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2,5-Dibromopyridine as a key building block in the synthesis of 2,5-disubstituted pyridine-based liquid crystals

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2,5-Dibromopyridine as a key building block in the synthesis of 2,5-disubstituted pyridine-based liquid crystals

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Fifteen 2,5-disubstituted pyridine based liquid crystals were synthesized exploiting the different reactivities of the bromine atoms in 2,5-dibromopyridine under Negishi coupling conditions. Convenient approaches to both 2-iodo-5-alkyl-pyridines and 2-alkyl-5-bromo-pyridines were also developed. The liquid crystalline behaviour of the synthesized materials was investigated using DSC and polarizing microscopy. The charge mobility of 2-(4-heptyloxyphenyl)-5-heptylpyridine was measured using the time of flight technique.

1. Introduction

Organic semiconductors have been intensively studied in recent decades from the viewpoint of their potential applications as the active media in electronic and electro-optical devices such as field effect transistors, photovoltaic cells and organic light-emitting diodes (OLEDs) [1]. These important technological applications have driven much of the materials research and engineering in this field.

Organic semiconductors can be divided into two main groups, namely, small molecules and oligomers/polymers, based on their size alone. They can be further classified by their state of organization, namely, single crystals, polycrystals, liquid crystals and amorphous materials including glasses. These structure categories are not exclusive but rather represent a continuum; each has its own respective relevance and advantages and disadvantages in their variety of physical properties and applications.

Historically, the single crystal organics have received most attention as semiconductors. The main advantage of single crystals is the high charge mobility that may result from their relative density and high degree of uniformity. Small molecules can be systematically modified and can sometimes be synthesized in the high purities required. However, the growth and processing of bulk single crystals, and their incorporation into device structures, is often difficult and thus limits the applications of single crystal semiconductors in practical applications. The deposition of thin films of polymorphic crystalline small molecule materials is a possible means to simplify the processing, but usually occurs at the expense of reduction of function, as in the case of the charge mobility. The class of acenes, especially pentacene, is a case in point. The relatively high charge mobility of crystalline pentacene has been recognized for decades but the intrinsic mobility of this material still appears not to have been realized. Most reports place the hole mobility of this substance in the vicinity of $1\,cm^2\,V^{-1}\,s^{-1}$ at room temperature but one recent report describes specially purified material with a mobility determined by the space-charge-limited-current technique (SCLC) of $35\,cm^2\,V^{-1}\,s^{-1}$ [2]. Thus, even in the case of a material studied for decades, there are still uncertainties about some fundamental semiconductor properties that are critically influenced by purity and processing.

Conjugated polymers are a second main class of organic semiconductors that are often much easier to process, but their charge mobility properties are overall poorer than for single crystals due to the lack of order. Of course polymers are themselves a diverse continuum of structures, from the amorphous systems through semicrystalline and finally highly ordered systems with crystalline domains. For this class of materials large one-dimensional mobilities $\Sigma\mu_{1D}$ of 0.125 and $0.108\,cm^2\,V^{-1}\,s^{-1}$ determined by pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) at room temperature were reported for liquid crystalline polyfluorene and poly(phenylenevinylene) derivatives, respectively; while polydiacetylenes in single crystal form are reported to have mobility $\Sigma\mu_{1D}$ in the range 1 to $7.2\,cm^2\,V^{-1}\,s^{-1}$ [3]. Some disadvantages of polymers

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include forbidding purification issues preventing the achievement of intrinsic large mobilities, in some cases low solubility and the necessity to chemically modify structures to increase solubility and, finally, difficulties in obtaining materials with well defined macroscopic structure.

In many respects liquid crystals interpolate between polymers and crystals, both structurally and in terms of their properties. The discovery of the high drift mobilities of the order of $1 \times 10^{-3}\,cm^{-2}\,V^{-1}\,s^{-1}$ (determined by the time-of-flight, TOF, technique) in the discotic mesophase of hexapentyloxytriphenylene and $0.1\,cm^{-2}\,V^{-1}\,s^{-1}$ in the helical plastic phase of the hexakis(hexylthio) derivative of triphenylene reported by Adam *et al.* [4] gave rise to a new class of organic semiconductors and also stimulated research on discotic liquid crystals in general. Later, it was also demonstrated that calamitic smectic liquid crystals, such as benzothiazole [5] and phenylnaphthalene derivatives [6] also could possess rather large charge mobilities. Features that make smectic liquid crystals attractive as organic semiconductors include the formation of different degrees of molecular ordering and the availability of liquid-like isotropic phases that permit processing with large-area uniformity. It has been shown by Hanna *et al.* that charge mobility systematically increases upon a transition from a less ordered phase to a higher ordered smectic phase. The mobility of the phenylnaphthalene 8-PNP-012 increases from $10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ for the SmA phase to $10^{-3}\,cm^2\,V^{-1}\,s^{-1}$ for the SmB phase. A high carrier mobility of $1 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$ was also observed for the more ordered SmE phase of 8-PNP-04 [6]. More recently, carrier mobilities of $1 \times 10^{-1}\,cm^2\,V^{-1}\,s^{-1}$ have been found in higher ordered smectic phases of thiophene oligomers at ambient temperature [7], which makes them good candidates for practical applications. O'Neill and Kelly reviewed developments in charge-transporting liquid crystals and outlined some of the issues of application of LCs in electronic and photonic devices [8]. Karl has summarized experimental methods that are currently used for the mobility measurements [9].

Our primary interest here lies in the synthesis and carrier transport examination of calamitic liquid crystals. It is known that some phenylpyridine liquid crystals have a propensity for formation of higher ordered smectic phases at or near room temperatures [10]. Thus, it was our goal to find a convenient synthetic approach for 2,5-disubstituted pyridines, to investigate their liquid crystalline behaviour and to examine their carrier transport properties. This paper is primarily devoted to the synthesis of pyridine containing liquid crystals, and investigation of their liquid crystalline behaviour along with some preliminary studies of charge mobility.

The literature provided several possible approaches to the construction of the requisite 5-substituted-2-arylpyridines [10–16]. The traditional general method for the synthesis of 2,5-disubstituted pyridines is based on the transformation of pyrylium salts obtained from acyclic precursors [11]. A more recent non-catalytic method reported by Chia *et al.* is based on the regioselective addition of a Grignard reagent to acylpyridinium salts followed by oxidation of the intermediate with *o*-chloranil with overall 40–68% yield [12]. With the recent developments in palladium mediated chemistry, new approaches to 2,5-disubstituted pyridines have been reported, for example, the crosscoupling of arylboronic acids with chloropyridines catalysed by a polymer-bound palladium complex [13], the selective palladium-catalysed coupling of 2-bromo-5-chloropyridine with bromobenzene in the presence of hexamethylditin [14], the selective coupling of 2,5-dichloropyridine with phenylboronic acids catalysed by $PdCl_2$(dppb) [15], and the selective coupling of 2,5-dibromopyridine with 4-octylphenyl boronic acid [10]. Tilley and Zawoiski reported a selective palladium-catalysed coupling of 2,5-dibromopyridine with phenyl- or (3,4-dimethoxyphenyl)-zinc chlorides under Negishi coupling conditions [16]. The desired 5-bromo-2-arylpyridines were formed in 72–74% yield. The possibility of further functionalization at position 5 of these 5-bromo-2-arylpyridines, the good yields obtained for these intermediates and the selectivity and convenience of the procedure were the reasons for our choice of this approach to prepare the desired 2,5-disubstituted pyridines (figure 1).

A disconnection analysis of the proposed pyridine containing liquid crystals led us to two important types of intermediates: 2-halo-5-alkylpyridines and 2-alkyl-5-halopyridines. Two methods for the synthesis of 2-iodo-5-alkylpyridines were found in the literature. Mathieu *et al.* reported a convenient method for the synthesis of 2-halo-5-methylpyridines by selective lithiation of 3-picoline at position C-6 using *n*-BuLi-$Me_2N(CH_2)_2OLi$ base followed by trapping with halo-containing electrophiles [17]. Unfortunately, this approach had been tested only for 3-methylpyridine. Also, it has been shown that the availability of the methyl proton was crucial for successful ring functionalization, therefore the reaction conditions may give different results if a longer alkyl chain is attached to the pyridine ring (*vide infra*). Another method for the preparation of 2-iodo-5-butyl-(*or* hexyl)-pyridines was recently reported by Schwab *et al.*, and although these valuable

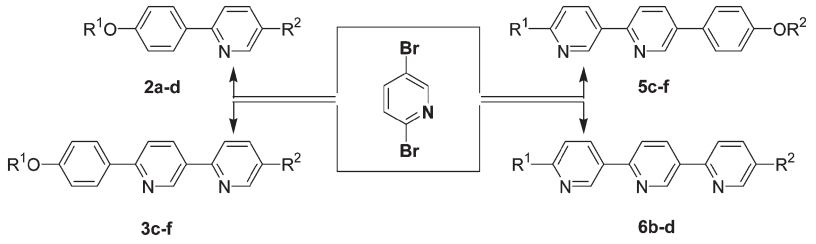


Figure 1. 2,5-Disubstituted pyridines **2a–d**, **3c–f**, **5c–f**, **6b–d** obtained from 2,5-dibromopyridine.

intermediates were synthesized with good yields the procedure is overall a multistep and multicomponent synthesis [18]. An examination of the literature found no convenient method for the synthesis of 2-alkyl-5-bromopyridines. One of the few examples is the direct bromination of 2-alkylpyridines, which gives a mixture of isomers [19]. This paper deals with the synthesis and examination of the liquid crystalline behaviour of the 2,5-disubstituted pyridines outlined in figure 1.

2. Experimental

2.1. *Materials and methods*

The solvents THF and Et_2O were freshly distilled from sodium benzophenone ketyl. $ZnCl_2$ was dried by melting and cooling under vacuum. After the addition of freshly distilled THF to dried $ZnCl_2$ the resulting mixture was stirred at room temperature under an inert atmosphere until the entire solid was dissolved. This freshly prepared solution of $ZnCl_2$ was then used for the transmetallation reaction. The 3-alkylpyridines **8a–d** were prepared according to the literature procedure [20]. The 4-heptyloxy-1-bromobenzene **13a** was prepared from 4-bromophenol and 1-bromoheptane using K_2CO_3 as a base and NMP as solvent [21]. The 4-(tetrahydropyran-2-yloxy)-1-bromobenzene **13b** and 4-(tetrahydropyran-2-yloxy)-1-iodobenzene **14** were prepared according to a literature procedure [22].

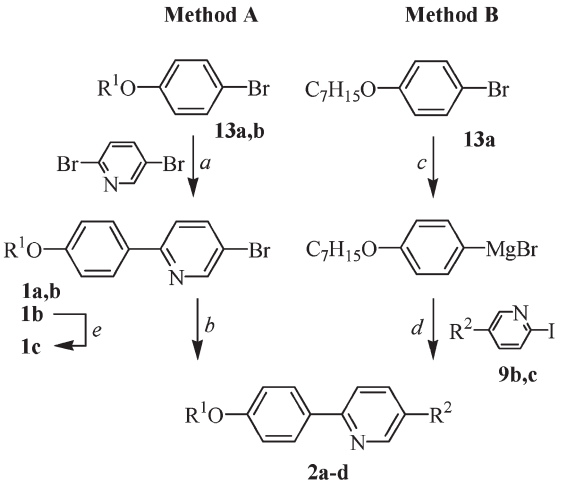
Both ^1H and ^{13}C NMR spectra were recorded using a Bruker 300 MHz spectrometer (TMS as internal standard). A differential scanning calorimeter (TA Instruments DSC, scanning rate of 5 or 10°C min^{-1}) and a polarizing microscope equipped with a Mettler FP90 and FP28HP hot stage were used to study the phase transitions (0.5–1°C min^{-1} cooling rate at transition temperatures determined by DSC). Phase assignments were made based on microscopic observations but transitions below 30°C were not observed by microscopy due to instrument limitations. Photographs were taken with a 35 mm film camera fitted to the microscope (ISO 400, 2–6 s exposure) or with a CCD camera using Studio Capture software.

Charge mobilities were measured using the pulsed-laser time-of-flight (TOF) technique. A Nd/YAG 10 ns pulse was quadrupled in frequency (266 nm) and fed into an 8-bar H_2 stimulated Raman shifter. The 340 nm Stokes line was used to photogenerate charges on a timescale much shorter than the charge transit time. The samples were contained in 10 µm cross-rubbed liquid crystal cells (EHC Inc.).

2.2. *Synthesis of 2-(4-alkoxylphen-1-yl)-5-alkylpyridines 2a–d [scheme 1]*

2.2.1. 2-(4-Heptyloxyphen-1-yl)-5-bromopyridine (1a). 4-Heptyloxy-1-bromobenzene **13a** (12 mmol, 3.25 g) was placed in a three-necked 50 ml flask and freshly distilled THF (20 ml) was added under a nitrogen atmosphere. The reaction mixture was cooled in a CO_2/acetone bath and *n*-BuLi (2.5 M, 4.8 ml) was added dropwise. After 30 min of stirring a solution of $ZnCl_2$ (12 mmol, 1.64 g) in 15 ml of freshly distilled THF was added, and the reaction mixture warmed to room temperature and stirred for 2 h (nitrogen atmosphere). 2,5-Dibromopyridine (10 mmol, 2.33 g) and $Pd(PPh_3)_4$ (1 mol%, 0.1 mmol, 0.115 g) were added and the reaction mixture was stirred for several hours. After the completion of reaction the mixture was poured into water, filtered and extracted with Et_2O (3 × 15 ml). The organic solution was washed with brine and then dried with $MgSO_4$. After vacuum filtration and evaporation of the solvent the crude product was chromatographed (silica gel, CH_2Cl_2) and a white solid (2.94 g) was isolated in 84.4% yield. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.85–1.00 (t, J=6.58 Hz, 3H), 1.23–1.39 (m, 6H), 1.39–1.50 (m, 2H), 1.73–1.84 (m, 2H), 3.95–4.03 (t, J=6.57 Hz, 2H), 6.94–7.02 (d, J=8.80 Hz, 2H), 7.50–7.56 (d, J=8.52 Hz, 1H), 7.74–7.82 (dd, J=8.51 Hz, 2.41 Hz, 1H), 7.87–7.93 (d, J=8.84 Hz, 2H), 8.65–8.69 (d, J=2.27 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.29, 22.80, 26.18, 29.26, 29.14, 31.96, 68.28, 114.91, 118.47, 120.98, 128.20, 130.69, 139.30, 150.64, 155.79, 160.51.

