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Hexaazatriisothianaphthenes: new electron-transport mesogens?

Matthias Lehmann,[a] Vincent Lemaur,[b] Jérôme Cornil,[b,c] Jean-Luc Brédas,[b,c] Simon Goddard,[d] Ilaria Grizzi[d] and Yves Geerts[a,*]

[a]*Laboratoire de Chimie des Polymères CP206/1, Université Libre de Bruxelles, Boulevard du Triomphe, 1050 Bruxelles, Belgium*
[b]*Laboratory for Chemistry of Novel Materials, Center for Research in Molecular Electronics and Photonics, University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium*
[c]*School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA*
[d]*CDT Limited, Greenwich House, Madingley Rise, Madingley Road, Cambridge CB3 0HJ, England, UK*

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Abstract—Hexaazatriisothianaphthenes substituted with six alkylsulfanyl chains (propyl and dodecylsulfanyl) have been synthesised and their thermotropic, photophysical and oxidation–reduction properties characterised. Their synthesis has been motivated by the results of quantum-chemical calculations that point to efficient transport properties for these new electron-deficient mesogens since electron transport is predicted to be only slightly affected by rotational degrees of freedom in the discotic mesophase.

1. Introduction

Discotic aromatic compounds emerge as attractive materials to promote efficient transport properties in organic-based devices such as light-emitting diodes, photovoltaic cells, or field effect transistors. Columnar liquid crystals combine the advantages of ease of preparation of oriented thin films, high order in the columns upon self-assembly, and self-healing capacity. Since such functional materials are used as one-dimensional semiconductors, both the orientation of the columnar structures at interfaces and the intracolumnar order of the aromatic cores play an important role in defining the device performance.[1] While a large number of p-type semiconducting columnar mesogens is known, few n-type materials have been reported to date.[2] Hexaazatriphenylenes (HAT), incorporating six nitrogen heteroatoms within a triphenylene core, are known to be electron-deficient and should thus facilitate electron injection. Columnar liquid crystals of derivatives based on a hexaazatriphenylene core have been obtained by supplying the electron-deficient core with three to six lateral chains.[3] In contrast, the electron-rich thiophene unit yields p-type semiconductivity in polythiophenes. Enhanced electron transport has been observed recently in conjugated polymers containing both thiophene and electron deficient units;[4] the substitution of sexithienyl with perfluorated carbon chains has also provided n-type semiconducting materials.[5] Our interest in electron-deficient columnar mesogens[3a] has led us to combine the HAT and thiophene building blocks to generate compound **1** (Fig. 1) as potential electron transport material. We have introduced peripheral alkylsulfanyl chains to increase solubility, stabilise the radical anions,[6] and induce supramolecular columnar liquid crystalline order. The preparation of **1** has also been triggered by the results of quantum-chemical calculations indicating that the electron transport properties are expected to be improved in hexaazatriisothianaphthene compounds

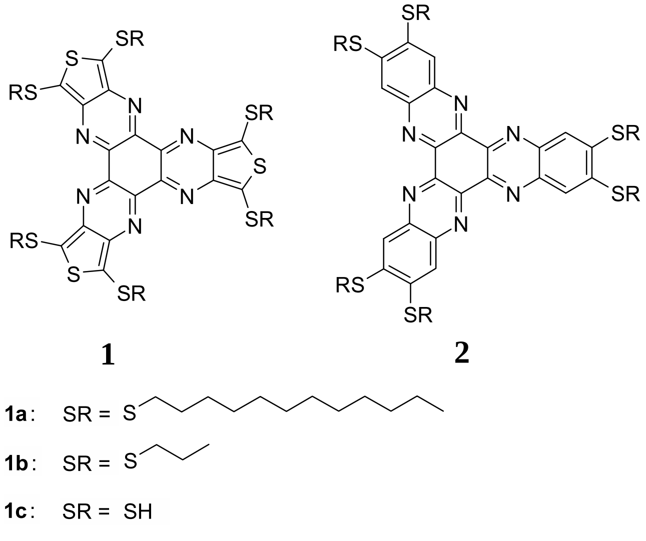

Figure 1. Chemical structure of hexaazatriisothianaphthenes **1** not forming LC phases and of hexaazatrinaphthalenes **2** forming LC phases for R=C_nH_{2n+1} (n=6, 8, 10, 12).[3a]

Keywords: Discotic mesogens; n-Type semiconductor; Electron mobility; Electronic splitting.

[*] Corresponding author. Tel.: +32-2-650-5390; fax: +32-2-650-5410; e-mail address: ygeerts@ulb.ac.be

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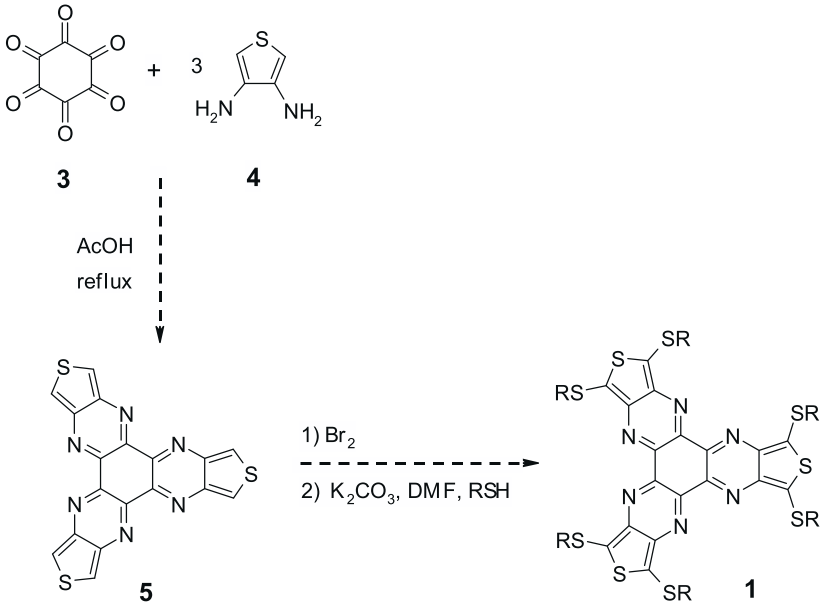

Scheme 1. Unsuccessful divergent synthesis of alkylsulfanyl-substituted **1**.

compared to triphenylene derivatives, as described below. The convergent synthesis of the new electron-deficient potential mesogen **1** containing linear lateral alkylsulfanyl chains is reported here and its thermotropic, photophysical and electrochemical properties are characterised.

