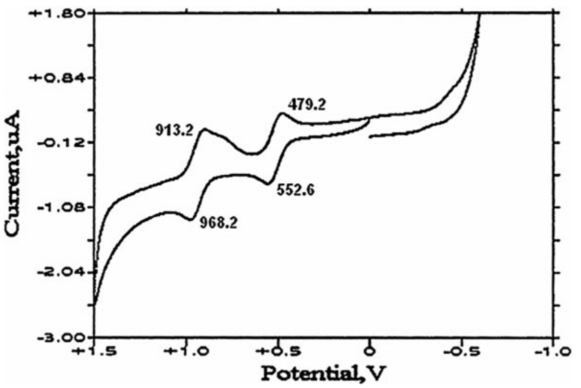

**Fig. 1** Cyclic voltammogram (CV) for **10a** (DCM, electrolyte TBAPF$_6$; working electrode: Pt; reference electrode: Ag/AgCl; 80 mV s$^{-1}$ (for CV of **10b** and **10c**, see Fig. S1 and S2, ESI†).

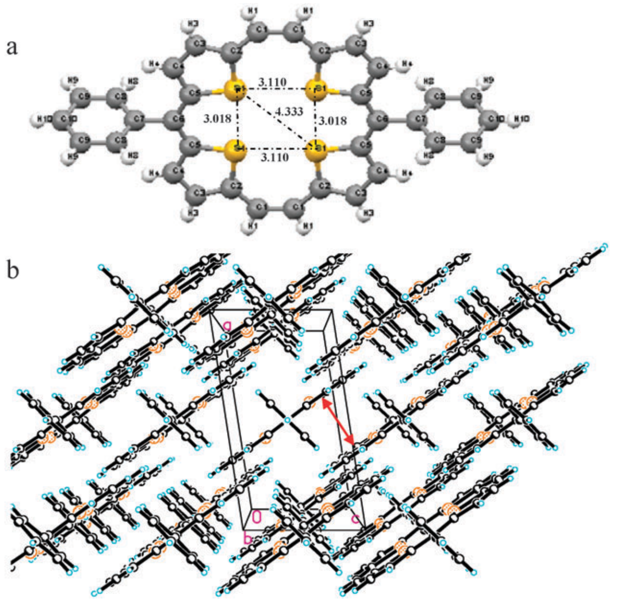

**Fig. 2** Crystal structure of **10a**. (a) Molecular structure of **10a** showing distances between sulfur atoms in the crystal. (b) Stacking pattern of **10a** in the crystal view along the *b*-axis (π–π interaction was observed with an interplanar distance of 3.526 Å (red arrow)).

Crystals of **10a** suitable for an X-ray structure determination were obtained from a methylene chloride–toluene solution of the purified product. The compound crystallizes in a monoclinic unit cell and belongs to the *C*2/*m* space group with unit cell parameters $a$ = 10.8683, $b$ = 20.9734, $c$ = 5.9459 Å, $\beta$ = 98.702°. The four sulfur atoms of the macrocycle are in the same plane (Fig. 2), as are the thiophene rings, unlike the [18]annulene analogue **1** in which the three thiophene units are totally out of plane. Of the two sets of sulfur atoms, the ones intercepted by four-carbon atoms are 3.110 Å distance apart, while the distance between the neighbouring sulfur atoms separated by a three-carbon bridge is 3.018 Å. These distances are marginally shorter than twice the van der Waals radius of sulfur (3.60 Å). The distance between the opposite sulfur atoms is 4.333 Å. Since the compound is purple and is planar, as also indicated by the torsion angles (0°) between all sulfur atoms, 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, very markedly showed[10] the above bond length relationship. Further, we have found that the *meso*-substituents around the annulene core do not induce any ring puckering of the molecule and/or affect aromaticity. The molecules of **10a** stacked in a face-to-face pattern along the *c*-axis into columns. The intermolecular π–π interactions could be observed as the interplanar distance between the adjacent molecules in one column is 3.526 Å. Such a column stacking and π–π overlapping will provide the path for electrical transport.

The aromaticity of **10a** was further evidenced by its $^1$H NMR and UV-visible absorbance spectra. In the $^1$H NMR spectrum, a singlet is observed at 11.08 ppm, corresponding to the protons on the ethene carbons and an AB system corresponding to the thiophene protons at 10.38 and 10.01 ppm. The aromatic protons appeared at 8.48 (6H) and 8.00 (4H) ppm. In contrast, no protons of the dihydro compound appeared below 7.39 ppm. The FAB mass spectrum of **10a** was very simple and showed a strong molecular ion peak (100%) and no fragmentation. In the UV-visible spectrum, recorded in DCM (Fig. 3), there are sharp and strong absorption maxima at 429 nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$ 222 860), compared to **9a**, and several weaker absorptions at longer wavelength [519, 557, 600 and 777 nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$ 2900, 9200, 57380 and 1700)]. The first absorption (at 429 nm) is analogous to the typical Soret band of the porphyrins and porphycenes, while the absorptions at longer wavelengths are similar to the Q-bands, but with a bathochromic shift with respect to porphycene. These spectra are clearly typical of an aromatic porphyrinoid macrocycle.

