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Molecular recognition-induced liquid crystals from complementary diaminopyridine and flavin dyads

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Complementary diaminopyridine–flavin dyads that provide liquid crystalline systems have been synthesised. The mesophases possess well-defined molecular architectures, thermal stability and wide ranges. Furthermore, chiral centres have been introduced to explore the role chirality plays on the end morphology. The introduction of stereo-centres into these systems offers effective control over mesophase morphology and generates well-defined columnar liquid crystals.

Keywords: molecular self-assembly; liquid crystal; supramolecule

Introduction

Molecular self-assembly provides an effective approach to assemble building blocks via non-covalent interactions (*1*). The attributes inherent in the self-assembly process such as directionality, specificity and tunability provide new directions for the development of liquid crystals (LCs). For example, the ability to engage components precisely at the molecular level offers routes for diverse molecular shapes including classical rod and disc-like topologies as well as other interesting structures (*2*). These LC materials build upon the integration of non-covalent interactions, exhibiting useful physical properties that make them attractive candidates in nanotechnology and materials science (*3*).

Non-covalent interactions such as hydrogen bonding (*4*), π–π stacking (*5*) and metal coordination (*6*) have been used to provide supramolecular LC systems. These processes can effectively create discotic LCs featuring disc-like topology (*7*). Hydrogen-bonded dyads (*7a–b*, *i*), triads (*7c*), and tetrads (*7d–g*) decorated with long aliphatic side chains can self-organise into a hexagonal columnar phase through the stacking of the discs. Furthermore, use of chiral mesogens allows for the regulation of helical ordering of LCs (*8*) providing access to materials with attractive physical properties. For example, chiral smectic and columnar phases have been developed extensively due to their attractive ferroelectric properties (*9*). The organisation of molecules in this way facilitates pragmatic applications such as materials with large non-linear optical effects (*10*). In addition, chiral columnar phases are particularly important to provide synthetic templates for the development of robust polymeric networks with helical channels and pores (*11*). Ordered porous materials fabricated from columnar phases have led to the development of highly selective catalysis (*12*), gas separation (*13*) and imprinting materials (*14*).

The complementary diaminopyridine (DAP) and flavin dyads offer high fidelity of molecular recognition and the ability to generate ordered aggregates, providing an ideal platform to create hydrogen-bonded LC systems (*15*). Recently, we have synthesised appropriately functionalised DAP–flavin systems that have the propensity to self-assemble, via hydrogen-bonding interactions, to create discrete helically stacked systems in hydrocarbon solvents (*15*). Herein, we demonstrate: (a) LC formation through DAP–flavin self-assembly; (b) the role molecular recognition has on determining the nature of the mesophases; and (c) the formation of DAP–flavin LC complexes whereby either both, one or neither of the complementary units possess a chiral centre, thereby allowing us to investigate, in a systematic manner, the specific role chiral centres play in the resulting mesophase architecture.

The DAP derivatives and complementary flavin derivatives used in this study are shown in Figure 1. *N*-Methyl flavin was prepared to create a non-hydrogen-bonding control. Mixtures (1:1) of complementary DAP and flavin recognition dyads **1**–**6** with achiral and chiral side chains were prepared in hexane. This methodology allowed us to produce systems whereby neither (**1** and **2**), both (**3** and **6**) or only one of the complementary dyads (**4** and **5**) were functionalised with a chiral centre, thereby allowing us to investigate the importance of increasing the chiral gradient has on the mesophase architecture. Moreover, systems **4** and **5** allow us to investigate the implications of attaching the chiral centre to either the DAP or flavin moieties, while

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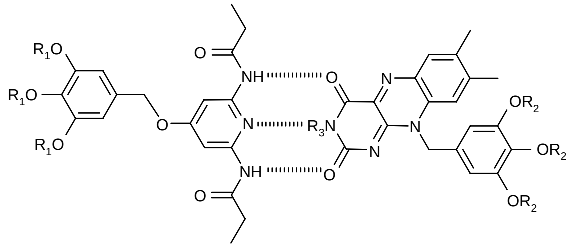


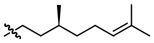
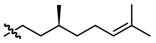
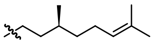
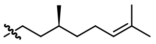
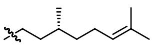
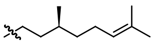
Dyad	R_1	R_2	R_3
1	$C_{12}H_{25}$	$C_{12}H_{25}$	H
2	$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
3			H
4		$C_{12}H_{25}$	H
5	$C_{12}H_{25}$		H
6			H

Figure 1. Structure of DAP–flavin systems.

systems **3** and **6** provide an insight into the role homo- and heterochirality play, respectively.

