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New bent core mesogens with exceptionally high clearing points

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A homologous series of novel two-ring alkoxythiophene-containing liquid crystals has been synthesized using a recently developed cyclization methodology to construct the heterocyclic core. The new heterocyclic unit is expected to confer high negative dielectric anisotropy and high dielectric biaxiality when incorporated into suitable mesogenic structures. The materials reported here possess nematic phases, with the longer chain homologues displaying smectic mesomorphism. In all cases the clearing points are significantly enhanced when compared with other two-ring thiophene-based mesogens. The synthesis, mesomorphic behaviour and stability are discussed, and the mesomorphic behaviour is compared with the analogous 4-alkoxy-4′-cyanobiphenyl derivatives synthesized by Gray.

1. Introduction

Mesogenic structures containing heterocyclic rings are finding increasing interest in the field of liquid crystal synthesis, as chemists attempt to optimize molecular properties for displays and optical applications. Heterocyclic units such as thiophene often possess unique physical properties. Liquid crystalline heterocyclic structures can be designed to exhibit mesogenic behaviour similar to or even superior to linear phenyl analogues and the like. For example, suitably substituted heterocycles such as 2,5-1,3,4-thiadiazoles [1], 2,5-pyridines [2–6], 2,5-thiophenes [7–12] and 2,5-benzofurans [13] have large lateral dipoles that contribute to enhanced negative dielectric anisotropy and dielectric biaxiality, whereas 2,5-pyrimidines [14, 15] and 2,5-dithianes [16–18] have large longitudinal dipoles that increase positive dielectric anisotropy. The core heterocyclic unit is compact and a large dipole may thus be incorporated into a liquid crystal structure through heterocycle use, with minimal impact on the transition temperatures (when compared with the analogous phenyl-based mesogens).

In linear systems such as 1,4-phenyl and 2,6-naphthyl-based mesogens, negative dielectric anisotropy and dielectric biaxiality are often enhanced with the incorporation of lateral substituents such as fluoro [19, 20], chloro [21], nitrile [21], trifluoromethoxy [22] and nitro [19] moieties. The inclusion of such substituents (especially the large units) leads to a decrease in the magnitude of the lateral molecular interactions, and consequently gives rise to substantially reduced mesomorphic behaviour. Exceptions to this rule may occur when molecular shielding prevents the lateral substituent from projecting out from the core. Examples of materials that exemplify the shielding effect have been published by Gray and Jones [23], and Eidenschink *et al.* (figure 1) [24, 25].

Heterocycle-based liquid crystals are thus excellent potential candidates for use in displays that require high negative dielectric anisotropy and/or high dielectric biaxiality. In order further to expand the heterocycle field of liquid crystals we have therefore targeted alkoxythiophenes as potential subunits capable of conferring high negative dielectric anisotropy and high dielectric biaxiality.

Recently our laboratory has initiated the first synthetic studies into both achiral and chiral non-racemic alkoxythiophene-containing liquid crystals for such use. The synthetic strategy used to access these new heterocycles employs the use of Lawesson's reagent as a sulphurization source for the ring closure of appropriately substituted γ-keto esters [11, 26]. In mainstream organic chemistry the efficient and reproducible synthesis of alkoxythiophenes has been elusive. Use of the classical Williamson ether

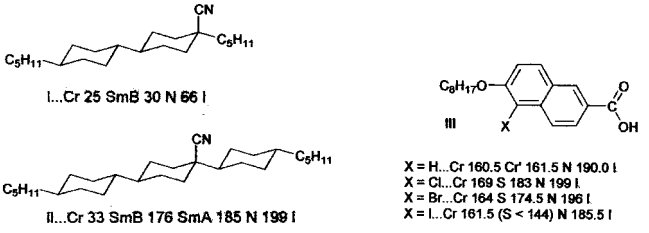

Figure 1. Molecular shielding of lateral substituents: axial hydrogen shielding (I and II, Eidenschink) and naphthyl core shielding (III, Gray).

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synthesis in the formation of alkoxythiophenes from hydroxythiophenes is nearly impossible due to hydroxythiophenes existing almost exclusively as the keto tautomers (for example, 3-thiolen-2-one and 4-thiolen-2-one). A recent paper by Sonpatki *et al.* highlights synthetic difficulties encountered in the synthesis of alkoxythiophenes [27–32] and shows that alkoxythiophenes may be prepared in excellent yields through the cyclization of γ-keto esters [26]. A subsequent paper describes the use of microwave irradiation in the formation of alkoxythiophenes from γ-keto esters under solvent-free conditions [11].

