Liquid-crystalline terpyridines†

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5,5″-Disubstitution of the terpyridine core leads to the first inherently liquid-crystalline terpyridines. Mesophases characteristic of bent-core and calamitic systems may be obtained depending on the core structure employed.

2,2′:6′,2″-Terpyridines (terpy) are ubiquitous in coordination chemistry as ligands in families of metal complexes with real or potential applications.[1] The idea of designing and synthesising liquid-crystalline terpys and then combining their excellent physical properties with the benefits of self organisation, is very attractive and attempts have been made to obtain such materials. Certain compounds containing the terpy fragment are known to be mesomorphic, mainly after complexation to metal centres. For example, 4′-alkylterpyridines lead to lyotropic Ru^{II} and Rh^{III} complexes,[2] while extended 6,6″-terpyridines formed intriguing motifs when coordinated to Cu^{I}.[3] As free ligands, however, terpyridines have not been found to be useful in this regard. To best of our knowledge the only example of mesomorphic terpy is reported by Ziessel *et al.* where the terpy is attached in the 4′-position to a hexacatenar diamide, which is clearly responsible for the mesomorphism as the free ligand[4] and in metal complexes.[5]

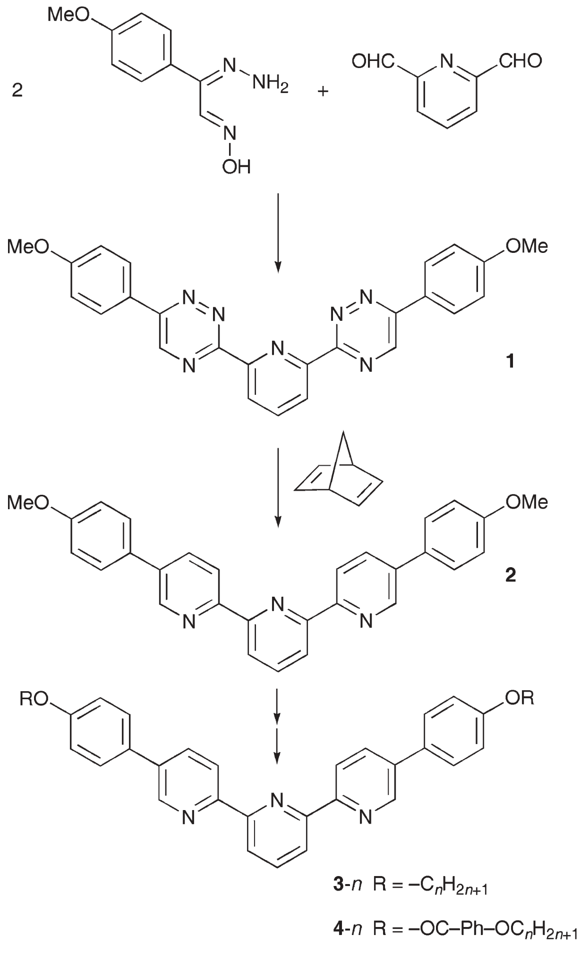
The literature shows that, in the design of mesogenic terpyridines, it is the 4′-position or the 6- and 6″-positions that have been functionalised. However, in considering how terpy-based liquid crystals might be realised, it is important to recall its bent nature, which suggests that any mesogens that do result will have mesomorphism characteristic of bent-core systems.[6] Bent-core liquid crystals tend to form lamellar or columnar phases and are of particular interest as they can show spontaneous symmetry breaking and are implicated as possible biaxial nematic materials.[7] Thus, the 5,5″-disubstituted pattern is the most attractive, yet save for one report[8] of terpy functionalised with cholesteryl groups at the 5,5″-positions (which was not mesomorphic), there are no other examples in the literature. This was also noted by Piguet and co-workers when they initially described mesomorphism in structurally analogous bis(benzimidazolyl)pyridines.[9]

Previously, some of us have accessed 5,5″-difunctionalised terpyridines using established and flexible chemistry in which a hydrazone is reacted with an aldehyde to give a 1,2,4-triazine, which is then reacted with norbornadiene to give the product (Scheme 1).[10] Using an anisyl-based hydrazone (**1**) leads to compound **2** whose methyl group is readily removed to allow for further substitution.

Mesomorphism in bent-core mesogens is a delicate function of the number of rings, the central bend angle and the functional groups that link the various rings.[6] The minimum number of rings required for mesomorphism in such systems appears to be five and so the first target compounds were **3**-*n* ($8 \leqslant n \leqslant 16$). None of these derivatives was mesomorphic and all melted directly (ESI†) to the isotropic liquid between 232 °C ($n = 6$) to 184 °C ($n = 18$).

Unlike compounds **3**, esters **4**-*n* were liquid crystalline and mesomorphism was investigated using polarised optical microscopy and DSC; thermal data are collected in the Table. It seems that the octyloxy homologue (**4**-8) is not mesomorphic and the texture formed on cooling, while reminiscent of a Col_r (B_1) phase, showed very sharp edges (ESI†). Preliminary X-ray analysis[12] also showed several peaks in the wide-angle region.

