Liquid-crystalline Terpyridines

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Supplementary Information

Experimental.

Nuclear magnetic resonance spectra were recorded on a Jeol JNM-EX 270 FT NMR system at 270 MHz for ^{1}H NMR and 68 MHz for ^{13}C NMR. Microanalyses were performed at Department of Chemistry, University of Newcastle upon Tyne using a Carlo Erba 1108 Elemental Analyzer controlled with CE Eager 200 software. Phase transition temperatures were determined using a Mettler Toledo DSC-822^e differential scanning calorimeter with a heating and cooling rate of 10 K min^{-1} (the apparatus was calibrated with indium for which T_m = 156.6 ^{o}C). Texture observations were made using Olympus BX50 polarizing microscope in conjunction with a Linkam LTS 350 hot stage and Linkam TMS 92 control unit. Literature procedures were followed for the preparation of **1**, **2** and **5**.[1]

General procedure for the demethylation reaction.

5,5''-Di(4-hydroxyphenyl)-2,2':6',2''-terpyridine

The mixture of anhydrous pyridine hydrochloride[2] (35.0 g) and 5,5''-di(4-methoxyphenyl)-2,2':6',2''-terpyridine **2** (2.5 g, 5.62 mmol) was stirred at 200 °C for 5 h. The hot solution was quenched carefully with water (50 cm^3). The resulting yellow precipitate was filtered off, washed thoroughly with water, hot acetone, and dried under vacuum to yield a yellow solid (2 g, 87 %). δ_H (DMSO-d_6) = 6.98 (AA'XX', *J* = 8.2 Hz, 2H, aromatic), 7.77 (AA'XX', *J* = 8.2 Hz, 2H, aromatic), 8.26 (t, 1H, *J* = 8.0 Hz, $H^{4'}$), 8.50 (dd, J = 8.2, 1.9 Hz, 2H, H^4 and $H^{4''}$), 8.58 (d, *J* = 8.0 Hz, 2H, $H^{3'}$ and $H^{5'}$), 8.85 (d, *J* = 8.2 Hz, 2H, H^3 and $H^{3''}$), 9.05 (d, *J* = 1.9 Hz, 2H, H^6 and $H^{6''}$)

General procedure for preparation of 5,5''-di(4-alkoxyphenyl)-2,2':6',2''-terpyridines, 3

5,5''-Di(4-octyloxyphenyl)-2,2':6',2''-terpyridine, 3-8.

A mixture of 5,5''-di(4-hydroxyphenyl)-2,2':6',2''-terpyridine (104 mg, 0.25 mmol), potassium carbonate (207 mg, 1.5 mmol), 1-bromooctane (100 mg, 0.51 mmol) and DMF (10 cm^3) was stirred at 80 °C for 12 hours. Water was added and the precipitated solid separated by filtration. The filter cake was washed with water, ethanol and crystallized from DMF to give the desired compound. Yield 135 mg, 84%. δ_H ($CDCl_3$) = 0.89 (**m**, 6H, $C\underline{H}_3(CH_2)_5CH_2CH_2$-O), 1.2-1.5 (m, 10H, $CH_3(C\underline{H}_2)_5CH_2CH_2$-O), 1.82 (m, 4H, $CH_3(CH_2)_5C\underline{H}_2CH_2$-O), 4.02 (t, *J* = 6.7 Hz, 4H, $CH_3(CH_2)_5CH_2C\underline{H}_2$-O), 7.00 (AA'XX', 4H, *J* = 8.2 Hz, Ar), 7.51 (AA'XX', 4H, *J* = 8.2 Hz ,Ar), 7.95 (t, *J* = 7.8 Hz, 1H, pyr $H^{4'}$), 8.01 (dd, J = 8.2, 1.8 Hz, 2H, H^4 and $H^{4''}$), 8.42 (d, *J* = 8.0 Hz, 2H, $H^{3'}$ and $H^{5'}$), 8.63 (d, *J* = 8.2 Hz, 2H, H^3 and $H^{3''}$), 8.90 (d, *J* = 1.8 Hz, 2H, H^6 and $H^{6''}$).