This initial study has been designed to examine the effect of the alkoxythiophene core on the mesophase thermal stability of simple achiral materials, and consequently to evaluate the potential of these materials in device applications including ferroelectric, nematic and high birefringence optics.

2. Synthesis

The synthesis of final products **13**–**17** is given in the scheme. The experimental details for the preparation of compounds **2**–**12** are found in references [26] (solution phase ring-closure of the γ-keto esters **3**–**7**) and [11] (microwave assisted ring closure).

The synthesis of the γ-keto acid **2** involved the Friedel–Crafts acylation of bromobenzene with succinic anhydride. The reaction conditions give complete regioselectivity and very high consistently reproducible yields. In addition, dehalogenation was not observed as has been previously reported [33].

γ-Keto esters **3**–**7** were prepared from the requisite γ-keto acid **2** using *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) as described by Hassner and Alexanian [34]. Crystallization of the products from methanol following chromatography ensured purity of the materials.

Synthesis of alkoxythiophenes **8**–**12** was carried out via ring closure of appropriate γ-keto esters using Lawesson's reagent as the source of sulphur. Microwave irradiation was used in the absence of solvent.

Synthesis of the final cyanated products **13**–**17** was carried out using the method of Friedman and Schechter [35] in *N*,*N*-dimethylformamide (DMF). The yields were not optimized and ranged from 45% to 75%. The use of *N*-methylpyrrolidin-2-one (NMP) as solvent did not give a reaction at 145°C. Purification of the final products was carried out using chromatography. Side-products that were not removed by chromatography were successfully removed by crystallization from methanol.

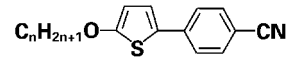
3. Results and discussion

3.1. *Transition temperatures*

3.1.1. *Mesogenic behaviour of alkoxythiophenes **13**–**17***

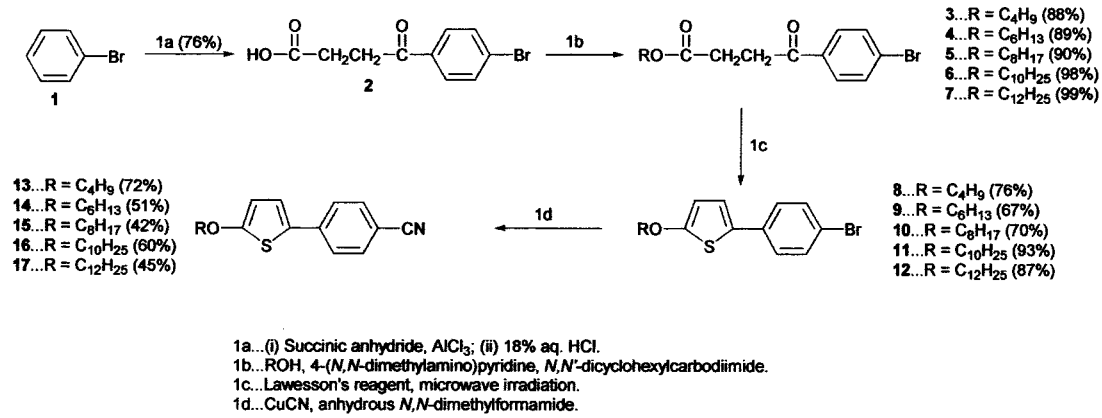
The transition temperatures of the alkoxythiophene products **13**–**17** are given in table 1. The analogous alkoxybiphenyls **18**–**22** synthesized by Gray [36] have the transition temperatures given in table 2.

Table 1. Transition temperatures (°C) of the 2-alkoxy-5-(4-cyanophenyl)thiophenes **13**–**17** obtained from polarizing optical microscopy (cooling rate of 5°C min^{-1}).



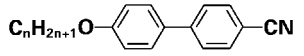
Compound	*n*	Cr	SmA	N	I
13	4	62.9	—	(• 30.7)	•
14	6	51.1	—	(• 36.8)	•
15	8	54.3	(• 36.8[a])	• 45.7)	•
16	10	70.4	—	[• 36]	•
17	12	69.1	(• 61.7)	—	•

[a] Cooling rate of 10°C min^{-1}.



