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Mesomorphism of a tetrahedral zinc complex†

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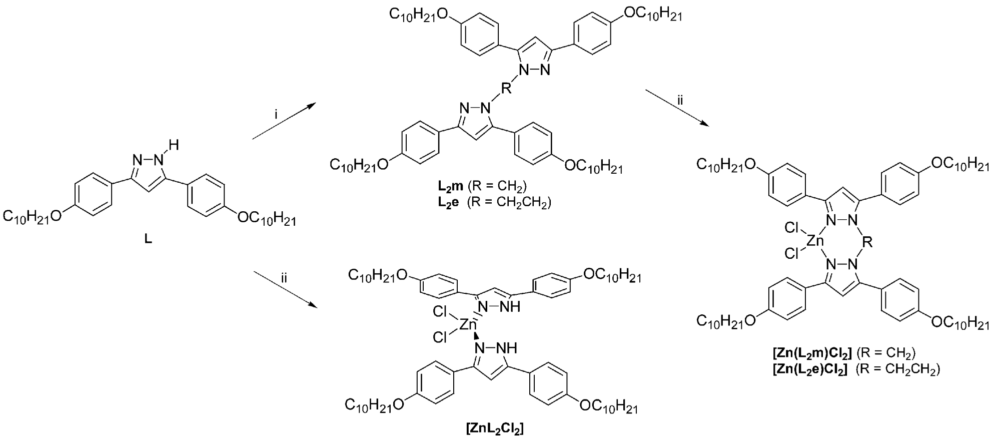
Thermotropic smectic phases have been observed for the first time in a zinc coordination complex with tetrahedral geometry; this complex, which contains the pyrazole dimer bis[3,5-bis(*p*-decyloxyphenyl)pyrazolyl]ethane as the ligand, exhibits fluorescence.

Zinc(II) can coordinate with a vast number of N and N,O donor ligands that display interesting luminescent properties for LED devices and sensors.[1] In most of these compounds, the zinc atom adopts a tetrahedral geometry, which has been proven to be a major drawback for mesomorphism.[2] Indeed, in the liquid crystalline zinc complexes described to date the metal centre is in a different geometry, *e.g.* forced into a planar coordination (with porphyrin ligands[3] and extended analogues) or pentacoordinated in a trigonal bipyramidal geometry (with dithiobenzoates[4] or tridentate pyridines[5]). Only one report concerning columnar phases in tetrahedral 2,2′-bipyridine zinc complexes has been communicated and this only appeared very recently.[6] By means of ligand design it is possible to obtain controlled supramolecular assemblies with coordination metal complexes.[7] This idea has been exploited in the work described here to generate smectic order in a fluorescent tetrahedral zinc complex. The combination of fluidity and orientational ability of liquid crystals with the particular properties of the complexes may lead to new candidates for multifunctional materials.

We prepared several compounds derived from 3,5-bis(*p*-decyloxyphenyl)pyrazole (**L**, Scheme 1). This ligand was chosen for several reasons: it can be coordinated to zinc through the pyridine-type nitrogen, it is liquid crystalline[8] and it can be modified through chemistry on the N1 nitrogen. Therefore, it is possible to synthesize pyrazole dimers in which a pyrazole is joined to its twin by a spacer (methylene or ethylene group in this work) and prepare the corresponding zinc complexes.

