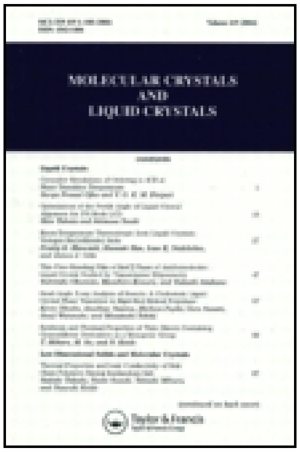

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Synthesis of 4-alkoxy and 4(4′-alkoxyphenyl)-2,6-di(hydroxymethyl) pyridines and their Applications as Liquid Crystals and Polymer Electrolyte Liquid Crystals

Ali R. Tajbakhsh [a] , Felix B. Dias [b] , Y. Zheng [b] & Peter V. Wright [a]

[a] Centre for Molecular Materials, Department of Chemistry, University of Sheffield, Sheffield, UK

[b] Department of Engineering Materials, University of Sheffield, Sheffield, UK

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Synthesis of 4-alkoxy and 4(4′-alkoxyphenyl)-2,6-di(hydroxymethyl) pyridines and their Applications as Liquid Crystals and Polymer Electrolyte Liquid Crystals

ALI R. TAJBAKHSH[a], FELIX B. DIAS[b], Y. ZHENG[b] and PETER V. WRIGHT[b,*]

[a] *Centre for Molecular Materials, Department of Chemistry, University of Sheffield, Sheffield, UK;*
[b] *Department of Engineering Materials, University of Sheffield, Sheffield, UK*

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4-Octyloxy-2,6-di(hydroxymethyl)pyridine (2), 4(4′-octyloxyphenyl)-2,6-di(hydroxymethyl)pyridine (4), and 4(4′-octadecyloxyphenyl)-2,6-di(hydroxymethyl)pyridine (3) were synthesised. By modification of a literature method the dimethyl (or ethyl) 4-hydroxypyridine-2,6-dicarboxylate (6) was synthesised with yield greater than 90%, using thionyl chloride/DMF catalyst mixture, compared with 55–85% using methanol or ethanol/H_2SO_4 mixture as reported in literature.

Williamson etherification of (6) using alkyl halide/acetone/K_2CO_3 mixture gave a poor yield, whereas, in a different synthesis using alkyl halide/toluene/Ag_2O mixture, the yield was improved to about 85%. Reduction of the 4-alkoxy-2,6-pyridine dicarboxylate (7) using $NaBH_4$/EtOH or MeOH was found to reduce only one ester and to hydrolyse the other one to acid. Using $NaBH_4$ or $LiBH_4$ THF/MeOH mixture, successfully reduced the diesters (7) and (8). The compounds synthesised were characterized by thermal analysis, FTIR, ^{1}H nmr, and mass spectroscopy.

The monomeric diol (3) exhibited both thermotropic and lyotropic (smectic A) behaviour. The polyether prepared from (3) and tetraethylene glycol dichloride gave a smectic A liquid crystal phase when both uncomplexed and complexed with $LiBF_4$ and $LiClO_4$. The complexes were characterized by DSC, small- and wide- angle X-ray diffraction and ionic conductivity–temperature measurements.

Keywords: Concave pyridines; thermotropic and lyotropic liquid crystal; polymeric electrolyte liquid crystals

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*Corresponding author: Tel.: +44 114 222 5499; Fax: +44 114 222 5943; e-mail: p.v.wright@sheffield.ac.uk

The 2,6-di(hydroxymethyl)pyridines (so called 'concave pyridines') are important compounds which have found extensive use in the synthesis of 'crown ethers' [1-6] where the nitrogen atom is geometrically disposed alongside neighbouring oxygens to partake in the coordination of the cation. The inclusion of the pyridyl residue permits the attachment of a substituent group, usually in the 4-position, which may perform a function, for example in molecular self-organisation.

We have found cause to incorporate these compounds into polyethoxy chains which form helical conformations about alkali cations. The regular occurrence of one pyridyl residue at each rotation of the helix allows the attachment of an alkyl chain, or other substituent, at the 4-position. As we have demonstrated [7-9] using the analogous derivatives of di (hydroxymethyl) benzene, the resulting two-dimensional (lamellar) organisation of the substituents interposed by the helical polymer ligands for the coordination of an alkali salt gives rise to a novel class of polymer electrolytes which may be organised as smectic liquid crystals [7, 8] or Langmuir Blodgett films [9] of high ionic conductivity.

However, in applying procedures recommended in the literature [1-6, 10-13] for the preparation of 4-alkoxy-2,6-di(hydroxymethyl) pyridines we have encountered some difficulties in synthesis, in particular for the preparation of compounds with the long alkyl side groups required for our self-assembling systems.

In this publication we discuss some observations on the procedures recommended by the literature and report a novel synthetic procedure which has given the desired compounds in good yield.

We also describe two applications for these monomeric compounds: (i) as novel liquid crystal systems and (ii) as novel polymer electrolytes when copolymerised with tetraethylene glycol and complexed with lithium salts.

SYNTHESIS OF CONCAVE PYRIDINES

Chelidamic acid (1) was chosen as starting material for synthesis of these monomers.

It has been reported in literature [10, 11] that treatment of chelidamic acid with methanol or ethanol in the presence of sulphuric acid as a catalyst would give the corresponding dimethyl or diethyl 4-hydroxypyridine-2,6-dicarboxylate (6) with a yield of between 55-85% [12, 13]. However, we have repeated the above procedures and isolated the diester (6) with low yield. In order to increase the yield of the diester (6), (see Scheme I) the