Table S1 Analytical data and melting points for compounds **3.**

	Calculated (Found)/%			
compound	**C**	**H**	**N**	**transitions**
3-1	known[1]			Cr 283 **I**
3-6	79.97 (79.78)	7.40 (7.51)	7.17 (7.24)	Cr 232 **I**
3-8	80.46 (80.32)	8.01 (8.08)	6.55 (6.57)	Cr 225 **I**
3-10	80.88 (80.75)	8.52 (8.53)	6.02 (6.03)	Cr 217 **I**
3-12	81.23 (80.79)	8.96 (8.94)	5.57 (5.67)	Cr 198 **I**
3-14	81.53 (81.57)	9.33 (9.54)	5.19 (5.29)	Cr 197 **I**
3-16	81.80 (81.50)	9.66 (9.90)	4.85 (4.94)	Cr 183 **I**
3-18	82.03 (82.06)	9.94 (9.95)	4.56 (4.67)	Cr 184 **I**

General procedure for the preparation of 5,5''-bis[4-(4-alkyloxybenzoyloxy)phenyl]-2,2':6',2''-terpyridines, 4.

5,5''-bis[4-(4-octyloxybenzoyloxy)phenyl]-2,2':6',2''-terpyridine, 4-8.

N,N'-Diisopropylcarbodiimide (0.185 cm^3, 151 mg, 1.2 mmol) was added to a stirring mixture of 4-octyloxybenzoic acid (165 mg, 0.66 mmol), 5,5''-di(4-hydroxyphenyl)-2,2':6',2''-terpyridine **2** (125 mg, 0.3 mmol), 4-(*N,N*-dimethylamino)pyridine (37 mg, 0.3 mmol), and dichloromethane (25 cm^3). The reaction mixture was stirred at room temperature for 2 d. The solvent and all other volatile reaction components were removed by rotary evaporation under reduce pressure and the residue was crystallised twice from DMF to yield the title compound as a colorless crystalline solid (185 mg, 77%). δ_H ($CDCl_3$): 0.88 (t, *J* = 6.6 Hz, 6H, $C\underline{H}_3(CH_2)_5CH_2CH_2$-O), 1.2-1.5 (m, 10H, $CH_3(C\underline{H}_2)_5CH_2CH_2$-O), 1.82 (m, 4H, $CH_3(CH_2)_5C\underline{H}_2CH_2$-O), 4.05 (t, *J* = 6.7 Hz, 4H, $CH_3(CH_2)_5CH_2C\underline{H}_2$-O), 6.96 (AA'XX', *J* = 8.2 Hz, 4H, Ar), 7.31 (AA'XX', *J* = 8.2 Hz, 4H, Ar), 7.72 (AA'XX', *J* = 8.2 Hz 4H, Ar), 8.00 (t, *J* = 7.8 Hz, 1H, pyr $H^{4'}$), 8.01 (dd, J = 8.2, 1.8 Hz, 2H, H^4 and $H^{4''}$), 8.19 (AA'XX', *J* = 8.2 Hz, 4H, Ar), 8.50 (d, *J* = 8.0 Hz, 2H, $H^{3'}$ and $H^{5'}$), 8.72 (d, *J* = 8.2 Hz, 2H, H^3 and $H^{3''}$), 9.05 (d, *J* = 1.8 Hz, 2H, H^6 and $H^{6''}$)

