In-plane Orientation in Langmuir–Blodgett Films of Triazolephthalocyanines

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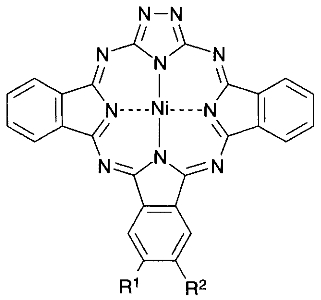
Langmuir–Blodgett experiments are carried out on a new class of non-symmetric amphiphilic azaporphyrins; in-plane orientation of the macrocycles is obtained when nickel(II) acetate salts are introduced into the subphase to complex the polar 1,2,4-triazole subunit.

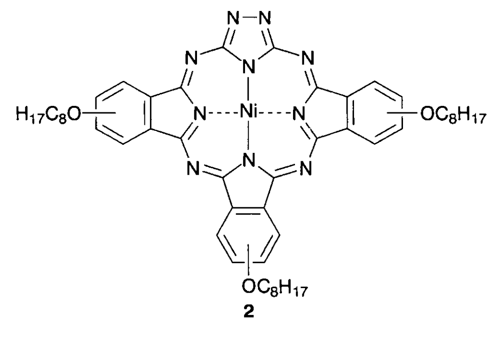
The Langmuir-Blodgett technique, while providing monomolecular layer-like structures, has been widely used as a very efficient way to build supramolecular architectures.[1] However, it has been shown that macroscopic order can be obtained not only in the direction perpendicular to the substrate but also inside each molecular plane. The reason for this phenomenon has been explained as the molecular flow in the vicinity of the substrate during the deposition process.[2] The molecules that lead to this in-plane orientation are disk-like aromatic molecules,[3,4] such as phthalocyanines and triarylpyrilium salts peripherally substituted with aliphatic chains, which are suitable for forming columnar aggregates by strong π–π interactions. The factors influencing molecular organization within the film assembly have been studied in phthalocyanine and porphyrin systems.[5] The use of such systems as templates to orient precursors of conducting polymers, *e.g.* thiophene subunits, many lead to well-oriented molecular wires; this is of the highest interest considering that the orientation was shown to be a condition necessary for high conductivity in molecular systems.[6]

We have recently described the preparation, characterization and properties of nickel(II) triazolephthalocyanines **1**, which are soluble in organic solvents.[7–9] These novel metallomacrocycles present an amphiphilic structure (polar 1,2,4-triazole subunit/aromatic macrocycle/hydrophobic chains) which is particularly suitable for Langmuir film formation.

We report here on the monomolecular layer behaviour of compounds **1a–c** and **2**, representative examples of this new class of phthalocyanine analogues. In-plane oriented Langmuir–Blodgett films of some of these triazolephthalocyanines have been obtained when Ni^{II} ions were introduced into the subphase to complex the 1,2,4-triazole moiety; this method appears to be a new way to provide preferential orientation and ordering of molecules.



1a $R^1 = R^2 = OC_{12}H_{25}$
b $R^1 = H, R^2 = Bu^t$
c $R^1 = H, R^2 = OC_8H_{17}$



2

The synthesis of compounds **1a–c** has been described in detail recently.[7–8] Trioctyloxy derivative **2** was prepared by the reaction of 3,5-diamino-1,2,4-triazole with 5-octyloxy-1,3-diiminoisoindoline in the presence of nickel(II) acetate tetrahydrate in a 1 : 3 : 1 molar ratio. The crude product was purified by column chromatography on silica gel and triturated with hot methanol to yield a dark solid (35% yield). The compound was characterized by elemental analysis, IR and UV–VIS, FAB MS and NMR spectroscopies.†

Compounds **1a–c** and **2** were found to be soluble in common spreading solvents such as chloroform and were therefore used in Langmuir–Blodgett experiments. Pressure–area isotherms (π/*A* curve) at 20 °C are presented in Fig. 1; they were reproducible and the Langmuir films were stable up to collapse pressures of *ca.* 40 mN m^{-1}. The molecular area obtained for solid monolayers of macrocycle **1a** was *ca.* 60 Å^2 which corresponds to the theoretical molecular cross-section obtained by CPK models for triazolephthalocyanines standing vertically on the aqueous subphase with the polar 1,2,4-triazole unit in

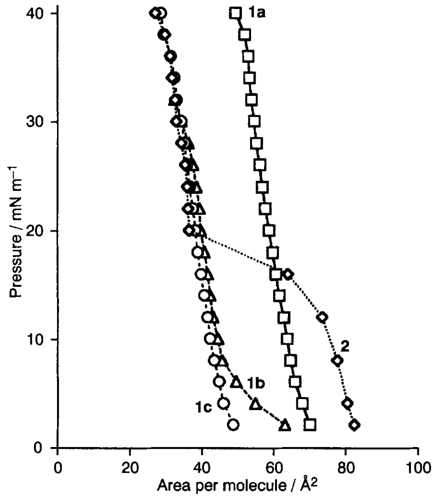


Fig. 1 Pressure–area isotherms at 20 °C for molecules **1a–c** and **2**

Table 1 Characteristics of the transfer of molecules **1a–c** and **2** onto fluorine substrates

	Surface pressure for deposition/ mN m^{-1}	Transfer ratio	Periodicity of the film
1a	25	1 (up and down stroke)	40 Å
1b	20	1 (up stroke only)	
1c	no transfer		
2	10	1 (up and down stroke)	

contact with the water. This result suggests the formation of a well-packed monolayer. In the case of the trisubstituted macrocycle **2**, the first part of the π/A curve also corresponds to an edge-on orientation of the macrocycle; however, at a pressure of *ca.* 16 mN m^{-1}, a phase transition occurred with a decrease of the molecular area to half its original value. This step in the curve is probably due to the formation of a double layer at the air–water interface. Such behaviour is not unusual for hydrophobic macrocycles.[3] Monosubstituted triazolephthalocyanines **1b,c** presented similar isotherms with a reproducible molecular area of *ca.* 34 Å^2 for the solid phase; this suggests the formation of a bilayer even at low surface pressures.