Scheme. Synthesis route to the 2-alkoxy-5-(4-cyanophenyl)thiophenes **13**–**17**.

Table 2. Transition temperatures (°C) of the 4-alkoxy-4′-cyanobiphenyls **18**–**22** synthesized by Gray.



Compound	*n*	Cr	SmA	N	I
18	4	78.0	—	(• 75.5)	•
19	6	58.0	—	• 76.5	•
20	8	54.5	• 67.0	• 80.0	•
21	10	61.0	—	• 84.5	•
22	12	69.0	• 89.0	—	•

The alkoxythiophenes **13**, **14**, **16** and **17** all exhibit the nematic phase. Compound **16** showed a nematic phase upon rapid cooling (isolated droplets) by optical microscopy; however, crystallization was so rapid following nucleation of the nematic phase that an accurate value of the $T_{N\text{-}I}$ could not be determined. A virtual $T_{N\text{-}I}$ value was therefore recorded from mixtures in E48 as described in a previous paper [37]. A maximum solubility of 39% of **16** in E48 was noted (an associated error bar of ± 0.4°C was determined).

Compounds **15** and **17** (C_8 and C_{12} homologues, respectively) have an additional SmA phase. The SmA phase was observed in **15** only upon rapid cooling (10°C min^{-1}), as crystallization precluded the observation of this phase at slower rates of cooling. In comparing the transition temperatures of the alkoxythiophenes **13**–**17** with the analogous alkoxyphenyl systems **18**–**22** it is clear that the mesomorphic behaviour is identical between the series.

3.1.2. *Comparison of the melting points*

The early members of the alkoxythiophene series (**13**–**15**) have melting points 15.1, 6.9 and 0.2°C lower than the analogous alkoxyphenyl derivatives (**18**–**20**). This result is in accord with earlier studies on alkylsulphanylthienyl [38], alkylthienyl [39–41] and related systems when compared with the corresponding phenyl systems. In contrast, the late members of the series (**16** and **17**) have melting points 9.4 and 0.1°C higher than the analogous alkoxyphenyl systems (**21** and **22**). Previous studies on a ferroelectric alkoxythiophene showed a similar trend with the melting point of the alkoxythiophene-based system being greater than the analogous phenyl system [42].

3.1.3. *Comparison of nematic and smectic A phase thermal stabilities*

Alkoxythiophenes **13**–**15** all possess monotropic nematic phases that are in all cases lower than those of the analogous alkoxyphenyl derivatives **18**–**20** (44.8, 39.7 and 34.3°C lower, respectively). Compound **16** has a virtual $T_{N\text{-}I}$ value approximately 48°C lower than alkoxyphenyl derivative **21**. These results are in full agreement with previous studies on 2,5-disubstituted thiophene-containing liquid crystals (relative to phenyl analogues).

The 2,5-disubstitution pattern imparts a deviation from linearity that is thought to give rise to less efficient molecular packing that is manifested by the low $T_{N\text{-}I}$ values exhibited by such systems. However, the $T_{N\text{-}I}$ values observed in these new materials are substantially greater than seen in any other thiophene derivatives that contain two adjacent rings in the core. This is likely to be due to a combination of the on-axis nature of the alkoxy substituent, combined with the highly polarizable combination of the alkoxy and thiophene units. Related alkylsulphanyl thiophene derivatives had considerably lower $T_{N\text{-}I}$ values than the new systems reported here [38]. Although the alkylsulphanyl substituent is more polarizable than the alkoxy unit, and would thus be expected to have a higher $T_{N\text{-}I}$ value according to the Maier–Saupe theory, the C–S–C bond angle in the alkylsulphanyl unit is smaller than the C–O–C bond angle in the alkoxy unit. As a consequence the alkyl chain in the former system will reside in a more off-axis position than the analogous alkoxy chain, giving a reduced aspect ratio and diminished anisotropic molecular interactions. Related alkyl systems are likely to have lower $T_{N\text{-}I}$ values than the alkoxythiophenes due to reduced values of polarizability anisotropy.