2.2.2. 2-[4-(Tetrahydropyran-2-yloxy)-phen-1-yl]-5-bromopyridine (1b). The intermediate **1b** was synthesized



For the intermediates: R^1=C_7H_{15} (**13a, 1a**), tetrahydropyran-2-yl (**13b, 1b**), C_8H_{15} (**1c**); R^2=C_6H_{13} (**9b**), C_7H_{15} (**9c**)

Reagents: *a*) *i*) *n*-BuLi, THF, -78 ºC; *ii*) $ZnCl_2$, THF, -78 ºC→rt; *iii*) 2,5-dibromopyridine, $Pd(PPh_3)_4$ (1 mol%), THF, rt; *b*) R^2MgBr, $NiCl_2$(dppe) (5 mol%), Et_2O, reflux; *c*) Mg, THF, reflux; *d*) $NiCl_2$(dppe) (5 mol%), THF, reflux; *e*) *i*) HCl (cat.), EtOH, reflux; *ii*) 1-bromooctane, K_2CO_3, NMP, heating.

Scheme 1. Synthetic approaches to mesogens **2a**–**d** utilizing the Negishi coupling and Ni(II)-catalyzed coupling of aryl halides with aryl or alkyl Grignards.

in the same manner as **1a** using 4-(tetrahydropyran-2-yloxy)-1-bromobenzene **13b** as starting material. The product was isolated as a white solid in 67% yield (1.12 g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.50–1.60 (m, 4H), 1.60–1.90 (m, 2H), 1.90–2.05 (m, 2H), 3.52–3.65 (m, 1H), 3.86–4.00 (m, 1H), 5.47–5.52 (t, J=3.31 Hz, 1H), 7.10–7.16 (d, J=8.90 Hz, 2H), 7.52–7.57 (d, J=8.52 Hz, 1H), 7.75–7.83 (dd, J=8.52 Hz, 2.42 Hz, 1H), 7.86–7.93 (d, J=8.86 Hz, 2H), 8.67–8.72 (d, J=2.40 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.82, 25.32, 30.41, 62.19, 96.33, 116.80, 118.66, 121.25, 128.19, 131.67, 139.41, 150.65, 155.80, 158.36.

2.2.3. 2-(4-Octyloxyphenyl)-5-bromopyridine (1c). A round bottom flask was charged with **1b** (1.8 mmol, 0.61 g) and 10 ml of EtOH. After addition of three drops of HCl the reaction mixture was heated for 30 min, and then cooled. K_2CO_3 was added to neutralize the HCl and the solvent was evaporated. The product 2-(4-hydroxyphen-1-yl)-5-bromopyridine was extracted with CH_2Cl_2, and after evaporation of the solvent was used in the alkylation reaction without further purification. A flask was charged with 2-(4-hydroxyphen-1-yl)-5-bromopyridine (1.75 mmol, 0.44 g), NMP (10 ml), K_2CO_3 (4 mmol, 0.54 g), and 1-bromooctane (2.2 mmol, 0.43 g). The reaction mixture was heated (~80°C) until no starting material remained (monitored by TLC). After completion of reaction the mixture was cooled and poured into 125 ml of ice water. The resulting white precipitate was separated and purified by column chromatography (silica gel, CH_2Cl_2 as eluant) to give 0.42 g (63.5% yield for two steps). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.77–0.90 (t, J=6.76 Hz, 3H), 1.10–1.31 (m, 8H), 1.31–1.50 (m, 2H), 1.68–1.82 (m, 2H), 3.90–4.00 (t, J=6.59 Hz, 2H), 6.87–6.98 (d, J=8.81 Hz, 2H), 7.45–7.51 (d, J=8.52 Hz, 1H), 7.70–7.79 (dd, J=8.52 Hz, 2.45 Hz, 1H), 7.79–7.90 (d, J=8.80 Hz, 2H), 8.58–8.61 (d, J=2.31 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.26, 22.81, 26.19, 29.39 (2C), 29.52, 31.97, 68.29, 114.93, 118.46, 120.98, 128.19, 130.72, 139.29, 150.64, 155.82, 160.51.

2.2.4. 2-(4-Heptyloxyphenyl)-5-pentylpyridine (2a). *Method A*. 2-(4-Heptyloxyphen-1-yl)-5-bromopyridine **1a** (3 mmol, 1.04 g) was placed into an oven-dried flask. Freshly distilled Et_2O (15 ml) and $NiCl_2$(dppe) (5 mol%, 0.15 mmol, 0.080 g) were added under nitrogen atmosphere. Freshly prepared *n*-pentylmagnesium bromide solution (3.3 mmol in 5 ml of Et_2O) was added dropwise to the reaction mixture, which was heated under reflux for several hours. The reaction mixture then was cooled and poured into 20 ml of water. The organic layer was separated; and the water layer was extracted with Et_2O (3 × 10 ml). The organic

layers were combined and the solvent was evaporated; the crude product was purified by column chromatography (silica gel, CH_2Cl_2 as eluant) (white solid, 0.92 g, 91% yield), and then recrystallized from MeOH. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.83–1.00 (m, 6H, $2CH_3$), 1.25–1.51 (m, 12H), 1.53–1.70 (m, 2H), 1.75–1.85 (m, 2H), 2.56–2.73 (t, J=7.65 Hz, 2H), 3.90–4.10 (t, J=6.58 Hz, 2H), 6.93–7.10 (d, J=8.88 Hz, 2H), 7.46–7.52 (dd, J=8.17 Hz, 2.23 Hz, 1H), 7.52–7.63 (dd, J=8.06 Hz, 0.74 Hz, 1H), 7.85–8.00 (d, J=8.88 Hz, 2H), 8.41–8.50 (d, J=1.51 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.18, 14.27, 22.65, 22.78, 26.18, 29.25, 29.45, 31.04, 31.49, 31.96, 32.79, 68.23, 114.78, 119.48, 128.01, 132.03, 135.80, 136.71, 149.77, 154.91, 159.91.

2.2.5. 2-(4-Heptyloxyphenyl)-5-hexylpyridine (2b). *Method B*. 4-Heptyloxy-1-bromobenzene **13a** (5.5 mmol, 1.50 g), magnesium turnings (9 mmol, 0.22 g) (activated by heating with a crystal of iodine), and freshly distilled THF (20 ml) were placed in an oven-dried flask equipped with magnetic stirbar, bubbler, and condenser (nitrogen atmosphere). The reaction mixture was heated under reflux for 1.5 h and then cooled. This freshly prepared Grignard was transferred via syringe dropwise into a separate flask charged with a solution of 2-iodo-5-hexylpyridine **9b** (5 mmol, 1.21 g) in freshly distilled THF (15 ml) and $NiCl_2$(dppe) (5 mol %, 0.5 mmol, 0.26 g). During the addition of the Grignard, the reaction mixture became yellow, then orange, then red and then greenish. The resulting solution was stirred overnight and then poured into water (15 ml). The mixture was vacuum filtered, the organic layer separated, and the water layer extracted with Et_2O (3×10 ml). The combined organic layers were evaporated and the product purified by column chromatography (silica gel, CH_2Cl_2 as eluant). The compound **2b**, isolated after column chromatography, was recrystallized from MeOH (1.3 g, 74% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.77–1.00 (m, 6H, $2CH_3$), 1.23–1.40 (m, 12H), 1.40–1.52 (m, 2H), 1.56–1.75 (m, 2H), 1.76–1.83 (m, 2H), 2.54–2.73 (t, J=7.66 Hz 2H), 3.90–4.03 (t, J=6.57 Hz, 2H), 6.93–7.03 (d, J=8.69 Hz, 2H), 7.48–7.54 (dd, J=8.12 Hz, 2.06 Hz, 1H), 7.55–7.62 (dd, J=8.12 Hz, 2.06 Hz, 1H), 7.86–7.96 (d, J=8.68 Hz, 2H), 8.41–8.50 (d, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.26 (2C), 22.77 (2C), 26.18, 29.00, 29.26, 29.45, 31.33, 31.81, 31.96, 32.82, 68.22, 114.77, 119.52, 128.02, 132.00, 135.81, 136.73, 149.73, 154.90, 159.92.

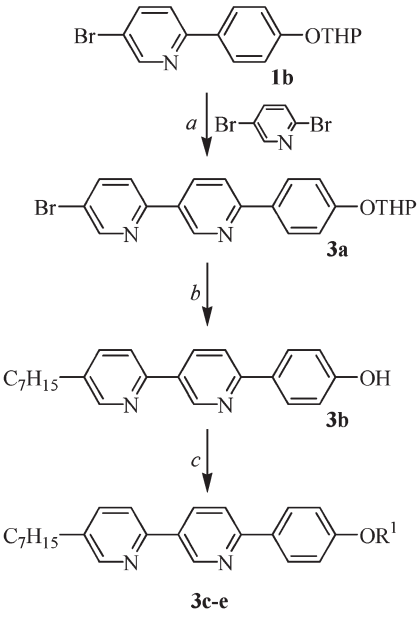
2.2.6. 2-(4-Heptyloxyphenyl)-5-heptylpyridine (2c). *Method A*. Compound **2c** was prepared in the same manner as **2a** except that *n*-heptylmagnesium bromide was used for the alkylation. The product was purified by column chromatography (silica gel, CH_2Cl_2 as eluant, 93% yield). The purified product was Kugelrohr distilled (230–245°C/0.1 mm Hg), and then recrystallized twice from electronic grade MeOH to obtain a sample for mobility measurements.

Method B. The product **2c** was also obtained in 74% yield by $NiCl_2$(dppe)-catalysed coupling of 2-iodo-5-heptylpyridine **9c** (0.01 mol, 3.03 g) with 4-heptyloxyphenylmagnesium bromide, freshly prepared from 4-heptyloxy-1-bromobenzene **13a** (0.012 mol, 3.25 g) and Mg (0.018 mol, 0.44 g) in the same manner as **2b**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.83–0.95 (m, 6H, $2CH_3$), 1.20–1.40 (m, 14H), 1.40–1.55 (m, 2H), 1.57–1.71 (m, 2H), 1.70–1.83 (m, 2H), 2.55–2.70 (t, J=7.65 Hz, 2H), 3.90–4.05 (t, J=6.58 Hz, 2H), 6.94–7.03 (d, J=8.83 Hz, 2H), 7.48–7.54 (dd, J=8.13 Hz, 2.21 Hz, 1H), 7.55–7.70 (d, J=8.09 Hz, 1H), 7.85–7.95 (d, J=8.85 Hz, 2H), 8.45–8.50 (d, J=1.65 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.27 (2C), 22.80 (2C), 26.18 (2C), 29.28 (3C), 29.44, 31.37, 31.96, 32.82, 68.22, 114.77, 119.52, 128.02, 132.00, 135.81, 136.73, 149.73, 154.90, 159.92.

2.2.7. 2-(4-Octyloxyphenyl)-5-heptylpyridine (2d). The same procedure as for **2a** was used to synthesize **2d** using 2-(4-octyloxyphenyl)-5-bromopyridine **1c** (1.1 mmol, 0.4 g) and *n*-heptylmagnesium bromide (1.21 mmol in 5 ml of Et_2O). The product was isolated as a white solid (0.4 g, 95% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–1.00 (m, 6H, $2CH_3$), 1.20–1.34 (m, 18H), 1.34–1.51 (m, 2H), 1.52–1.74 (m, 2H), 1.75–1.85 (m, 2H), 2.52–2.65 (t, J=7.65 Hz, 2H), 3.95–4.10 (t, J=6.59 Hz, 2H), 6.85–7.02 (d, J=8.82 Hz, 2H), 7.40–7.54 (dd, J=8.16 Hz, 2.22 Hz, 1H), 7.55–7.61 (d, J=8.06 Hz, 1H), 7.87–7.94 (d, J=8.82 Hz, 2H), 8.45–8.47 (d, J=1.94 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.27 (2C), 22.82 (2C), 26.22 (2C), 29.28 (2C), 29.44, 29.55, 31.37, 31.95, 31.99, 32.82, 68.22, 114.77, 119.47, 128.00, 132.02, 135.79, 136.69, 149.75, 154.90, 159.91.

2.3. *Synthesis of 2-(4-alkoxyphen-1-yl)-5-(5-alkylpyridin-2-yl-)pyridines 3a–f [schemes 2, 3]*

2.3.1. 2-[4-(Tetrahydropyran-2-yloxy)phen-1-yl]-5-(5-bromopyrid-2-yl)pyridine (3a). Compound **1b** (10.5 mmol, 3.51 g) was placed in a flask and freshly distilled THF (20 ml) was added under a nitrogen atmosphere. The reaction mixture was cooled in a CO_2/acetone bath and *n*-BuLi (2.5M in hexanes, 4.4 ml) was added dropwise. After addition of a few drops of *n*-BuLi the reaction mixture became purple; after stirring, the colour disappeared, but addition of the next portion of *n*-BuLi resulted in change of colour again. After 30 min of stirring a solution of $ZnCl_2$ (12 mmol, 1.64 g) in 15 ml of freshly distilled THF (nitrogen atmosphere)

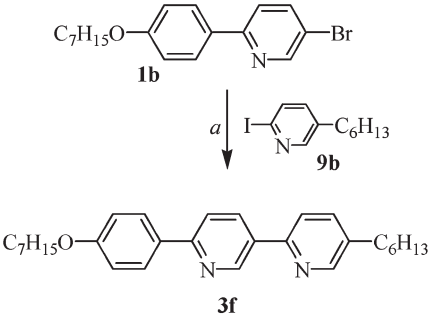


R^1=C_6H_{13}, C_7H_{15}, C_8H_{15}

Reagents: *a*) *i*) *n*-BuLi, THF, -78 ºC; *ii*) $ZnCl_2$, THF, -78 ºC→rt; *iii*) 2,5-dibromopyridine, $Pd(PPh_3)_4$ (1 mol%), THF, rt; *b*) *i*) $C_7H_{15}MgBr$, $NiCl_2$ (dppe) (5 mol%), Et_2O, reflux; *ii*) HCl (3 drops), EtOH, heating; *c*) R^1Br, K_2CO_3, acetone, reflux.

Scheme 2. Synthesis of 2-(4-alkyloxyphen-1-yl)-5-(5-alkylpyridin-2-yl)pyridines **3c**–**f** from versatile intermediate **3a** constructed by selective Negishi coupling of 2,5-dibromopyridine with arylzinc chloride derived from **1b**.

was added, and the red reaction mixture was stirred for 30 min. The reaction mixture was warmed to room temperature and stirred for 1 h. 2,5-Dibromopyridine (10 mmol) and a catalytic amount of $Pd(PPh_3)_4$ (1 mol %, 0.1 mmol, 0.12 g) were then added and the reaction mixture stirred for several hours. After completion of the reaction the mixture was poured into water, filtered and extracted with Et_2O (3 × 15 ml). The organic solution was dried with brine and then with $MgSO_4$. After evaporation of the solvent the crude product was chromatographed (silica gel, CH_2Cl_2) and the pure product was isolated as a white solid (2.8 g, 68% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.55–1.80 (m, 3H), 1.85–1.95 (m, 2H), 1.98–2.10 (m, 1H), 3.58–3.70 (m, 1H), 3.95–4.05 (m, 1H), 5.45–5.60 (t, J=3.01 Hz, 1H), 7.12–7.20 (d, J=8.80 Hz, 2H),



Reagents: *a*) *i*) *n*-BuLi, THF, -78 ºC; *ii*) $ZnCl_2$, THF, -78 ºC→rt; *iii*) 2-iodo-5-hexylpyridine (**9b**), $Pd(PPh_3)_4$ (1 mol%), THF, rt.