The longer-chain homologues, however, showed a different, but common behaviour. Thus, heating the materials led to a transition



Scheme 1 Synthesis of the mesomorphic terpyridines.

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Table 1 Mesomorphism of the new compounds

Compound	Transition	T/°C	ΔH/kJ mol^{-1}
4-8	Cr–I	285	35.7
4-10	Cr–Cr′	199	5.4
	Cr′–B_2	252	8.9
	B_2–I	256	18.2
4-12	Cr–Cr′	192	6.2
	Cr′–B_2	245	10.4
	B_2–I	253	18.9
4-14	Cr–Cr′	186	6.5
	Cr′–B_2	242	9.1
	B_2–I	249	17.8
4-16	Cr–Cr′	182	5.9
	Cr′–B_2	238	9.2
	B_2–I	244	17.7
6-4	Cr–N	190	56.5
	N–I	256	2.4
6-8	Cr–N	163	42.4
	N–I	204	1.8
	(SmC–N)	(93)	(−4.2)
6-12	Cr–N	139	27.7
	N–I	175	1.8
	(SmC–N)	(111)	(−2.8)
6-16	Cr–SmC	143	29.5
	SmC–N	150	2.4
	N–I	161	1.4

to an ordered phase with a wide temperature range, after which a more fluid phase was seen followed by the isotropic liquid. Slow cooling from isotropic gave a texture that grew dendritically and then coalesced gradually and was characteristic of a B_2 mesophase. The chiral nature of the phase[11] was evident using polarised optical microscopy where domains of opposite handedness were observed when the polarisers were uncrossed (Fig. 1). The high temperatures have so far prevented us carrying out a switching study to determine the exact symmetry of the B_2 phase. Cooling from the B_2 phase gave rise to a texture that appeared to have defects consistent with a columnar phase yet, as with compound **4**-8, the edges were rather sharp. Despite the relatively low enthalpy of transition, this phase is assigned as crystalline. Note that X-ray has so far been unable to 'catch' the B_2 phase in these compounds due to its narrow range of existence.[12]

The synthetic route employed in realising these terpyridines allows the central five-ring unit to be varied with a good degree of flexibility. In order to widen the range of materials available for study, the dieneophile 1-morpholinocyclopentene[13] was employed which, in reaction with **1**, led to annelated terpyridines **5** in 70% yield (Scheme 2). Demethylation of **5** followed by esterification using 4-alkoxybenzoic acids led to the new liquid crystals, **6**-*n*.

Thus, in total contrast to **4**-*n*, these annelated terpyridines, **6**-*n*, showed nematic and smectic C phases, phases characteristic of rod-like materials. This result was checked carefully and microscopy showed an absence of chiral domains in the N phase and both broken-fan and schlieren textures in the SmC phase, with the classic striated texture at the transition (Fig. 3). Further, the nematic phase of **6**-8 was found to be continuously miscible with that of 4-pentyl-4″-cyanoterphenyl at 190 °C. An X-ray single crystal structure[14] of **5** helped in understanding this change in mesomorphic nature. Thus, the two pentalene rings occupy the central space (Fig. 2) and, in this way, begin to transform the shape the core from bent to rod-like, preventing a chevron-like arrangement in a layered phase. In addition, the angle that the two peripheral oxygen atoms make with the centroid of the central pyridine ring is 135°, which is approaching the upper limit for behaviour characteristic of bent-core mesogens that do not possess substantial dipoles. Subsequent addition of the two ester groups is, on the basis of previous studies,[16] predicted to open out the central angle further. The combination of these three factors contribute to the observation of nematic and smectic mesophases.

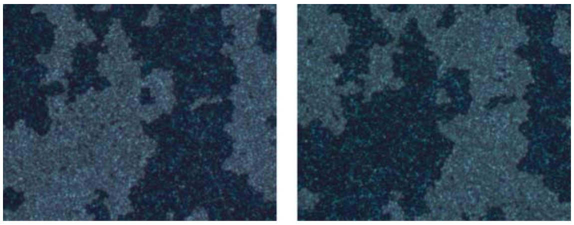
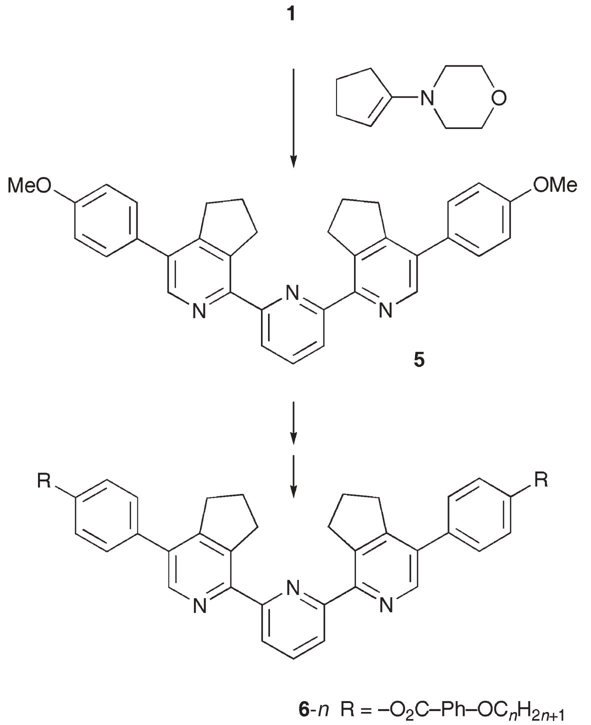


