

## Synthesis of Triphenylene-based Porphyrazinato Metal(II) Complexes which display Discotic Columnar Mesomorphism

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The synthesis of mesogenic triphenylene-based porphyrazine complexes bearing sixteen decyloxy side-chains is described; the widely extended core-system present leads to an enhanced stability of the mesophases formed by these complexes.

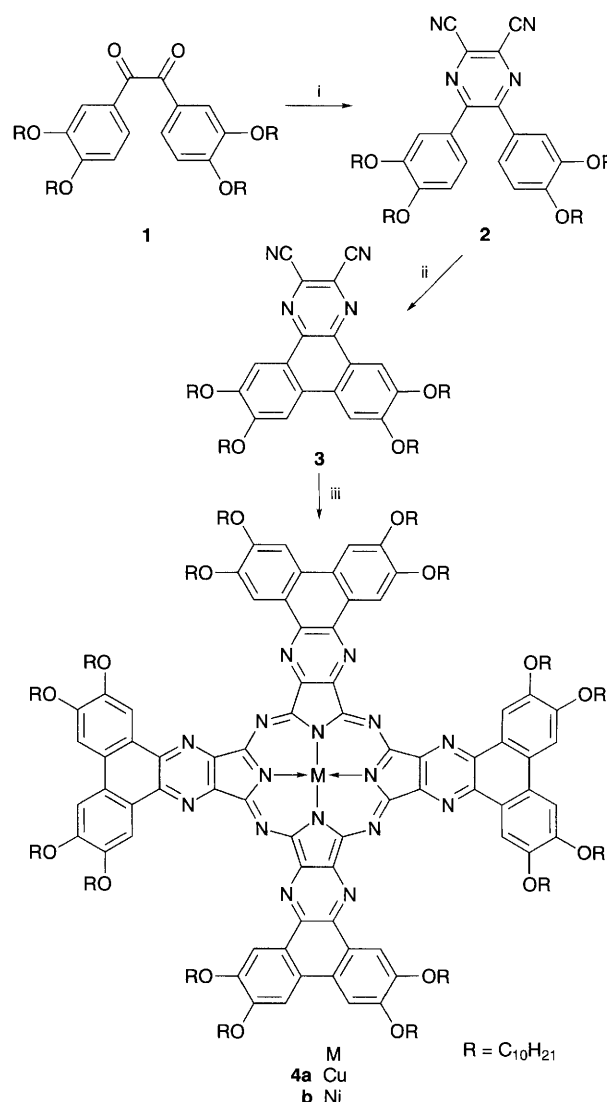
Liquid crystals incorporating transition-metal complexes promise to significantly increase the range of properties currently exhibited by mesomorphic materials.<sup>1</sup> Phthalocyanines and their derivatives have been demonstrated to be particularly attractive materials due to their extended two-dimensional  $\pi$ -conjugated electron system and their alignment in columnar stacks. The high electron density present in these systems usually leads to a large polarizability, establishing the fundamental requirements for the occurrence of linear and non-linear optical effects.<sup>2</sup> The one-dimensional interactions resulting from their columnar superstructures have been discussed in the context of conducting and photoconducting bulk materials and as the basis of conductive and capacitive elements in molecular electronic devices.<sup>3</sup>

We now report the synthesis of mesogenic triphenylene-based porphyrazine complexes with a widely extended planar core peripherally bearing sixteen *n*-decyloxy chains. The aromatic moiety of these macrocycles has a diameter of approximately 24 Å and contains 86  $\pi$ -electrons. Scheme 1 depicts the procedure used in the synthesis of the substituted tetrakis(1,4-diazatriphenylene)porphyrazinato metal(II) complexes **4** ( $R = C_{10}H_{21}$ ,  $M = Cu$  **4a** or  $Ni$  **4b**).