2. Results and discussion

2.1. Synthesis

Hexaazatriisothianaphthene is a molecule with a threefold symmetry built on the hexaazatriphenylene core. This class of compounds can be prepared by a threefold condensation of either 1,2-diketones with hexaaminobenzene[7] or of 1,2-diamines with hexaketocyclohexane.[8] Since hexaketocyclohexane **3** is commercially available and the preparation of diaminothiophenes is well established, we have chosen the latter route to reach our synthetic goal. A first attempt to obtain the parent hexaazatriisothianaphthene **5** by the condensation of 3,4-diaminothiophene **4** with hexaketone **3** is shown in Scheme 1. A subsequent hexabromination and nucleophilic substitution with mercaptoalkanes should give the alkylsulfanyl-substituted molecules. This approach offers as an advantage that the thermotropic properties can be easily tuned in the final reaction step by introduction of different lateral, flexible groups, as recently achieved for hexaalkylsulfanyltriphenylenes[9] and hexaalkylsulfanylhexaazatrinaphthylenes.[3a] After the threefold condensation, a black insoluble powder was obtained, from which the hexaazatriisothianaphthene **5** could not be isolated. In order to improve the solubility of the final product, a convergent strategy has been adopted (Scheme 2). By nucleophilic substitution of the chlorine atoms of thiophene **6** in *N*,*N*-dimethylformamide, the symmetric 2,5-dialkylsulfanyl-3,4-dinitrothiophenes **7a**,**b** were obtained in much lower yields than those previously reported for similar compounds.[10] In addition, non-C_2 symmetric isomers **8a**,**b** with a nitro group shifted to the vicinal position were isolated; this side product was not described by Erker,[10] although it forms even at reaction temperatures as low as 10 °C.[†][11] The modification of the reaction conditions, using methanol as a protic solvent and triethylamine as a base yielded the symmetrical thiophenes **7a**,**b** almost quantitatively.[12] The reduction of **7a**,**b** with Fe/AcOH afforded the dialkylsulfanyldiaminothiophenes **9a**,**b** in 35 and 49% yields, respectively. The target compounds **1a**,**b** were obtained by the subsequent threefold condensation of **9a**,**b** with hexaketocyclohexane **3**. It is known that 3-aminothiophene can undergo a transamination reaction in the presence of catalytic amounts of acid.[13] In order to avoid this side reaction, which can lead to undesirable oligomers, the condensation has been carried out only with molecular sieves 4 Å; no transformation was observed unless a small amount of methylsulfonic acid was added. Under these conditions, the yield of **1a**,**b** ranges from 6 to 9%. Reaction conditions could be optimised using freshly prepared hexaketocyclohexane octahydrate[8b] **3** and a mixture of acetic acid and ethanol as reaction medium, which resulted in up to 31% isolated pure product. The purity and symmetry of the discotic product is demonstrated by NMR, FT-IR spectroscopy and elemental analysis. ^{1}H NMR spectra of **1a**,**b** show only protons of the lateral chains