Scheme 3. Alternative approach to mesogens of type **3**: synthesis of 2-(4-heptyloxyphen-1-yl)-5-(5-hexylpyridin-2-yl)pyridine (**3f**).

7.62–7.70 (d, J=8.48 Hz, 1H), 7.75–7.82 (d, J=8.38 Hz, 1H), 7.87–7.93 (dd, J=8.46 Hz, 2.37 Hz, 1H), 7.98–8.05 (d, J=8.78 Hz, 2H), 8.30–8.37 (dd, J=8.37, 2.35 Hz, 1H), 8.73–8.80 (d, J=2.29 Hz, 1H), 9.18–9.22 (d, J=2.19 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.83, 25.34, 30.43, 62.18, 96.34, 116.80, 119.83, 119.98, 121.46, 128.39, 131.55, 132.24, 135.01, 139.64, 147.92, 151.26, 153.44, 157.72, 158.41.

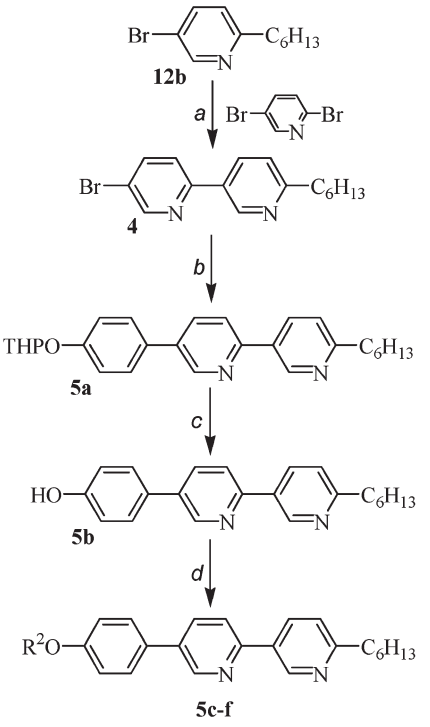
2.3.2. 2-(4-Hydroxyphen-1-yl)-5-(5-heptylpyridin-2-yl) pyridine (3b). The $NiCl_2$(ddpe)-catalysed alkylation of **3a** (2 mmol, 0.82 g) with freshly prepared *n*-heptylmagnesium bromide was performed in the same manner as for **2a**. The crude alkylated product was heated under reflux in EtOH with 3 drops of HCl until all starting material disappeared (monitored by TLC). The product **3b** was isolated in 80% yield in two steps. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–0.95 (t, J=6.73 Hz, 3H, CH_3), 1.24–1.45 (m, 8H), 1.51–1.75 (m, 2H), 2.60–2.72 (t, J=7.64 Hz, 2H), 6.85–6.91 (d, J=8.60 Hz, 2H), 7.58–7.65 (dd, J=8.17 Hz, 2.06 Hz, 1H), 7.65–7.77 (m, 2H), 7.85–7.92 (d, J=8.58 Hz, 2H), 8.32–8.40 (dd, J=8.34 Hz, 2.22 Hz, 1H), 8.52–8.57 (d, J=1.95 Hz, 1H), 9.13–9.20 (d, J=2.17 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.26, 22.81, 29.26 (2C), 31.30, 31.93, 32.91, 116.05, 120.20, 120.29, 128.73, 131.04, 132.73, 135.37, 137.15, 137.51, 147.63, 150.23, 152.30, 157.25, 157.74.

2.3.3. 2-(4-Heptoxyphen-1-yl)-5-(5-heptylpyridin-2-yl) pyridine (3c). Compound **3b** (0.5 mmol, 0.17 g) was heated at reflux in acetone with 1-bromoheptane (0.55 mmol, 0.1 g) and K_2CO_3 (1 mmol, 0.138 g) for several hours (monitored by TLC). After completion of the reaction the solvent was evaporated and the product extracted with Et_2O. After evaporation of the solvent the product was recrystallized from EtOH (0.061 g, 27% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.80–1.00 (m, 6H, $2CH_3$), 1.20–1.40 (m, 14H), 1.40–1.55 (m, 2H), 1.60–1.73 (m, 2H), 1.75–1.84 (m, 2H), 2.60–2.71 (t, J=7.65 Hz, 2H), 3.95–4.10 (t, J=6.59 Hz, 2H), 6.95–7.05 (d, J=8.84 Hz, 2H), 7.55–7.65 (dd, J=8.12 Hz, 2.20 Hz, 1H), 7.67–7.73 (d, J=8.00 Hz, 1H), 7.74–7.80 (d, J=8.32 Hz, 1H), 7.96–8.03 (d, J=8.84 Hz, 2H), 8.33–8.39 (dd, J=8.35 Hz, 2.33 Hz, 1H), 8.50–8.57 (d, J=1.70 Hz, 1H), 9.17–9.23 (d, J=1.64 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.26 (2C), 22.78 (2C), 26.17 (2C), 29.26 (3C), 29.43, 31.31, 31.95, 32.92, 68.27, 114.87, 119.67, 120.02, 128.36, 131.52, 132.65, 134.94, 136.92, 137.26, 147.89, 150.35, 152.50, 157.09, 160.37.

2.3.4. 2-(4-Octyloxyphen-1-yl)-5-(5-heptylpyridin-2-yl) pyridine (3d). The preparation of **3d** was performed in the same manner as **3c** but using 1-bromooctane as the alkylating agent. The product was isolated as a white solid after recrystallization from EtOH (0.028 g, 13% yield; some additional product could be isolated from the mother liquor). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–1.00 (m, 6H, $2CH_3$), 1.20–1.40 (m, 16H), 1.40–1.53 (m, 2H), 1.60–1.71 (m, 2H), 1.75–1.85 (m, 2H), 2.60–2.76 (t, J=7.63 Hz, 2H), 3.90–4.05 (t, J=6.58 Hz, 2H), 6.97–7.04 (d, J=8.88 Hz, 2H), 7.56–7.62 (dd, J=8.11 Hz, 2.24 Hz, 1H), 7.67–7.74 (d, J=8.08 Hz, 1H), 7.74–7.81 (dd, J=8.43 Hz, 0.72 Hz, 1H), 7.97–8.08 (d, J=8.93 Hz, 2H), 8.32–8.40 (dd, J=8.35 Hz, 2.33 Hz, 1H), 8.53–8.57 (d, J=1.66 Hz, 1H), 9.18–9.21 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.27 (2C), 26.21 (2C), 29.28 (2C), 29.42 (3C), 29.54, 31.31, 31.93, 31.99, 32.92, 68.28, 114.88, 119.67, 120.02, 128.36, 131.53, 132.65, 134.95, 136.92, 137.26, 147.90, 150.35, 152.50, 157.09, 160.37.

2.3.5. 2-(4-Hexyloxyphen-1-yl)-5-(5-heptylpyridin-2-yl) pyridine (3e). The preparation of **3e** was performed in the same manner as **3c** using 1-bromohexane as the alkylating agent. The product was isolated as a white solid after recrystallization from EtOH (0.047 g, 21.4% yield an additional amount of the product could be isolated from the mother liquor). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–1.00 (m, 6H, $2CH_3$), 1.20–1.40 (m, 12H), 1.40–1.52 (m, 2H), 1.53–1.75 (m, 2H), 1.75–1.83 (m, 2H), 2.56–2.70 (t, J=7.61 Hz, 2H), 3.90–4.05 (t, J=6.56 Hz, 2H), 6.95–7.05 (d, J=8.74 Hz, 2H), 7.57–7.61 (dd, J=8.04 Hz, 1.75 Hz, 1H), 7.67–7.74 (d, J=8.02 Hz, 1H), 7.75–7.81 (d, J=8.32 Hz, 1H), 7.95–8.06 (d, J=8.72 Hz, 2H), 8.31–8.38 (dd, J=8.36 Hz, 2.16 Hz, 1H), 8.50–8.62 (s, 1H), 9.17–9.23 (d, J=1.36 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.22, 14.26, 22.78, 22.81, 25.89, 29.28 (2C), 29.39, 31.32, 31.77, 31.94, 32.92, 68.27, 114.86, 119.67, 120.02, 128.35, 131.52, 132.64, 134.94, 136.92, 137.26, 147.89, 150.34, 152.49, 157.08, 160.36.

2.3.6. 2-(4-Heptyloxyphen-1-yl)-5-(5-hexylpyridin-2-yl) pyridine (3f). Compound **1a** (1.2 mmol, 0.42 g) was placed in an oven-dried flask equipped with magnetic stirbar (nitrogen atmosphere). Freshly distilled THF (10 ml) was added and the reaction mixture cooled in a CO_2/acetone bath. *n*-BuLi (2.5M in hexanes, 0.53 ml) was added dropwise and the reaction mixture stirred for 30 min. Zinc chloride (1.32 mmol, 0.18 g) in 10 ml of freshly distilled THF was added to the reaction mixture. After stirring for 30 min, the CO_2/acetone bath was removed and the reaction mixture allowed to warm to room temperature. 2-Iodo-5-hexylpyridine **9b** (1 mmol, 0.29 g) and $Pd(PPh_3)_4$ (1 mol%, 12 mg) were added to



R^2=C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}

Reagents: *a*) *i*) *n*-BuLi, THF, -78 °C; *ii*) $ZnCl_2$, THF, -78 °C→rt; *iii*) 2,5-dibromopyridine, $Pd(PPh_3)_4$ (1 mol%), THF, rt; *b*) *i*) *n*-BuLi, THF, -78 °C; *ii*) $ZnCl_2$, THF, -78 °C→rt; *iii*) 4-(tetrhydropyran-2-yloxy)-1-iodobenzene (**14**), $Pd(PPh_3)_4$ (1 mol%), THF, rt; *c*) HCl (3 drops), EtOH, heating; *d*) R^2Br, K_2CO_3, acetone, reflux.

Scheme 4. Synthesis of 2-(2-alkylpyridin-5-yl)-5-(4-alkyloxyphen-1-yl)pyridines **5c**–**f** utilizing Negishi coupling as key steps for the construction of the aromatic core.

the reaction mixture and it was left overnight. It was then poured into 20 ml of water and vacuum filtered. The organic layer was separated and the water layer extracted twice with Et_2O. The combined organic phases were dried with brine and then over $MgSO_4$. The product was recrystallized twice from EtOH (0.18 g, 40% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–1.00 (m, 6H, $2CH_3$), 1.20–1.40 (m, 12H), 1.40–1.50 (m, 2H), 1.51–1.63 (m, 2H), 1.64–1.89 (m, 2H), 2.60–2.69 (t, J=7.63 Hz, 2H), 3.95–4.06 (t, J=6.55 Hz, 2H), 6.95–7.05 (d, J=8.80 Hz, 2H), 7.57–7.61 (dd, J=8.04 Hz, 2.03 Hz, 1H), 7.67–7.80 (d, J=8.08 Hz, 1H), 7.75–7.81 (d, J=8.28 Hz, 1H), 7.95–8.06 (d, J=8.82 Hz, 2H), 8.31–8.38 (dd, J=8.36 Hz, 2.28 Hz, 1H), 8.50–8.62 (d, J=1.58 Hz, 1H), 9.17–9.23 (d, J=1.92 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.27 (2C), 22.76, 22.79, 26.18, 29.00, 29.26, 29.43, 31.28, 31.80, 31.96, 32.92, 68.26, 114.86, 119.66, 120.02, 128.35, 131.51, 132.64, 134.94, 136.91, 137.25, 147.90, 150.34, 152.49, 157.07, 160.36.

2.4. *Synthesis of 2-(2-hexylpyridin-5-yl)-5-(4-(alkoxyphen-1-yl)pyridines 5c–f [scheme 4]*

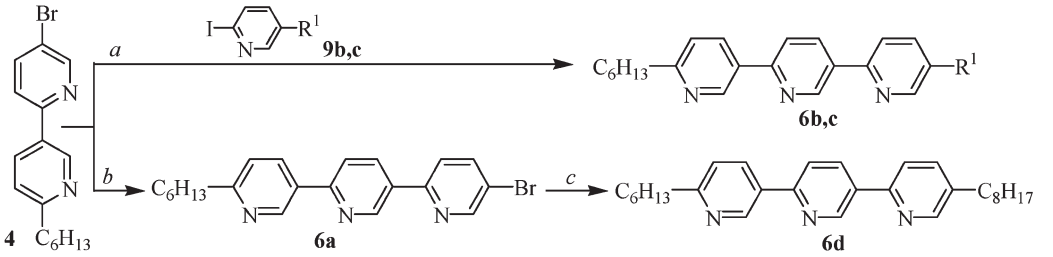
2.4.1. 2-(2-Hexylpyridin-5-yl)-5-bromopyridine (4). 2-Hexyl-5-bromopyridine **12a** (11.56 mmol, 2.80 g) was placed in an oven-dried flask equipped with magnetic stirbar (nitrogen atmosphere). Freshly distilled THF (15 ml) was added and the reaction mixture cooled in a CO_2/acetone bath. *n*-BuLi (2.5M in hexanes, 4.62 ml) was added dropwise, keeping the temperature below −70°C, and the deep red reaction mixture was stirred for 10 min. Zinc chloride (13.9 mmol, 1.89 g) in 10 ml of freshly distilled THF was added to the reaction mixture, keeping the temperature below −60°C. After 15 min of stirring the CO_2/acetone bath was removed and the orange–red reaction mixture allowed to warm to room temperature. This freshly prepared arylzinc chloride solution was added dropwise via syringe to the a THF solution (10 ml) of 2,5-dibromopyridine (9.5 mmol, 2.25 g) and $Pd(PPh_3)_4$ (1 mol %, 0.11 g), and the

reaction mixture was stirred overnight at room temperature (nitrogen atmosphere). The reaction mixture was poured into 20 ml of water, and vacuum filtered. The organic layer was separated, and the water layer was extracted with Et_2O (2 × 15 ml). The combined organic phases were dried with brine and then over $MgSO_4$. After evaporation of the solvent the residue was dissolved in a mixture of 75 ml of hexanes and 5 ml of EtOAc, and then heated under reflux with several grams of clay (Montmorillonite KSF). After vacuum filtration and solvent evaporation the residue was Kugelrohr distilled (120°C, 0.06 mm Hg) to give a white solid (2.25 g, 64%). DSC analysis: m.p. 38.1°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.83–0.91 (t, J=6.99 Hz, 3H), 1.21–1.37 (m, 6H), 1.70–1.76 (m, 2H), 2.81–2.87 (t, J=7.77 Hz, 2H), 7.22–7.30 (d, J=8.36 Hz, 1H), 7.59–7.64 (dd, J=8.44 Hz, 0.65 Hz, 1H), 7.84–7.91 (dd, J=8.46 Hz, 2.39 Hz, 1H), 8.20–8.28 (dd, J=8.14 Hz, 2.36 Hz, 1H), 8.73–8.77 (dd, J=2.36 Hz, 0.60 Hz, 1H), 9.05–9.10 (dd, J=2.29 Hz, 0.55 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.24, 22.72, 29.19, 29.96, 31.83, 38.11, 120.06, 121.50, 123.12, 131.54, 135.13, 139.68, 147.03, 151.25, 153.38, 163.38.