6,7,10,11-Tetrakis(decyloxy)-1,4-diazatriphenylene-2,3-dinitrile **3** is prepared either by direct conversion of the corresponding phenanthrene-9,10-dione<sup>4</sup> with diaminomaleodinitrile or in a two-step synthesis by reaction of the benzil **1**<sup>4</sup> with diaminomaleodinitrile and subsequent oxidative aryl-aryl coupling with  $VOF_3$  in the presence of boron trifluoride-diethyl ether. The overall yield is much better in the latter case (60 vs. 10%).

Compound **3** shows mesomorphic behaviour in the temperature range 57.5–258.1 °C as revealed by differential scanning calorimetry, polarized optical microscopy and X-ray diffraction experiments. The mesophase texture viewed under crossed polarizers is best described as focal conic or fan-shaped, frequently observed for hexagonal columnar mesogens.<sup>5</sup> X-ray diffraction studies confirm a hexagonal columnar arrangement in ordered stacks ( $D_{6h}$ ). The three reflections in the narrow angle region can be assigned to (100), (110) and (200) in a two-dimensional hexagonal array with lattice constant  $a = 22.75$  Å. A broad halo centred at  $d \approx 4.8$  Å is typical of liquid correlations between molten hydrocarbon side-chains, while a narrow reflection at  $d = 3.50$  Å represents the stacking distance of the aromatic discs within the columns. This hexagonal columnar mesomorphism is rather exceptional for molecules with  $C_{2v}$  symmetry,<sup>6</sup> and most examples known to date are restricted to mesogens with  $D_{nh}$  symmetry ( $n = 3, 4$  and  $6$ ).<sup>1</sup> Since molecules with  $C_{2v}$  symmetry cannot exhibit a disc shape independently, they may organize into a superstructure which on time average leads to an antiparallel alignment of nearest neighbours (*discotic antiphase*), as recently suggested by Swager and coworkers.<sup>6</sup> We think that the increased van der Waals interactions of the triphenylene-core units in a superstructure of this type appear to be responsible for the extraordinary mesogenic stability of **3** compared to hexaalkoxy-substituted triphenylenes, which exhibit liquid-crystalline behaviour over a significantly smaller range of temperature.<sup>7</sup>

Conversion of **3** with either  $CuCl_2$  or  $NiCl_2$  in a template synthesis catalysed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) yielded the desired complexes **4** as ductile, dark solids. The complexes were purified by repeated reprecipitation from acetone and subsequent Soxhlet extraction using dichloromethane (18% yield). Structural proof was accomplished through high resolution FD-mass spectrometry, elemental analysis, and UV-VIS spectroscopy. Attempts to synthesize the metal-free macrocycle failed, most likely due to enhanced steric obstructions in the peripheral region.



**Scheme 1** Reagents and conditions: i, 1.25 equiv. diaminomaleodinitrile, acetic acid, reflux, 4 h; ii, 3 equiv.  $VOF_3$ , 2.1 equiv.  $BF_3 \cdot Et_2O$ ,  $CH_2Cl_2$ , room temp., 45 min; iii, 0.25 equiv.  $MCl_2$ , 0.5 equiv. DBU, 2-methylbutan-2-ol, reflux, 72 h

It could be shown by differential scanning calorimetry and X-ray diffraction experiments that these complexes exhibit liquid crystalline behaviour over the whole range of temperature accessible for our investigations ( $-100$  to  $300$  °C). Even upon annealing for several hours at temperatures as low as  $-100$  °C no evidence for crystallization could be observed. X-Ray diffraction studies at various temperatures reveal a tetragonal ordered columnar structure ( $D_{tet.o}$ ) for both the copper and nickel complexes **4a** and **4b**. Fig. 1 depicts the X-ray diffraction diagram of the copper(II) complex **4a** at  $25$  °C. The first six reflections in the low-angle region could be unambiguously assigned in a two-dimensional tetragonal array with lattice constant  $a = 46.44$  Å, whereas some of the reflections at higher angles still remain unassigned. The broad halo at  $d \approx 4.4$  Å reflects the disorder of the aliphatic chains, while the narrow peak at  $d = 3.72$  Å is assigned to core-core correlations. Interestingly, an additional broad peak is centred at twice the