Results and discussion

Molecular recognition studies

The hydrogen-bonding properties of dyad **1** were characterised using ^{1}H NMR and IR. The downfield shifts of the imide peak of the flavin-functionalised unit in $CDCl_3$ were measured upon the addition of the complementary DAP derivative, and gave rise to an association constant (K_a) of 1050 M^{-1}. In films, the NH stretching frequencies of DAP and flavin shift from 3320 to 3280 cm^{-1}, and from 3160 to 3220 cm^{-1}, respectively, and are indicative of the hydrogen bonding for the 1:1 mixture of DAP and flavin in the bulk state.

Mesophase behaviour

To investigate LC properties of DAP–flavin dyads, differential scanning calorimetry (DSC) and polarised optical microscopy (POM), solid-phase circular dichroism (CD) and X-ray diffraction (XRD) studies were performed. DSC analyses showed that transitions from mesophases to isotropic liquids were in the range of 129–185°C. The transition enthalpies ranged from 14.2 to 17.4 kJ/mol, and these values are intermediate between those found in other hydrogen-bonding LCs (1–37 kJ/mol) (Table 1) (*16*). The DAP–flavin systems with chiral centres showed supercooling for the isotropic–mesophase transition under DSC conditions due to their space-demanding structures (*16a*).

Table 1. Thermal properties of DAP–flavin systems (**1**–**6**).

Dyad	Transition temperature (°C)
1	M-185 (17)-I
2	M-129 (10)-I
3	M-177 (17)-I
4	M-185 (14)-I
5	M-173 (14)-I
6	M-174 (14)-I

Notes: I, isotropic state; M, mesophase. The values were determined by DSC (heating and cooling rate; 10°C/min). Parentheses indicate enthalpy changes in kJ/mol.

POM studies proved to be very valuable in probing the role molecular recognition as well as chirality plays in mesophase formation. No mesophase were observed for solutions of any of the non-complexed DAP or flavin derivatives as evidenced by the lack of shearable birefringent textures (e.g. the constituents of complex **1** (DAP (Cr-65-I), flavin (Cr-205-I)). However, with the exception of dyad **2**, the DAP–flavin dyads were all highly birefringent, showing shearable mesophases at room temperature. This behaviour indicates a wide mesophase range, which is in contrast to most other molecular recognition LCs. As expected, a variety of highly birefringent and shearable textures were visualised upon cooling from the isotropic melt (Figure 2). Observed conical fan textures for dyad **1** (Figure 2(a)) and rectilinear textures for dyads **3**, **4** and **6** (Figure 2 (b), (c) and (e)) are typical for hexagonal phases (*16a–c*, *17*). The dyad **1** was able to evolve highly birefringent domains even after cooling from the clearing point. In sharp contrast to the rest, non-specific control dyad **2** failed to develop birefringent domains, demonstrating that molecular recognition significantly improves thermal stability of the mesophase region.

X-ray diffraction studies

Given the breadth and diversity of LC textures obtained for the DAP–flavin systems, XRD experiments were conducted. The XRD profile of **1** showed sharp reflection peaks characteristic of hexagonal columnar packing corresponding to the (100) and (110) reflections with a intercolumnar spacing of 3.0 nm (Figure 3). However, the control **2** did not show any sharp reflections (Figure 3(a)). This apparent distinction demonstrates that molecular recognition induces the formation of well-defined hexagonal columnar phases. Broad peaks in the wide-angle area correspond to disordered arrangements of dodecyl side chains.