The synthesis of the novel ligands **L_2m** and **L_2e** was approached by solid–liquid phase-transfer catalysis by adapting a method described by Diez Barra *et al.*[9] The zinc complexes were prepared using anhydrous zinc(II) chloride in a stoichiometric amount in THF.[10] Polarising optical microscopy and DSC studies (Table 1) reveal that compound **L** is mesomorphic, displaying SmC and SmA phases, but its zinc complex **[ZnL_2Cl_2]** is not liquid crystalline. The structural analysis of a similar compound [Zn(3,5-dimethylpyrazole)$_2Cl_2$][11] shows that the zinc atom in the complex is in a tetrahedral geometry, which introduces an unfavourable angle between the mesogens at the N1 position and precludes mesomorphism. Similar behaviour is observed for the ligand **L_2m** with a tetrahedral methylene bridge, although it has the same melting point as **L**. In the complex **[Zn(L_2m)Cl_2]** the pyrazole dimer **L_2m** coordinates to the metal through its two pyridinic nitrogen atoms and generates a compound that is not mesomorphic. The absence of mesomorphism is probably due to the non-planar shape of the central metallacycle, a situation previously described in similar derivatives [Zn[2,2-bis(pyrazolyl)propane]Cl_2][12] or [Zn[bis(3,4,5-trimethylpyrazolyl)methane]Br_2],[13] where the six-membered C(NN)$_2$Zn ring adopts a boat form with a fold angle of 140° and 126°, respectively. Ligand **L_2e** displays a monotropic smectic A phase, probably due to the increased degree of freedom introduced by the ethylene spacer with respect to the methylene one. However, the short range of the mesophase indicates that the L units are still far from being independent. In contrast, the zinc complex **[Zn(L_2e)Cl_2]** shows enantiotropic smectic C and A phases, indicating that the liquid crystalline phases are significantly favoured by complexation. The combination of the metal centre, which closes a seven-membered ring, and the flexibility of the ethylene spacer are crucial to minimise the steric demands of the tetrahedral centre and allow the organisation of the molecules in layers.

Examples of similar structures have not been described previously so, in an attempt to confirm our hypotheses, we attempted to grow crystals of **[Zn(L_2e)Cl_2]**. Unfortunately, all efforts to



Scheme 1 *Reagents and conditions*: (i) $ClCH_2CH_2Cl$ or CH_2Br_2, K_2CO_3, NBu_4Br, 90 °C, 64–70%; (ii) $ZnCl_2$, THF, r.t., 60–70%.

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† Electronic supplementary information (ESI) available: characterization data for the novel compounds; microphotographs of the mesophase textures of compound [Zn(L_2e)Cl_2] and absorption and emission spectra for L_2e and [Zn(L_2e)Cl_2]. See http://www.rsc.org/suppdata/cc/b4/b407652d/

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Table 1 Transition temperatures and thermodynamic data[a]

Compound	T_{onset}/°C (ΔH/kJ mol^{-1})
L [Ref. 8]	Cr 79 (31.8) Cr′ 130 (13.1) SmC 180[b] SmA 183 (6.1) I
L_2m	Cr 129 (59.7) I
L_2e	Cr [122 (7.2) SmA][c] 124 (56.1) I
[ZnL_2Cl_2]	Cr 108 (95.0) Cr′ 178 (53.2) I
[Zn(L_2m)Cl_2]	Cr 97 (16.0) Cr′ 164 (27.2) I
[Zn(L_2e)Cl_2]	Cr 95 (10.6) SmC 134 (13.7[d]) SmA 154[b] I

[a] Cr, Cr′: crystal phases, I: isotropic liquid, SmA: smectic A, SmC: smectic C. [b] Optical microscopy data. [c] Monotropic transition. [d] Transitions SmC–SmA and SmA–I appear by DSC as a single peak.

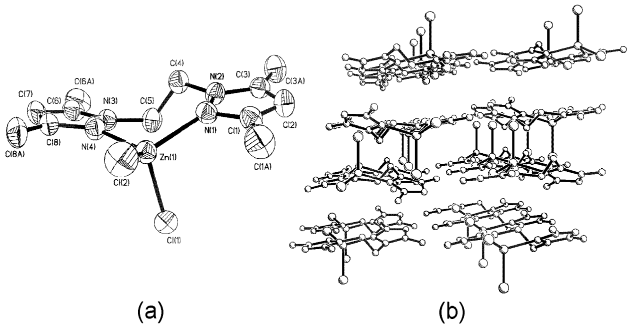

Fig. 1 (a) ORTEP representation of [Zn(bmpze)Cl_2] (50% probability ellipsoids) with atom numbering scheme. (b) Packing diagram showing two kinds of planes parallel to *bc*.