Long chain alkoxythiophenes **15** and **17** additionally have a SmA phase that is 30.2 and 27.3°C lower than the SmA phase observed in alkoxyphenyls **20** and **22**, respectively.

3.2. *Stability of the materials*

The following observations of material stability were specifically made with reference to alkoxythiophene **15** (C8 chain) although they are likely to be applicable to the entire homologous series. When the alkoxythiophene is stored in a dark jar the material is stable for an indefinite period. However, exposure to strong sunlight for a week or more causes the neat material to turn brown in colour. A mixture of the alkoxythiophene in E48 (8 wt %) also turned brown on exposure to strong sunlight (within a week). Thermal stability was much better as both the neat material and the mixture ($T_{N\text{-}I} = 82.0$°C) were stable at 80°C in the absence of light (enclosed Mettler oven) for four days (prolonged evaluation was not undertaken). Long term studies to evaluate the chemical changes taking place are currently underway.

4. Conclusions

We have presented the first synthesis of a new class of nematic thermotropic mesogens that incorporate the alkoxythiophene moiety into the rigid core. The clearing

points are substantially higher than any previously reported two-ring systems that contain thiophene as a core unit. The materials are photochemically unstable in strong sunlight and will require the use of a filter for use in display applications.

5. Experimental

Compounds **2**–**12** were prepared by methods described in [26]; only characterization details are given here.

5.1. *3-(4-Bromobenzoyl)propanoic acid (2)*

Yield 39.07 g (76%), m.p. 147–148°C (lit. [33] 149.5–150.2°C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.59 (2H, t, $J = 6.35$ Hz), 3.21 (2H, t, $J = 6.35$ Hz), 7.88 (2H, d, $J = 8.79$ Hz), 7.96 (2H, d, $J = 8.79$ Hz), 12.19 (1H, s). IR (KBr) ν_{max} 2600–3400, 1730, 1670, 1585, 1479, 1447, 1410, 1105, 1074, 840 cm^{-1}. Anal: calcd for $C_{10}H_9BrO3$ C 46.72, H 3.53; found C 46.69, H 3.49%.

5.2. *Butyl 4-(4-bromophenyl)-4-oxobutanoate (3)*

Yield 5.21 g (88%), m.p. 30–31°C, purity (GLC) > 96%. ^{1}H NMR ($CDCl_3$) δ 0.85 (3H, t, $J = 7.20$ Hz), 1.30–1.41 (2H, sext, $J = 7.20$ Hz), 1.55–1.65 (2H, quint, $J = 7.20$ Hz), 2.75 (2H, t, $J = 6.60$ Hz), 3.25 (2H, t, $J = 6.60$ Hz), 4.10 (2H, t, $J = 7.20$ Hz), 7.60 (2H, d, $J = 8.50$ Hz), 7.82 (2H, d, $J = 8.50$ Hz). IR (KBr) ν_{max} 3000, 1726, 1685, 1588, 1467, 1174, 1071, 808 cm^{-1}. Anal: calcd for $C_{14}H_{17}BrO_3$ C 53.69, H 5.47; found C 53.67, H 5.46%.

5.3. *Hexyl 4-(4-bromophenyl)-4-oxobutanoate (4)*

Yield 5.74 g (89%), m.p. 32–33°C, purity (GLC) > 99%. ^{1}H NMR ($CDCl_3$) δ 0.85 (3H, t, $J = 6.70$ Hz), 1.25 (6H, m), 1.60 (2H, quint, $J = 6.70$ Hz), 2.75 (2H, t, $J = 6.60$ Hz), 3.25 (2H, t, $J = 6.60$ Hz), 4.05 (2H, t, $J = 6.70$ Hz), 7.60 (2H, d, $J = 8.40$ Hz), 7.85 (2H, d, $J = 8.40$ Hz). IR (melt) ν_{max} 2956, 2924, 1731, 1671, 1583, 1417, 1398, 1177, 842 cm^{-1}. Anal: calcd for $C_{16}H_{21}BrO_3$ C 56.32, H 6.20; found C 56.28, H 6.15%.