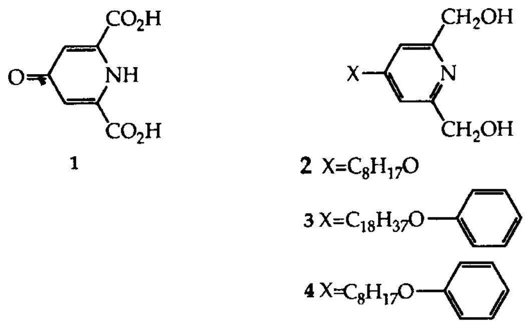
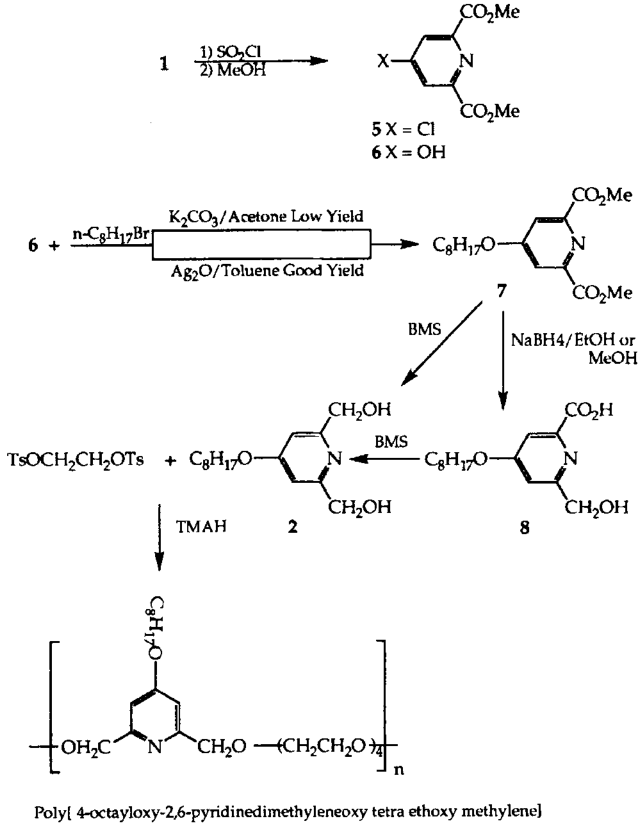


FIGURE 1 The starting material, Chelidamic acid (1) and target compounds.

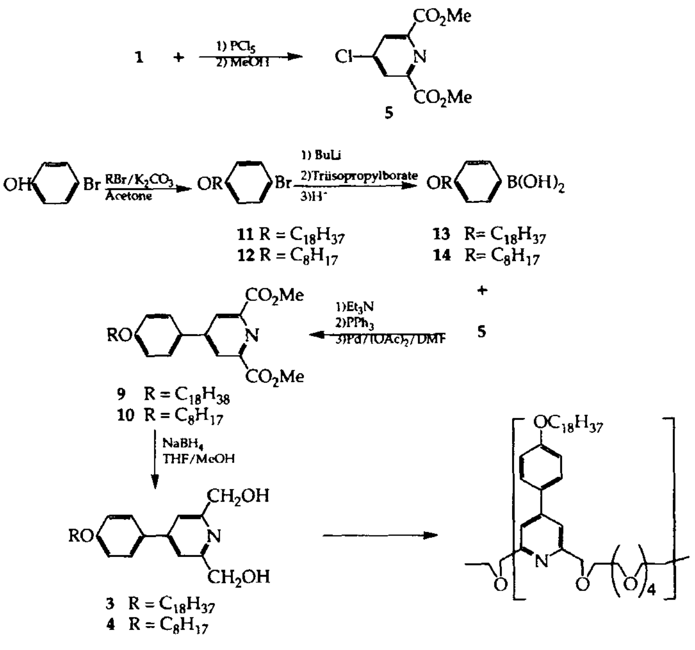


Poly[4-octayloxy-2,6-pyridinedimethyleneoxy tetra ethoxy methylene]

SCHEME I Synthetic pathways to alkoxy-2,6-dimethylpyridine and the polyether.

chelidamic acid was reacted with excess of thionyl chloride in the presence of 1, or 2 drops of DMF as catalyst at room temperature overnight. Cold evaporation of the thionyl chloride followed by treatment of the residue with methanol gave the dimethyl 4-hydroxypyridine-2,6-dicarboxylate (6) in greater than 90% yield.

Williamson etherification of the hydroxy diester (6) using *n*-alkylhalide in acetone and K_2CO_3 gave a very low yield of dimethyl 4-alkoxypyridine-2,6-dicarboxylate (7). However, mixture of the compound (6) and *n*-alkyl halide in the presence of Ag_2O in refluxed toluene for 6 h. gave the compound (7) in a very good yield. There are many reagents for reduction of an ester to the corresponding alcohol such as $LiAlH_4$, $NaBH_4$, *etc*. In our case, reduction of compound (7) with $LiAlH_4$ gave a tarry material which was difficult to work up. Treatment of the compound (7) with $NaBH_4$ in dry EtOH or MeOH at room temperature reduced only one ester and hydrolysed the other one to the 6-(hydroxymethyl)-4-octyloxypyridine-2-carboxylic acid (8). However, the same reagent in the mixture of THF and MeOH with the ratio of 4:1 successfully reduced the two esters in the compounds (9) and (10) (see Scheme II), into corresponding dialcohols (3) and (4) respectively. A possible explanation for this behaviour of $NaBH_4$ in our case could be the complexation of Na^+ with the nitrogen and ester in EtOH which impedes reduction of the carboxyl group by hydronium ions. Heating the mixture



SCHEME II Synthetic pathways to monomers 3 and 4.

under refluxed ethanol for 2 days failed to give further reduction of the carboxyl to the alcohol.

However, treatment of the compound (8) with borane dimethyl sulphide (BMS) gave the dialcohol (2) [14]. Reaction of the compound (7) with BMS also gave the dialcohol (2).

Polymerisation of the compound (2) with the tetraethylene glycol ditosylate in the presence of tetramethylammonium hydroxide (TMAH) gave the water soluble polymer (see Scheme I).

To decrease solubility of the polymer in water and increase the order of the system, we have introduced alkoxyphenyl substituents. Self organisation of the side groups promotes helical formation in the polyether chain and extends two dimensional order throughout the system [8, 9].

Thus compounds (3) and (4) were synthesised. The synthetic pathways to these compounds are outlined in Scheme II.

Treatment of the chelidamic acid with PCl_5 in refluxed dichloromethane (DCM) for 5 h. gave a pink solution. The DCM was carefully removed from the reaction mixture and the residue was cautiously added to ice-cooled dry MeOH. Evaporation of MeOH after 30 min. gave white crystalline (5) with the yield greater than 90%. The alkoxy boronic acid (13) and (14) was prepared by modification of the literature method [15]. Palladium catalysed cross coupling between the compound (5) and boronic acids (13) and (14) gave the corresponding compounds (9) and (10). Reduction of (9) and (10) using $LiBH_4$ or $NaBH_4$ in refluxed THF and MeOH with the ratio of 4:1 gave the compounds (3) and (4).

The polyether was prepared by polycondensation of (3) with tetraethylene glycol dichloride in solution of dimethyl sulphoxide in the presence of potassium hydroxide.

THERMOTROPIC BEHAVIOUR OF THE MONOMERS

Samples of 4-octyloxy-2,6-di(hydroxymethyl)pyridine (2) and 4(4′-octyloxyphenyl)-2,6-di(hydroxymethyl) pyridine (4) melted directly into isotropic liquid at 89.5°C and 115°C respectively when viewed in a hot-stage microscope. 4(4′-Octadecyloxyphenyl)-2,6-di(hydroxymethyl)pyridine (3) melted at 95°C into a smectic A (SA) and an isotropic liquid at 104.8°C. Both textures of SA can be identified on cooling from isotropic by the appearance of battonets which coalesced and gave focal conics as well as homeotropic textures (Plate 1).