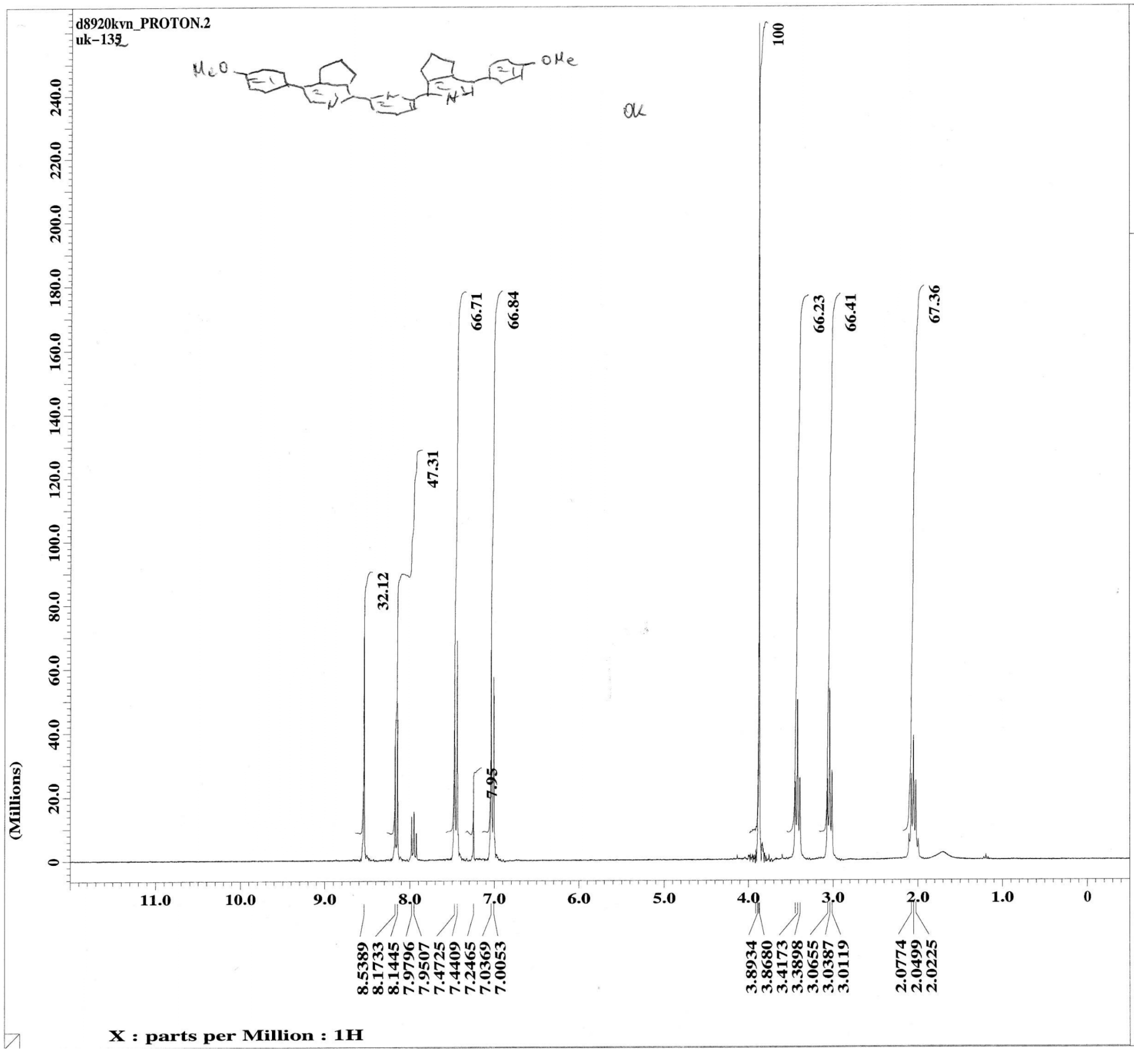
The same experimental procedure were followed for the preparation of **6**.

Table S2 Analytical data for compounds **4** and **6**

	Calculated (Found)/%		
Compound	**C**	**H**	**N**
4-8	77.61 (77.40)	6.74 (6.83)	4.76 (4.81)
4-10	78.09 (78.00)	7.20 (7.29)	4.48 (4.57)
4-12	78.52 (78.59)	7.60 (7.78)	4.23 (4.26)
4-14	78.90 (78.95)	7.96 (8.18)	4.00 (4.09)
4-16	79.24 (79.30)	8.29 (8.16)	3.80 (3.90)
6-4	77.72 (77.56)	6.05 (6.12)	4.94 (4.95)
6-8	78.64 (78.54)	7.02 (7.12)	4.37 (4.38)
6-12	79.37 (79.24)	7.79 (7.74)	3.91 (3.95)
6-16	79.96 (79.99)	8.41 (8.55)	3.54 (3.56)

Compound **5**

Melting point: 254-255 °C. ^{1}H and ^{13}C NMR spectra below:



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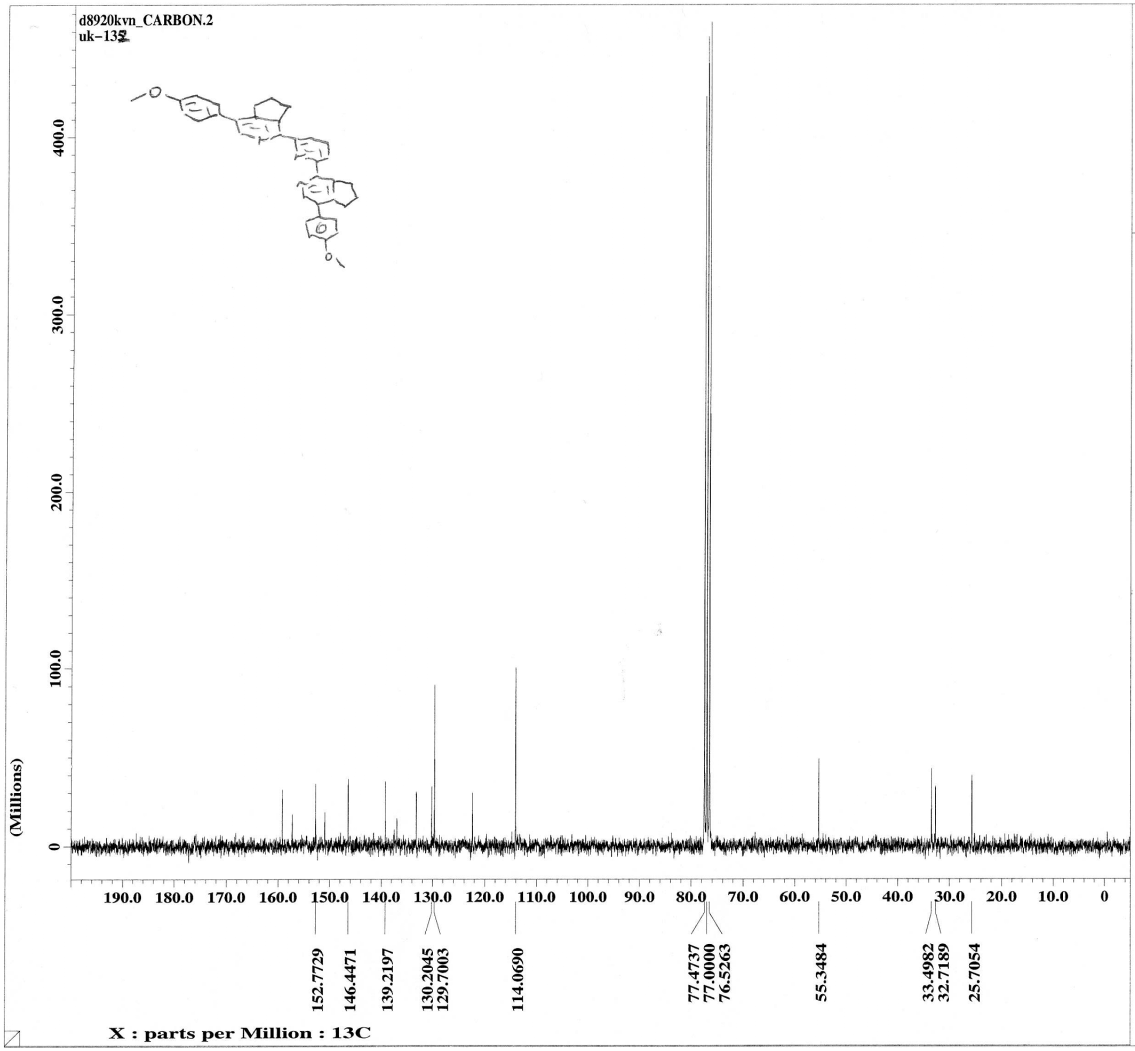

