Mesogenic dipyrrins—building blocks for the fabrication of fluorescent and metal-containing materials†

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A new class of mesogenic dipyrrins is reported and their use in the fabrication of fluorescent and metal-containing self assembling materials is demonstrated.

Since the early 1990's there has been a consistent and growing interest in the chemistry of 4,6-dipyrrins (2-(2*H*-pyrrol-2-ylidenemethyl)pyrroles) as bi-dentate ligands for the formation of metal complexes.[1] Most commonly used for this purpose are the 5-aryl-4,6-dipyrrins derived by oxidation of the readily available 5-aryl-dipyrromethanes.[2] Manipulation of the aryl group and/or metal ion has yielded many interesting complexes with differing metal : ligand ratios and geometries. Examples include 2 : 1 ligand : metal complexes of Zn(II), Cu(II), and Ni(II), which show either distorted tetrahedral or distorted square planar geometries;[3] distorted octahedral complexes with 3 : 1 ligand : metal ratios for Fe(III),[4] and 2 : 2 zinc(II) complexes of 5-(2-pyridyl)dipyrrin with tetrahedral geometry.[5] The ability of dipyrrins to form complexes has also been exploited in the formation of supramolecular complexes, such as zinc containing porphyrin–dipyrrin assemblies with applications in light harvesting.[6]

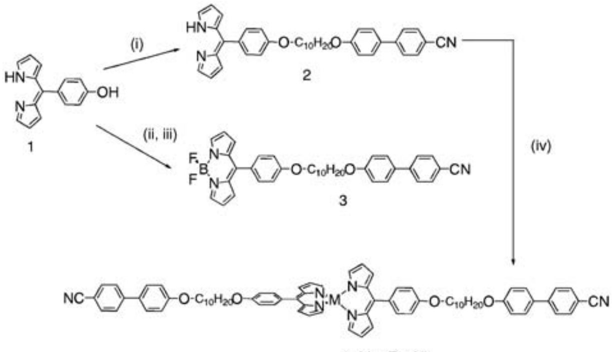
In parallel with the interest in metal complexes of dipyrrins there has been an explosive growth in research involving boron complexes of dipyrrins. Unusually, complexes formed from dipyrrins and boron trifluoride give a 1 :1 ligand to boron complex, often referred to by the generic term BODIPY.[7] The most noteworthy property of BODIPY is its intense fluorescence in the green region of the visible spectrum; and this has been the driving force behind efforts to exploit BODIPYs as markers for biological macromolecules,[8] and as components of sensors for nitric oxide,[9] potassium,[10] zinc,[11] and in light harvesting arrays.[12]

Recently, two reports of materials with gelation and liquid crystalline properties have appeared.[13] In these articles mesogenic units were attached to the BODIPY core by acetylenic or amide bonds, and liquid crystalline behaviour of the resulting conjugates was reported to exhibit columnar mesophases. In parallel with this work we have been studying the effects of attachment of mesogenic cyanobiphenyl units and report here the formation of liquid crystalline BODIPY containing materials. The corresponding cyanobiphenyl substituted dipyrrin, without boron, can also be used in the formation of Zn(II) and Ni(II) complexes. Interestingly, the dipyrrin, BODIPY and Ni(II) complex all display nematic behaviour, while the Zn(II) complex shows no liquid crystalline properties, an effect which is ascribed to differences in packing associated with complex geometries.

The core building block used in these studies comprised a 5-(4-hydroxyphenyl)dipyrrin (**1**) linked to a cyanobiphenyl unit *via* a ten carbon aliphatic chain. Synthesis of this material was achieved by treatment of **1**, derived from (4-hydroxyphenyl)dipyrromethane[2] by DDQ oxidation,[3a] with 1.1 eq. of 4′-(10-bromodecyloxy)biphenyl-4-carbonitrile in the presence of potassium carbonate and potassium iodide in butanone, yielding the 4′-(10-(4-dipyrrin-phenoxy)decyloxy)biphenyl-4-carbonitrile (**2**) in 49% yield (Scheme 1).

4′-(10-(4-(4,4-Difluoro-4-bora-3a,4a-diazaindacen-8-yl)phenoxy)decyloxy)biphenyl-4-carbonitrile (**3**) was derived from the boron complex of **1** using the same coupling procedure (Scheme 1). Metal complexes were derived from **2** by heating in dichloromethane in the presence of 20 eq. of either zinc or nickel acetate, followed by purification by size exclusion chromatography, to give the Zn(II) (**4Zn**) and Ni(II) (**4Ni**) complexes in 90% yield (Scheme 1).