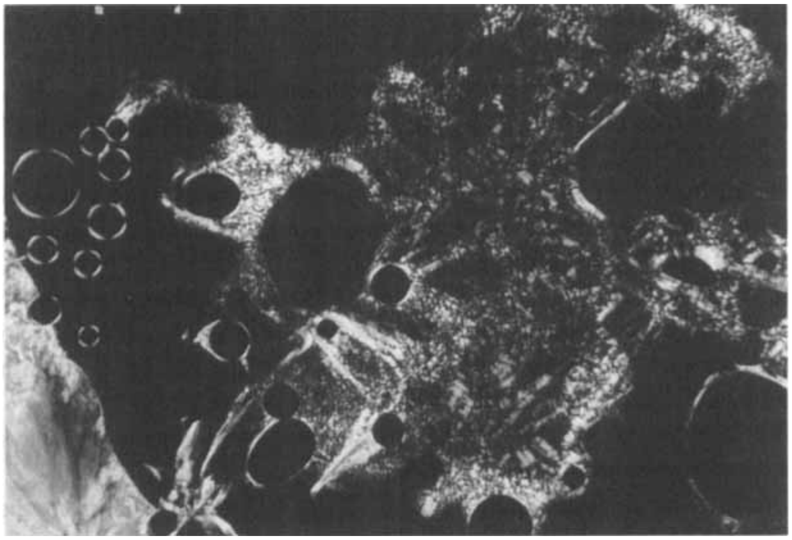


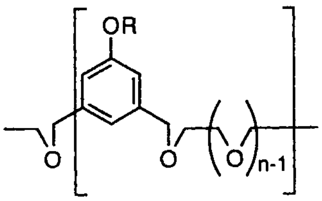
PLATE 1 Micrograph of both homeotropic and focal conic textures of smectic A (SA) under polarising optical microscope at a magnification factor of 100. (See Color Plate I).

LYOTROPIC BEHAVIOUR OF MONOMERS

Compounds (2) and (4) were soluble in water and ethylene glycol and lyotropic liquid crystal properties were not observed. However, compound (3) dissolved slowly in water at 86.7°C and revealed an SA texture. A sample of (3) in ethylene glycol also gave lamellar SA (Plate 2). Two distinct focal conic, homeotropic textures of the SA texture of compound (3) were observed in a contact experiment with ethylene glycol.

STRUCTURE, THERMOTROPIC BEHAVIOUR AND IONIC CONDUCTIVITY OF A REGULAR POLYETHER FROM MONOMER 3 AND ITS COMPLEXES WITH $LiBF_4$ AND $LiClO_4$

We have previously reported [7, 8] the synthesis and characterisation of poly(oligoethoxymethyleneoxy(5-alkoxy-1,3-phenylene)methylene)s where $R = a$ long alkyl chain $—C_{12}H_{25}$ or $—C_{16}H_{33}$ and $n = 5$ or 6. These polymers form 1:1 complexes with Li, Na or Mg salt having univalent anions. The polymer having $R = —C_{16}H_{33}$ and $n = 5$ has been most



Poly[oligoethoxymethyleneoxy(5-alkoxy-1,3-phenylene) methylene

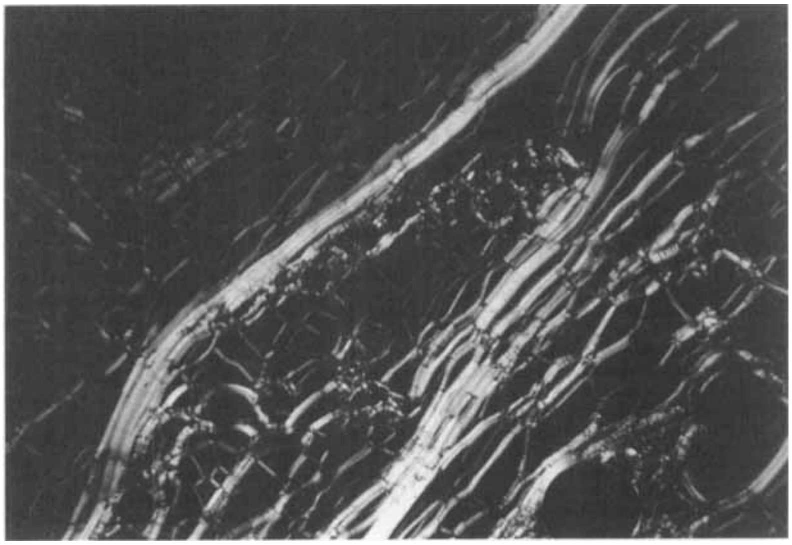
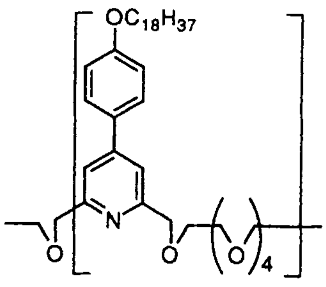


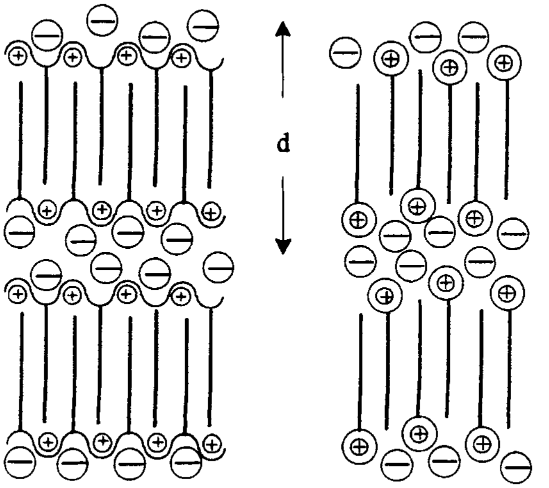
PLATE 2 Micrograph of lamellar texture of compound (3) in ethylene (3) in ethylene glycol under polarizing microscope at a magnification factor of 100. (See Color Plate II).

extensively studied and is coded $C_{16}O_5$. Its equimolar complex with $LiClO_4$ is denoted $C_{16}O_5: LiClO_4$ (1:1). The complexes form smectic polymer liquid crystal systems above the side chain melting point temperatures (*e.g.*, 42°C for $—C_{16}H_{33}$). The coalescence of the side chains creates helical polyether tubes surmounted by the alkyl side chains which interdigitate to create a hexagonal lattice as shown by the schematic structure of Figure 2. The cations occupy the helical tubes and the anions create an interlamellar layer.