2.4.2. 2-(2-Hexylpyridin-5-yl)-5-[4-(tetrahydropyran-2-yloxy)-phen-1-yl]pyridine (5a). Compound **4** (4 mmol, 1.28 g) was placed in an oven-dried flask equipped with magnetic a stirbar (nitrogen atmosphere). Freshly distilled THF (15 ml) was added and the reaction mixture cooled in a CO_2/acetone bath. *n*-BuLi (2.5M in hexanes, 1.6 ml) was added dropwise and the reaction mixture (the colour of carrot juice) was stirred for 10–15 min. A solution of zinc chloride (4.8 mmol, 0.66 g) in 10 ml of freshly distilled THF was added to the reaction mixture. After 15 min of stirring the CO_2/acetone bath was removed and the red reaction mixture allowed to warm to room temperature. This freshly prepared arylzinc chloride solution was added dropwise to a THF solution (10 ml) of 4-(tetrahydropyran-2-yloxy)-1-iodobenzene **14** (4 mmol, 1.21 g) and $Pd(PPh_3)_4$ (1 mol%), and the mixture was stirred overnight at room temperature (nitrogen atmosphere). The reaction mixture was poured into 20 ml of water and vacuum filtered. The organic layer was separated, dried with brine, then over $MgSO_4$. After vacuum filtration and solvent evaporation the mixture was chromatographed to give 0.61 g (37% yield) of the pure product. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85–0.89 (t, J=6.95 Hz, 3H, CH_3), 1.25–1.45 (m, 6H), 1.55–1.82 (m, 6H), 1.83–1.95 (m, 2H), 2.80–2.92 (t, J=7.76 Hz, 2H), 3.55–3.70 (m, 1H), 3.80–4.00 (dt, J=10.36 Hz, 3.01 Hz, 1H), 5.45–5.52 (t, J=3.08 Hz, 1H), 7.15–7.22 (d, J=8.72 Hz, 2H), 7.24–7.30 (d, J=8.14 Hz, 1H), 7.53–7.60 (d, J=8.76 Hz, 2H), 7.74–7.81 (dd, J=8.26 Hz, 0.74 Hz,, 1H), 7.90–7.96 (dd, J=8.25 Hz, 2.39 Hz, 1H), 8.22–8.30 (dd, J=8.11 Hz, 3.4 Hz, 1H), 8.88–8.93 (d, J=2.34 Hz, 1H), 9.11–9.15 (d, J=2.15 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.26, 18.85, 22.75, 25.33, 29.24, 30.05, 30.44, 31.88, 38.43, 62.23, 96.46, 117.25, 120.25, 122.84, 128.18, 130.79, 132.12, 134.64, 134.88, 135.17, 147.65, 148.22, 153.34, 157.47, 163.14.

2.4.3. 2-(2-Hexylpyridin-5-yl)-5-(4-hydroxyphen-1-yl) pyridine (5b). The protected phenol **5a** (0.61 g, 1.46 mmol) isolated from the coupling reaction was placed in 25 ml Erlenmeyer flask. Ethanol (10 ml) and three drops of HCl (conc.) were added and the reaction mixture heated under reflux for one hour. After cooling, K_2CO_3 (0.5 g) was added and the solvent was evaporated under vacuum. The product was washed with water and vacuum filtered to give 0.49 g of the crude material. A white solid was isolated after recrystallization from EtOH (0.39 g, 80% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.83–0.90 (t, J=7.01 Hz, 3H), 1.23–1.37 (m, 6H), 1.73–1.79 (m, 2H), 2.86–2.92 (t, J=7.75 Hz, 2H), 6.98–7.03 (d, J=8.63 Hz, 2H), 7.28–7.33 (d, J=8.02 Hz, 1H), 7.47–7.53 (d, J=8.65 Hz, 2H), 7.66–7.74 (broad s, OH), 7.74–7.80 (dd, J=8.28 Hz, 0.65 Hz, 1H), 7.90–7.98 (dd, J=8.25 Hz, 2.40 Hz, 1H), 8.28–8.32 (dd, J=8.13 Hz, 2.33 Hz, 1H), 8.88–8.91 (dd, J=2.28 Hz, 0.68 Hz, 1H), 9.10–1.15 (d, J=1.82 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.23, 18.55, 22.72, 29.17, 30.11, 31.80, 37.93, 116.61, 120.56, 123.33, 128.40, 128.69, 132.53, 134.94, 135.32, 135.77, 147.01, 147.95, 152.55, 157.91, 162.86.

2.4.4. 2-(2-Hexylpyridin-5-yl)-5-(4-pentyloxyphen-1-yl) pyridine (5c). Phenol **5b** (0.31 mmol, 0.104 g) was heated under reflux in 7 ml of acetone with 1-bromopentane (0.34 mmol, 0.05 g) and K_2CO_3 (0.62 mmol, 0.07 g) for several hours until all the starting phenol was consumed (monitored by TLC). After completion of reaction the acetone was evaporated and the organic product extracted with Et_2O. After evaporation of the solvent the product was recrystallized from EtOH to give a white solid (0.04 g, 33% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.88–0.98 (m, 6H, $2CH_3$), 1.33–1.50 (m, 10H), 1.72–1.86 (m, 4H), 2.83–2.89 (t, J=7.66 Hz, 2H), 3.99–4.05 (t, J=6.53 Hz, 2H), 6.98–7.05 (d, J=8.59 Hz, 2H), 7.20–7.29 (d, J=5.93 Hz, *the signal overlaps with the $CHCl_3$ signal*, 1H), 7.50–7.61 (d, J=8.60 Hz, 2H), 7.73–7.79 (d, J=8.24 Hz, 1H), 7.90–7.98 (dd, J=8.12 Hz, 2.23–2.27 Hz, 1H), 8.23–8.29 (dd, J=8.12 Hz, 2.19 Hz, 1H), 8.80–8.90 (d, J=1.92 Hz, 1H), 9.11–9.14 (d, J=1.86 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.20, 14.25, 22.63, 22.75, 28.36, 29.10,



R^1=C_6H_{13}, C_7H_{15}

Reagents: *a*) *i*) *n*-BuLi, THF, -78 ºC; *ii*) $ZnCl_2$, THF, -78 ºC→rt; *iii*) 2-iodo-5-alkylpyridine (**9b** or **9c**), $Pd(PPh_3)_4$ (1 mol%), THF, rt; *b*) *i*) *n*-BuLi, THF, -78 ºC; *ii*) $ZnCl_2$, THF, -78 ºC→rt; *iii*) 2,5-dibromopyridine, $Pd(PPh_3)$ (1 mol%), THF, rt; *c*) $C_8H_{17}MgBr$, $NiCl_2$(dppe) (5 mol%), Et_2O, reflux.

Scheme 5. Two different approaches to tripyridine liquid crystals: synthesis of 2-(2-alkylpyridin-5-yl)-5-(5-alkylpyridin-2-yl)pyridines **6b**–**d**.

29.24, 30.06, 31.88, 38.43, 68.31, 115.33, 120.26, 122.84, 128.20, 129.71, 132.13, 134.63, 134.78, 135.20, 147.64, 148.14, 153.22, 159.60, 163.13.

2.4.5. 2-(2-Hexylpyridin-5-yl)-5-(4-hexyloxyphen-1-yl) pyridine (5d). The liquid crystal **5d** was prepared in the same manner as **5c** (0.03 g, 23% yield) except that 1-bromohexane was used as alkylating agent. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.82–0.95 (m, 6H, $2CH_3$), 1.22–1.40 (m, 10H), 1.40–1.51 (m, 2H), 1.70–1.82 (m, 4H), 2.80–2.90 (t, J=7.62 Hz, 2H), 3.98–4.05 (t, J=6.56 Hz, 2H), 6.99–7.06 (d, J=8.77 Hz, 2H), 7.24–7.29 (d, J=7.85 Hz, 1H, *the signal overlaps with a $CHCl_3$ signal*), 7.53–7.59 (d, J=8.75 Hz, 2H), 7.74–7.80 (d, J=8.29 Hz, 1H), 7.88–7.95 (dd, J=8.25 Hz, 2.40 Hz, 1H), 8.23–8.30 (dd, J=8.10 Hz, 2.35 Hz, 1H), 8.88–8.92 (dd, J=2.33 Hz, 0.66 Hz, 1H), 9.10–9.14 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.22, 14.26, 22.77 (2C), 25.89, 29.24, 29.37, 30.07, 31.75, 31.89, 38.43, 68.32, 115.33, 120.28, 122.86, 128.21, 129.70, 132.14, 134.65, 134.80, 135.21, 147.63, 148.15, 153.21, 159.60, 163.12.

2.4.6. 2-(2-Hexylpyridin-5-yl)-5-(4-heptyloxyphen-1-yl) pyridine (5e). The liquid crystal **5e** was prepared in the same manner as **5c** (0.046 g, 35% yield) except that 1-bromoheptane was used as alkylating agent. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.86–0.95 (m, 6H, 2 CH_3), 1.20–1.50 (m, 14H), 1.70–1.90 (m, 4H), 2.75–2.95 (t, J=7.76 Hz, 2H), 3.95–4.05 (t, J=6.54 Hz, 2H), 7.00–7.05 (d, J=8.62 Hz, 2H), 7.24–7.30 (d, J=8.06 Hz, 1H, *overlaps with $CHCl_3$ signal*), 7.51–7.59 (d, J=8.61 Hz, 2H), 7.75–7.80 (d, J=8.27 Hz, 1H), 7.88–7.96 (dd, J=8.24 Hz, 2.41 Hz, 1H), 8.23–8.30 (dd, J=8.13 Hz, 2.32 Hz, 1H), 8.88–8.93 (d, J=2.34 Hz, 1H), 9.11–9.14 (d, J=2.24 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.27 (2C), 22.76, 22.78, 26.17, 29.24 (2C), 29.41, 30.07, 31.89, 31.95, 38.43, 68.33, 115.33, 120.27, 122.85, 128.21, 129.70, 132.13, 134.64, 134.79, 135.21, 147.64, 148.15, 153.22, 159.60, 163.13.

2.4.7. 2-(2-Hexylpyridin-5-yl)-5-(4-octyloxyphen-1-yl) pyridine (5f). The liquid crystal **5f** was prepared in the same manner as **5c** using phenol **5b** (0.5 mmol, 0.17 g), K_2CO_3 (1 mmol, 0.136 g), and 1-bromooctane (0.6 mmol, 0.11g). A white solid was obtained after recrystallization of the crude material from EtOH (0.09 g, 41% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–0.96 (m, 6H, $2CH_3$), 1.20–1.40 (m, 14H), 1.40–1.51 (m, 2H), 1.70–1.85 (m, 4H), 2.82–2.89 (t, J=7.77 Hz, 2H), 3.95–4.05 (t, J=6.57 Hz, 2H), 7.00–7.05 (d, J=8.75 Hz, 2H), 7.24–7.30 (d, J=8.00 Hz, 1H, *overlaps with $CHCl_3$ signal*), 7.53–7.59 (d, J=8.74 Hz, 2H), 7.75–7.81 (dd, J=8.25 Hz, 0.63 Hz, 1H), 7.88–7.91 (dd, J=8.25 Hz, 2.40 Hz, 1H), 8.23–8.30 (dd, J=8.12 Hz, 2.36 Hz, 1H), 8.87–8.92 (dd, J=2.31 Hz, 0.61 Hz, 1H), 9.11–9.14 (d, J=2.13 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.27 (2C), 22.76, 22.83, 26.21, 29.24, 29.41 (2C), 29.53, 30.07, 31.89, 31.98, 38.43, 68.33, 115.33, 120.28, 122.86, 128.21, 129.70, 132.14, 134.65, 134.80, 135.21, 147.64, 148.15, 153.22, 159.60, 163.13.

2.5. *Synthesis of 2-(2-Alkylpyridin-5-yl)-5-(5-alkyl–pyridin-2-yl)-pyridines 6b-d [scheme 5]*

2.5.1. 2-(2-Hexylpyridin-5-yl)-5-(5-bromopyridin-2-yl) pyridine (6a). Compound **4** (3.07 mmol, 0.98 g) was placed in an oven-dried flask equipped with magnetic stirbar (nitrogen atmosphere). Freshly distilled THF (15 ml) was added and the reaction mixture cooled in a CO_2/acetone bath. *n*-BuLi (2.5M in hexanes, 1.23 ml) was added dropwise and the orange–red reaction mixture was stirred for 10 min. $ZnCl_2$ (3.7 mmol, 0.5 g)

in 5 ml of freshly distilled THF was added to the reaction mixture. After 15 min of stirring (reaction temperature −70–72°C) the CO_2/acetone bath was removed and the red reaction mixture allowed to warm to room temperature. This freshly prepared arylzinc chloride solution was added dropwise via syringe to a THF solution (10 ml) of 2,5-dibromopyridine (3.07 mmol, 0.727 g) and $Pd(PPh_3)_4$ (1.7 mol%, 60 mg). The reaction mixture was stirred overnight at room temperature (nitrogen atmosphere) and then poured into 20 ml of water and vacuum filtered. The organic layer was separated, dried with brine and then over $MgSO_4$. The product was chromatographed (silica gel, CH_2Cl_2/acetone=14/1. The product was recrystallized from EtOH to give 0.17 g, (14% yield) of shining white flakes, m.p. 84°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.86–1.00 (t, J=6.87 Hz, 3H), 1.25–1.45 (m, 6H), 1.74–1.85 (m, 2H), 2.83–2.90 (t, J=7.76 Hz, 2H), 7.26–7.30 (d, J=8.22 Hz, 1H), 7.68–7.72 (d, J=8.44 Hz, 1H), 7.83–7.86 (d, J=8.33 Hz, 1H), 7.91–7.98 (ddd, J=8.47 Hz, 2.39 Hz, 1.13 Hz, 1H), 8.27–8.33 (dd, J=8.13 Hz, 2.28 Hz, 1H), 8.37–8.43 (ddd, J=8.31 Hz, 2.36 Hz, 1.07 Hz, 1H), 8.78–8.81 (m, 1H), 9.14–9.20 (d, J=2.14 Hz, 1H), 9.23–9.28 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.25, 22.75, 29.23, 30.03, 31.87, 38.45, 120.29, 120.33, 121.58, 122.90, 131.79, 132.62, 134.87, 135.23, 139.73, 147.85, 148.30, 151.48, 153.05, 155.65, 163.66.