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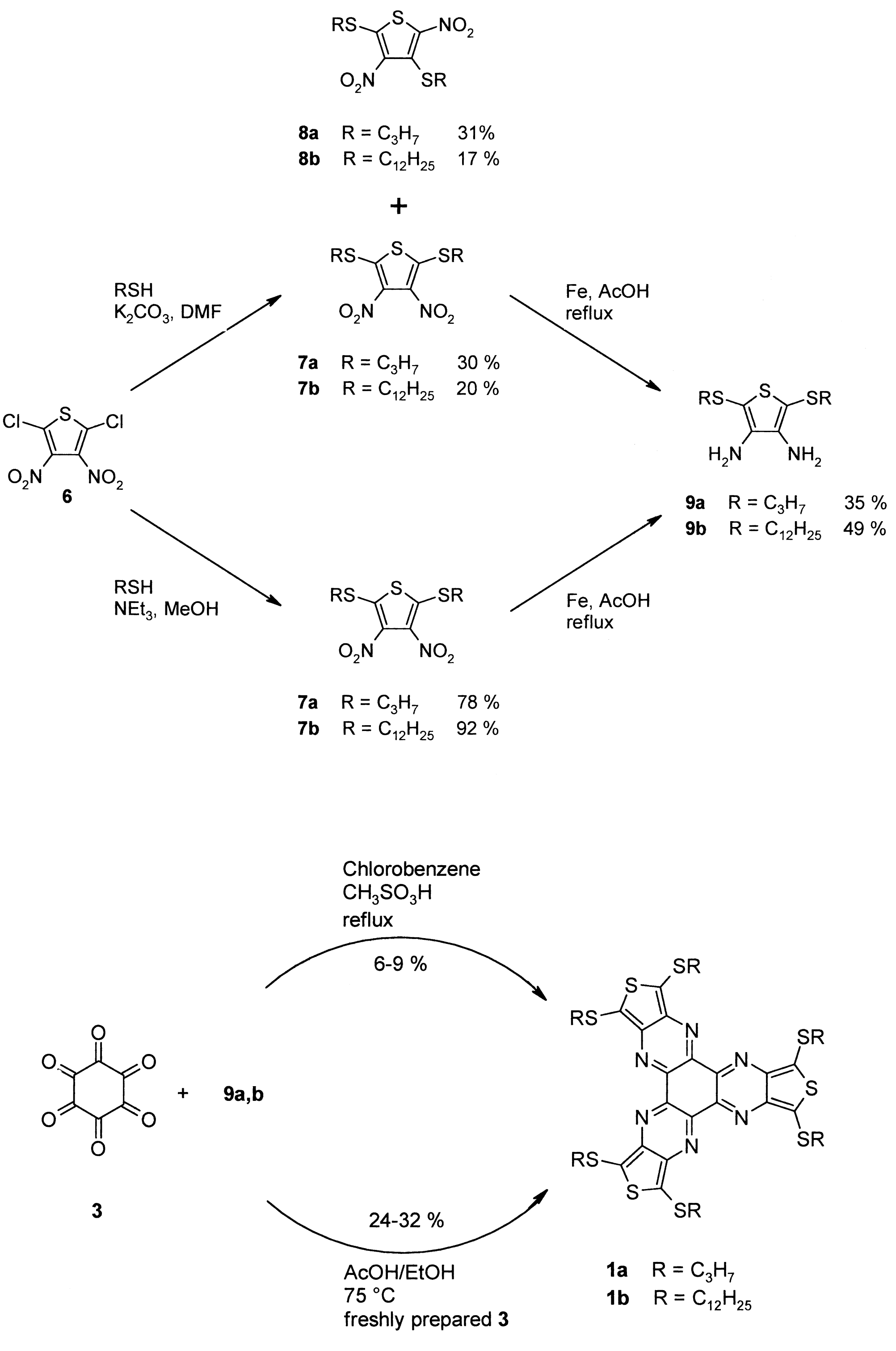
[†] Analytical data confirm the composition of the product **8a**,**b**. ^{1}H NMR spectra present signals corresponding to two distinguishable α-CH_2 groups, ^{13}C NMR shows four different signals for the carbon atoms of the thiophene ring, while EI mass spectra exhibit the same molecular mass peak as in the symmetrical product **7a**,**b**. Since FT-IR spectra are similar for **7a**,**b** and **8a**,**b**, no rearrangement from a nitro to a nitrite group (at 1610–1680 cm^{-1}) takes place. Thus, we find an unusual process where the nucleophilic substitution is accompanied by a shift of a nitro group. The reaction process and mechanism have not been further investigated. With the conditions given in Ref. 10 (DMF, RSH, K_2CO_3, 0 °C) the non-symmetric products **8a**,**b** were always isolated. The reaction at lower temperature is very slow, but even at −10 °C the side product was formed. Cine substitutions on 3,4-dinitro-substituted thiophenes, where the leaving groups are at a neighbouring position of the incoming nucleophile, were observed previously, see Ref. 11.



Scheme 2. Convergent synthesis of alkylsulfanyl-substituted hexaazatriisothianaphthenes **1**.

and the FT-IR data confirm the absence of amino groups. Interestingly, the IR spectra show a signal at 1734 cm^{-1}, which cannot be attributed to the absorption of a keto group according to mass analysis and ^{13}C NMR spectra. Thus, this signal is probably a combination or overtone of vibrations of the polycyclic aromatic system. The threefold symmetry of the product is verified by the ^{13}C NMR data where only three signals are found for the aromatic core, as expected (Table 1).

2.2. Theoretical support

Charge transport in discotic liquid crystals is generally considered to operate via a hopping mechanism whereby charges move from disc to disc down the one-dimensional stacks. The hopping rate, and hence the charge mobility, strongly depends on the intermolecular transfer integrals that describe the strength of the electronic coupling between adjacent neighbours. The transfer integrals can be

Table 1. ^{13}C NMR data obtained in $CDCl_3$ for the C_3-symmetric molecules **1a**,**b**

Compound	Aromatic carbons[a]	Aliphatic carbons
1a	131.4 (C_{ia}) 142.8, 143.7 (C_{ta})	13.3 (CH_3) 23.0 (CH_2) 40.1 (SCH_2)
1b	131.3 (C_{ia}) 142.7, 143.6 (C_{ta})	14.1 (CH_3) 22.7, 28.7, 29.2–29.7, 31.9 (CH_2) 37.9 (SCH_2)

[a] C_{ia} quaternary carbons of the inner aromatic ring, C_{tA} quaternary carbons of the thiophene unit; peaks were assigned by increment estimation of chemical shifts.

calculated to a good approximation for holes [electrons] as half the splitting of the HOMO [LUMO] levels in a dimer formed by two neutral molecules;[14] they are highly sensitive to the relative positions of the interacting units, in particular to ring rotations and displacements within the stacks, that are expected in mesophases.[15] In the case of the triphenylene molecules, we have shown that the transfer integrals become vanishingly small for specific rotational angles, a feature that is strongly detrimental to the transport properties. This motivated us to characterise, prior to chemical synthesis, the charge transport properties in hexaazatriisothianaphthene. We have thus calculated at the semiempirical Intermediate Neglect of Differential Overlap (INDO) level[16] the electronic splittings in dimers made of two hexaazatriisothianaphthene cores substituted by six sulfanyl groups, **1c** (Fig. 1) and have compared the results to those previously obtained for triphenylene derivatives. The geometry of the hexaazatriisothianaphthene core has been optimised at the Density Functional Theory (DFT) level using the B3LYP functionals and a 6-31G** basis set.