The corresponding polyether prepared by the polycondensation of (3) and tetraethylene glycol dichloride, poly[4(4′-octadecyloxyphenyl)-2,6-pyridine dimethyleneoxy tetraethoxymethylene] coded $C_{18}BPyO_5$ is described here.



The Polyether of C18BPyO5



Side view of helices

End view of helices

FIGURE 2 Schematic structure for $C_{16}O_5$ and its equimolar complexes with lithium salts.

DSC traces of $C_{18}BPyO_5$ and its complexes with equimolar proportions of the repeating unit and $LiClO_4$ or $LiBF_4$ are shown in Figure 3. In the pure polymer the side chains melt at *ca.* 45°C increasing to *ca.* 56°C in the complexes $C_{18}BPyO_5:LiClO_4$ (1:1) and $C_{18}BPyO_5:LiBF_4$ (1:1). These are similar melting temperatures to those of the corresponding phenylene system with C_{18} side chains [16]. This suggests a similar interdigitated hexagonal lattice structure for the C_{18} side chains in the complexes with $C_{18}BPyO_5$. The enthalpies of the endotherm, 25–29 kJ (mole repeating unit)$^{-1}$ are similar to those of the $C_{16}O_5$ complexes. Plate 3 shows a focal conic texture of $C_{18}BPyO_5:LiClO_4$ (1:1) in the liquid crystal phase at 105°C. This suggest an SA structure for the polyether complexes.

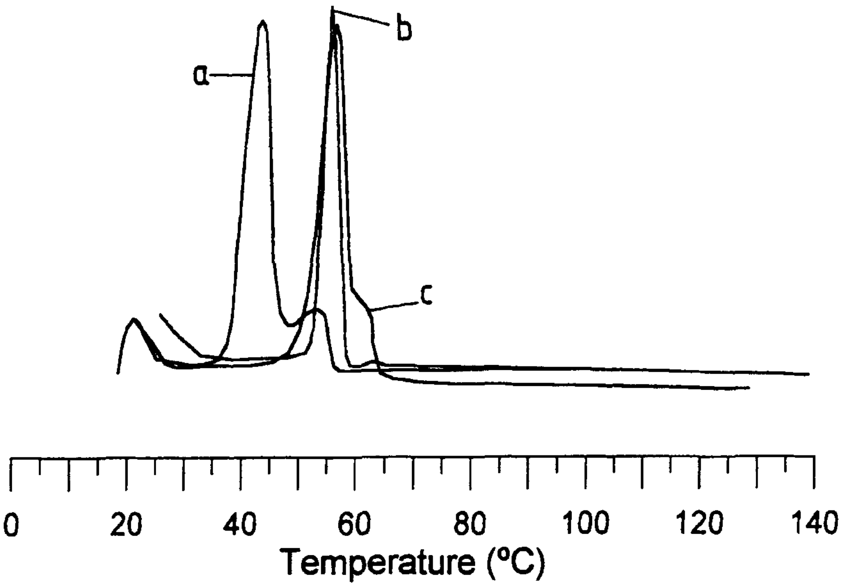


FIGURE 3 DSC traces of $C_{18}BpyO_5$ and its equimolar complexes with $LiBF_4$ and $LiClO_4$ (a) $C_{18}BPyO_5$ $\Delta H = 25.0\,kJ\,mol^{-1}$ (b) $C_{18}BPyO_5 : LiBF_4$ (1:1) $\Delta H = 29.4\,kJ\,mol^{-1}$ (c) $C_{18}BPyO_5$: $LiClO_4$ (1:1) $\Delta H = 24.9\,kJ\,mol^{-1}$.

PLATE 3 Micrograph of focal conic texture of complex C18BPyO5 : $LiClO_4$ under polarising microscope at magnification factor of 100. (See Color Plate III).

X-ray scattering traces for $C_{18}BPyO_5$: $LiBF_4$(1:1) are shown in Figure 4. The traces at $q = 1.4 - 1.5$ show a peak denoting a spacing, D, of 4.15 Å at 20°C but only a broad band at 100°C. The peak corresponds to the hexagonal lattice parameter in the crystalline state of the $—C_{18}H_{37}$ side chains. However, broad wide-angle bands at 56°C (not shown), 100°C and 120°C arise from side chain melting. The sharp peak at low q for temperatures 20°C and 100°C indicate regular periodicities, d, of 56.4 Å and 51.0 Å respectively in the crystalline and liquid crystalline states of the system. The trace recorded at 120°C, however, shows a less intense peak at low q concurring with the absence of birefringence in the hot-stage polarising microscope at this temperature. The $C_{18}BPyO_5$: $LiClO_4$(1:1) complex shown in Plate 3 behaves similarly to the complex with $LiBF_4$

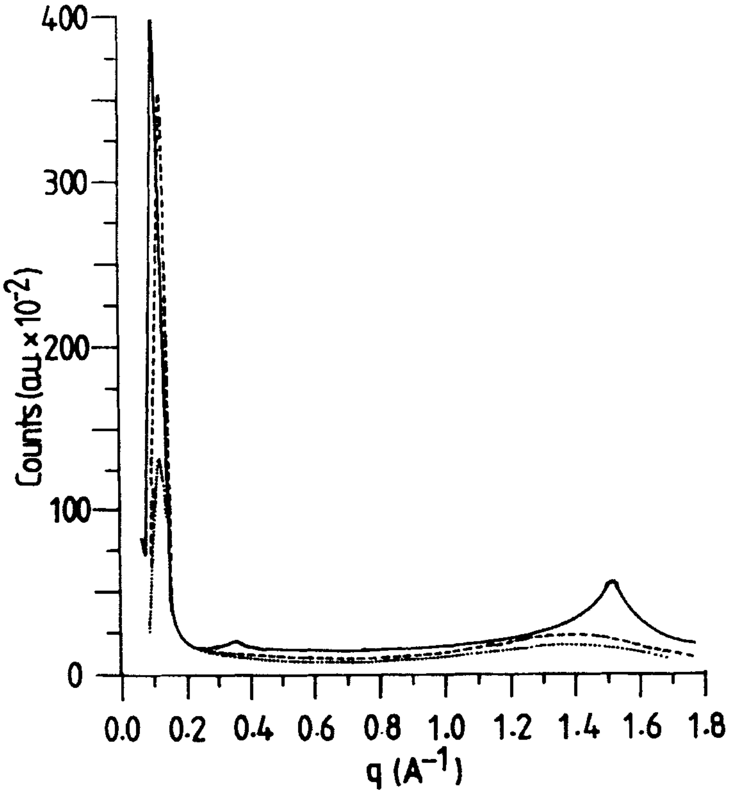


FIGURE 4 X-ray scattering traces for $C_{18}BPyO_5$: $LiBF_4$ (1:1) solid line: 20°C dashed line: 100°C dotted line: 120°C $q = 4\pi\ (\sin\theta)/\lambda$.

becoming non birefringent in the hot-stage polarising microscope at temperatures above *ca.* 112°C.