Using a vertical dipping method, macrocycles **1a,b** and **2** were deposited onto calcium fluoride hydrophilic substrates which were made hydrophobic by the predeposition of three fatty acid monolayers. The surface pressure for the deposition, the transfer ratio and the structures of the films for the compounds are listed in Table 1. UV–VIS and IR dichroism measurements were attempted on these films, but they did not show any preferential orientation of the molecules. On the contrary, if nickel(II) acetate is introduced in a 10^{-3} mol dm^{-3} concentration into the water subphase, Langmuir–Blodgett films of **1a** and **2** lead to in-plane oriented Langmuir–Blodgett layers. The IR dichroism spectra presented in Fig. 2 clearly show that the molecular planes are preferentially oriented perpendicularly to the dipping direction. This result was confirmed by X-ray diffraction in a transmission geometry (wavelength 0.1542 nm): a Langmuir film of compound **1a** on a nickel(II) acetate subphase was deposited onto hydrophobic silica. Crescent-like reflections are observed at 0.338 nm (see Fig. 3). This is a typical value for the distance between the planes of adjacent macrocycles, which suggests columnar organization. The crescent-like aspect reflects the preferential orientation of the columns along the dipping direction. However, no reflection corresponding to an intercolumnar distance was observed at smaller angles. A very small beam-stop was used to explore this region, which explains the additional rings caused by some beam-stop diffraction. The in-plane orientation could be explained considering the complexing ability of the 1,2,4-triazole subunit towards Ni^{II} ions.[10,11] The Ni^{II} ions may bridge two triazolephthalocyanines leading to a preorganized polymer-like structure at the air–water interface; on deposition, this would induce a preferential in-plane orientation of the molecules.

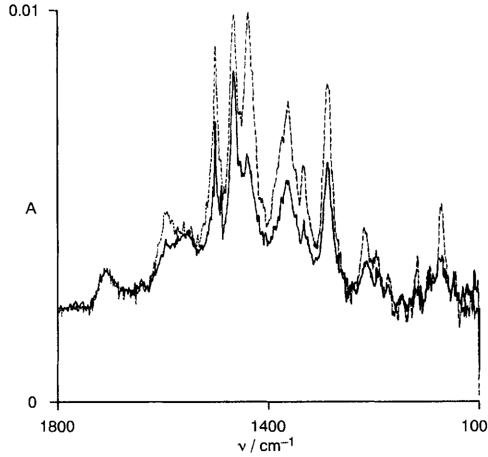


Fig. 2 IR dichroism of an LB film of **1a** onto a fluorine substrate. The Langmuir film was realized on a Ni(acetate)$_2$ subphase (10^{-3} mol dm^{-3}). —— = polarization parallel to the dipping direction, ------ = polarization perpendicular to the dipping direction.

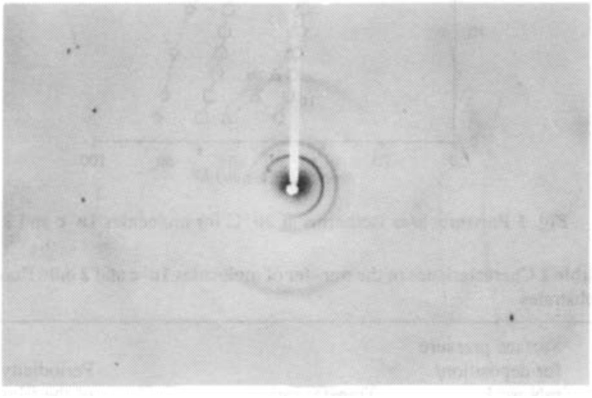


Fig. 3 X-Ray diffraction pattern in a transmission geometry realized on LB films of **1a** deposited onto hydrophobic silica (wavelength 0.1542 nm). The substrate is oriented perpendicularly to the X-ray incident direction. The third diffraction circle, which corresponds to a periodicity, of 3.38 Å, clearly shows an in-plane anisotropy; this periodicity, attributed to the distance between the macrocycles, is mainly present in the direction of transfer.

The non-centrosymetric and aromatic characteristics of triazolephthalocyanines and the organization found in LB films of these compounds holds a great potential for their use as templates to orient other molecules and therefore may find interesting electric or optical applications. Currently, work is focussed on exploring further this kind of induced in-plane orientation on similar molecules substituted with dyes or precursors of conducting polymers.

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Footnote

† mp >250 °C. IR ν/cm^{-1} (KBr): 1600, 1490, 1470, 1450 (C=N), 1390, 1250, 760 cm^{-1} (C–H). UV–VIS I_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 270 (4.42), 363 (4.17), 409 (sh), 535 (3.87), 640 (3.93), 676 (sh). FAB-MS (*m*-NBA, *m*/*z*) 907, 909 (M + H$^+$), 795, 797 ([M − C_8H_{16}] + H$^+$), 683, 685 ([M− 2C_8H_{16}] + H$^+$), 571, 573 ([M − 3C_8H_{16}] + H$^+$). ^{1}H NMR ($CDCl_3$) δ: 7.8, 6.5, 6.3 (3m, 9H arom), 4.1–3.5 (m, 6H, OCH_2), 2.0–1.1 (m, 36H, CH_2), 0.97 (m, 9H, CH_3).

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