Comparison across the chiral gradient in these systems clearly shows that introduction of chirality promotes the formation of well-defined hexagonal columnar mesophases.

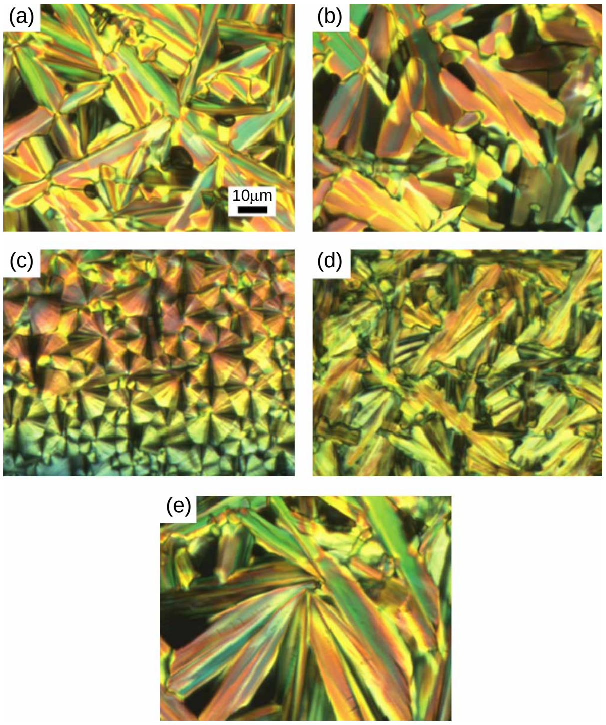


Figure 2. Representative POM images of dyads (a) **1**, (b) **3**, (c) **4**, (d) **5** and (e) **6**.

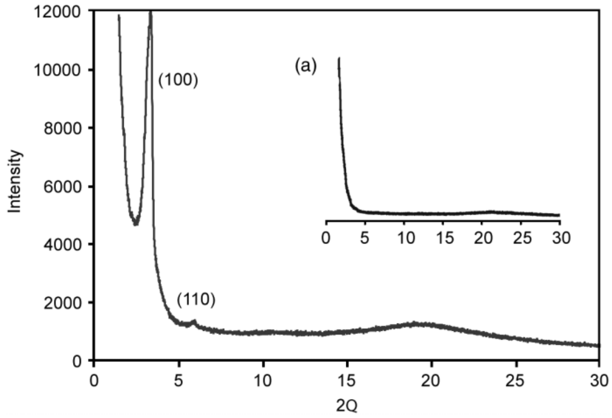


Figure 3. X-ray diffractogram for **1**; inset (a) shows XRD for **2**.

System **1** showed sharp reflection peaks in the wide-angle area characteristic of well-defined hexagonal columnar packing. In sharp contrast, dyads **4** and **5** showed only two sharp peaks corresponding to the (100) and (110) reflections. XRD data for dyad **6** provided supportive evidence for propensity of chirality to promote well-defined hexagonal columnars, as very sharp reflection peaks were observed in the wide-angle area for system **6** that were almost identical to those found in system **3**. These results essentially demonstrate that the dyads with chiral centres on both DAP and flavin units form more ordered LC columnar phases.

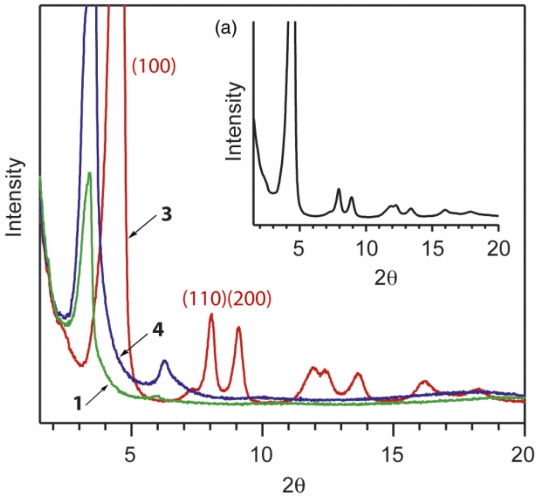


Figure 4. X-ray diffractograms for **2**, **3** and **4**. Inset (a) shows XRD diffractogram for **6**.