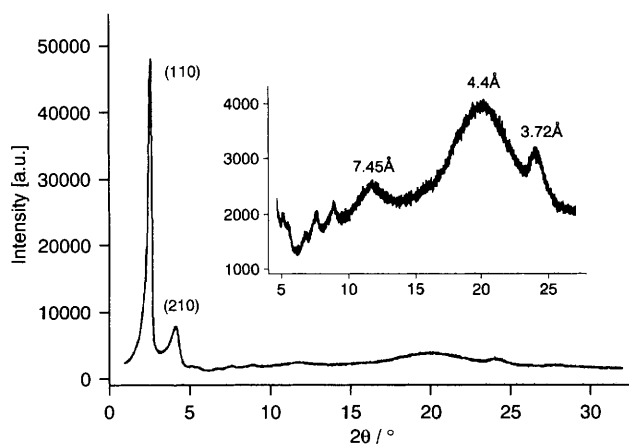


Fig. 1 X-Ray diffraction diagram of the copper(II) complex **4a** at  $25$  °C

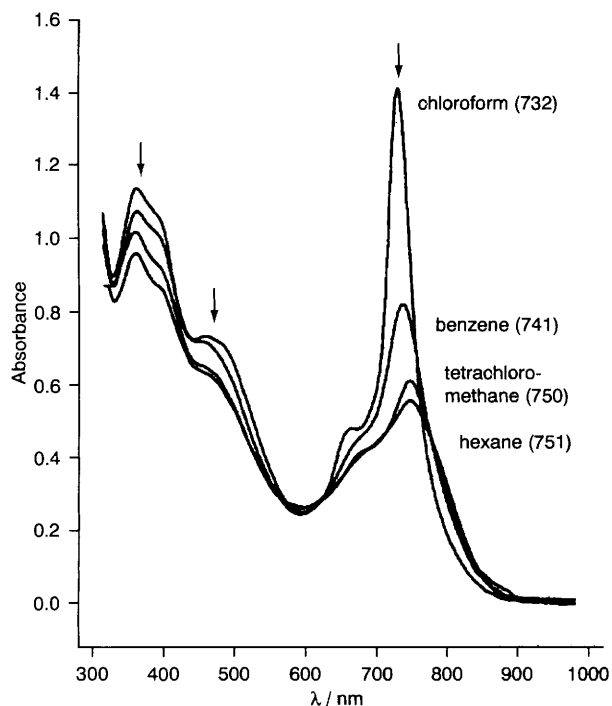


Fig. 2 UV-VIS spectra of the copper(II) complex **4a** at  $25$  °C ( $c = 1.3 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , values in parentheses indicate  $\lambda_{\text{max}}$ )

core-core correlation distance or  $d = 7.45$  Å. This halo is likely due to a doubling of the period along the columns pointing to a staggered or spiral arrangement of adjacent units. However, the exact superstructure could not be unequivocally clarified yet, and it will be necessary to explore the precise structure by additional physical methods. The nature of the mesophase does not change until slow thermal decomposition occurs at temperatures above  $300$  °C.

The appearance of the UV-VIS spectra for the complexes **4a** and **4b** correspond to those typically observed for phthalocyanines<sup>8</sup> and tetrapyrzino-porphyrazines.<sup>9</sup> However, the Q bands for the complexes **4a** and **4b** in chloroform solution are found at  $732$  and  $720$  nm, respectively, demonstrating a significant red shift in comparison with the corresponding values reported for octaalkyl-substituted tetrapyrzino-porphyrazines.<sup>9</sup> This shift reflects the influence of the extended core  $\pi$ -system and is in good agreement with recent theoretical studies on the electronic spectra of various benzo-substituted phthalocyanines.<sup>10</sup> A decrease in solvent polarity is accompanied by increasing aggregation between the complexes, evidenced by the decrease of the absorbance and a slight red shift of the Q band (Fig. 2). This coupling between aggregation and metachromic effect is quite general for dye molecules with delocalized aromatic systems<sup>11,12</sup> and has been recently employed to determine aggregation equilibria of an octa-substituted phthalocyanine in dodecane solution.<sup>13</sup>

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