The First Aluminium Discotic Metallomesogen: Hydroxo[5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrinato]aluminium(III)

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Hydroxo[5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrinato]aluminium(III) exhibits a disordered discotic hexagonal columnar (D_{hd}) phase, the first example of a discotic metallomesogen having an aluminium nucleus.

Metallomesogens have been extensively studied in view of their potential as novel advanced materials.[1] In view of their characteristic molecular ordering of a stacking columnar array and the extended π-conjugation electron system for the rigid core moiety, discotic metallomesogens are particularly attractive for their electronic properties.[2]

An interesting and important feature of metallomesogens is that they have the potential to induce a variety of supramolecular assemblies as the mesophase resulting from specific molecular interactions derived from the presence of the metal species, even for molecular geometries which are unlikely to form such a characteristic ordering of molecules to form a mesophase. It is recognised that in general a hexagonal columnar array (D_h phase) will be formed for molecules with six or eight aliphatic substituents peripherally attached to the core moiety. This requirement also applies to discotic metallomesogens. Phthalocyanines[3] and porphyrins[4] octa-substituted with aliphatic chains are reported to show a D_h phase. Furthermore, for some dithiolene metal complexes, the number of peripheral aliphatic chains is critical for the occurrence of a D_h phase.[5]

Recently it was reported that tetra-substituted tetraphenylporphyrins and their metal complexes (Co, Ni, Cu, Zn and Pd) with square planar geometry exhibit only a discotic lamellar (D_L) phase.[6] For tetra-substituted discotic metallomesogens, only dinuclear copper soaps[7] and vanadyl β-diketonate derivatives[8] are known to show a D_h phase in which molecular stacking is induced by metal-derived specific interactions along the columnar axis.

We now report the first example of an aluminium discotic metallomesogen with four alkyl tails giving rise to a discotic hexagonal disordered columnar phase (D_{hd}), hydroxo-[5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrinato]aluminium(III), (C_{12}tpp)Al(OH). This compound does not appear to have any functional groups capable of taking part in intermolecular specific interactions relevant to the formation of columnar stacks.

The complex was synthesised and purified by a slight modification of the literature method.[9] The metal-free ligand was dissolved in benzonitrile and the solution heated under reflux with $AlCl_3$; the resulting aluminium chloride complex was passed through an alumina column with CH_2Cl_2 as eluent to give the hydroxo complex. The identity of the product was confirmed by spectroscopic analyses: IR(KBr) ν_{max}/cm^{-1} 3654(OH str.); ^{1}H NMR δ_H ($CDCl_3$, 500 MHz) −6.48 (s, 1H, OH), 0.88 (t, 12H, CH_3), 1.31 (m, 56H, $[CH_2]_7$), 1.47 (m, 8H, $C_6H_4CH_2CH_2CH_2CH_2$), 1.55 (m, 8H, $C_6H_4CH_2CH_2CH_2$), 1.90 (m, 8H, $C_6H_4CH_2CH_2$), 2.93 (t, 8H, $C_6H_4CH_2$), 7.54 (d, 8H, *meta meso* Ph), 8.08 (br s, 8H, *ortho* Ph), 9.05 (s, 8H, β pyrrole-H); UV–VIS ($CHCl_3$) λ_{max}/nm (ε_{max}/l mol^{-1} cm^{-1}) 587.5 (4100), 548.1 (19800), 511.1 (2960), 418.3 (527000); satisfactory elemental analyses.

Fig. 1 shows a DSC thermogram of the first heating run (heating rate: 5 °C min^{-1}). Two peaks can be seen starting at 84 °C (peak maximum 101 °C; ΔH 74 kJ mol^{-1}) and *ca.* 150 °C (peak maximum 177 °C, shoulder at 185 °C), corresponding to the melting and clearing points, respectively. These phase transitions were confirmed by polarized microscopic observations. Once the complex had been heated above the clearing point, the phase transition sequence changed to another type (non-enantiotropic), indicating that μ-oxo dimerization[10] occurs above *ca.* 140 °C.[11]

Powder X-ray diffraction studies showed that the mesophase is of discotic hexagonal disordered columnar (D_{hd}) type because of the presence of the characteristic three peaks in the narrow angle region. For these peaks, corresponding to (100), (110) and (200), the *d*-spacing ratio is $1 : 1/\sqrt{3} : 1/2$, typical for

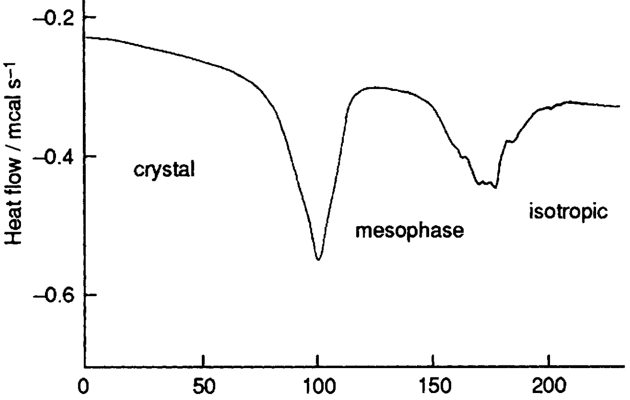
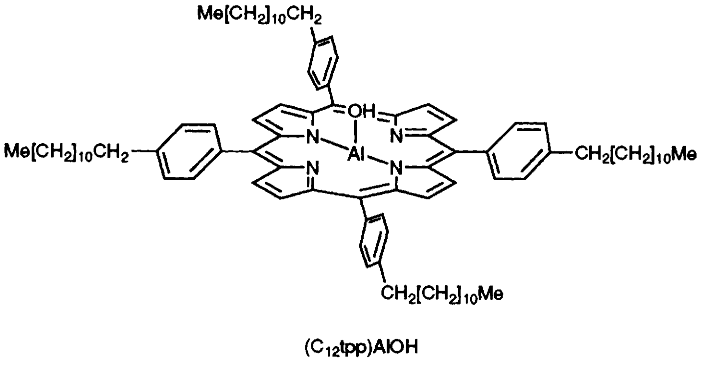


Fig. 1 DSC thermogram of (C_{12}tpp)Al(OH) for the first heating run (heating rate: 5 °C min^{-1})



(C_{12}tpp)AlOH

a discotic hexagonal array. Furthermore, sharp reflections in the wider angle region are absent, although there is a broad peak centred at 2θ = *ca.* 20° (4.4 Å) derived from alkyl chain melting.

The occurrence of the D_h phase in this aluminium complex seems to indicate the existence of some specific molecular interaction along the direction of the column axis, suitable for the formation of an appropriate columnar structure for hexagonal alignment. Further studies on the intermolecular specific interaction giving the D_h phase are now in progress to probe the formation of the supramolecular mesomorphic structure.

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Footnotes

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