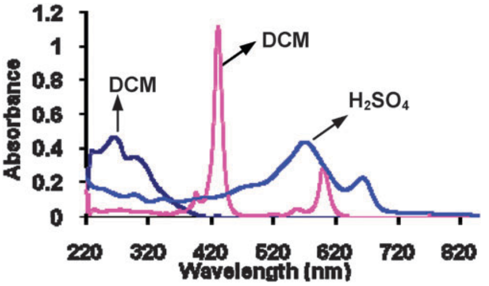

**Fig. 3** UV/VIS spectra of **10a** (DCM and $H_2SO_4$) and **9a** in DCM.

**Table 1** Detailed performance of OFETs based on thin films of **10a–c** on OTS-treated $SiO_2$/Si substrates with different substrate temperatures ($T_{sub}$)

| | $T_{sub}$/°C | $\mu^a$/cm$^2$ V$^{-1}$ s$^{-1}$ | $I_{on}/I_{off}$ | $V_T$/V |
|---|---|---|---|---|
| **10a** | 25 | 0.25 (0.29) | $1.34 \times 10^3$ | −12.9 |
| | 60 | $1.58 \times 10^{-2}$ | $1.48 \times 10^3$ | −5.11 |
| **10b** | 25 | 0.44 (0.63) | $3 \times 10^2$ | −7.47 |
| | 60 | 0.28 (0.31) | $1.34 \times 10^3$ | −17.6 |
| **10c** | 25 | $5.04 \times 10^{-3}$ ($9.68 \times 10^{-3}$) | $8.96 \times 10^5$ | −49.0 |
| | 60 | $2.45 \times 10^{-2}$ ($3.16 \times 10^{-2}$) | $3.03 \times 10^4$ | −50.1 |

[a] The maximum values of mobilities are given in parentheses alongside the average values.

Compared to the thiophene derived [18]annulene, this macrocycle is less crowded, enabling it to have a planar or near-planar structure with its π-electrons fully conjugated around the periphery. Recording of UV-visible spectrum in $H_2SO_4$ resulted in considerable broadening of the peaks, suggestive of formation of dicationic 20π antiaromatic species **11**.

Thin films of **10a–c** were prepared by vacuum deposition on octadecyltrichlorosilane (OTS) modified or bare $SiO_2$. The AFM (Fig. S4, ESI†) and XRD (Fig. S5, ESI†) characterizations revealed that, in contrast to **10c**, the films of both **10a** and **10b** are highly crystalline. The substrate temperature also has significant influence on the morphology, crystallinity and the corresponding transport properties of the films. The first intense reflection was observed at $2\theta = 5.43$, 5.09 and 5.11° for **10a**, **10b** and **10c**, respectively, corresponding to *d*-spacings of 1.62, 1.73 and 1.73. These *d*-spacings are close to that of the molecular lengths along the longer axis (1.86, 2.02 and 2.00 nm for **10a**, **10b** and **10c**, Fig. S6, ESI†). Thus, **10a**, **10b** and **10c**, position on the substrate with their long axes inclined at angles of 60.6, 59.0 and 59.0, respectively, w.r.t the substrate. This is different from what has been previously observed,[7] where the *meso*-unsubstituted tetrathia[22]annulene **6** was positioned almost perpendicular to the substrate.

The electrical transport properties of thin films of **10a–c** were characterized by FET devices (Fig. S7, ESI†). All of these materials behaved as p-type organic semiconductors. Data of device performance (for full data with a variety of substrates, see Table S1, ESI†) are summarized in Table 1. The highest performance with a mobility as high as 0.65 cm$^2$ V$^{-1}$ S$^{-1}$ was observed on thin films of **10b** deposited on OTS-modified $SiO_2$ at a substrate temperature of 25 °C. This value is among the highest of thin film OFETs. Comparing with *meso*-unsubstituted tetrathia[22]annulene **6**, the *meso*-substituents (substituted and unsubstituted phenyl group) significantly improved the transport properties of these materials. This could presumably be attributed to the change of molecular stacking pattern of **10a–c** w.r.t the *meso*-unsubstituted counterpart **6**,[7] as specified above, in the thin films.

In conclusion, three new *meso*-elaborated neutral, aromatic tetrathia[22]annulene[2,1,2,1] derivatives, derived solely from thiophene, have been synthesized. Introduction of substituents at the *meso*-position significantly alters the stacking pattern in the solid state and improves the electrical transport properties of these aromatic macrocylic molecules. It has been revealed that these sulfur bridged annulenes are promising active materials for OFETs.

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