2.5.2. 2-(2-Hexylpyridin-5-yl)-5-(5-hexylpyridin-2-yl) pyridine (6b). Compound **4** (7.0 mmol, 2.23 g) was placed in an oven-dried flask equipped with a magnetic stirbar (nitrogen atmosphere). Freshly distilled THF (60 ml) was added, and the reaction mixture cooled in a CO_2/acetone bath. *n*-BuLi (2.5M in hexanes, 2.8 ml) was added dropwise over 15 min (the reaction temperature was kept below −70°C during this addition); the reaction mixture was stirred for 30 min. A solution of $ZnCl_2$ (8.4 mmol, 1.15 g) in 10 ml of freshly distilled THF was added to the reaction mixture, and it turned brown–yellow. After 40 min of stirring the CO_2/acetone bath was removed and the yellow reaction mixture (with brown precipitate) was allowed to warm to room temperature. During the warming process the brown precipitate dissolved and the reaction mixture became orange–yellow. After an hour of stirring 2-iodo-5-hexylpyridine **9b** (7.0 mmol, 2.02 g) in 2 ml of hexanes and $Pd(PPh_3)_4$ (1 mol%, 0.08 g) were added, and the reaction mixture stirred overnight at room temperature (nitrogen atmosphere). Solvents were evaporated from the resulting yellow solution under reduced pressure. Water (20 ml) was added, and the products extracted with CH_2Cl_2 (3 × 30 ml). The organic phases were combined, dried with brine and then over $MgSO_4$, and the solvents evaporated under reduced pressure. The crude product mixture was dissolved in 10 ml of CH_2Cl_2 and chromatographed (silica gel, hexanes/Et_2O=2/3 as eluant). The fractions containing pure material were combined, the solvents were evaporated under reduced pressure, and the product was recrystallized from 150 ml of hexanes to give 0.85 g of shining white crystals (30.2% yield). The fractions containing slightly contaminated product were also combined, the solvents evaporated, and an additional quantity of product was obtained after recrystallization from hexanes (0.3 g, 40.9% total yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–0.94 (m, 6H, $2CH_3$), 1.20–1.44 (m, 12H), 1.63–1.74 (m, 2H), 1.74–1.79 (m, 2H), 2.64–2.70 (t, J=7.66 Hz, 2H), 2.83–2.88 (t, J=7.76 Hz, 2H), 7.23–7.30 (d, J=8.08 Hz, 1H), 7.55–7.64 (dd, J=8.08 Hz, 2.21 Hz, 1H), 7.68–7.74 (d, J=8.06 Hz, 1H), 7.78–7.85 (dd, J=8.31 Hz, 1.03 Hz, 1H), 8.26–8.33 (dd, J=8.11 Hz, 2.34 Hz, 1H), 8.38–8.43 (dd, J=8.30 Hz, 2.34 Hz, 1H), 8.52–8.56 (d, J=1.96 Hz, 1H), 9.15–9.17 (d, J=2.28 Hz, 1H), 9.24–9.27 (d, J=2.29 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.24 (2C), 22.74 (2C), 28.99, 29.23, 30.05, 31.25, 31.78, 31.88, 32.92, 38.44, 120.17, 120.24, 122.83, 132.02, 133.79, 134.81, 135.13, 136.97, 137.61, 147.82, 148.32, 150.44, 152.08, 154.95, 163.38.

2.5.3. 2-(2-Hexylpyridin-5-yl)-5-(5-heptylpyridin-2-yl) pyridine (6c). Compound **6c** was prepared in the same manner as **6b** using 2-(2-hexylpyridin-5-yl)-5-bromopyridine **4** (2.5 mmol, 0.8 g) and 2-iodo-5-heptylpyridine **9c** (0.76 g, 2.5 mmol,) as starting materials. The product was recrystallized from MeOH (white solid, 0.22 g, 21.4% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.86–0.91 (t, J=6.84 Hz, $2CH_3$), 1.20–1.48 (14H, m), 1.60–1.70 (m, 2H), 1.70–1.90 (m, 2H), 2.64–2.70 (t, J=7.66 Hz, 2H), 2.83–2.89 (t, J=7.76 Hz, 2H), 7.25–7.30 (d, J=8.38 Hz, 1H), 7.59–7.64 (dd, J=18.08 Hz, 12.23 Hz, 1H), 7.68–7.74 (d, J=8.06 Hz, 1H), 7.81–7.86 (d, J=1H), 8.27–8.33 (dd, J=8.10 Hz, 2.34 Hz, 1H), 8.38–8.44 (dd, J=8.31 Hz, 2.33 Hz, 1H), 8.54–8.58 (d, J=1.92 Hz, 1H), 9.14–9.17 (d, J=2.15 Hz, 1H), 9.25–9.28 (d, J=2.08 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.26 (2C), 22.76, 22.81, 29.27 (3C), 30.07, 31.31, 31.89, 31.93, 32.93, 38.46, 120.20, 120.28, 122.86, 132.04, 133.81, 134.84, 135.16, 137.00, 137.64, 147.83, 148.33, 150.46, 152.10, 154.97, 163.40.

2.5.4. 2-(2-Hexylpyridin-5-yl)-5-(5-octylpyridin-2-yl) pyridine (6d). Compound **6d** was prepared by the standard alkylation of 2-aryl-5-bromopyridine **6a** (0.3 mmol, 0.12 g) with *n*-octylmagnesium bromide in the presence of $NiCl_2$(dppe) (for the procedure see the

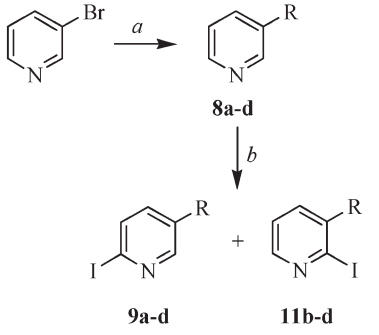
synthesis of **2a**). The product was purified by column chromatography and recrystallized from EtOH (0.077 g, 60% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.84–0.94 (t, J=6.40 Hz, 6H, $2CH_3$), 1.24–1.44 (m, 16H), 1.62–1.71 (m, 2H), 1.71–1.83 (m, 2H), 2.63–2.71 (t, J=7.65 Hz, 2H), 2.82–2.90 (t, J=7.75 Hz, 2H), 7.26–7.30 (d, 1H, *the signal overlaps with $CHCl_3$ signal*), 7.60–7.66 (dd, J=8.15 Hz, 2.06 Hz, 1H), 7.70–7.76 (d, J=8.06 Hz, 1H), 7.81–7.87 (d, J=8.36 Hz, 1H), 8.28–8.34 (dd, J=8.11 Hz, 2.30 Hz, 1H), 8.38–8.45 (dd, J=8.30 Hz, 2.28 Hz, 1H), 8.54–8.59 (d, J=1.69 Hz, 1H), 9.14–9.17 (d, J=2.17 Hz, 1H), 9.24–9.28 (d, J=2.12 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.27 (2C), 22.76, 22.82, 29.23, 29.33, 29.39, 29.55, 30.07, 31.31, 31.88, 32.01, 32.93, 38.43, 120.22, 120.30, 122.88, 132.06, 133.83, 134.88, 135.17, 137.01, 137.65, 147.79, 148.33, 150.46, 151.47, 154.95, 163.38.

2.6. *Synthesis of 2-iodo-5-alkylpyridines 9a–d [scheme 6]*

2.6.1. 2-Iodo-5-hexylpyridine (9b). *N*,*N*-Dimethylaminoethanol (0.03 mol, 2.67 g) and 10 ml of hexanes were placed in an oven-dried flask; *n*-BuLi (2.5M in hexanes, 0.06 mol, 24 ml) was added dropwise (−30–35°C, $(CH_2Cl)_2/CO_2$) and the reaction mixture stirred for 20 min. A solution of 3-hexylpyridine (0.01 mol, 1.63 g) in 5 ml of hexanes was added dropwise and the reaction mixture stirred for 30–40 min, cooled to −78°C (acetone/CO_2) and a solution of iodine (8.88 g, 0.035 mol) in freshly distilled THF (15 ml) added dropwise. The reaction mixture was stirred for 1 h, warmed and poured into aqueous $Na_2S_2O_3$. The resulting mixture was vigorously stirred for 15 min, and the organic layer separated. The water layer was extracted twice with CH_2Cl_2 and the organic phases were combined, washed with brine, and dried over $MgSO_2$. After evaporation of the solvent the desired product was isolated in 5.08 g (70%) yield by column chromatography (silica gel, CH_2Cl_2). R_f=0.5 (CH_2Cl_2 as eluant). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.70–0.90 (t, J=6.66 Hz, 3H), 1.17–1.45 (m, 6H), 1.50–1.72 (m, 2H), 2.47–2.80 (t, J=7.69 Hz, 2H), 7.10–7.20 (dd, J=8.02 Hz, 2.51 Hz, 1H), 7.58–7.63 (d, J=8.06 Hz, 1H), 8.18–8.21 (d, J=2.43 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.21, 22.69, 28.87, 31.04, 31.70, 32.48, 114.64, 134.49, 137.84, 138.01, 151.10.

2.6.2. 2-Iodo-3-hexylpyridine (11b). The minor regioisomer **11b** was isolated by column chromatography as a yellow oil in 8% yield from the synthesis of 2-iodo-5-hexylpyridine **9b**. R_f=0.38 (CH_2Cl_2 as eluant). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.65–0.82 (m, 3H), 1.10–1.31 (m, 6H), 1.40–1.52 (m, 2H), 2.45–2.60 (t, J=7.85 Hz, 2H), 6.95–7.08 (dd, J=7.52 Hz, 4.64 Hz, 1H), 7.20–7.28 (dd, J=7.59 Hz, 1.95 Hz, 1H), 7.98–8.20 (dd, J=4.63 Hz, 1.96 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.22, 22.72, 29.09, 29.86, 31.69, 39.19, 123.06, 125.17, 136.38, 143.05, 148.08.

2.6.3. Attempt to prepare 3-(1-iodohexyl)pyridine (10). *n*-BuLi (2.5M, 0.06 mol, 24 ml) was added dropwise to solution of *N*,*N*-dimethylaminoethanol (30 mol, 2.67 g) in 40 ml of hexanes (0°C). The mixture was cooled to −78°C (acetone/CO_2 bath) and a solution of 3-hexylpyridine (10 mmol, 1.63 g) in 15 ml of hexanes was added dropwise. The orange reaction mixture was stirred for 1 h, and then a solution of I_2 (35 mmol, 8.88 g) in dry THF (50 ml) was added dropwise (acetone/CO_2 bath). After completion of the addition



R=C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}

Reagents: *a*) RMgBr, $NiCl_2$(dppe), Et_2O, reflux; *b*) *i*) *n*-BuLi–$Me_2NCH_2CH_2OLi$ (3 eq), -30-35 °C, hexanes; *ii*) I_2, THF-hexanes, -78 °C.

Scheme 6. Synthesis of 2-iodo-5-alkylpyridines **9a**–**d** from readily available 3-alkylpyridines.

the reaction mixture was stirred for 1 h, then allowed to warm to room temperature. The mixture was poured into 50 ml of agueous $Na_2S_2O_3$ and vigorously stirred for 15 min. The product was extracted with Et_2O (3×20 ml). The combined organic phases were dried over $MgSO_4$, vacuum filtered, and the solvent evaporated to give 2.40 g of the crude material. Unreacted starting material was isolated as a yellow oil (1.5 g, 92% recovery) by column chromatography (silica gel, CH_2Cl_2, then CH_2Cl_2/MeOH, 5/1 as eluant). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–1.00 (m, 3H, CH_3), 1.25–1.45 (m, 4H), 1.51–1.73 (m, 2H), 2.53–2.70 (t, J=8.0 Hz, 2H), 7.10–7.35 (m, 1H), 7.45–7.55 (m, 1H), 8.40–8.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.18, 22.69, 28.95, 31.24, 31.73, 33.14, 123.33, 135.87, 138.09, 147.30, 150.11.

2.6.4. 2-Iodo-5-pentylpyridine (9a). The intermediate **9a** was synthesized from 3-pentylpyridine **8a** in the same way as described for **9b**. The product was purified by column chromatography (silica gel, CH_2Cl_2 as eluant) and isolated with 67.3% yield as a yellow oil. R_f=0.5 (CH_2Cl_2 as eluant). The minor isomer 2-iodo-3-pentylpyridine (**11a**) was detected by TLC (R_f=0.32, CH_2Cl_2 as eluant), but was not isolated. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.82–0.98 (t, J=6.85 Hz, 3H), 1.20–1.40 (m, 4H), 1.50–1.67 (m, 2H), 1.45–2.60 (t, J=7.70 Hz, 2H), 7.10–7.21 (dd, J=8.07 Hz, 2.59 Hz, 1H), 7.56–7.65 (d, J=8.05 Hz, 1H), 8.15–8.20 (d, J=2.48 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.12, 22.56, 30.78, 31.36, 32.45, 114.62, 134.52, 137.88, 138.05, 151.14.

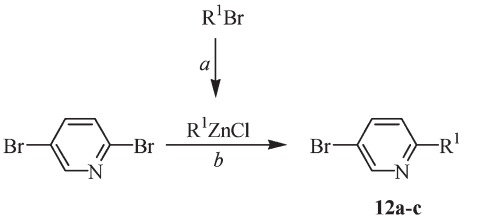
2.6.5. 2-Iodo-5-heptylpyridine (9c). The intermediate **9c** was prepared in the same manner as **9b**, using 3-heptylpyridine **8c** as starting material. A yellow oil was isolated after column chromatography (silica gel, CH_2Cl_2 as eluant) in 63% yield. R_f=0.5 (CH_2Cl_2 as eluant). The minor isomer 2-iodo-3-heptylpyridine (**11c**) was detected by TLC (R_f=0.41, CH_2Cl_2 as eluant), but was not isolated in a pure form. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–0.95 (t, J=6.82 Hz, 3H), 1.15–1.40 (m, 8H), 1.50–1.65 (m, 2H), 2.50–2.60 (t, J=7.68 Hz, 2H), 7.12–7.19 (dd, J=8.05 Hz, 2.59 Hz, 1H), 7.58–7.65 (d, J=8.04 Hz, 1H), 8.17–8.23 (d, J=2.50 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.24, 22.77, 29.18 (2C), 31.11, 31.88, 32.49, 114.62, 134.51, 137.89, 138.05, 151.15.