As expected, the HOMO and LUMO splittings calculated in cofacial dimers (where the two molecules are exactly superimposed on top of one another) decrease with the intermolecular distance. The splittings are found to be rather high, 0.6 and 0.4 eV for the HOMO and LUMO levels, respectively, for an intracolumnar separation of 0.35 nm. The HOMO splitting of molecule **1** is smaller than the corresponding value calculated for the triphenylene derivatives (~0.8 eV);[15] in contrast, the LUMO splittings are similar, in the order of 0.4 eV, in the two compounds. In all cases, the electronic splittings decrease when going away from a cofacial conformation by laterally displacing one molecule with respect to the other.

We report in Figure 2 the evolution of the HOMO and LUMO splittings in a dimer built with two hexaazatriisothianaphthene cores substituted by six sulfanyl groups **1c** when rotating one disc with respect to the other around the stacking axis, together with the corresponding evolution obtained for the triphenylene molecule. While the HOMO

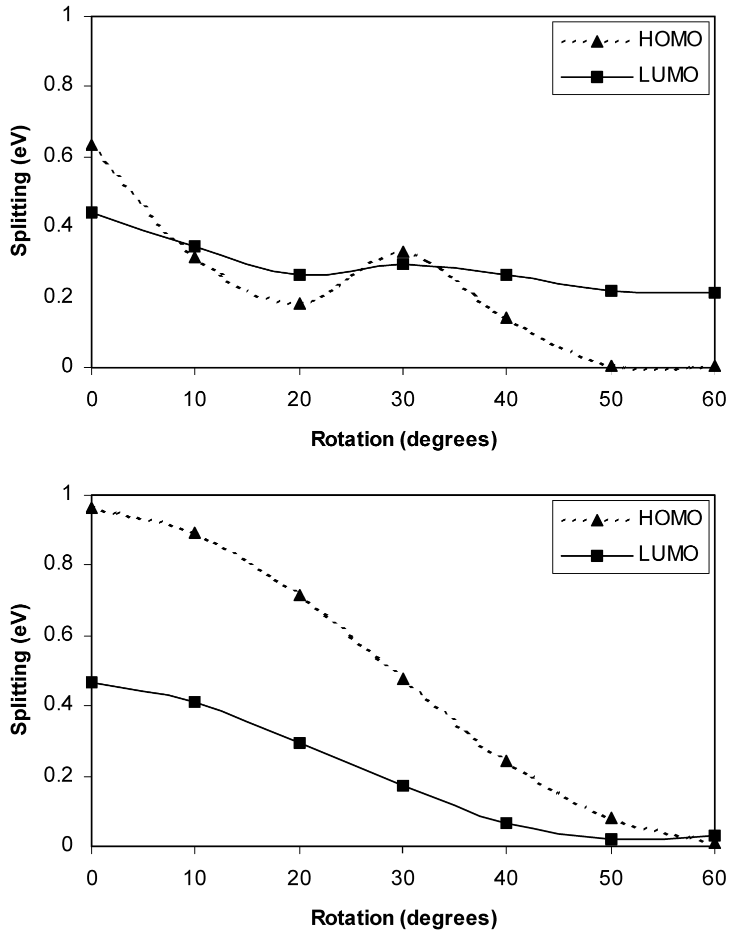


Figure 2. INDO-calculated angular dependence of the HOMO and LUMO splittings in a dimer made of: (top) two hexaazatriisothianaphthene cores substituted by six sulfanyl groups; and (bottom) two triphenylene molecules. The intermolecular distance is fixed here at 0.35 nm.

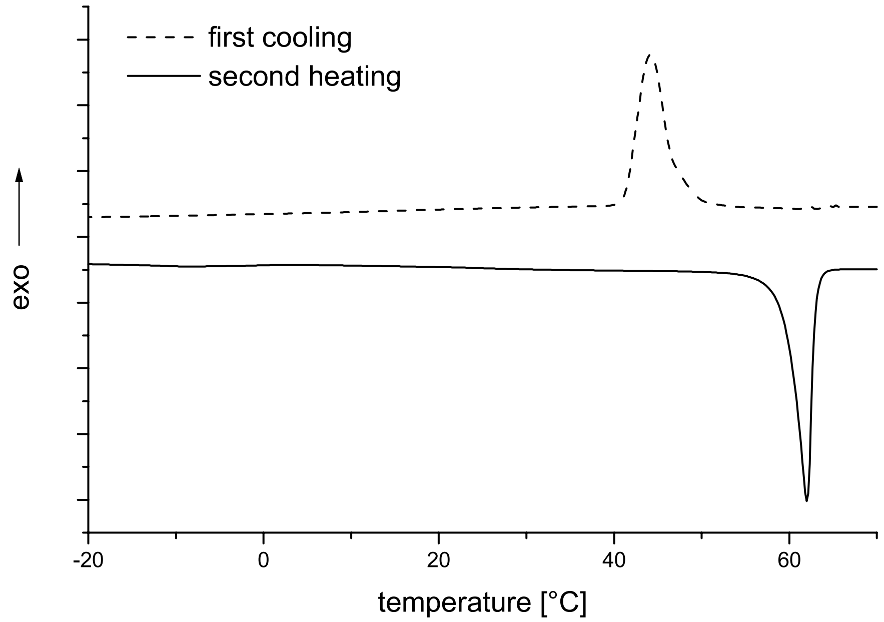


Figure 3. DSC curves (first cooling and second heating) of hexaazatriisothianaphthene **1b** (heating rate 10°/min).

splitting exhibits clear maxima and minima, the LUMO splitting is almost constant between 0 to 60 °, in contrast to the results obtained for the triphenylene derivatives. That the calculated LUMO splittings are large and insensitive to rotational degrees of freedom thus makes molecule **1** a potentially very attractive electron-transport mesogen.