The pure polymer $C_{18}BPyO_5$ gives an intense sharp peak at low *q* only at temperatures below the endotherm at *ca.* 45°C above which the system is *optically* isotropic in the polarising microscope. The X-ray data for $C_{18}BPyO_5$ and both complexes is summarised in Table I. The long spacings, *d*, at all three temperatures increase as salt is added to the pure polymer and with increase in anion size. In a given system the spacings decrease with increase in temperature. These observations are consistent with expectation from the schematic structure of Figure 2 if lateral expansion of the inter-helical distance within a layer creates more space for accommodation of the anions between the layers.

However, the X-ray trace recorded at 120°C is typical of those observed in the optically isotropic states of all these systems. Whilst there is a loss of order indicated by the less intense peak at low *q*, a long spacing close to that of the liquid crystal phase clearly remains within the system. This presumably corresponds to a morphology of fragmented lamellae or 'micelles'. These structures, also present in the phenylene-based polymers, are under further investigation.

The ionic conductivities of both $C_{18}BPyO_5$: $LiBF_4$ (1:1) and $C_{18}BPyO_5$:-$LiClO_4$ (1:1) are shown as $\log_{10}\sigma$ *versus* 1/T in Figure 5. Also indicated in Figure 5 is the conductivity plot for a sample of $C_{16}O_5$: $LiClO_4$ (1:1) which, like both of the $C_{18}BPyO_5$ complexes presently considered, had not received any thermal treatment or mechanical shearing intended to optimise the organisation of the system. Recent work has shown [16] that the conductivities of $C_{16}O_5$: $LiClO_4$ systems are significantly higher the more ordered the system. This behaviour contrasts with that of conventional polymer electrolytes in which the ion-conductivity pathways are found in the amorphous component of the materials and which become less conductive with crystallinity. There are steep rises in the plots for both $C_{18}BPyO_5$ systems in the temperature region 35–50°C. This is within a similar temperature range to the corresponding rise in the conductivity data

TABLE I X-ray scattering data for $C_{18}BPyO_5$ and its complexes with $LiBF_4$ and $LiClO_4$

Temperature/°C	*dÅ* 20	*d/Å* 59	*d/Å* 100	*D/Å* 20	*Anion size /Å*
$C_{18}BPyO_5$	53.8	diffuse	diffuse	4.18	...
$C_{18}BPyO_5$: $LiBF_4$ (1:1)	56.4	53.4	51.0	4.15	···4.64
$C_{18}BPyO_5$: $LiClO_4$ (1:1)	59.9	56.6	55.9	4.15	···4.72

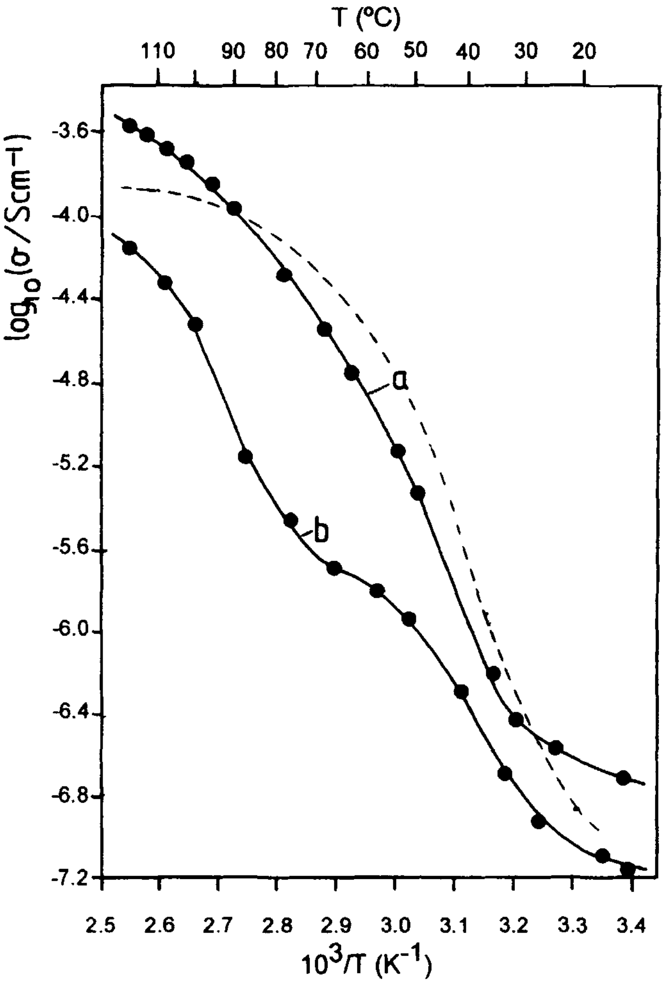


FIGURE 5 Conductivity of $C_{18}BPyO_5$ complexes with $LiBF_4$ and $LiClO_4$ (a) $C_{18}BPyO_5$:$LiBF_4$ (1:1) (b) $C_{18}BPyO_5$:$LiClO_4$ (1:1) dashed line $C_{16}O_5$:$LiClO_4$ (1:1) (no mechanical or thermal treatments have been applied to these systems).

for $C_{16}O_5$: $LiClO_4$ (1:1) which was attributed to increase in the mobility of the ions brought about by the apparently simultaneous melting of the side chains at *ca.* 42°C. In $C_{18}BPyO_5$: $LiBF_4$ (1:1) and $C_{18}BPyO_5$: $LiClO_4$ (1:1) the endotherm peaks are at a higher temperature (*ca.* 56°C) but they occur *above* the initial rise in the conductivity. Further investigations of ion mobility in the region of side chain melting are required. In $C_{16}O_5$: $LiClO_4$ systems (including those with a third long alkyl component incorporated in the side chain layer) a second transition in the conductivity plots has been identified in the region of 60°C which has been tentatively attributed to an 'ion-loosening' process involving a degree of cation-helix dissociation and/or cation-anion dissociation [16]. The presence of the nitrogen atoms along the helical cavity of $C_{18}BPyO_5$ might be expected to increase the strength of the helix interaction with the lithium ion. The presence of a second transition in the conductivity data at a somewhat higher temperature (*ca.* 90°C) in $C_{18}BPyO_5 : LiClo_4$ (1:1) may therefore tentatively be attributed to a process analogous to that occurring at the lower temperature in $C_{16}O_5 : LiCO_4$ (1:1).