2.6.6. 2-Iodo-5-octylpyridine (9d). The preparation of **9d** was performed in the same manner as for **9b**. The product was isolated in 72% yield as a yellow oil by column chromatography (silica gel, CH_2Cl_2 as eluant). R_f=0.51 (CH_2Cl_2 as eluant). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–0.92 (t, J=6.86 Hz, 3H, CH_3), 1.20–1.45 (m, 10H), 1.50–1.64 (m, 2H), 2.48–2.55 (t, J=7.69 Hz, 2H), 7.10–7.19 (dd, J=8.07 Hz, 2.01 Hz, 1H), 7.57–7.63 (d, J=8.02 Hz, 1H), 8.15–8.21 (appears as s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.26, 22.80, 29.21, 29.34, 29.48, 31.10, 31.97, 32.48, 114.63, 134.50, 137.88, 138.04, 151.14.

2.6.7. 2-Iodo-3-octylpyridine (11d). The minor isomer **11d** (6% yield) was isolated as a byproduct from the synthesis of **9d** by column chromatography. R_f=0.4 (CH_2Cl_2 as eluant). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.75–0.95 (m, 3H), 1.10–1.45 (m, 10H), 1.50–1.70 (m, 2H), 2.58–2.70 (t, J=7.86 Hz, 2H), 7.10–7.21 (dd, J=7.57 Hz, 4.65 Hz, 1H), 7.33–7.42 (dd, J=7.54 Hz, 1.90 Hz, 1H), 8.10–8.20 (dd, J=4.60 Hz, 1.84 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.27, 22.82, 29.37, 29.44, 29.49, 29.91, 32.00, 39.22, 123.07, 125.20, 136.41, 143.11, 148.13.

2.7. *Synthesis of 2-alkyl-5-bromopyridines (12a–d) [scheme 7]*

2.7.1. 2-Hexyl-5-bromopyridine (12a). 1-Bromohexane (57.7 mmol, 9.45 g) was added dropwise to an oven-dried flask charged with magnesium (62.7 mmol, 1.52 g) and freshly distilled THF (50 ml). After completion of the addition, the reaction mixture was stirred under nitrogen for about an hour. In another flask, zinc chloride (62.7 mmol, 8.55 g,) was dried by melting and then cooling under vacuum; freshly distilled THF (60 ml) was added and the resulting mixture stirred until solution was complete. The Grignard reagent was added dropwise to the zinc chloride solution with cooling (ice-water bath). The reaction mixture was stirred for 30 min and then warmed to room temperature. The resulting *n*-hexylzinc chloride was added dropwise to a solution of 2,5-dibromopyridine (47.7 mmol, 11.3 g) and $Pd(PPh_3)_4$ (1 mol%, 0.55 g) in 40 ml of freshly distilled THF (N_2 atmosphere). The reaction mixture was stirred overnight, and then poured into 100 ml of water. After vacuum filtration the organic phase was separated and dried over $MgSO_4$. The solvent was evaporated and the product purified by vacuum distillation (colourless oil, 84–88°C/0.10–0.11 mm Hg, 8.40 g, 73% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85–0.90 (t, J=6.98 Hz, 3H), 1.27–1.36 (m, 6H), 1.65–1.75 (m, 2H), 2.70–2.76 (t, J=7.77 Hz, 2H), 6.95–7.10 (d, J=8.29 Hz, 1H), 7.60–7.75 (dd, J=8.29 Hz, 2.42 Hz, 1H), 8.55–8.65 (d, J=1.56 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.22, 22.70, 29.11, 29.89, 31.80, 37.90, 117.85, 124.19, 138.91, 150.31, 161.25.



R^1=C_5H_{11}, C_6H_{13}, C_8H_{17}

Reagents: *a*) *i*) Mg, THF; *ii*) $ZnCl_2$, THF; *b*) $Pd(PPh_3)_4$, THF, rt

Scheme 7. Synthesis of 2-alkyl-5-bromopyridines **12a**–**c** by the Negishi coupling of 2,5-dibromopyridine with alkylzinc chlorides.

2.7.2. 2-Pentyl-5-bromopyridine (12b). Compound **12b** was prepared in the same manner as described for **12a** using 1-bromopentane as precursor for preparation of the alkylzinc chloride. The product was isolated as a colourless oil in 54% yield (b.p. 95°C/0.45 mm Hg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80–0.93 (t, J=6.80 Hz, 3H, CH_3), 1.25–1.40 (m, 4H), 1.63–1.75 (m, 2H), 2.70–2.75 (t, J=7.77 Hz, 2H), 7.00–7.07 (d, J=8.28 Hz, 1H), 7.65–7.73 (dd, J=8.28 Hz, 2.37 Hz, 1H), 8.53–8.60 (d, J=2.26 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.14, 22.64, 29.60, 31.61, 37.86, 117.85, 124.18, 138.88, 150.31, 161.24.

2.7.3. 2-Octyl-5-bromopyridine (12c). Compound **12c** was made in the same way as described for **12b** using 1-bromooctane as precursor for preparation of the alkylzinc chloride. The product was isolated in 30% yield as a colourless oil (115°C/0.22 mm Hg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.83–0.91 (t, J=6.68 Hz, 3H, CH_3), 1.23–1.32 (m, 10H), 1.64–1.73 (m, 2H), 2.68–2.78 (J=7.77 Hz, 2H), 7.00–7.11 (d, J=8.30 Hz, 1H), 7.67–7.72 (dd, J=8.28 Hz, 2.43 Hz, 1H), 8.50–8.60 (d, J=2.21 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.26, 22.81, 29.36, 29.45, 29.56, 29.94, 31.99, 37.88, 117.86, 124.20, 138.94, 150.28, 161.24.

3. Results and discussion

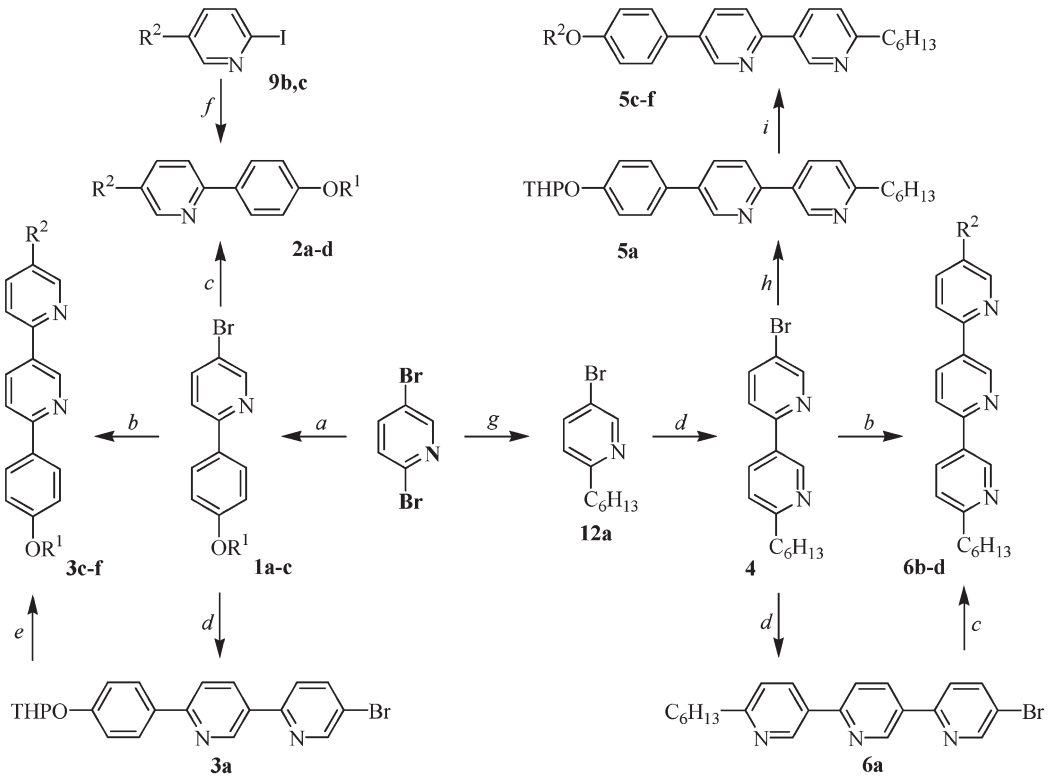
3.1. *Synthesis of 2,5-disubstituted pyridine liquid crystals*

The four classes of 2,5-disubstituted pyridines shown in scheme 8 were synthesized using mainly the selective coupling of 2,5-dibromopyridine with arylzinc chloride as a key step. Known 2-(4-alkoxyphen-1-yl)-5-alkylpyridines **2a**–**d** were made using two different approaches. The first approach was based on the Pd(0)-catalysed coupling reaction of 4-alkoxyphenylzinc chloride with 2,5-dibromopyridine to give the desired intermediates **1a**,**b** with good yields (67–84%) (scheme 1, *Method A*). Although 2-[4-(tetrahydropyran-2-yloxy)phen-1-yl]-5-bromopyridine **1b** was isolated in the relatively low yield of 67%, it produced a versatile intermediate 2-(4-hydroxyphen-1-yl)-5-bromopyridine after removal of the THP-protection group. Alkylation of this intermediate with *n*-octylbromide under standard conditions gave **1c**, and the following alkylation with alkyl Grignard under Ni(II)-catalysis produced the desired **2a**,**d**. The second approach was based on the $NiCl_2$(dppe)-catalysed coupling reaction of 2-iodo-5-alkylpyridines **9b** and **9c** with 4-alkoxyphenylmagnesium bromide to give **2b** and **2c** in 74% yield.

Liquid crystalline 2-(4-alkyloxyphen-1-yl)-5-(5-alkyl–pyridin-2-yl)-pyridines **3c**–**f** could be prepared using two approaches: Negishi coupling of arylzinc chloride prepared from intermediates **1** with (i) 2-iodo-5-alkylpyridines to give final products (this approach was used for the preparation of **3f**) or (ii) with 2, 5-dibromopyridine. In the latter case the isolated 2-[4-(tetrahydropyran-2-yloxy)phen-1-yl]-5-(5-bromo-pyrid-2-yl)pyridine (**3a**) underwent Ni-catalyzed alkylation with alkyl Grignard followed by THP-removal to give phenol **3b**. Alkylation of 2-(4-hydroxypheny-1-yl)-5-(5-heptylpyridin-2-yl)pyridine (**3b**) with alkylbromides in the presence of K_2CO_3 proceeded cleanly but with low isolated yields of the desired products **3c**–**e** (13–40%) due to losses during small scale recrystallization.

A convenient approach to 2-alkyl-5-bromopyridine intermediates **12** required for the synthesis of liquid crystals **5c**–**f** and **6b**–**d** was also developed. Here, 2,5-dibromopyridine was reacted selectively with alkylzinc chlorides in the presence of a catalytic amount of $Pd(PPh)_3$ to give the desired products **12** in moderate to good yields (30–73%).

The key intermediate **4** for the synthesis of both types of compounds **5** and **6** was obtained by the standard Negishi coupling reaction of 2-hexylpyridin-5-ylzinc chloride, itself derived from 2-hexyl-5-bromopyridine (**12b**), with 2,5-dibromopyridine. The arylzinc chloride obtained from 2-(2-hexylpyridin-5-yl)-5-bromopyridine (**4**) underwent Negishi coupling reaction with THP-protected 4-bromophenol to provide 2-(2-hexylpyridin-5-yl)-5-(4-(tetrahydropyran-2-yloxy)phen-1-yl)pyridine



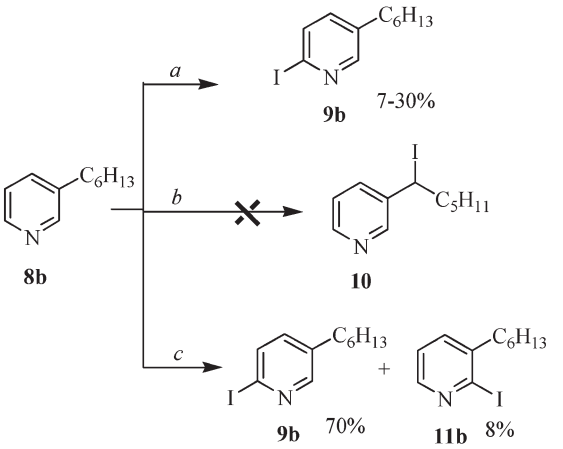
Reagents: ***a***) 4-alkoxyphen-1-yl-zinc chloride, $Pd(PPh_3)_4$, THF; ***b***) *i*) *n*-BuLi, THF, -78 °C; *ii*) $ZnCl_2$, THF, -78 °C→rt; *iii*) 2-iodo-5-alkylpyridine **9**, $Pd(PPh_3)_4$ (1 mol%), THF, rt; ***c***) R^2MgBr, $NiCl_2$(dppe), Et_2O, reflux; ***d***) *i*) *n*-BuLi, THF, -78 °C; *ii*) $ZnCl_2$, THF, -78 °C→rt; *iii*) 2,5-dibromopyridine, $Pd(PPh_3)_4$, THF, rt; ***e***) *i*) R^2MgBr, $NiCl_2$(dppe), Et_2O, reflux; *ii*) HCl (cat.), EtOH, heating; *iii*) R^1Br, K_2CO_3, acetone, reflux; ***f***) 4-alkoxyphen-1-yl-magnesium bromide, $NiCl_2$(dppe), THF; ***g***) $C_6H_{13}ZnCl$, $Pd(PPh_3)_4$ (1 mol%), THF; ***h***) *i*) *n*-BuLi, THF, -78 °C; *ii*) $ZnCl_2$, THF, -78 °C→rt; *iii*) 4-(tetrahydropyran-2-yloxy)-1-iodobenzene (**14**), $Pd(PPh_3)_4$ (1 mol%), THF, rt; ***i***) *i*) HCl (cat.), EtOH, heating; *ii*) R^2Br, K_2CO_3, acetone, reflux.

Scheme 8. Summarized strategy for the synthesis of pyridine-based liquid crystals.

(**5a**) in a moderate 37% yield, which was THP-deprotected to obtain phenol **5b**. Its alkylation with alkylbromides gave mesogens **5c**–**f** in 23–41% yield; no side reactions were observed and the moderate yields are the result of loss during recrystallization. Negishi coupling of **4** with 2-iodo-5-alkylpyridines **9b**,**c** resulted in the construction of the aromatic core with three pyridine rings. The final products **6b**,**c** were isolated in low 18–40% yields. A better yield of 40% was observed for the synthesis of liquid crystal **6b**, when a more diluted solution of arylbromide **4** (0.12M in THF) underwent the lithiation-transmetallation-coupling sequence, while the same reaction with a higher concentration of **4** (0.25M in THF) led to the isolation of the desired product **6b** in 18% yield. A slightly lower yield of 14% was observed for the coupling of aryl bromide **4** (0.2M initial concentration) with 2,5-dibromopyridine, which resulted in 2-(2-hexylpyridin-5-yl)-5-(5-bromopyridin-2-yl)pyridine (**6a**), which itself was reacted with alkyl Grignard to obtain the desired liquid crystal **6d**. Consistently low yields observed for the Negishi coupling of arylzinc chlorides derived from **4** are probably the result of the poor selectivity during the bromine–lithium exchange. The reaction requires further optimization of conditions to be truly useful for the synthesis of this type of liquid crystal on a larger scale.