2.3. Thermotropic and photophysical properties

The thermotropic properties were investigated by means of polarised optical microscopy (POM) and differential scanning calorimetry (DSC). The hexaalkylsulfanylhexaazatriisothianaphthenes **1a**,**b** do not show liquid crystalline behavior despite the fact that similar systems, such as hexaalkylsulfanylhexaazatrinaphthalene **2** (Fig. 1), possess a rich mesomorphism.[3a] Compound **1a** is crystalline under POM and shows a melting transition in the second heating cycle of DSC (onset at 147 °C, $\Delta H = 33.8$ kJ/mol). After the first heating cycle where crystals melt at 69 °C, compound **1b** is a rather waxy material. However, this material also shows in the second heating trace a transition at 59 °C (onset) with a large enthalpy of 87.9 kJ/mol (Fig. 3). Subsequent heating and cooling cycles show a hysteresis of 12 °C. POM studies reveal a typical crystal growth upon cooling from the isotropic phase. The non-mesogenic behavior is surprising; it could be related to Coulomb repulsion effects linked to the charge distribution found on the aromatic cores (a Mulliken population analysis performed from the DFT calculations yields atomic charges of $-0.54|e|$ on the nitrogen atoms, see Fig. 4), which could dominate over the stabilizing forces induced by van der Waals interactions.

The photophysical properties of **1a** and **1b** were investigated by UV–Vis and emission spectroscopy. The absorption spectrum of **1b** in $CHCl_3$ is displayed in Figure 5; as expected, the same spectrum is obtained for compound **1a** since the size of the alkyl side chains does not impact the optical properties. The absorption spectrum is characterised by two maxima at 290 nm (with a molar extinction coefficient $\varepsilon = 4.6 \pm 0.1 \times 10^4$ l/mol cm) and at 373 nm (with $\varepsilon = 6.0 \pm 0.1 \times 10^4$ l/mol cm). In addition, we observe a shoulder around 400 nm which appears as a vibronic satellite of the lowest intense absorption band as well as a tail extending down to 770 nm, which corresponds to a small optical bandgap of 1.6 eV (Fig. 5, insert). A thin solid film of **1** shows essentially the same absorption features as in the dilute solution. However, when the absorption is measured at room temperature in the crystalline phase, a strong bathochromic shift of 23 nm is observed (Fig. 5), which points to a strong interaction between chromophores in the crystal. In contrast, such a shift is not present in the spectra recorded in the isotropic liquid. Since it has been suggested from X-ray data that aromatic mesogens maintain columnar aggregates in the isotropic phase,[17] the similarity of the spectra in dilute solution and in the isotropic liquid in

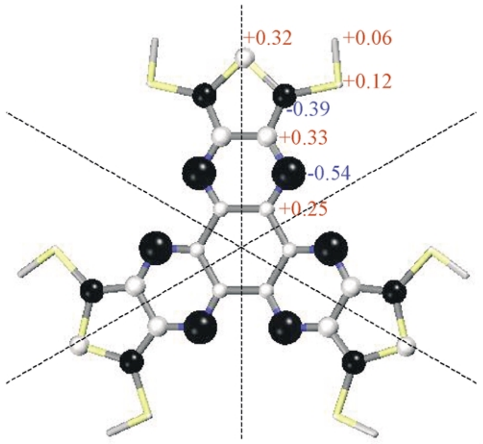


Figure 4. Charge distribution in the hexaazatriisothianaphthene molecule substituted by six sulfanyl groups **1c**, as calculated at the DFT level from Mulliken population analysis. The size of the spheres is proportional to the net charge on each atom; black [white] spheres relate to negative [positive] charges. The charge on the nitrogen atoms is calculated to be $-0.54|e|$.

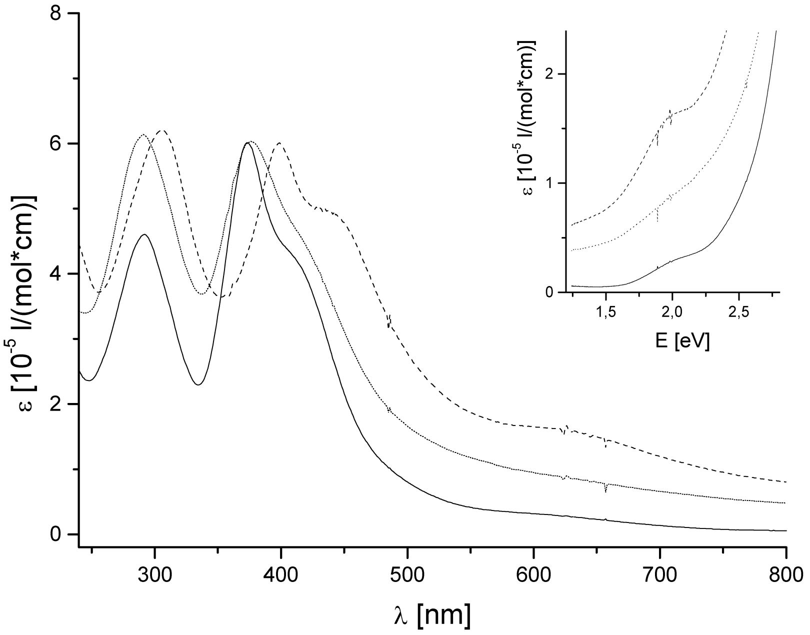


Figure 5. UV–Vis absorption spectra of hexaazatriisothianaphthene **1b** in CHCl$_3$ (solid line) and normalised spectra in a neat thin film heated to the isotropic liquid (dotted line) and cooled to the crystalline phase (dashed line). The insert shows the absorption edge of the same spectra versus the energy in eV.

vicinity of the melting transition for molecule **1** points to a weak interaction of mesogens and thus to a small tendency towards aggregation. The emission of compounds **1a**,**b** is so weak that reliable fluorescence spectra could not be recorded.