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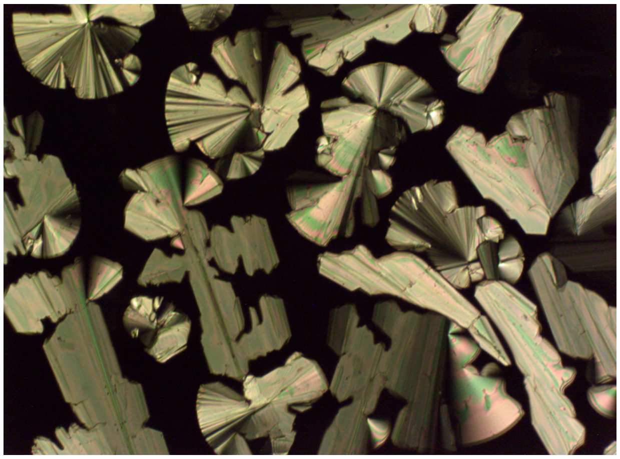
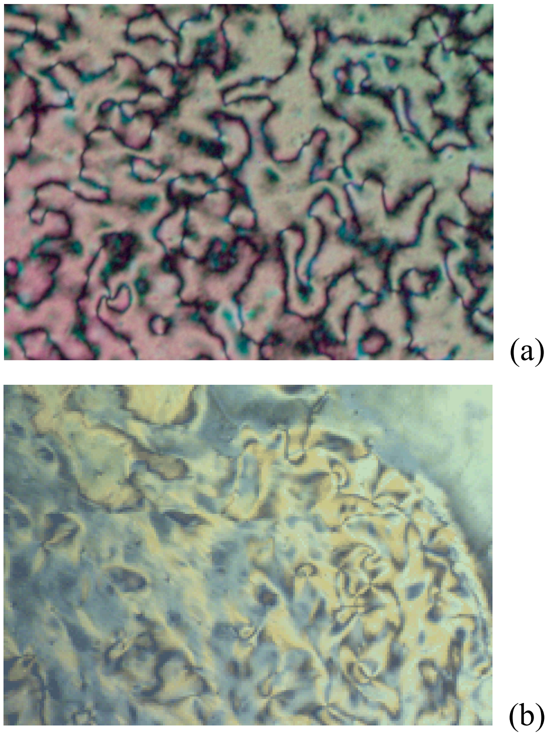


Fig. S1 Optical texture of **4**-8 on cooling from isotropic liquid at 259 °C.



(a)

(b)

Fig. S2 Optical textures of (a) **6**-8 in the nematic phase at 170 °C on cooling, (b) **6**-16 in the SmC phase at 145 °C on cooling.

Crystallography

Compound **5** crystallized as colorless, monoclinic plates in the C2/c space group (Fig. S3). The molecule has C_2 rotational symmetry about the N_1–C_3 axis with the asymmetric unit comprising half the molecule. The aromatic rings are twisted out of coplanarity with the angle between the central pyridine and the pyridine portion of the 6,7-dihydro-5H-[2]pyrindine ring being 23.61(6)°. The terminal 4-methoxyphenyl ring is further twisted by 49.49(5)°. The methoxy group lies in the plane of the phenyl ring allowing full conjugation. The cyclopentyl ring of the pyrindine is orientated away from the pyridine ring presumably to reduce steric crowding. The cyclopentyl ring of the pyridine exhibited disorder in the position of C_{10}. This was modelled in two positions which the relative occupancy of which was allowed to refine and found to be ~ 3:1. C_9 and C_{11} were each modelled as two coincident atoms to allow use of a riding model for their hydrogens; the position of the latter being dependent upon the position of C_{10}.

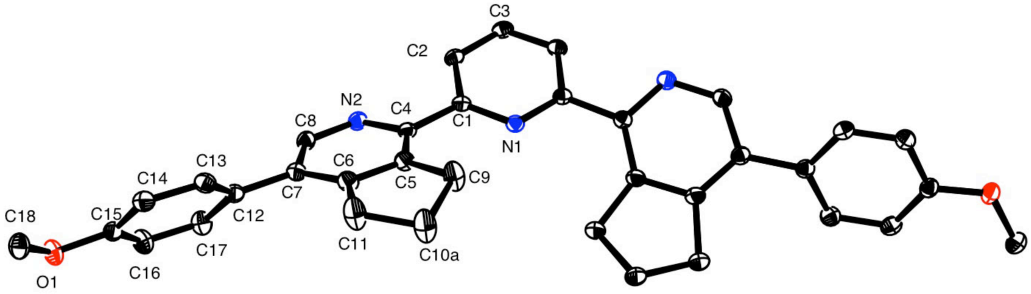


Fig. S3 Numbered ORTEP of **5**

References

1 V.N. Kozhevnikov, D.N. Kozhevnikov, O.V. Shabunina, V.L. Rusinov, O.N. Chupakhin, *Tetrahedron Lett.,* **2005**, *46*, 1521.

2 Pyridinium hydrochloride is a classical reagent for cleavage of aryl methyl ethers at 200-220 °C avoiding strongly acidic or basic conditions. V. Prey, *Chem. Ber.,* **1942**, *75B*, 350.