5.4. *Octyl 3-(4-bromobenzoyl)propanoate (5)*

Yield 6.42 g (90%), m.p. 39–40°C. ^{1}H NMR ($CDCl_3$) δ 0.77 (3H, t, $J = 6.70$ Hz), 1.25 (10H, m), 1.70 (2H, quint, $J = 6.70$ Hz), 2.75 (2H, t, $J = 6.60$ Hz), 3.25 (2H, t, $J = 6.60$ Hz), 4.10 (2H, t, $J = 6.70$ Hz), 7.60 (2H, d, $J = 7.70$ Hz), 7.80 (2H, d, $J = 7.70$ Hz). IR (KBr) ν_{max} 3080, 2917, 2851, 1728, 1667, 1581, 1466, 1419, 1177, 842 cm^{-1}. Anal: calcd for $C_{18}H_{25}BrO_3$ C 58.54, H 6.82; found C 58.49, 6.83%.

5.5. *Decyl 4-(4-bromophenyl)-4-oxobutanoate (6)*

Yield 9.56 g (99%), m.p. 48–49°C, purity (GLC) > 99%. ^{1}H NMR ($CDCl_3$) δ 0.85 (3H, t, $J = 6.70$ Hz), 1.25 (14H, m), 1.60 (2H, quint, $J = 6.70$ Hz), 2.75 (2H, t, $J = 6.60$ Hz), 3.25 (2H, t, $J = 6.60$ Hz), 4.08 (2H, t, $J = 6.70$ Hz), 7.60 (2H, d, $J = 7.70$ Hz), 7.85 (2H, d, $J = 7.70$ Hz). IR (KBr) ν_{max} 3091, 2916, 2389, 2287, 1736, 1666, 1581, 1464, 1421, 1176, 1069, 842 cm^{-1}. Anal: calcd for $C_{20}H_{29}BrO_3$ C 60.45, H 7.36; found C 60.49, 7.54%.

5.6. *Dodecyl 4-(4-bromophenyl)-4-oxobutanoate (7)*

Yield 13.30 g (99%), m.p. 50–52°C, purity (GLC) > 99%. ^{1}H NMR ($CDCl_3$) δ 0.93 (3H, t, $J = 6.70$ Hz), 1.13–1.40 (20H, m), 2.76 (2H, t, $J = 6.60$ Hz), 3.27 (2H, t, $J = 6.60$ Hz), 4.09 (2H, t, $J = 6.70$ Hz), 7.61 (2H, d, $J = 8.60$ Hz), 7.87 (2H, d, $J = 8.60$ Hz). IR (NaCl) ν_{max} 2800–3000, 1727, 1679, 1584, 787 cm^{-1}. Anal: calcd for $C_{22}H_{33}BrO_3$ C 62.11, H 7.82; found C 62.23, H 7.96%.

5.7. *2-(4-Bromophenyl)-5-butoxythiophene (8)*

Yield 3.77 g (76%), m.p. 74–75°C. ^{1}H NMR ($CDCl_3$) δ 0.95 (3H, t, $J = 7.30$ Hz), 1.50 (2H, sext, $J = 7.30$ Hz), 1.80 (2H, quint, $J = 7.30$ Hz), 4.20 (2H, t, $J = 7.30$ Hz), 6.15 (1H, d, $J = 4.00$ Hz), 6.95 (1H, d, $J = 4.00$ Hz), 7.35 (2H, d, $J = 8.70$ Hz), 7.50 (2H, d, $J = 8.70$ Hz). ^{13}C NMR ($CDCl_3$) δ 165.7, 134.0, 132.0, 129.0, 126.4, 121.3, 120.2, 105.9, 73.8, 31.3, 19.3, 14.0. IR (KBr) ν_{max} 3080, 2868, 2265, 1585, 1551, 1500, 1465, 1390, 1271, 1202, 1112, 817 cm^{-1}. Anal: calcd for $C_{14}H_{15}BrOS$ C 54.03, H 4.86; found C 54.05, H 5.00%.