3.2. *Synthesis of 2-iodo-5-alkylpyridines 9a–d*

The key intermediates for the synthetic approach to liquid crystals **2c** and **6b**,**c** are 2-iodo-5-alkylpyridines, which were obtained using the optimized method reported by Fort *et al* [17]. The original conditions



Reagents: *a*) *i*) *n*-BuLi–$Me_2NCH_2CH_2OLi$ (3 equiv.), **0 ºC**, hexanes, 1h; *ii*) I_2, THF-hexanes, -70 ºC; *b*) *i*) *n*-BuLi–$Me_2NCH_2CH_2OLi$ (3 equiv.), **-70 ºC**, hexanes, 1h; *ii*) I_2, THF-hexanes, -65-70 ºC; *c*) *i*) *n*-BuLi–$Me_2NCH_2CH_2OLi$ (3 equiv.), **-30-35 ºC**, hexanes, 1h; *ii*) I_2, THF-hexanes, -70 ºC.

Scheme 9. Lithiation of 3-hexylpyridine (**8b**) with *n*-BuLi–LiDMAE under different temperature conditions followed by trapping with iodine.

used for the lithiation of 3-methylpyridine worked poorly for 3-hexylpyridine (**8b**), producing a complex mixture of more than four products with a low yield of the desired 2-iodo-5-hexylpyridines (**9b**) (scheme 9). The lithiation of 3-hexylpyridine **8b** with *n*-BuLi-Me_2N-$(CH_2)_2$-OLi (denoted *n*-BuLi-DMAE) at −70°C followed by trapping with iodine led to recovery of the starting material. An increase of the lithiation reaction time up to 2 h did not change the outcome of the reaction and led to recovery of the starting material. Lithiation of 3-hexylpyridine (**8b**) at −30°C, followed by the reaction with the electrophile at −70°C produced the desired 2-iodo-5-hexylpyridine **9b** with good yield along with regioisomer **11b** as a minor byproduct. This optimized reaction temperature profile was used for the synthesis of all the other alkylpyridines **8a**,**c**,**d**. In all cases formation of minor 2-iodo-3-alkylpyridines **11** was observed with <10% yield.

3.3. *Liquid crystalline phase behaviour of the pyridine-based liquid crystals*

All the target molecules **2a–d**, **3c–f**, **5c–f**, and **6b–d** exhibited liquid crystalline behaviour. Transition temperatures observed by DSC analysis and microscopy are summarized in table 1. Phase assignments were made based on analysis of the textures observed and are preliminary for the new materials **3**, **5**, **6**.

3.3.1. Liquid crystalline behaviour of the known phenylpyridines 2a–d. Preparation methods and phase assignments of the known 2-(4-alkoxyphen-1-yl)-5-alkylpyridines **2a–d** have been described previously [11, 23–28]. The DSC thermogram (figure 2) of 2-(4-heptyloxyphenyl)-5-hexylpyridine **2b** clearly exhibits two peaks between 43 and 69.1°C, while Pavluchenko *et al.* reported only these two transition temperatures: Cr 40 S 68 I (°C) [11].

The phase assignment for liquid crystal **2b** was based on the microscopy observations of the material on a slide and as a free-standing film. The transition from SmC to SmI (slide) on cooling was difficult to observe in the fan texture, but was clearly evident on cooling the free-standing film, figure 3 (*b*). A highly coloured mosaic texture, characteristic of the SmG phase formed on cooling from the SmC or SmF phases [29], was observed on cooling the SmI phase, figures 3 (*c*) and 3 (*d*).

The phase assignment of 2-(4-heptyloxyphenyl)-5-heptylpyridine **2c** found in the literature is somewhat controversial (table 1, entry **2c**). Our data and observations are in full agreement with an assignment made by Decher *et al*. [23]. No DSC event at 24°C was observed, the temperature at which a transition from SmG to SmH takes place according to Heinemann *et al.* [24] and Inoue *et al*. [25]. The phase that forms on cooling from the SmI phase exhibits zigzag lines, which are usually indicative of the SmH phase [29].

A contradiction with the literature was also found for 2-(4-octyloxyphenyl)-5-heptylpyridine **2d**. The DSC thermogram clearly shows only four peaks (the peak at 33.5°C probably is due to a crystal to crystal

Table 1. DSC analysis and microscopy observations for pyridine liquid crystals.

Compound	R^1	R^2		DCS peaks/°C (the second heating-cooling cycle)	Transition temperatures/°C (by microscopy on cooling)
2a	C_7H_{15}	C_5H_{11}	heating	57.9, 65.0, 73.0	Cr 57.9 SmC 62.9 N 69.9 I
			cooling	45.1, 55.8, 72.8	(Cr 56.9 S 61.8 N 68.2) [27]
2b	C_7H_{15}	C_6H_{13}	heating	19.1, 43.0, 47.2, 51.4, 69.1	Cr 40.5 SmG 46.0 SmI 49.9 SmC 69.6 I
			cooling	18.2, 41.8, 45.8, 50.5, 68.5	(Cr 40 S 68 I) [11]
2c	C_7H_{15}	C_7H_{15}	heating	16.3, 30.5, 32.3, 41.0, 53.9, 77.8	Cr 31.1 SmH 41.1 SmI 52.3 SmC 76.6 I (Cr 31 SmG 40 SmI 52 SmC 77) [23]
			cooling	15.2, 31.2, 40.2, 53.1, 77.2	(Cr 24 SmH 31.5 SmG 40.3 SmF 53 SmC 76.6 I) [25] (Cr 24 H 31 SmG 40 SmF 53 SmC 77 I) [24]
2d	C_8H_{17}	C_7H_{15}	heating	33.5 46.5, 57.4, 81.2	Cr 43.8 SmI 54.9 SmC 79.8 I (Cr 47 SmI 58 SmC 81) [26]
			cooling	31.6 45.2, 56.7, 80.7	(Cr 45 G 45.4 F 56.5 C 80.4) [25] (Cr 46.5 H 45 G 56 C 80.5) [28] (Cr 45 G 45.5 F 56 C 80) [24]
3c	C_7H_{15}	C_7H_{15}	heating	46.1, 117.1, 151.1, 209.0, 211.5	Cr 39.8 *SmG*114.8 SmI 149.4 SmC
			cooling	41.4, 115.9, 149.7, 207.4, 210.2	207.8 N 210.5 I
3d	C_8H_{17}	C_7H_{15}	heating	54.2, 117.0, 151.7, 210.1	Cr 49.1 *SmF* 116.6 SmI 150.3 SmC
			cooling	50.2, 116.1, 150.3, 208.5	207.1 N 210.5 I
3e	C_6H_{13}	C_7H_{15}	heating	40.3, 53.6, 128.0, 153.4, 206.7, 212.6	Cr 33.4 *SmG* 123.2 SmI 149.2 SmC
			cooling	34.1, 126.5, 151.8, 205.3, 211.4	206.6 N 212.5 I
3f	C_7H_{15}	C_6H_{13}	heating	55.0, 58.7, 126.4, 150.9, 198.9, 205.8	Cr 50.2 *SmF* 123.7 SmI 149.3 SmC
			cooling	51.3, 123.9, 149.5, 194.7, 199.3, 204.5	194.2 SmC+N 198.7 N 204.1 I
5c	C_6H_{13}	C_5H_{11}	heating	66.1, 172.4, 230.9	Cr (12.9)[b] *SmB* 170.2 SmA 228.4 I
			cooling	12.9, 170.3, 228.4	
5d	C_6H_{13}	C_6H_{13}	heating	60.1[a] 63.9 171.9 177.7 225.0	Cr1 (23.6)[b] Cr2 42.9 *S1* **153.6** SmF
			cooling	23.6 44.2 170.9 178.7 223.6	171.6 SmI 177.2 SmA 225.0 I
5e	C_6H_{13}	C_7H_{15}	heating	75.0, 172.2, 189.7, 220.9	Cr1 (22.5)[b] Cr2 35.7 K3 51.9 S1 **147.9**
			cooling	22.5, 35.4, 54.9, 170.3, 186.7 219.2	SmF 168.8 SmC 186.3 SmA 219.2 I
5f	C_6H_{13}	C_8H_{17}	heating	60.3, 170.8, 190.1, 217.1	Cr1 (18.6)[b] Cr2 49.3 *S1* **145.8** SmF
			cooling	18.6, 49.4, 168.8, 187.9, 215.0	167.8 SmC 187.1 SmA 215.4 I
6b	C_6H_{13}	C_6H_{13}	heating	60.5, 123.3, 142.6, 184.4, 205.9	Cr 46.5 SmF 119.2 SmI 139.0 SmC
			cooling	46.5, 121.9, 141.3, 183.1, 203.9	180.7 SmA 205.1 I
6c	C_6H_{13}	C_7H_{15}	heating	45.7, 123.9, 142.9, 185.3, 205.0	Cr 33.8 SmF 123.2 SmI 142.3 SmC
			cooling	33.0, 122.1, 141.3, 183.9, 202.4	186.2 SmA 205.0 I
6d	C_6H_{13}	C_8H_{17}	heating	39.6[a], 144.96, 191.37, 202.46	Cr (28.24)[b] SmF 141.3 SmC 189.9 SmA
			cooling	28.24, 142.92, 189.37, 200.21	203.2 I

[a]**5d** transition at 70.5°C was observed during the first heating-cooling cycle; **6d** transition at 52.45°C was observed during the first heating-cooling cycle. [b]The transition was not observed by microscopy due to instrument limitations; the phase assignment shown in italic.

transition). Microscopy observations led us to the following sequence: I→SmC→SmI→Cr, which is in an agreement with the assignment made by Kelly *et al*. [26].

3.3.2. Liquid crystalline behaviour of the materials 3c–f, 5c–f, and 6b–d. All the synthesized 2,5-disubstituted pyridines **3**, **5**, **6** have quite low melting point in the range 40–75°C and become isotropic liquids in the range 202–230°C. All these compounds, except **5c** and **6d**, form at least four liquid crystalline phases. Liquid crystals **3c**–**f** exhibit the following sequence of the first three phases on cooling from isotropic liquid: I→N→SmC→SmI. For compound **3d** and **3f** the phase formed on cooling of SmI was identified as SmF, based on the observation of a *schlieren*-mosaic texture formed from the *schlieren* texture of the previous phase. The liquid crystalline phase formed on cooling of the *schlieren* texture of the SmI phases of **3c** and **3e** appeared as a true highly coloured mosaic texture characteristic of SmG. The observed ΔH of transition from SmI to the next phase on cooling for compounds **3c**–**f** is in the range 0.11–0.19 kJ mol^{-1}.

Materials of type **5** exhibit more diverse liquid crystalline behaviour, but they all formed the SmA phase on cooling from the isotropic liquid. Only one more phase, with ΔH (SmA→*Sm1*)=3.55 kJ mol^{-1}, was observed for **5c**. The focal-conic texture of the SmA after transition to *S1* became broken. Supercooling was

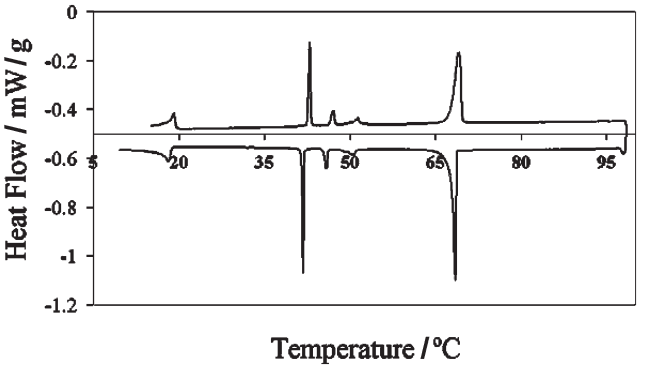


Figure 2. DSC thermogram of 2-(4-heptyloxyphenyl)-5-hexylpyridine (**2b**).

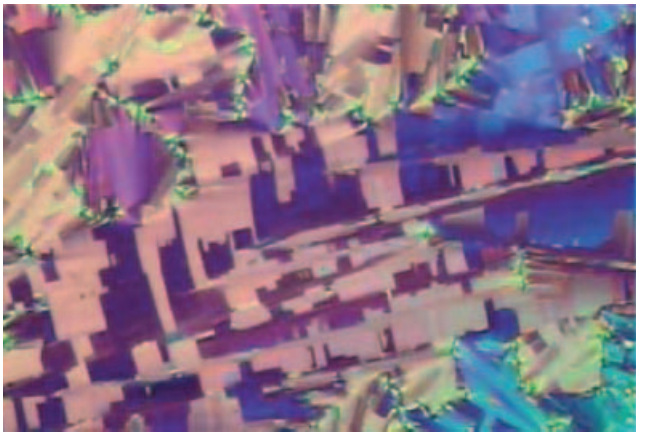


Figure 4. Texture of compound **5f**, SmF (166.1°C, slide).

observed by DSC as the transition from the crystalline phase to *Sm1* was detected at 66.1°C on heating and at 12.9°C on cooling. Three other liquid crystals of the type **5d**–**f** have still more complicated behaviour. One more transition not seen in DSC was observed for **5d**–**f** by observation of *schlieren*-mosaic texture of the SmF phase (the temperature at which transition was observed is shown in bold in table 1). The texture formed on cooling the *schlieren*-mosaic texture was a highly coloured mosaic. No changes were seen in the broken focal-conic texture. The following sequence of the first three phases was observed for **5e**,**f**: I→SmA→SmC→SmF, with ΔH(SmA→SmC)=0.12–0.16 kJ mol^{-1}. A different sequence was exhibited by **5d**: I→SmA→SmI→SmF, with ΔH(SmA→SmI)=1.37 kJ mol^{-1}. For all three liquid crystals **5d**–**f** the fan texture of the SmF phase had the characteristic elongated L-shaped patterns (figure 4).