Initial studies of compounds **2**, **3**, **4Zn** and **4Ni** by differential scanning calorimetry (DSC) revealed liquid crystalline behaviour for **2**, **3** and **4Ni**, while **4Zn** exhibited only a crystalline to isotropic liquid transition at 139 °C. Compounds **2** and **3** showed monotropic mesophases at 41 °C and 47 °C on



Scheme 1 *Reagents and conditions:* (i) 1.1 eq. 4′-(10-bromodecyloxy)biphenyl-4-carbonitrile, K_2CO_3, KI, butanone, rt; (ii) 15 eq. triethylamine, $BF_3{\cdot}OEt_2$, toluene, 70 °C; (iii) 1.1 eq. 4′-(10-bromodecyloxy)biphenyl-4-carbonitrile, K_2CO_3, KI, butanone, rt; (iv) 20 eq. zinc(II) or nickel(II) acetate, dichloromethane–methanol (4 : 1), reflux.

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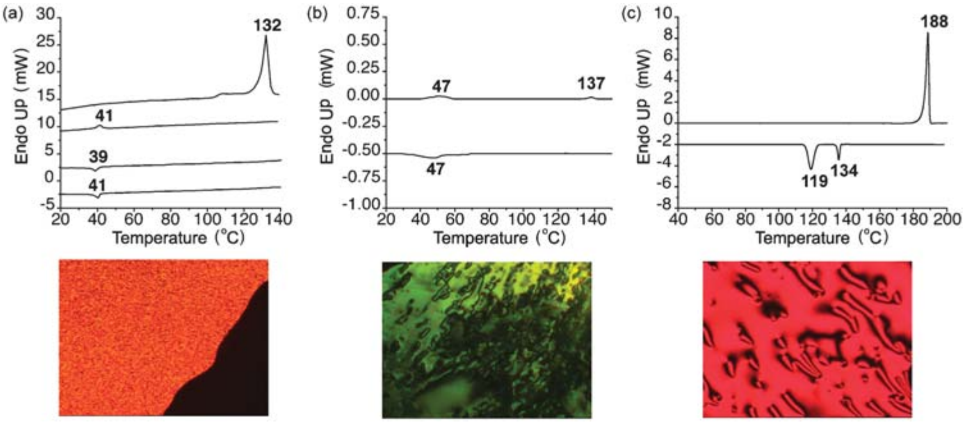

Fig. 1 (a) DSC trace for compound **2** and optical polarising microscopy (OPM) image at 25 °C (b) DSC trace for compound **3** and OPM image at 25 °C (c) DSC trace for compound **4Ni** and OPM image at 133 °C.

cooling, while **4Ni** exhibited similar behaviour at 134 °C (Fig. 1), Optical polarising microscopy (OPM) images of compounds **2**, and **3** showed classical nematic thread textures while compound **4Ni** shows typical 2 and 4 brush disclinations associated with the nematic phase (Fig. 1).

The similarity of the LC properties of **2** and **3** are also demonstrated by transition enthalpies (ΔH) at the N–Iso transition, which are a measure of the difference of ordering between the two phases. ΔH values of 0.9 kJ mol^{-1} for **2** and 1.06 kJ mol^{-1} for **3** were observed. The BODIPY system **3** contains two fluorine groups perpendicular to the plane of the π system of the dipyrrin; the impact on the LC properties is, however, very small. Significant differences are apparent when **2** and **3** are compared to **4Ni**, where the dipyrrin core is dimerised by complexation with Ni(II) and, as a result, the cyanobiphenyl groups are at both ends of the longest axis of the molecule. Here the highest N–Iso transition, 134 °C, and also the highest ΔH value at 18.0 kJ mol^{-1}, of the series is found (Table 1).

To understand the surprisingly different LC phase stability of the systems **3** and **4Ni**, investigation by XRD at temperatures where the supercooled nematic phase remains stable over extended periods (**3**: 35 °C; **4Ni**: 125 °C) of time were carried out. Both systems show scattering patterns typical of the nematic phase (Fig. 2). For compound **3** a signal at wide angles q = 14.6 (4.3 Å) is associated with the lateral distances of the molecules (for nematics values between 4.2 Å–4.8 Å are normally observed). Additionally the very weak intensity in the small angle region at q = 4.26 (14.7 Å) is in line with two overlapping antiparallel oriented cyanobiphenyl groups forming a supramolecular dimer. Previously this has been observed for cyanobiphenyl containing polymers forming a nematic phase.[14] For **4Ni** intensities at q = 13.75 (4.57Å), for the lateral packing, and small angle scattering at q = 2.34 (27 Å), which is relatively sharp, were recorded. The small angle scattering value is approximately half that of the molecular length, which is estimated to be 54 Å. This result points to a local SmA$_d$-like organization, however it is noted that such smectic-like fluctuations are strictly local, accounting for a sharper small angle signal in **4Ni** when compared to **3**. Typically such systems are described as cybotactic nematic and have been observed for a large number of systems ranging from rod shaped to disc shaped mesogens.[15] The subtle differences in the structure of the supramolecular assemblies of the compounds **3** and **4Ni**, which form the base units assembling the nematic phase, are likely to be responsible for the differences in ordering as well as the transition temperatures.