The level of conductivity of the $C_{18}BPyO_5$ and $C_{16}O_5$ based systems are apparently similar in the samples described here, none of which have received any treatment to optimise their morphological organisation. In common with the $C_{16}O_5$ based systems, the conductivities of the $C_{18}BPyO_5$ complexes show no indication of declining in the optically isotropic temperature region. A 'micellar structure' in this region such as described above, would provide a pseudo 3-dimensional network of conducting surfaces over which ions may readily migrate [16]. This should render less critical the desirability for the 2-dimensional conductive pathways to be oriented normal to the electrodes. Investigations on the influence of organisation on conductivity in these systems are underway.

EXPERIMENTAL SECTION

Melting points of monomeric compounds were determined on a Linkam hot-stage and temperatures were controlled by a Linkam temperature controller PR600, and are uncorrected. IR spectra were obtained on a Perkin-Elmer FT-IR Spectrometer (Paragon 1000) and positions of absorbtion bands are reported in cm^{-1}. ^{1}Hnmr were recorded on a Bruker AC250 instrument and chemical shifts are reported in ppm down field from TMS. High resolution Mass spectra were determined on a VG Prospec Mass spectrometer. Small-to wide-angle X-ray diffraction was carried out with a MAR Research Image Plate area detector using graphite-monochromatised CuKa radiation ($\lambda = 1,54\,\text{Å}$). Differential scanning calorimetry was performed using a Perkin-Elmer DSC7 series Thermal Analysis System. Polarised light microscopy was carried out in association with a Lincam PR600 heated stage. Complex impedance measurement on the complexes were performed using a Solartron 1286 electrochemical interface and 1250 frequency response analyser operating over the frequency range 5 Hz–64 kHz. The measurements were performed with predried samples coated with sputtered gold electrodes under vacuum and sandwiched between copper electrodes using a silicon rubber spacer with a fine vent giving the vacuum access to the sample. Prior to measurement over a range of temperatures the samples were held at a temperature of approximately 110°C under vacuum for several hours in the conductivity measuring cell. The conductivity was monitored throughout this period and when it became sensibly constant the sample was slowly cooled in order to develop the texture and the conductivity data was recorded on the heating cycle.

Dimethyl 4-hydroxypyridine-2,6-dicarboxylate (6)

To a suspension of chelidamic acid (1 g; 5.5 m mol.) in excess freshly distilled thionyl chloride (20 ml) was added one or two drops of DMF. The mixture was stirred at room temperature overnight which during this period gave a homogeneous solution. The excess of thionyl chloride was removed under reduced pressure and the solid residue was cooled in an ice-bath and then an excess amount of dry methanol was carefully added. The methanol was removed and the solid was crystallised from water giving dimethyl 4-hydroxypyridine-2,6-dicarboxylate (6) as needles; yield 91%;. mp 177.2°C; ^{1}Hn.m.r. ($CDCl_3$) 4.01 (6H, s, 2 CO_2CH_3) and 7.48 (2H, s, Py); IR. (KBr), 3437, 3138, 1723.8 and 1605 cm^{-1}.

Dimethyl 4-octyloxypyridine-2,6-dicarboxylate (7)

A mixture of dimethyl 4-hydroxypyridine-2,6-dicarboxylate (6) (1.55 g; 8 m mol.), l-bromooctane (1.6g; 8.2 m mol.) and silver (I) oxide (2 g; 8.5 m mol.) in toluene (40 ml) was heated under reflux in a dean-stark apparatus overnight. The solid was filtered off and the filtrate was evaporated to dryness giving off-white crystals. Recrystallisation from ethanol gave dimethyl 4-octyloxypyridine-2,6-dicarboxylate (7), 2.1 g; yield 85%; mp 71°C; ^{1}Hn.m.r. ($CDCl_3$) 0.83 (3H, t, J6.9, CH_3), 1.25 (8H, m, $CH_3C_4H_8$), 1.4 (2H, qn, J5.0, $CH_2CH_2CH_2O$), 1.87 (2H, qn, J7.0, CH_2 CH_2O), 3.93 (6H, s, 2 CO_2Me), 4.08 (2H, t, J7.5, CH_2O), 7.74 (2H, s, Py); IR. (KBr) 2954.8, 2919.6, 2871, 1718 and 1599 cm^{-1}; HRMS Calc. for $C_{17}H_{25}NO_5$ 323.1733, Found: 323.1736.

6(Hydroxymethyl)-4-octyloxypyridine-2-carboxylic acid (8)

To a solution of dimethyl 4-octyloxypyridine-2,6-dicarboxylate (7) (1.19 g; 3.7 m mol.) in dry ethanol (20 ml) was added in portions $NaBH_4$ (0.31 g; 8.0 m mol). The mixture was stirred at room temperature for 2 h. The excess of $NaBH_4$ was destroyed by addition of water. Evaporation of the solvent under reduced pressure gave 6(hydroxymethyl)-4-octyloxypyridine-2-carboxylic acid (8), which was purified by column chromatography on silica gel using methanol as eluent. Evaporation of the solvent followed by recrystallisation of the residue from methanol gave the pure compound (8), 0.88 g; yield 85%, mp 50°C; ^{1}Hn.m.r. ($CDCl_3$), 0.86 (3H, t, J6.9, CH_3), 1.3 (8H, m, $CH_3C_4H_8$), 1.41(2H, qn, j5.2, $CH_2CH_2CH_2O$), 1.86 (2H, qn, J6.25, CH_2CH_2O), 4.24 (2H, t, J7.8, CH_2O), 4.98 (2H, s, CH_2OH), 7.12 (1H, d, J3.1, Py) and 7.74 (1H, d, J3.1, Py); IR. (KBr) 3377, 2928, 2856, 1724 and 1600 cm^{-1}; HRMS Calc. for $C_{15}H_{23}NO_4$ 281.2549, Found: 281.1627.

4-Octyloxy-2,6-di(hydroxymethyl)pyridine (2)

Reduction of the compounds (7) and (8) to the corresponding 4-octyloxy-2,6-di(hydroxymethyl)pyridine (2) was achieved by using borane dimethyl sulphide complex (BMS) [14].