2.4. Oxidation–reduction properties

Cyclic voltammetry traces were recorded for thin films of **1a**, casted on the working electrode from a toluene solution, versus the standard calomel electrode (SCE). The first half wave potential for reduction amounts to −0.89 V and the one for oxidation to 0.28 V. From the onset of these reduction and oxidation waves, the LUMO and HOMO energies can be estimated to −3.9 and −4.8 eV, respectively,[18] in reference to ferrocene. The energy of the LUMO level is relatively low compared to other electron deficient aromatic disks, such as tributoxycarbonylhexaazatrinaphthylenes[3b] (−3.4 eV), perylenediimide[19] (−3.3 eV) and even tris-8-hydroxyquinoline aluminium[20] (−2.9 eV), a commonly used electron-transport material in light emitting diodes.[21] Consequently, hexaalkylsulfanyltriisothianaphthene **1** exhibits an inherent electron deficient nature and is therefore a potential n-type semiconductor.

3. Conclusions

In view of their promising electron transport properties suggested by quantum-chemical calculations, the electron-deficient and potentially mesogenic hexaazatriisothianaphthene cores substituted by propylsulfanyl and dodecylsulfanyl chains have been prepared in a convergent synthesis by condensation of diamines with hexaketocyclohexane. Cyclic voltammetry on thin films demonstrates the electron-deficient nature of the new material, with a surprisingly low energy for the LUMO level estimated at −3.9 eV. Despite the fact that the closely related hexaazatrinaphthalene discs substituted by six alkylsulfanyl chains form columnar LC phases, POM and DSC studies do not establish the existence of liquid crystalline phases for the new compounds; this has probably to be attributed to strong Coulombic repulsion among the conjugated cores. Lateral substituents other than alkylsulfanyl chains should be found to promote supramolecular columnar organisation.

4. Experimental

Solvents and reagents were purchased from Aldrich and used as received. Column chromatographies were performed on silica gel (Merck silica gel 60, mesh size 0.2–0.5 mm). ^{1}H NMR spectra were recorded on a Bruker Avance 300 with solvent signal as internal standard. Mass spectra were recorded on a VG Micromass 7070F instrument (electron impact, 70 eV) and a VG instruments ZAB 2-SE-FPD using FD. Elemental analysis was carried out at the micro analytical laboratory of the University of Mainz (Germany). UV/Vis absorption measurements were carried out with a HP 8453 spectrophotometer. The thermal behaviour of the materials synthesised was investigated by polarizing optical microscopy (JENA microscope equipped with a Mettler FP 52 hot stage) and differential scanning calorimetry (Mettler Toledo DSC) with heating and cooling scans performed at 10 °C min^{-1}. The cyclic voltammograms reported here were recorded with a computer controlled EG&G potentiostat/galvanostat at a constant scan rate of 1000 mV/s. A three electrode configuration undivided cell was used. The working electrode was glassy carbon (3 mm diameter), with a Pt wire auxiliary electrode and a non-aqueous reference electrode containing 0.01 M AgNO$_3$, 0.1 M tetrabutylammoniumperchlorate (TBAP) in acetonitrile, and silver wire. The electrolyte was 0.1 M TBAP in acetonitrile. The oxidation voltage sweeping range was from −1.0 to 1.3 V. The polymer film is casted directly on the working electrode from a toluene solution (3 mg/ml).

Bubbling Argon through the electrolyte for 20 min prior to the experiment purges the solution of dissolved oxygen. The measurements were carried out under a positive pressure of Argon. HOMO and LUMO levels were measured at the onset of, respectively, the first oxidation and reduction events of the second cycle. The potentials were referenced to the ferrocene half wave potential ($-E_{\text{HOMO/LUMO}} = E_{\text{oxidation/reduction}} - E_{\text{ferrocen}} + 4.8$ eV).

4.1. General procedures

In a first attempt, dinitro and diamino derivatives **7**, **8** and **9** have been prepared following the procedure reported in the literature.[10] However, since the nucleophilic substitution of **6** afforded a mixture of products, which were difficult to purify, the synthesis had to be modified. In the following the original and modified procedures are described, which were used for the synthesis of **7** and **9**. Moreover, a general optimised synthesis for the final step of the reaction scheme, the condensation of **9** with hexaketocyclohexane, is given.

General procedure (1). Nucleophilic substitution of 2,5-dichloro-3,4-dinitrothiophene **6**.

Method 1.[10] Alkylthiol (11.0 mmol) was added to a suspension of K_2CO_3 (1.5 g) in dry DMF (10 ml) under nitrogen and stirred at ambient temperature for 20 min. The mixture was cooled with an ice bath and a solution of thiophene **6** (4.1 mmol) in DMF (4 ml) was added dropwise. The reaction was controlled by thin layer chromatography. After 2 h, no further reaction could be observed. The mixture was poured on 100 g ice and the precipitate was collected and recrystallised from acetone. The crude product consisted of two different compounds, which were purified by column chromatography. In contrast to previous work,[10] a non-symmetrical product **8a**,**b** could be isolated in the same amount as symmetrical product **7a**,**b**.

Method 2.[12] To solution of thiophene **6** (12 mmol) and alkylthiol (27 mmol) in methanol (50 ml) at 5 °C, triethylamine (3 ml) was added. The ice bath was removed after 10 min and the mixture was stirred additional 2 h at room temperature.

General procedure (2). Reduction of 2,5-dialkylsulfanyl-3,4-dinitrothiophene **7**.

