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Unusual mesomorphic behaviour of an ethynyl-substituted phthalocyanine†

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An ethynyl-substituted nickel(II) phthalocyanine has been synthesised and its thermotropic properties studied; optical microscopy, differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques revealed an unusual mesomorphic behaviour observed for the first time in phthalocyanine systems where each disk of the hexagonal columnar mesophase is formed by two ethynyl-substituted phthalocyanine units.

Phthalocyanines (Pcs) and related aromatic macrocycles[1] are molecules intensively studied due to their unique structural, photophysical and electrochemical properties that make them attractive compounds for technological applications. These planar, aromatic macrocycles in fact have been successfully incorporated as active components of semiconductor and electrochromic devices, information storage systems and liquid crystal displays, among others.[2]

A crucial and delicate issue to be addressed in order to incorporate phthalocyanines into devices is how to control the spatial arrangement of these macrocycles with respect to each other, with the aim of extending or even improving the phthalocyanines' chemical and physical properties from the molecular to the macroscopic level.

Although several examples of phthalocyanine organisation have been reported using different molecular recognition motifs,[3] one of the most effective approaches towards this goal is the use of Pcs bearing long, flexible hydrocarbon chains. These macrocycles in fact are able to interact with each other *via* supramolecular interactions forming ordered columnar structures with a discotic mesomorphic behaviour.[4] Discotic mesomorphism makes this kind of compounds potentially interesting as one-dimensional conductors,[5] in which the conducting wire would be formed by the spine of the central conjugated system surrounded by an insulating region of hydrocarbon chains.

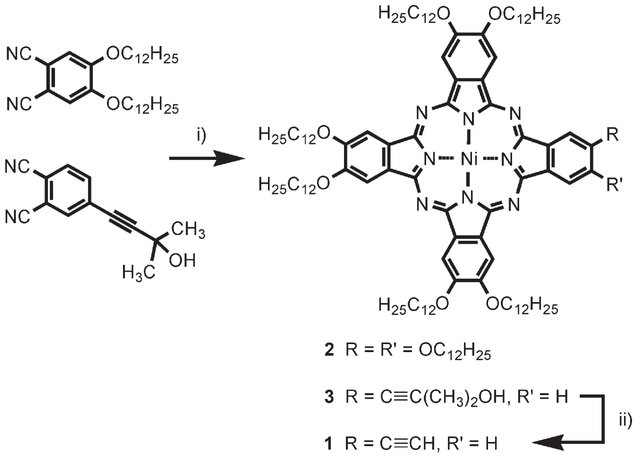
To date several studies have been reported on the liquid crystal behaviour of single[4a,6] as well as multi Pc derivatives.[7,8]

In this communication we report on the synthesis and the unusual thermotropic behaviour of an ethynyl-substituted nickel(II) phthalocyanine (**1**) (Scheme 1).

The first step towards the preparation of the ethynyl-substituted Ni(II)Pc **1** was the synthesis of the alkynyl-substituted Ni(II)Pc **3** by statistical tetramerisation reaction of 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile[9] and 4,5-didodecyloxyphthalonitrile‡ in the presence of $NiBr_2$. This reaction gives a mixture of Pcs among which the symmetric octadodecyloxy Ni(II)Pc **2** and the alkynyl-substituted Ni(II)Pc **3** could be isolated after column chromatography in 36% and 20% yield respectively (Scheme 1). The Ni(II)Pc **3** was then subjected to a NaOH treatment to obtain the ethynyl-substituted nickel(II) Pc **1** in 70% yield (Scheme 1).§ The three Ni(II)Pcs **1–3** were fully characterized by UV/vis, ^{1}H-NMR and IR spectroscopies, MALDI-TOF mass spectrometry and elemental analysis, and the mesomorphic properties of Ni(II)Pcs **1** and **2** investigated by polarizing optical microscopy and the transition temperatures confirmed by differential scanning calorimetry (DSC).

The ethynyl-substituted Ni(II)Pc **1** is a highly viscous liquid crystal at room temperature and becomes completely fluid at 70–74 °C (transition to the isotropic liquid). This transition is detected on heating in DSC as an endothermic peak at 70 °C with an associated enthalpy of 13 kJ mol^{-1} (Table S1, Supporting Information). Although a birefringent texture typical of a liquid crystal phase is not clearly visible, the observed viscosity and the enthalpy value of the transition to the isotropic liquid are characteristic of a mesophase.

On the other hand the symmetric octadodecyloxy Ni(II)Pc **2**, when heated on the hot stage of the microscope, melts into a birefringent fluid phase that shows a focal-conic texture with



Scheme 1 Synthesis of the ethynyl-substituted Ni(II)Pc **1**. i) $NiBr_2$, dimethylaminoethanol, argon, 135 °C, **2** (36% yield) and **3** (20% yield). ii) NaOH, toluene, argon, reflux, 70% yield.