A sample of the diester (7) was also successfully reduced to the dimethanol (2) by the following procedure using $NaBH_4$ or $LiBH_4$. To a solution of the diester (7) (1 g; 3.1 m mol.) in dry THF (20 ml) was added in one portion $NaBH_4$(0.12 g; 3.1 m mol) or $LiBH_4$(0.07 g; 3.1 m mol). Dry methanol (5 ml) to this mixture under reflux and under an atmosphere of nitrogen was then slowly added. The heating was continued for 2 h. Water was carefully added to the cooled mixture to destroy the excess of the reducing reagent. Evaporation of the solvent to dryness gave a solid which was purified by column chromatography on silica gel using methanol as eluent. Evaporation of the solvent followed by recrystallisation from methanol gave 4-octyloxy-2,6-di(hydroxymethyl)pyridine (2) as colourless crystals, 0.74 g; yield 90%, mp 89.3°C, ^{1}Hn.m.r. ($CDCl_3$) 0.9 (3H, t, J7.5, CH_3), 1.32 (8H, m, $CH_3C_4H_8$), 1.44 (2H, qn, J5.0, $CH_2CH_2CH_2O$), 1.79 (2H, qn, J6.3, CH_2CH_2O), 4.0 (2H, t, J7.5, CH_2O), 4.65 (4H, s, CH_2OH), 6.68 (2H, s, Py) IR. (KBr) 3333, 2918, 2850 and 1597.8 cm^{-1}; HRMS Calc. for $C_{15}H_{25}NO_3$, 267.1834, Found: 267.1829.

Dimethyl 4-chloropyridine-2,6-dicarboxylate (5)

To a suspension of chelidamic acid (1) (10 g; 50 m mol.) in dichloromethane (DCM) (150 ml) was added in one portion phosphorus pentachloride (56 g; 270 m mol.). The mixture was heated under reflux for 5 h. The DCM was removed under reduced pressure and the solid residue was cooled in an ice-bath. An excess volume of dry methanol (*ca.* 100 ml) was added and stirred for 30 min. Evaporation of some methanol followed by cooling of the solution gave the dimethyl 4-chloropyridine-2,6-dicarboxylate (5) as off-white crystals, 11.4 g; yield 91%; mp 152.3°C; ^{1}Hn.m.r. ($CDCl_3$) 4.05 (6H, s, 2 CO_2CH_3) and 8.27 (2H, s, Py); IR.(KBr) 3090.9, 3000, 2953, 1720 and 1575 cm^{-1}; HRMS Calc. for $C_9H_8NO_4Cl$, 229.0142, Found: 229.0133.

1-Bromo-4-octadecyloxybenzene (11)

A mixture of 4-bromophenol (17.3 g; 100 m mol), *n*-octadecylbromide (36.6 g; 110 m mol) and K_2CO_3 (27.6 g; 200 m mol) in acetone (150 ml) was heated under reflux with fast stirring for 20 h. The cooled mixture was filtered and the filtrate was then evaporated to dryness. The solid residue was recrystallised from ethanol giving 1-bromo-4-octadecyloxybenzene (11), 34.0; yield 80%, mp 58.6°C; ^{1}Hn.m.r. ($CDCl_3$) 0.86 (3H, t, J7.8, CH_3), 1.23 (28H, m, $CH_3C_{14}H_{28}$), 1.41 (2H, qn, J5.2, $CH_2CH_2CH_2O$), 1.75 (2H, qn, J6.1, CH_2CH_2O), 3.89 (2H, t, J6.25, CH_2O), 6.79 (2H, d, J9.4, AA'BB', C_6H_4), 7.35 (2H, d, J9.4, AA'BB', C_6H_4).

The same procedure was used for the preparation of 1-**bromo-4-octyloxybenzene** (12)- 28.5 g of bromophenol gave 24.23 g of 1-bromo-4-octyloxybenzene (12); yield 85%; b.p 62°C/0.1 torr; ^{1}Hn.m.r. ($CDCl_3$) 0.83 (3H, t, J7.8, CH_3), 1.25 (8H, m, $CH_3C_4H_8$), 1.37 (2H, qn, J6.0, CH_2CH_2 CH_2O), 1.68 (2H, qn, J6.25, CH_2CH_2O), 3.83 (2H, t, J6.25, CH_2O), 6.66 (2H, d, J9.8, AA'BB', C_4H_4) and 7.25 (2H, d, J9.8, AA'BB', C_6H_4).

4-Octadecyloxyphenylboronic acid (13)

A solution of butyl lithium (3 ml, 5 mmol; 1.6 M) in *n*-hexane in a three necked flask (250 ml) under an atmosphere of argon was cooled to −78°C. The 1-bromo-4-octadecyloxybenzene (2 g; 5 mmol) in THF (20 ml) was then added dropwise at such a rate as to keep the temperature at −78°C to −75°C. After 1 h the progress of the reaction was monitored by t.l.c. which showed only the starting material. At this stage another portion of butyl lithium (3 ml, 5 mmol; 1.6 M) was added dropwise. Stirring continued for a further 1 h and then the reaction once again monitored by t.l.c. which showed that more than 90% of starting materials had been consumed. Stirring was continued for another 1 h and then an excess of a solution of triisopropylborate (6 ml) in THF (10 ml) was slowly introduced into the reaction mixture at such a rate that the temperature did not rise above −70°C. The reaction was stirred for 2 h at −78°C and then allowed to warm to room temperature overnight. After cooling to 0°C, 120 ml of 10% hydrochloric acid was added, stirred for 30 min, organic layer was separated and the aqueous layer extracted into ether (2 × 50 ml). The combined organic extracts were washed with water (2 × 50 ml), brine (50 ml) and dried over magnesium sulphate. The desiccant was removed by filtration and the filtrate evaporated under reduced pressure giving a solid which was washed several times with petroleum ether (40 – 60) to give 4-octadecyloxyphenylboronic acid (13), 1.7 g; yield 95%; mp 58.6°C; ^{1}Hn.m.r. ($CDCl_3$), 0.87 (3H, t, J6.25, CH_3), 1.25 (28H, m, $CH_3C_{14}H_{28}$), 1.49 (2H, qn, J5.0, CH_2CH_2 CH_2O), 1.81 (2H, qn, J6.25, CH_2CH_2O), 4.05 (2H, t, J7.8, CH_2O), 6.97 (2H, d, J9.38, AA'BB', C_6H_4), 8.15 (2H, d, J9.38, AA'BB', C_6H_4); HRMS Calc. for $C_{24}H_{43}BO_3$ 390.4195, Found: 390.3287.

The same procedure was used for the preparation of **4-octyloxyphenylboronic acid** (14)- 13.5 g of 1-bromo-4-octyloxybenzene yielded 10.67 g, 90% boronic acid (14); mp 105.2°C; ^{1}Hn.m.r. ($CDCl_3$), 0.89 (3H, t, J6.25, CH_3), 1.38 (8H, m, $CH_3C_4H_8$), 1.48 (2H, qn, J5.0, $CH_2CH_2CH_2O$), 1.73 (2H, qn, J6.25, CH_2CH_2O), 4.05 (2H, t, J7.8, CH_2O), 7.0 (2H, d, J8.13, AA'BB', C_6H_4). 8.15 (2H, d, J8.13, AA'BB', C_6H_4); HRMS Calc. for $C_{14}H_{23}BO_3$ 249.1777, Found: 249.17767.