Fig. 1 Optical texture of the B_2 phase of **4**-12 at 250 °C on cooling. Polarisers are uncrossed as indicated on the the figures.



Scheme 2 Synthesis of the annelated terpyridines **6**-*n*.

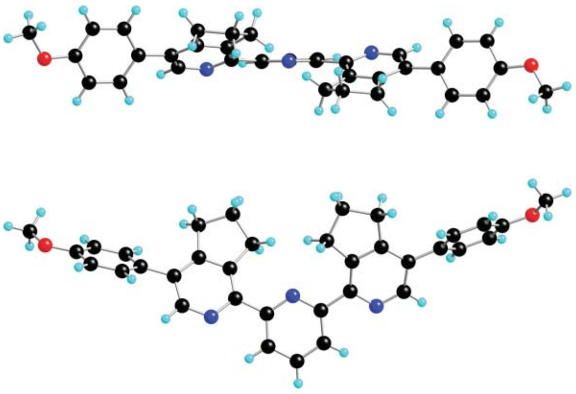


Fig. 2 Two views of the molecular structure of **5**.

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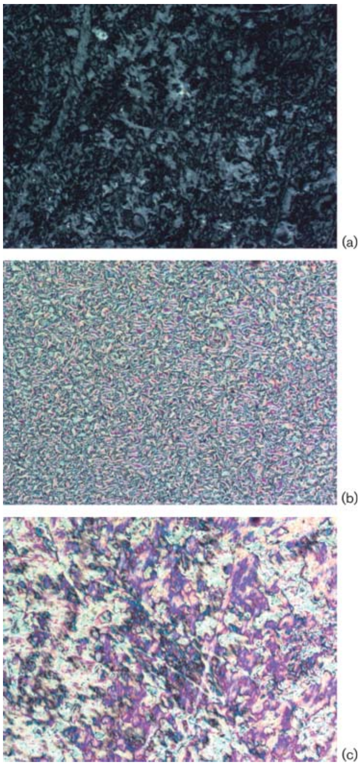

Fig. 3 Photomicrographs, taken over <0.5 °C, of the N–SmC transition of **6**-16: (a) nematic, (b) transition, (c) SmC phase.

The extra steric demands of the pentalene ring also caused noticeable destabilisation of the crystal phases and mesophases. For example, **6**-12 melts to nematic at 139 °C and clears at 175 °C, while **4**-12 melts to the B_2 phase at 245 °C and clears at 253 °C.

These new mesogens open up a wide and exciting prospect for functional metal complexes, particularly when coupling their photophysical properties with liquid-crystalline assembly.

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14 Summary crystal data for **5**: $C_{35}H_{31}N_3O_2$; formula weight M = 525.63 g mol^{-1}; T = 110(2) K; MoK_α radiation λ = 0.71073 Å; size 0.27 × 0.11 × 0.08 mm^3; monoclinic; space group *C2/c*; a = 16.1072(12) Å; b = 15.3466(12) Å; c = 11.0231(8) Å; $\alpha = \gamma = 90°$, β = 98.079(2)°; V = 2697.8(4) Å^3; Z = 4; D_c = 1.294 Mg m^{-3}; μ = 0.081 mm^{-1}; $F000$ = 1112; Crystal size; $1.84 < \theta < 28.36°$; 13663 reflections collected = 3362 unique (R_{int} = 0.0352); $-21 \leqslant h \leqslant 21$, $-20 \leqslant k \leqslant 20$, $-14 \leqslant l \leqslant 14$; Completeness to theta = 28.36° 99.5%; absorption correction – none; Solved using SHELXS-97 and refined with SHELXL-97[15] with full-matrix least squares on F^2 193 parameters; GoF = 1.052, $R_i[I > 2\sigma(I_0)]$ = 0.0456; $wR_2[I > 2\sigma(I_0)]$ = 0.1221; R_1(all reflections) = 0.0600; wR_2(all reflections) = 0.1311; $0.398 > \Delta\rho > -0.221$ e. Å^{-3}. CCDC 647485. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709730a.
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