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fan-shaped domains, characteristic of a columnar hexagonal mesophase (Table S1, Supporting Information). In DSC, melting into the mesophase is detected as an endothermic peak at 84 °C with an associated enthalpy of 77.2 kJ mol^{-1}. Further heating leads to the transformation of the mesophase into an isotropic liquid at about 300 °C. However, this transition is slow and is not detected by DSC, but only by optical microscopy. Compound **2** has been reported before,[10] and our results are in fair agreement with those described by Binnemans.[10b]

In order to obtain detailed information about the mesomorphic organisation of the Pc units, samples of compounds **1** and **2** were studied by X-ray diffraction (XRD) both at high and room temperature. In both cases the X-ray diffractograms displayed the features of a hexagonal columnar (Col_h) mesophase (Table S2, Supporting Information).

In the case of ethynyl-substituted Ni(II)Pc **1** the diffraction pattern taken at room temperature reveals the presence of a set of low-angle maxima with a reciprocal spacing ratio $1 : \sqrt{3} : \sqrt{4} : \sqrt{9} : \sqrt{13}$, characteristic of hexagonal packing of columns. Similarly, the XRD patterns of Ni(II)Pc **2** taken above 84 °C (temperature at which the compound becomes fluid and develops a texture) are characteristic of a hexagonal columnar mesophase, as revealed by the presence of a set of low-angle maxima with a reciprocal spacing ratio $1 : \sqrt{3} : \sqrt{4} : \sqrt{7}$. In both compounds the maxima can be indexed as the *hk* reflections of a two-dimensional hexagonal lattice (Table S2, Supporting Information). In addition to this, a broad diffuse halo corresponding to a distance of about 4.5 Å is observed for both Ni(II)Pc **1** and **2**. This halo is characteristic of the liquid-like arrangement of the conformationally-disordered alkyl chains and confirms the mesomorphic nature of these compounds. Finally, a high-angle reflection at 3.4 Å, corresponding to the stacking distance, is found in the patterns of both compounds. Although this reflection is not found in all columnar mesophases, its presence confirms the existence of stacks of molecules. The absence of any other reflection (in particular *hkl* reflections with *h* or *k*, and *l*, simultaneously different from 0) excludes the existence of a three-dimensional order.

Surprisingly the hexagonal lattice constant for compound **1** (a = 51.0 Å) is considerably larger than that for **2** (a = 36.5 Å), even though the molecular mass of the ethynyl-substituted Ni(II)Pc **1** is smaller than that of the symmetric Ni(II)Pc **2** (1699.2 and 2045.8 g mol^{-1} respectively). This suggests that, whereas for the symmetric Ni(II)Pc **2** the discotic mesogenic columns are formed *via* stacking of single phthalocyanine molecules along the central metal atom, in the case of compound **1** each disk of the columns is formed by two ethynyl-substituted Ni(II)Pc units. The proposed model is supported by the values of the area "S" of the hexagonal lattice deduced from the hexagonal lattice constant "a", which is equivalent to the cross-section of the column. "S" is 1153 Å^2 for compound **2** and 2253 Å^2 (*i.e.* approximately twice the value) for compound **1**.

The use of complementary molecular shapes to generate correlated structures having a disc-like organisation is not new and has been exploited to generate mesomorphism in some systems.[11] Similarly, several series of non-disc-like, metal-containing or pure organic molecules[4a,11] have been reported to display columnar mesomorphism due to some kind of intermolecular correlation through hydrogen bonding or dipole–dipole interactions, among others. To the best of our knowledge this is the first time a similar effect has been observed in a phthalocyanine system. It is probable that dipole–dipole interactions between the unsymmetric dipolar[12] Pc-molecules **1** are responsible for the intermolecular interactions that hold in place two ethynyl-substituted Ni(II)Pcs in each disk of the columnar mesophase (Fig. 1).

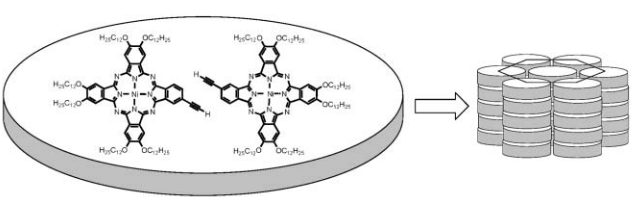

Fig. 1 Schematic representation of the proposed model for the stacking of molecules formed by Ni(II)Pc **1** in the Col_h mesophase.

Further studies are currently in progress in our laboratories on similar mesogenic Pc-based systems in order to gain a better understanding of the structural features of a phthalocyanine which are required in order to influence the resulting columnar organisation.

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‡ 4,5-Didodecyloxyphthalonitrile was prepared following the procedure used by I. Hisato, E. Katashi, O. Takahisa, N. Tumotu, Eur. Pat. Appl. EP. 373,643. (QCO7F7/00), 20 Jun. 1990, 15 Dec. 1988, *Chem. Abs.* 114:P1333092a, for the preparation of 4,5-dibutoxyphthalonitrile.

§ This synthetic strategy (*i.e.* synthesis of a propargylic-substituted Pc followed by base-treatment, thus obtaining an ethynyl-substituted Pc) has been previously reported by K. Ohta *et al.*, *Mol. Cryst. Liq. Cryst.*, 2003, **397**, 325.

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