In addition to the number of chiral centres introduced, our experiments have shown that the location of the chiral centres was also critical in influencing the DAP–flavin LC morphology. As dyad **5** has a chiral centre on the flavin whereas dyad **4** has the chiral unit on the DAP derivative, we have used these derivatives to demonstrate the role chiral centre location has on the mesophase morphology. XRD data revealed that system **4** exhibited a hexagonal columnar phase (Figure 4, blue line), whereas derivative **5** showed a substantially different mesophase morphology. As shown in Figure 5, the observed wave positions of the sharp reflection peaks for dyad **5** were of the ratio of 1:2:3:4:5, providing evidence for the smectic phase formation. This contrast in morphology clearly shows the important role the location of chirality plays in DAP–flavin LC.

Given that the DAP–flavin dyads can generate well-defined hexagonal columnar mesophases, we next focused

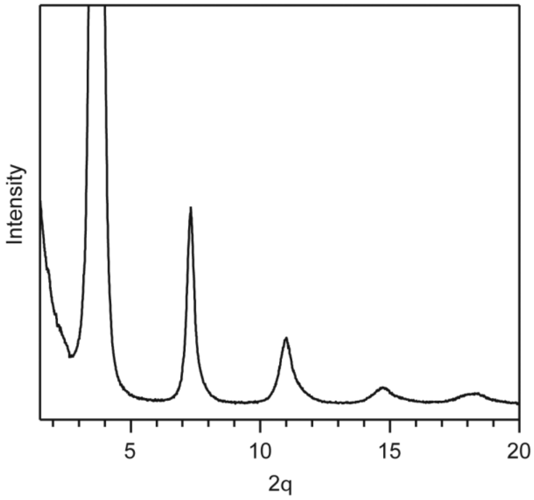


Figure 5. X-ray diffractogram for **5**.

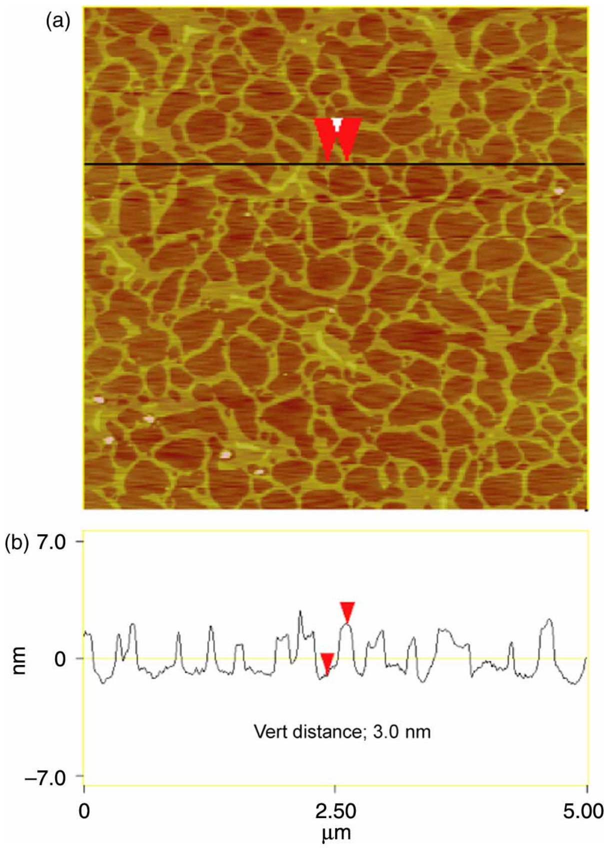


Figure 6. AFM image of dyad **1** on a silica substrate for a 100 µM solution; (a) height image and (b) corresponding cross-section profile.

our attention onto the surface morphology of material deposited onto surfaces using atomic force microscopy (AFM). A silica surface dipped in a dilute solution of dyad **1** showed an extremely interlinked network (Figure 6). The interlinked network provided multilayered structures at high concentrations (*9*). Cross-section profiles revealed a uniform thickness of 2.8–3.1 nm, showing excellent agreement with XRD results (Figure 4(a)). The columnar spacing and uniform thickness observed in XRD and AFM are essentially consistent with a dyad diameter predicted using molecular modelling studies (*8a*).