5.8. *2-(4-Bromophenyl)-5-hexyloxythiophene (9)*

Yield 3.32 g (67%), m.p. 67–68°C. ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, $J = 6.50$ Hz), 1.20–1.50 (6H, m), 1.80 (2H, quint, $J = 6.50$ Hz), 4.05 (2H, t, $J = 6.50$ Hz), 6.17 (1H, d, $J = 3.90$ Hz), 6.95 (1H, d, $J = 3.90$ Hz), 7.35 (2H, d, $J = 7.65$ Hz), 7.45 (2H, d, $J = 7.65$ Hz). ^{13}C NMR ($CDCl_3$) δ 165.7, 134.0, 132.0, 128.8, 126.4, 121.3, 120.2, 105.9, 74.1, 31.7, 29.3, 25.7, 22.7, 14.2. IR (KBr) ν_{max} 2926, 2854, 1892, 1639, 1586, 1550, 1499, 1465, 1391, 1269, 1199, 1115, 817 cm^{-1}. Anal: calcd for $C_{16}H_{19}BrOS$ C 56.64, H 5.64; found C 56.64, H 5.76%.

5.9. *2-(4-Bromophenyl)-5-octyloxythiophene (10)*

Yield 3.48 g (70%), m.p. 66–67°C. ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, $J = 6.50$ Hz), 1.20–1.50 (10H, m), 1.58 (2H, quint, $J = 6.50$ Hz), 4.05 (2H, t, $J = 6.50$ Hz), 6.17 (1H, d, $J = 3.90$ Hz), 6.94 (1H, d, $J = 3.90$ Hz), 7.33 (2H, d, $J = 8.70$ Hz), 7.44 (2H, d, $J = 8.70$ Hz). ^{13}C NMR ($CDCl_3$) δ 165.7, 134.0, 132.0, 128.8, 126.4, 121.3, 120.2, 105.9, 74.1, 32.0, 29.5, 29.4, 29.3, 26.0, 22.8, 14.3. IR (KBr) ν_{max} 3080, 2918, 2846, 1552, 1502, 1462, 1199, 817 cm^{-1}. Anal: calcd for $C_{18}H_{23}BrOS$ C 58.85, H 6.31; found C 58.84, H 6.60%.

5.10. *2-(4-Bromophenyl)-5-decyloxythiophene (11)*

Yield 2.80 g (93%), m.p. 66–67°C. ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, $J = 6.50$ Hz), 1.20–1.50 (14H, m), 1.80 (2H, quint, $J = 6.50$ Hz), 4.05 (2H, t, $J = 6.50$ Hz), 6.17

(1H, d, $J = 3.90$ Hz), 6.95 (1H, d, $J = 3.90$ Hz), 7.35 (2H, d, $J = 7.65$ Hz), 7.45 (2H, d, $J = 7.65$ Hz). ^{13}C NMR ($CDCl_3$) δ 165.7, 134.0, 132.0, 129.4, 126.4, 121.3, 120.2, 105.9, 74.1, 32.0, 29.7. IR (KBr) ν_{max} 2920, 2851, 1551, 1500, 1465, 1391, 1273, 1202, 1061, 819 cm^{-1}. Anal: calcd for $C_{20}H_{27}BrOS$ C 60.75, H 6.88; found C 60.95, H 7.15%.

5.11. *2-(4-Bromophenyl)-5-dodecyloxythiophene* (**12**)

Yield 3.74 g (87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (3H, t, $J = 6.80$ Hz), 1.22 (16H, br s), 1.40 (2H, quint, $J = 6.70$ Hz), 1.75 (2H, quint, $J = 6.70$ Hz), 4.01 (2H, t, $J = 6.70$ Hz), 6.14 (1H, d, $J = 3.70$ Hz), 6.90 (1H, d, $J = 3.70$ Hz), 7.31 (2H, d, $J = 8.80$ Hz), 7.41 (2H, d, $J = 8.80$ Hz). IR (NaCl) ν_{max} 3000–2800, 1548, 1501, 1261, 1202, 822 cm^{-1}. ^{13}C NMR ($CDCl_3$) δ 165.8, 134.0, 132.0, 128.9, 126.5, 121.3, 120.3, 106.0, 74.2, 32.1, 29.9, 29.8, 29.8, 29.6, 29.5, 29.4, 26.1, 22.9, 14.3. Anal: calcd for $C_{22}H_{31}BrOS$ C 62.40, H 7.38; found C 62.44, H 7.33%.