Dimethyl 4(4′-octadecyloxyphenyl)pyridine-2,6-dicarboxylate (9)

A mixture of dimethyl 4-chloropyridine-2,6-dicarboxylate (5) (2.15 g; 10 mmol), 4-octadecyloxy boronic acid (13) (4.0 g; 10 m mol), triethylamine (4.2 ml, 30 mmol), palladium(II) diacetate (0.063 g; 0.3 mmol), and triphenylphosphine (0.16 g; 0.62 mmol), in DMF (40 ml), was heated under reflux and an atmosphere of argon for 4 h. The solvent was evaporated under reduced pressure and the residue purified by column chromatography on silica gel using a mixture of DCM : ethylacetate (8:2) as eluent. The fluorescent band under UV. was collected. Evaporation of the solvent gave an off-white solid which was crystallised with ethanol to give dimethyl 4(4′-octadecyloxyphenyl)pyridine-2,6-dicarboxylate (9) as colourless crystals, 3.2 g; yield 60%; mp 147.7°C; ^{1}Hn.m.r. ($CDCl_3$), 0.89 (3H, t, J7.8, CH_3), 1.30 (28H, m, $CH_3C_{14}H_{28}$), 1.49 (2H, qn, J6.5, $CH_2CH_2CH_2O$), 1.82 (2H, qn, J9.38, CH_2CH_2O), 4.02 (2H, t, J7.5, CH_2O), 4.05 (6H, s, 2 CO_2CH_3), 7.02 (2H, d, J9.38,AA'BB', C_6H_4), 7.73 (2H, d, J9.38, AA'BB', C_6H_4), and 8.50 (2H, s, Py); IR.(KBr) 2910, 2825, 1720, 1600 cm^{-1}; HRMS Calc. for $C_{33}H_{49}NO_5$ 539.3611, Found: 539.3619.

The same procedure was used for the synthesis of the **dimethyl 4(4′-octyloxyphenyl)pyridine-2,6-dicarboxylate** (10)-(2 g; 8.7 mmol) of the chloro compound (5) and (2.64 g, 10 mmol) of the boronic acid (14) gave 2.44 g; yield 70% of the dimethyl 4(4-octyloxyphenyl)pyridine-2,6-dicarboxylate (10) mp. 93.8°C, ^{1}Hn.m.r. ($CDCl_3$), 0.90 (3H, t, J7.8, CH_3), 1.30 (8H, m, CH_3 C_4H_8), 1.50 (2H, qn, J6.5, $CH_2CH_2CH_2O$), 1.82 (2H, qn, J7.5, CH_2CH_2O), 4.02 (2H, t, J7.5, CH_2O), 4.05 (6H, s, $2CO_2CH_3$), 7.04 (2H, d, J9.38, AA'BB', C_6H_4), 7.75 (2H, d, J9.38, AA'BB', C_6H_4), 8.50 (2H, s, Py); IR.(KBr) 3002, 2953, 1747 cm^{-1}; HRMS Calc. for $C_{23}H_{29}NO_5$ 399.2046, Found: 399.2050.

4(4'-Octadecyloxyphenyl(-2,6-dimethanolpyridine(3)- and 4(4'-Octyloxyphenyl)-2,6-dimethanolpyridine (4)

The same procedure to reduce the compound (7) was used for the reduction of the compounds (3) and (4). To reduce (2.0 g; 3.7 mmol) of the diester (9), (0.4 g; 10.5 mmol) $NaBH_4$ was used and gave 1.25 g of the compound (3); yield 70%; mp 95°C; ^{1}Hn.m.r. ($CDCl_3$), 0.88 (3H, t, J9.38, CH_3), 1.31 (28H, m, $CH_3C_{14}H_{28}$), 1.51 (2H, qn, J6.2, $CH_2CH_2CH_2O$), 1.80 (2H, qn, J7.5, CH_2 CH_2O), 3.01–3.65 (2H, br, 2 OH), 4.00 (2H, t, J9.38, CH_2O), 4.84 (4H, s, $2\,CH_2OH$), 6.97 (2H, d, J9.38, AA'BB', C_6H_4). 7.41 (2H, s, Py) and 7.61 (2H, d, J9.38, AA'BB', C_6H_4); IR(KBr) 3185, 2960, 2845, 1610 cm^{-1}; HRMS Calc. for $C_{31}H_{49}NO_3$ 483.3712, Found: 483.3703. To reduce (1.18 g; 3 mmol) of the diester (10), (0.25 g; 6.6 mmol) $NaBH_4$ was used and gave 0.81 g of the compound (4); yield 80%, m.p. 115°C; ^{1}Hn.m.r. ($CDCl_3$), 0.9 (3H, t, J9.4, CH_3), 1.34 (8H, m, $CH_3C_4H_8$), 1.50 (2H, m, $CH_2CH_2CH_2O$), 1.86 (2H, qn, J6.2, CH_2CH_2O), 3.00 (2H, br, 2 OH), 4.00 (2H, t, J9.37, CH_2O), 4.80 (4H, s, $2\,CH_2OH$), 6.97 (2H, dd, J9.37, AA'BB', C_6H_4), 7.38 (2H, s, Py), 7.60 (2H, dd, J9.37, C_6H_4); IR (KBr) 3355, 3131, 2924, 2856, 1608 cm^{-1}; HRMS Calc. for $C_{21}H_{29}NO_3$ 343.2147, Found: 3432145.

Poly[(4-octadecyloxy-4'-phenyl)-2,6-pyridine dimethyleneoxytetraethoxymethylene] ($C_{18}BPyO_5$)

The polyether $C_{18}BPyO_5$ was prepared by the reaction of (3) with tetraethyleneglycol dichloride in KOH-dimethylsulphoxide at 90°C for 7 days under an atmosphere of nitrogen. The polymer was precipitated by adding water to the solution. After further washing in water unreacted monomer was removed by washing in MeOH.

The molecular weight of the polymer $C_{18}BPyO_5$ was estimated by gel permeation chromatography using chloroform as solvent and sharp fractions of polystyrene (Polymer Laboratories) as calibration standards;

the GPC peak maxima corresponding to approximately 5000 Daltons but the distribution was broad.

The complexes were prepared by dissolving the appropriate proportions of the salt and polymer repeating unit in acetone. After removal of the solvent the mixture was heated for several hours at 60°C to ensure uniform dissolution of the anhydrous salt in the polymer and then stored in dessicator.

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