On cooling the SmF phase of **5e**, changes in the appearance of the mosaic texture were observed as shown in figure 5. The mosaic platelets shown in figure 5 (*b*) are large with more defined borders and

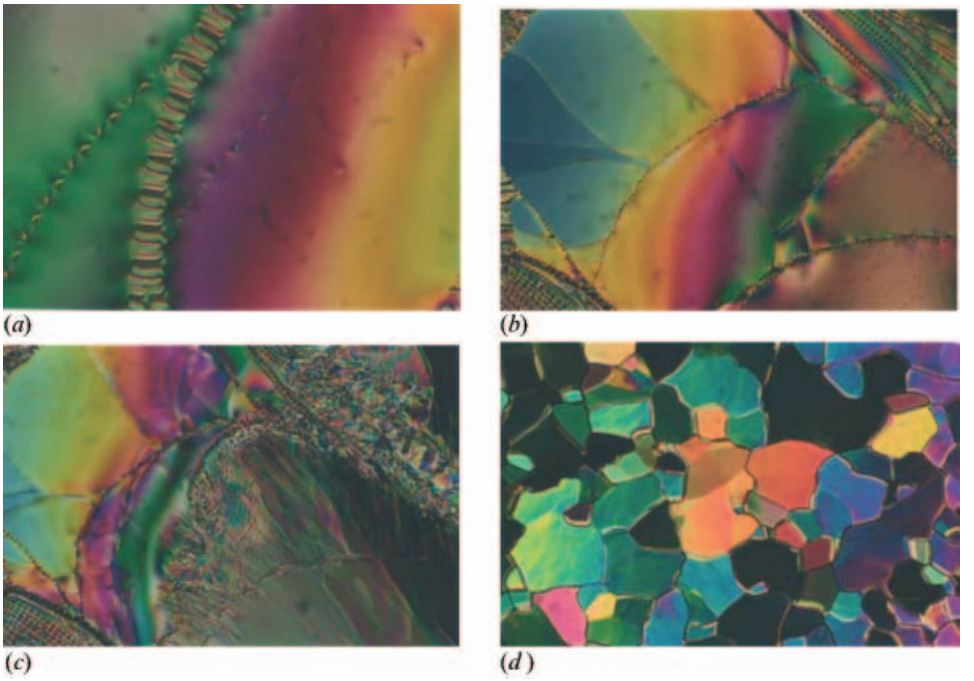


Figure 3. Textures of **2b**: (*a*) SmC (67.5°C, free-standing film); (*b*) SmI (48°C, free-standing film); (*c*) SmG (44°C, free-standing film); (*d*) SmG (44.9°C, slide).

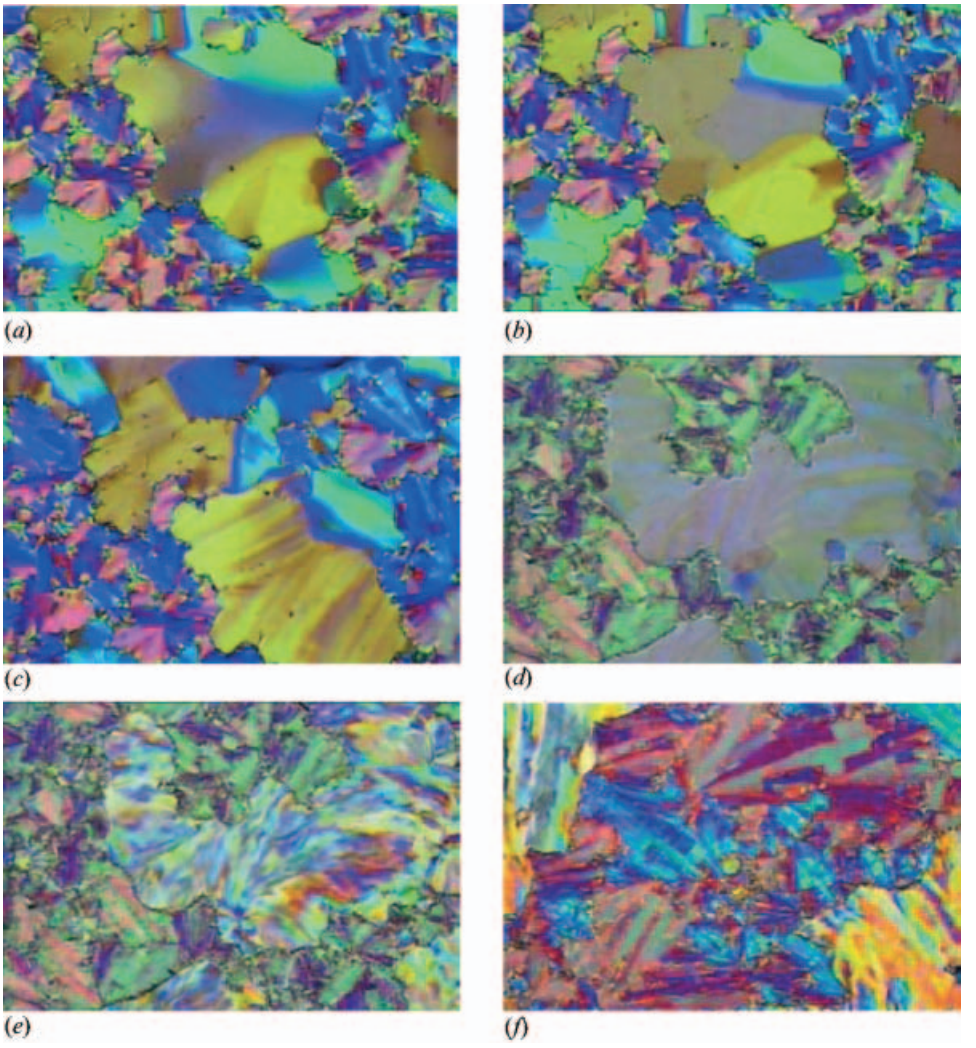


Figure 5. Textures of **5e**: (*a*) SmF (152.9°C, slide); (*b*) *S1* (144.7°C, slide); (*c*) *S2* (92.6°C, slide); (*d*) Cr3 (48.7°C, slide); (*e*) transition to Cr2 (36.3°C, slide); (*f*) Cr1 (32.1°C, slide).

colour, which is characteristic of the SmG phase formed on cooling of SmF. Coloured bands within the platelets start to develop around 120°C on cooling the mosaic texture of the *S1* phase, figure 5 (*c*). Further cooling brings more changes to the appearance of this texture (bright spots on the left upper and right lower corners in figure 5 (*f*) were originally *schlieren*-mosaic texture of the SmF phase). Liquid crystals with three pyridine rings **6b**,**c** exhibit the following phase sequence: I→SmA→SmC [figure 6 (*a*)] →SmI [figure 6 (*b*)] →SmF [figure 6 (*c*)], while **6d** lacks SmI in that sequence.

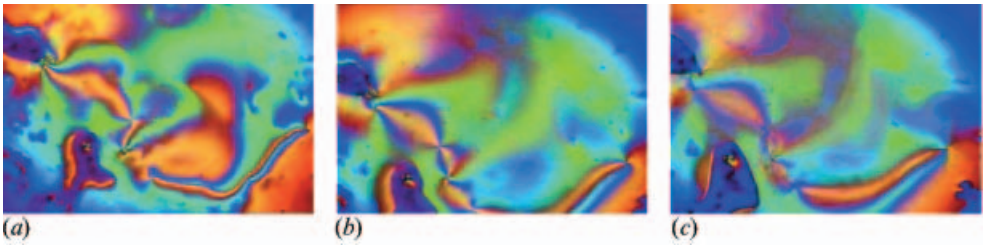


Figure 6. Textures of **6b**: (*a*) *schlieren* texture of SmC, (161.7°C, slide); (*b*) *schlieren* texture of SmI (137.7°C, slide); (*c*) *schlieren*-mosaic texture of SmF (107.1°C, slide).

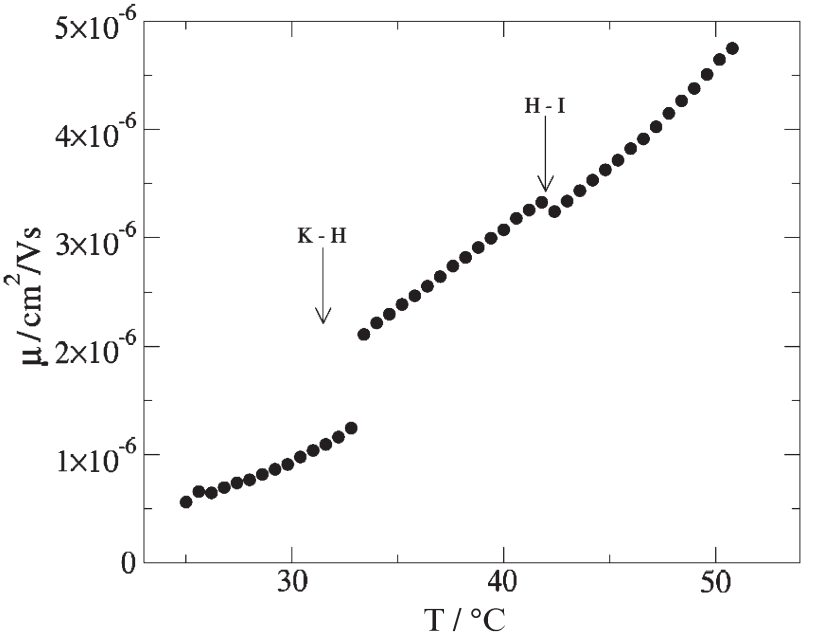


Figure 7. Time-of-flight mobility of positive charge carriers in 2-(4-heptyloxyphenyl)-5-heptylpyridine (**2c**).

3.3.3. Charge transport in the phenylpyridine smectic liquid crystal 2c. In figure 7 we show the mobility $\mu(T)$ of charge carriers in the phenylpyridine liquid crystal **2c** determined by the TOF technique. The mobility data were obtained on heating. A step function increase in μ is evident at the entry into the S_H phase at about 33°C while a small step decrease occurs at the S_H/S_I transition. The *increase* in mobility concurrent with a *decrease* in ordering (i.e. from a crystal to a liquid crystalline phase), along with the small magnitude of μ argues for the identification of the charge carriers as positive ions rather than holes.

To check this, we performed experiments on samples of **2c** intentionally 'doped' with 1% 8PNPO12 [6], a phenylnaphthalene liquid crystal. Note that 'doping' is an imprecise term here, since the 8PNPO12 plays the role of a hole trap, and does not contribute carriers as would a conventional dopant in inorganic semiconducting materials. As shown in figure 8, this doping qualitatively changes the time-of-flight transient from the typical ballistic form representative of the pure (not intentionally doped) sample to highly dispersive behaviour seen in the doped sample. Since we do not expect such low doping levels significantly to impact any ionic transport (i.e. 1% of the trap material should not affect the viscosity and therefore the ionic mobility), we conclude that the mobility shown in figure 7 is indeed that of *holes*. Furthermore, since repeated attempts at purification of **2c** (combinations of Kugelrohr distillation, recrystallization and chromatography) did not result in any significant change in the measured mobilities, we tentatively rule out multiple trapping as the cause of the low mobilities seen in figure 7.

This result is interesting since the analogous biphenyl materials [30] (4-octyloxy-4′-octylbiphenyl and 4-hexyloxy-4′-octylbiphenyl) have mobilities that are about 5–10 times higher than that of the phenylpyridine **2c**. The measurements of these smectic biphenyls also indicate that the measured mobilities were multiple trapping limited, and are therefore lower bounds on the intrinsic mobilities. Further measurements on both the phenylpyridines and biphenyls are required to answer the question of whether the nitrogen heteroatom substantially lowers the ability of these materials to transport charge. More work is also needed to explain the temperature dependence of, and anomalous S_H to S_I jump in $\mu(T)$. One interesting similarity between these two classes of liquid crystals is notable. As discussed in [30], biphenyl smectics with two alkyl chains, rather than one alkyl and one alkoxy chain, exhibit dispersive transport. The addition of the oxygen result in semiconductors with well defined times-of-flight. The phenylpyridine **2c**, with an alkyloxy tail, also exhibits non-dispersive transport, raising the question of whether this structure/function correlation is more general.

4. Conclusions

A general strategy for the synthesis of 2,5-disubstituted pyridine compounds was developed and applied to the

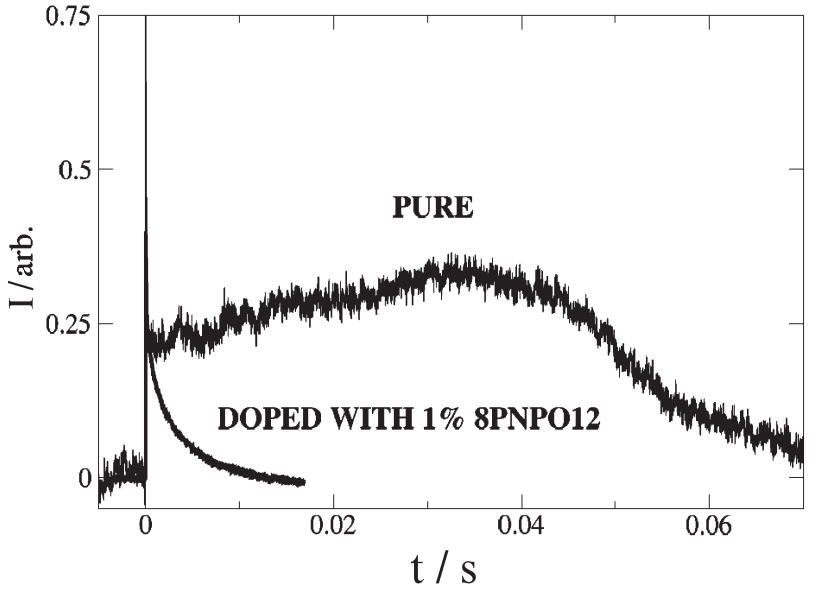


Figure 8. Time-of-flight charge transients in pure and doped 2-(4-heptyloxyphenyl)-5-heptylpyridine (**2c**).

synthesis of targeted pyridine containing liquid crystals. Negishi coupling of 2,5-dibromopyridine with arylzinc chlorides led to the formation of valuable 2-aryl-5-bromopyridines, which can be further functionalized exploiting the bromine at C-5 by alkylation with alkyl Grignards under $NiCl_2$(dppe) catalysis or by conversion into arylzinc chlorides and coupling with aryl halides.

Tuning of the reaction temperature conditions for the successful synthesis of 2-iodo-5-alkylpyridines and development of the convenient synthetic approach to 2-alkyl-5-bromopyridines complemented the developed strategy and allowed the preparation of 2,5-disubstituted pyridines with different position and number of nitrogen atoms in the desired products.

The time of flight experiment showed that the hole mobility of **2c** was low, of the order $10^{-6}\,cm^2\,V^{-1}\,s^{-1}$, and that it increased with a decrease of order of molecular arrangement. Further measurements on both the phenylpyridines and biphenyls are required to answer the question of whether the nitrogen heteroatom substantially lowers the ability of these materials to transport charge. More work is also needed to explain the temperature dependence of the anomalous S_H to S_I jump in $\mu(T)$.In comparing the two classes of compounds, the question arises as to whether non-dispersive transport in both may be related to the presence of an alkoxy chain.

X-ray diffraction experiments planned for the new liquid crystals will help to identify and hopefully confirm the phase assignments made by microscopy observations.

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