5.12. *2-Butoxy-5-(4-cyanophenyl)thiophene* (**13**)

Copper(I) cyanide (0.29 g, 0.0032 mol) was added in one portion to a stirred solution of compound **8** (1.00 g, 0.00321 mol) in dry DMF (50 ml) under dry argon at reflux. The reaction mixture was maintained under these conditions for a further 24 h (after reflux for approximately 3 h the green reaction mixture turned to a black solution). The cooled reaction mixture was poured into ice-cold hydrochloric acid (10%, 100 ml) and stirred for one hour. Dichloromethane (150 ml) was poured into the mixture with stirring and the organic layer was separated. The aqueous layer was washed with dichloromethane (50 ml) and the combined organic extracts were washed with water (3 × 50 ml) and dried ($MgSO_4$). The drying agent was filtered off and the solvent removed *in vacuo*. The crude product was purified twice by column chromatography (silica gel/hexane: ethyl acetate, 9:1) to afford a yellow product which was crystallized twice from ethanol. The product was then dried under reduced pressure (P_2O_5, paraffin, 24 h) to afford a white solid; yield 0.81 g (72%). ^{1}H NMR ($CDCl_3$) δ 1.00 (3H, t, $J = 7.5$ Hz), 1.51 (2H, sext, $J = 7.5$ Hz), 1.81 (2H, quint, $J = 6.5$ Hz), 4.10 (2H, t, $J = 6.3$ Hz), 6.23 (1H, d, $J = 4.2$ Hz), 7.11 (1H, d, $J = 4.2$ Hz), 7.54 (2H, d, $J = 6.6$ Hz), 7.60 (2H, d, $J = 6.6$ Hz). ^{13}C NMR ($CDCl_3$) δ 13.8, 19.1, 31.2, 73.8, 106.1, 109.2, 119.2, 123.5, 124.7 (2C), 127.5, 132.7 (2C), 139.2, 167.4. IR (KBr) ν_{max} 2250, 1620, 1075, 748 cm^{-1}. MS (*m*/*z*) 257.0 (M^+), 202.0, 201.0 (100%), 172.0, 140.2. Anal: calcd for $C_{15}H_{15}NOS$ C 70.01, H 5.87, N 5.44; found C 69.91, H 5.84, N 5.43%.

Compounds **14**–**17** were prepared as described for the preparation of **13** using the quantities stated.

5.13. *2-(4-Cyanophenyl)-5-hexyloxythiophene* (**14**)

Quantities: copper(I) cyanide (0.32 g, 0.0036 mol), compound **9** (1.00 g, 0.00295 mol) in dry DMF (50 ml). The crude product was purified twice by column chromatography (silica gel/hexane: ethyl acetate, 9:1) to afford a yellow product which was crystallized twice from ethanol. The product was dried under reduced pressure (P_2O_5, paraffin, 24 h) to afford a white solid; yield 0.43 g (51%). ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, $J = 7.5$ Hz), 1.35 (4H, m), 1.47 (2H, quint, $J = 6.5$ Hz), 1.82 (2H, quint, $J = 6.5$ Hz), 4.08 (2H, t, $J = 6.5$ Hz), 6.22 (1H, d, $J = 4.3$ Hz), 7.10 (1H, d, $J = 4.3$ Hz), 7.55 (2H, d, $J = 6.7$ Hz), 7.59 (2H, d, $J = 6.7$ Hz). ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 25.7, 29.3, 31.7, 74.3, 106.3, 109.4, 119.3, 123.6, 124.9 (2C), 127.7, 132.8 (2C), 139.4, 167.5. IR (KBr) ν_{max} 2250, 1620, 1075, 748 cm^{-1}. MS *m*/*z* 285.0 (M^+), 202.0, 201.0 (100%), 167.0, 149.0. Anal: calcd for $C_{17}H_{19}NOS$ C 71.54, H 6.71, N 4.91; found C 71.29, H 6.71, N 4.91%.