Thiophene **7** (0.8 mmol) was dissolved in acetic acid/water (4.4 ml, 10:1) and heated to 75 °C. 624 mg (11 mmol) iron powder were added in two portions, the mixture was refluxed for 1 h, poured on water and extracted with CH_2Cl_2. After drying the organic phase with Na_2SO_4 and evaporation of the solvent, the product was isolated by column chromatography.

General procedure (3). Condensation with hexaketocyclohexane octahydrate (optimised procedure).

Freshly prepared hexaketocyclohexane × $8H_2O$ (180 mg, 0.58 mmol) and 3,4-diamino-2,5-dialkylsulfanylthiophene (1.9 mmol) in ethanol/glacial acid (1:1, 40 ml) were stirred over night at room temperature under argon atmosphere. The reaction mixture was then poured on water (80 ml) and extracted with CH_2Cl_2 (2 × 50 ml). The combined organic phases were washed with a saturated solution of $NaHCO_3$ and water and dried over $NaSO_4$. Evaporation yielded a crude black product, which was purified as described below.

4.1.1. 2,5-Dipropylsulfanyl-3,4-dinitrothiophene (7a) and 2,4-dipropylsulfanyl-3,5-dinitro-thiophene (8a).

Method 1. The general procedure (1) (method 1) led to a yellow precipitate, which was purified by chromatography on silica (toluene/hexane/ethyl acetate). Compound **7a** (0.98 g) was isolated as a yellow solid, mp 92 °C, yield 30%. As a side product, non-symmetrical compound **8a** (1.02 g) was obtained in 31% yield, mp 73 °C; this was not reported in previous investigations.[10]

Method 2. The general procedure (1) (method 2), using 1-propanethiol, afforded a suspension of a yellow precipitate. Water (100 ml) was added to the reaction mixture and the precipitate was collected, washed with 20 ml cold methanol and dried to yield 3.10 g (78%) of a yellow solid **7a**.

Compound **7a**. ^{1}H NMR ($CDCl_3$, 300 MHz) 1.08 (t, 6H, CH_3), 1.78 (m, 4H, CH_2), 2.99 (t, 4H, SCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.2 (CH_3), 22.2 (CH_2), 38.5 (SCH_2), 138.5, 141.4 ($C_{\text{Thiophene}}$). FT-IR $\nu(\text{cm}^{-1}) = 2964$, 2933, 2869, 1508, 1461, 1367, 1321, 1304. Mass (EI) *m/z* (rel. intensity) = 322 (100), 126 (19), 112 (34), 101 (35), 84 (72).

Compound **8a**. ^{1}H NMR ($CDCl_3$, 300 MHz) 0.98, 1.13 (2t, 6H, CH_3), 1.59, 1.89 (2dt, 4H, CH_2), 2.97, 3.07 (2t, 4H, SCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.2, 13.4 (CH_3), 21.3, 22.7 (CH_2), 37.1, 38.3 (SCH_2), 136.8 (C–SR), 141.1 (C–NO_2), 141.4 (C–NO_2), 154.3 (C–SR). FT-IR $\nu(\text{cm}^{-1}) = 2979$, 2968, 2954, 2931, 2871, 1516, 1494, 1450, 1383, 1308, 1242. Mass (EI) *m/z* (rel. intensity) = 322 (28), 170 (43), 112 (60), 101 (100).

4.1.2. 2,5-Didodecylsulfanyl-3,4-dinitrothiophene (7b) and 2,4-didodecylsulfanyl-3,5-dinitrothiophene (8b).

Method 1. Following the general procedure (1) (method 1), a yellow precipitate was obtained, which was purified by column chromatography on silica (hexane/ethyl acetate). Compound **7b** (0.47 g) was isolated as a yellow solid, mp 77–79 °C, yield 20%. As a side product, non-symmetrical compound **8b** (0.40 g) was obtained in 17% yield, mp 60–63 °C; this was not reported in previous investigations.[10]

Method 2. The general procedure (1) (method 2) using 1-dodecanethiol afforded a yellow precipitate, which was collected by filtration and washed with methanol. Compound **7b** was obtained as a yellow solid (6.50 g, 92%).

Compound **7b**. ^{1}H NMR ($CDCl_3$, 300 MHz) 0.92 (t, 6H, CH_3), 1.20–1.85 (m, 40H, CH_2), 3.03 (t, 4H, SCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz) 14.1 (CH_3), 22.7, 28.6, 28.7, 29.0, 29.3, 29.5, 29.6, 29.7, 31.9 (CH_2), 36.6 (SCH_2), 141.4, 138.5 ($C_{\text{Thiophene}}$). FT-IR $\nu(\text{cm}^{-1}) = 2952$, 2818, 2850, 1512, 1467, 1427, 1371, 1327, 1304. Mass (EI) *m/z* (rel. intensity) = 574 (100), 544 (12), 402 (10), 389 (9), 201 (9).

Compound **8b**. ^{1}H NMR ($CDCl_3$, 300 MHz) 0.88 (t, 6H, CH_3), 1.10–2.00 (m, 40H, CH_2), 2.99, 3.08 (2t, 4H, SCH_2).

^{13}C NMR ($CDCl_3$, 75 MHz) 14.1 (CH_3), 22.7, 27.7, 28.6, 28.8, 28.96, 29.0, 29.3, 29.5, 29.6, 31.9 (CH_2), 35.3, 36.4 (SCH_2), 137.0 (C–SR), 141.1 (C–NO_2), 141.3 (C–NO_2), 154.5 (C–SR). FT-IR ν(cm^{-1}) = 2952, 2920, 2848, 1520, 1489, 1468, 1440, 1373, 1338, 1304, 1282, 1244. Mass (EI) *m/z* (rel. intensity) = 574 (4), 557 (12), 544 (10), 528 (11), 57 (100).