achieve this goal proved unsuccessful. However, we were able to solve the structure of [Zn(bmpze)Cl_2] [bmpze: 1,2-bis(3,5-dimethylpyrazolyl)ethane], in which the metal is in a similar environment, and use this as a model for comparison.‡ The molecular structure is shown in Fig. 1a. The zinc atom is in a tetrahedral environment and the planes containing the pyrazole rings are arranged with respect to one another at an angle of only 16°, indicating that the molecule is more planar than the ones with a methylene spacer. From the packing study (Fig. 1b) it appears that the chloro ligands are disposed in pseudoaxial and equatorial positions with respect to the main molecular plane and the molecules are arranged in layers in an antiparallel fashion.

The mesophase assignment was confirmed by powder X-ray diffraction[14] at different temperatures. In the smectic C phase layer spacings of 29 Å (108 °C) and 30 Å (118 °C) were measured. The smectic A phase was found to have a layer spacing of 32 Å at different temperatures (140, 145 and 150 °C). These values are in accordance with a packing model similar to the mesophases of **L** (measured layer spacing of 34.7 Å in the SmA and 32–33 Å for the SmC)[8] where the molecules are arranged with their long axes perpendicular (SmA) or tilted (SmC) to the layer. It seems reasonable that **[Zn(L_2e)Cl_2]** can lead to a smaller layer spacing as the dimeric nature of the compound may leave more free volume to accommodate the conformationally disordered decyloxy chains in the layer.

A preliminary study of the optical properties in dichloromethane solutions showed that the ligand **L_2e** exhibits fluorescence at 338 nm upon excitation at the absorption maximum (263 nm). The zinc complex **[Zn(L_2e)Cl_2]** fluoresces under similar conditions at 365 nm with a higher intensity. Thus, on complexation both a red-shift and a chelation-enhanced fluorescence, estimated to be multiplied by a factor of three, are observed (Fig. 2).

Following this work we will apply the "flexible ligand" approach to other structures in order to generate new phases as a way to study new multifunctional materials based on zinc-containing mesogens.

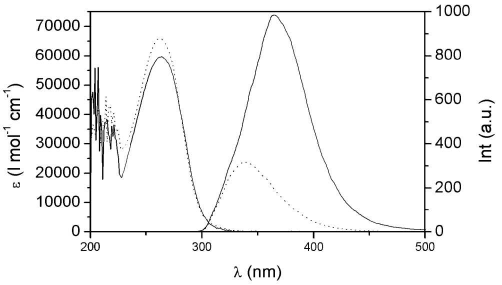

Fig. 2 Absorption and emission spectra for compound **L_2e** (dotted line) and **[Zn(L_2e)Cl_2]** (solid line).

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Notes and references

‡ Crystal data for **[Zn(bmpze)Cl_2]**: colourless crystals suitable for crystallographic analysis were obtained by slow diffusion of hexane into a solution of the compound in dichloromethane. $C_{24}H_{36}Cl_4N_8Zn_2$, M = 709.15, monoclinic, a = 14.976(3), b = 11.164(3), c = 18.877(3) Å, β = 101.590(9)°, V = 3091.8(10) Å^3, T = 293 K, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 1.926 mm^{-1}. The structure, refined on F^2, converged for 5434 unique reflections (R_{int} = 0.0376) to give R_1 = 0.0569, wR_2 = 0.1270 [$I > 2\sigma(I)$] and R_1 = 0.1112, wR_2 = 0.1536 (all data) and a goodness-of-fit = 1.033. CCDC 239724. See http://www.rsc.org/suppdata/cc/b4/b407652d/ for crystallographic data in .cif or other electronic format.

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