The striking differences in behaviour observed for the Zn(II) (**4Zn**) and Ni(II) (**4Ni**) complexes, in spite of the fact that the ligand (**2**) used to form both is identical, and itself exhibits liquid crystalline behaviour, may be explained by the geometry

Table 1 Transition temperatures for compounds displaying mesogenic properties (°C) as determined by DSC (1st cooling (10 °C min^{-1}))

Compound	Transition temperature/°C (Enthalpies (ΔH/kJ mol^{-1}))			
2	Cr	132	(N41 (0.9))	Iso
3	Cr	137	(N47 (1.06))	Iso
4Ni	Cr	188	(N134 (18.0))	Iso

Cr = crystalline, N = nematic, Iso = isotropic

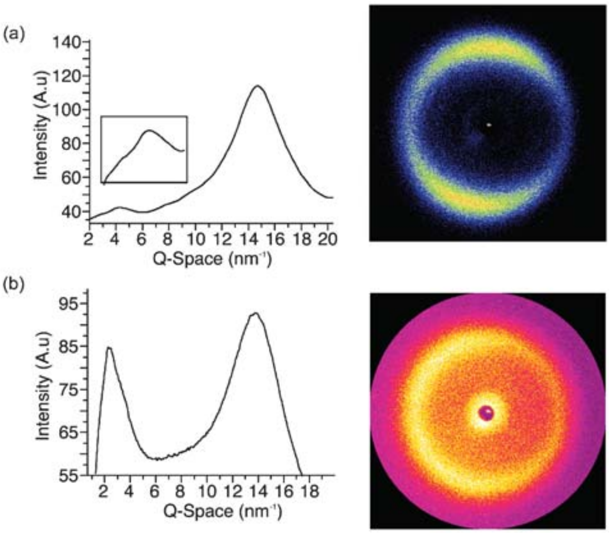

Fig. 2 XRD Patterns for compounds (a) **3** (at 35 °C) and (b) **4Ni** (at 125 °C).

of the metal core. The distorted square planar geometry displayed by Ni(II)[3,16] complexes allows for a closer packing in the condensed phase enhancing intermolecular interactions and thus stabilising mesophase formation, a factor which occurs to a lesser extent in the tetrahedral Zn(II) conformation.[6a]

The possibilities of combining self assembling characteristics with the high molar absorptivity and quantum yield of fluorescence of the BODIPY fluorophore are extremely exciting. BODIPYs, when compared to most other fluorophores, are relatively insensitive to environmental changes such as pH and polarity.[17] The deposition of liquid crystalline materials as thin films offers the possibility of utilising these materials as components in sensors,[18] however signal transduction is a problem with conventional liquid crystals due to the low sensitivity of absorbance based measurement. Fluorescent polymers offer excellent sensitivity, but often require the incorporation of complicated and expensive fluorescent sensors into polymers which play no active role in sensing.[19] BODIPYs, while relatively insensitive to chemical changes in their immediate environment, are very sensitive to changes in their relative orientations, as demonstrated by the extreme differences in fluorescence reported for D_I (non-fluorescent) and D_{II} (fluorescent with bathochromically shifted emission, λ_{emm} = 630 nm) orientations of BODIPY dimers.[20] It is also of interest that the fluorescence of BODIPYs bearing aryl rings in the 5 position, as described here, is extremely sensitive to the dihedral angle between the 5-aryl unit and the plane of the BODIPY,[6a] a factor which is expected to be intimately linked with the freedom of movement imposed by the supramolecular structure adopted at different temperatures.

From the fluorescence images (Fig. 3) it can be seen that the LC state is clearly fluorescent. Overlaying the two images indicates a difference in fluorescence between the dark homeotropic areas of nematic thread, where the molecules are aligned parallel to the beam, and the homogeneous areas, where the molecules are aligned perpendicular to the beam. This phenomenon has only previously been reported for columnar systems,[13] making this observation the first example of its type in the nematic phase. While the measurement of fluorescence in these early studies is qualitative it clearly demonstrates that fluorescence is not quenched in the nematic liquid crystalline state, and therefore represents a new class of materials incorporating fluorescent properties into orientationally ordered fluids. The fluorescent behaviour of the nematic phase also demonstrates that the relative orientation of the fluorophores is not of the D_I type, previously described for BODIPY aggregates, as this form is not fluorescent.[21] We are currently expanding the range of mesogenic units attached to the BODIPY core, and also their number and relative positions on the fluorophore, in order to further probe the effects of different liquid crystalline phases and supramolecular assemblies on fluorescence. Given the intimate link which has been shown by others between BODIPY orientation in aggregates and fluorescence yields, we believe the behaviour of these new fluorescent materials will be of great interest to a wide range of scientists.

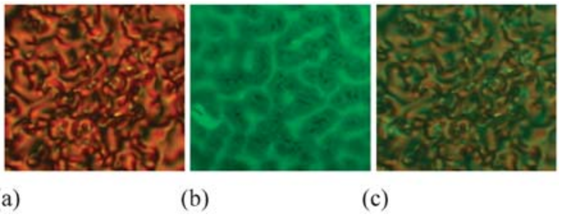

Fig. 3 OPM (a), fluorescence (b) (λ_{ex} = 488 nm; λ_{emm} > 505 nm; image width = 127 μm) and overlay (c) images for **3**.

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