4.1.3. 3,4-Diamino-2,5-dipropylsulfanyl-thiophene (9a). After reduction, following the general procedure (2), **9a** was obtained by column chromatography (silica/hexane/ethyl acetate/NEt_3) as a light brownish solid, yield 1.19 g (47%). The product was not stable in air and consequently used directly for the next reaction. ^{1}H NMR ($CDCl_3$, 300 MHz) 0.96 (t, 6H, CH_3), 1.61 (m, 4H, CH_2), 2.61 (t, 4H, SCH_2), 3.76 (broad, 4H, NH_2). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.2 (CH_3), 23.0 (CH_2), 40.0 (SCH_2), 108.1, 140.4 ($C_{Thiophene}$).

4.1.4. 3,4-Diamino-2,5-didodecylsulfanyl-thiophene (9b). After reduction, following the general procedure (2), **9b** was obtained by column chromatography (silica/hexane/ethyl acetate) as a light brownish waxy solid, yield 0.2 g (49%). The product was not stable in air and consequently used directly for the next reaction. ^{1}H NMR ($CDCl_3$, 300 MHz) 0.88 (t, 6H, CH_3), 1.20–1.40, 1.58 (m, 40H, CH_2), 2.62 (t, 4H, SCH_2), 3.75 (broad, 4H, NH_2). ^{13}C NMR ($CDCl_3$, 75 MHz) 14.1 (CH_3), 22.7, 28.6, 29.2, 29.3, 29.5, 29.6, 29.7, 31.9 (CH_2), 38.0 (SCH_2), 108.2, 140.3 ($C_{Thiophene}$).

4.1.5. 1,3,8,10,15,17-Hexapropylsulfanyl-4,7,11,14,18,20-hexaazatriisothianaphthene (1a). 300 mg (1.14 mmol) **9a**, 60 mg (0.19 mmol) hexaketocyclohexane × $8H_2O$ (Aldrich) (**3**) were dissolved in 10 ml chlorobenzene and 60 mg molecular sieves (4 Å) were added. The mixture was refluxed for 2 days. Since no reaction was observed by TLC control, one drop of methanesulfonic acid was added. After 2 h at reflux, the solvent was evaporated under vacuum and the product was purified by column chromatography (silica 60, hexane/ethyl acetate = 5:1). Compound **1a** (15 mg) was isolated as a dark yellow solid, yield 6%.

Optimised procedure. 550 mg of a crude product obtained by the general procedure was purified by column chromatography (silica 60, hexane/ethyl acetate/triethylamine = 80:4:1). The almost pure product (170 mg) was recrystallised from ethanol/methylene chloride by slow evaporation (approx. 2–3 days) of the solvent at room temperature. Filtration afforded 156 mg (32%) of black needle-like crystals, mp 147 °C (onset DSC). ^{1}H NMR ($CDCl_3$, 300 MHz) 1.29 (t, 18H, CH_3), 1.82 (m, 12H, CH_2), 3.03 (t, 12H, SCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.3 (CH_3), 23.0 (CH_2), 40.1 (SCH_2), 131.4, 142.8, 143.7 ($C_{aromatic}$). FT-IR ν (cm^{-1}) = 2957, 2924, 2851, 1734, 1459, 1379, 1288, 1125. Mass (EI) *m/z* (rel. intensity) = 848 (M^+, 12), 182 (52), 150 (100), 108 (73). Elemental analysis calcd for $C_{36}H_{42}N_6S_9$ (%): C 51.03, H 5.00, N 9.92; found: C 51.33, H 5.16, N 9.67.

4.1.6. 1,3,8,10,15,17-Hexadodecylsulfanyl-4,7,11,14,18,20-hexaazatriisothianaphthene (1b). 200 mg (0.39 mmol) **9b**, 20 mg (0.065 mmol) hexaketocyclohexane × $8H_2O$ (Aldrich) (**3**) were dissolved in 10 ml chlorobenzene and one drop of methanesulfonic acid was added. The mixture was refluxed for 2 h. Then the solvent was evaporated under vacuum and the product was purified by column chromatography (silica 60, hexane/ethyl acetate). Compound **1b** (9 mg) was isolated as a dark yellow solid, yield 9%.

Optimised procedure. The crude product, obtained by the general procedure (3), was purified by column chromatography (silica 60, hexane/ethyl acetate/triethylamine = 80:2:1). The purest fractions (136 mg) were again chromatographed to yield 95 mg of a dark yellow solid. The material was crystallised from ethanol/ methylene chloride by slow evaporation of methylene chloride at 40 °C and reduced pressure (800–500 mbar). Filtration afforded 72 mg (24%) of brown to black solid powder, mp 69 °C (Onset DSC). ^{1}H NMR ($CDCl_3$, 300 MHz) 0.89 (t, 18H, CH_3), 1.20–1.40, 1.55, 1.80 (m, 120H, CH_2), 3.36 (t, 12H, SCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz) 14.1 (CH_3), 22.7, 28.7, 29.2, 29.3, 29.5, 29.6, 29.7, 31.9 (CH_2), 37.9 (SCH_2), 131.3, 142.7, 143.6 ($C_{aromatic}$). FT-IR ν(cm^{-1}) = 2962, 2926, 2853, 1734, 1467, 1380, 1262, 1125, 1097, 1073, 1024, 803. Mass (FD) *m/z* (rel. intensity) = 1605 (17), 1618 (100). Elemental analysis calcd for $C_{90}H_{150}N_6S_9$ (%): C 67.36, H 9.42, N 5.24; found: C 67.39, H 9.45, N 5.16.

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