Circular dichroism

As molecular organisation is significantly dependent on the number and location of chiral centres in liquid crystalline DAP–flavin systems, solid-phase CD measurements were undertaken to further study these systems (*18*). Figure 7 displays CD spectra of dyads **3**, **4**, **5** and **6** on quartz plates. Dyads **3** and **6** showed strong negative Cotton effects, providing evidence for the formation of chiral LC phases. In clear contrast, no CD response was observed for systems **4** and **5**. These results clearly suggest that formation of chiral LC phases requires chiral centres on both recognition elements of the DAP–flavin dyads. Interestingly, the observed CD profiles for homochiral dyad **3** and heterochiral dyad **6** are essentially identical to each other, implying that significant segregation in the LC state is possibly overwhelming the delicate role chirality plays in solution.

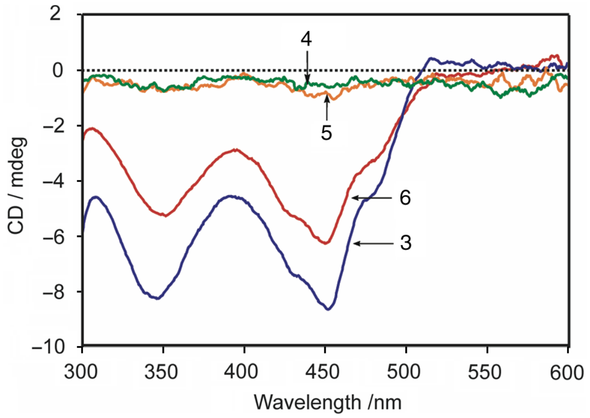


Figure 7. CD spectra of thin films of **3**, **4**, plates **5** and **6** on quartz.

Conclusions

In summary, we have demonstrated the formation of hydrogen-bonded LC, from complementary flavin–DAP recognition dyads. We have shown that specific molecular recognition plays a key role in providing thermal stability and a well-defined nature of the hexagonal columnar LCs. Furthermore, we have demonstrated that chirality significantly effects the liquid crystalline behaviour of DAP–flavin LC. The results clearly show that the introduction of chirality into both recognition elements of the hydrogen-bonded dyad is essential in enhancing and tailoring LC phase formation. We are currently extending these systems to probe whether tuneable systems can be developed, and our results will be reported in due course.

Experimental

Materials

All reagents were purchased from Aldrich (Milwaukee, WI, USA) and used without further purification. All DAP and flavin compounds used in this report were synthesised according to our previous report (*15*).

Instrumentation

DSC measurements were performed on TA instrument Q-1000 (scan rate 10°C/min) with hermetic aluminium pans. A polarised optical microscope Olympus BX-51 was used for visual observation. X-ray diffractograms were recorded on a PANalytical X'pert PRO XRD system with a flat stage. Tapping mode AFM was performed at ambient conditions with a Dimension 3100, Nanoscope III from Digital Instruments Corporation, Ahmedabad, India. Imaging was done at a scan rate of 1 Hz. IR spectra were recorded on MIDAC Corporation M1200-SP3 on KBr plates.

Preparation of dyads

A 1:1 mixture of DAP and flavin derivatives in *n*-hexanes was refluxed for 1 h, and evaporated under vacuum to yield a mesomorphic solid.

Polarised optical micrograph

All samples were placed on glass slides, and prepared through solvent saturation with hexanes for 3 days. The films were subsequently dried at room temperature for 3 days, and annealed at 150°C for 12 h.

XRD experiments

All samples were placed on glass slides, and subjected to solvent saturation with hexanes for 3 days in a desiccator. The solvent was allowed to evaporate slowly at room temperature.

Atomic force micrograph

Cleaned silica substrates were dipped in a solution of dyad **1** at variable concentrations (10 μM–1 mM).

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