5.14. *2-(4-Cyanophenyl)-5-octyloxythiophene* (**15**)

Quantities: copper(I) cyanide (0.14 g, 0.0016 mol), compound **10** (0.5 g, 0.001 mol) in dry DMF (50 ml). The crude product was purified twice by column chromatography (silica gel/hexane: ethyl acetate, 9:1) and then crystallized twice from ethanol to afford a white solid which was dried under reduced pressure (P_2O_5, paraffin, 24 h); yield 0.133 g (42%). ^{1}H NMR ($CDCl_3$) δ 0.85 (3H, t, $J = 6.9$ Hz), 1.28 (8H, m), 1.41 (2H, quint, $J = 7.3$ Hz), 1.76 (2H, quint, $J = 6.5$ Hz), 4.04 (2H, t, $J = 6.5$ Hz), 6.18 (1H, d, $J = 4.2$ Hz), 7.06 (1H, d, $J = 4.2$ Hz), 7.49 (2H, d, $J = 8.6$ Hz), 7.54 (2H, d, $J = 8.6$ Hz). IR (KBr) ν_{max} 2230, 1610, 1060, 745 cm^{-1}. ^{13}C NMR ($CDCl_3$) δ 14.3, 22.9, 26.1, 29.3, 29.4, 29.5, 32.0, 74.3, 106.3, 109.4, 119.3, 123.6, 124.9 (2C), 127.7, 132.9 (2C), 139.4, 167.6. MS (*m*/*z*) 313.0 (M^+), 201.1 (100%), 172.1, 140.1, 128.1. Anal: calcd for $C_{19}H_{23}NOS$ C 72.80, H 7.40, N 4.47; found C 72.76, H 7.44, N 4.47%.

5.15. *2-(4-Cyanophenyl)-5-decyloxythiophene* (**16**)

Quantities: copper(I) cyanide (0.72 g, 0.0080 mol) and compound **11** (2.64 g, 0.00668 mol) in dry DMF (50 ml). The crude product was purified twice by column chromatography (silica gel/hexane: ethyl acetate, 9:1) and then crystallized twice from ethanol to afford a white solid which was dried under reduced pressure (P_2O_5, paraffin, 24 h); yield 1.37 g (60%). ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, $J = 7.0$ Hz), 1.28 (12H, m), 1.45 (2H, quint, $J = 8.1$ Hz), 1.80 (2H, quint, $J = 6.9$ Hz), 4.08 (2H, t, $J = 6.5$ Hz), 6.22 (1H, d, $J = 4.2$ Hz), 7.10 (1H, d, $J = 4.2$ Hz), 7.52 (2H, d, $J = 6.7$ Hz), 7.58 (2H, d, $J = 6.7$ Hz). ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 25.9, 29.1, 29.3, 29.4, 29.6 (2C), 32.0, 74.1, 106.1, 109.2, 119.2, 123.5, 124.7 (2C), 127.5, 132.7 (2C), 139.3, 167.4. IR (KBr) ν_{max} 2245, 1610, 1060, 748 cm^{-1}.

MS m/z 341 (M^+), 325.1, 298.8, 284.9 (100%), 269.1. Anal: calcd for $C_{21}H_{27}NOS$ C 73.86, H 7.97, N 4.10; found C 73.80, H 7.96, N 4.09%.

5.16. *2-(4-Cyanophenyl)-5-dodecyloxythiophene (17)*

Quantities: copper(I) cyanide (0.21 g, 0.0023 mol) and compound **12** (0.84 g, 0.0020 mol) in dry DMF (50 ml). The crude product was purified twice by column chromatography (silica gel/hexane: ethyl acetate, 9:1) and then crystallized twice from ethanol to afford a white solid which was dried under reduced pressure (P_2O_5, paraffin, 24 h); yield 0.33 g (45%). ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, $J = 6.9$ Hz), 1.28 (16H, m), 1.46 (2H, quint, $J = 7.4$ Hz), 1.82 (2H, quint, $J = 7.0$ Hz), 4.10 (2H, t, $J = 6.5$ Hz), 6.23 (1H, d, $J = 4.2$ Hz), 7.11 (1H, d, $J = 4.2$ Hz), 7.54 (2H, d, $J = 8.8$ Hz), 7.60 (2H, d, $J = 8.8$ Hz). ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 25.9, 29.1, 29.3, 29.4, 29.6 (3C), 29.7, 32.0, 74.1, 106.1, 109.2, 119.2, 123.5, 124.7 (2C), 127.5, 132.7 (2C), 139.3, 167.4. IR (KBr) ν_{max} 2250, 1625, 1060, 750 cm^{-1}. MS (m/z) 370.0 (M^+), 279.0, 167.0, 149.0 (100%), 55.1. Anal: calcd for $C_{23}H_{31}NOS$ C 74.75, H 8.45, N 3.79; found C 73.64, H 8.46, N 3.61%.

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