Organization of triazolephthalocyanines in Langmuir–Blodgett films

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Langmuir monolayers were prepared using a new class of non-centrosymmetric macrocycles, the triazolephthalocyanines, differently substituted with aliphatic chains and/or thiophene subunits. Different monolayer behaviour and film deposition have been observed among the different macrocycles. Compounds substituted with two long aliphatic chains on the isoindole ring opposite to the triazole unit have shown the best monolayer behaviour. Stable monolayers were successfully transferred onto CaF_2 substrates which had been made hydrophobic. The Langmuir–Blodgett films were characterized by IR and UV–VIS linear dichroism. In-plane orientation of some of the macrocycles was observed when nickel(II) acetate was added to the aqueous subphase.

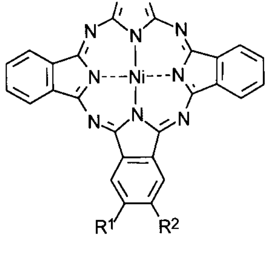
The Langmuir–Blodgett (LB) technique has been widely used as a tool to assemble supramolecular architectures into well-controlled lamellar structures[1] which present interesting applications in the fields of molecular electronics and chemical sensors.[2] Further organization within the layers of the built-up LB films can also be achieved in some circumstances. It has been established that this in-plane anisotropy is clearly related to the dynamic processes involved during the transfer of the Langmuir monolayer onto the solid substrate.[3] It was predicted that macromolecules or molecular aggregates of elongated shape would be orientated by the flow and lie parallel to the dipping direction after deposition. Therefore, rod-like polymers were the first macromolecules able to produce in-plane orientated LB films.[4] In particular, peripherally substituted phthalocyaninatopolysiloxanes $(PcSiO)_n$ form stable monolayers that can be transferred onto hydrophobic solid substrates to yield macroscopically-orientated LB films with the long axis of the polymer parallel to the dipping direction.[5]

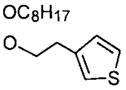
However, it seems that the limiting factor in the preparation of highly in-plane orientated LB films based on $(PcSiO)_n$ resides in the difficulty to prepare these polymers. It has been observed that the dichroic ratio that indicates the degree of order within the layer is related to the size of the rod. However, disk-like aromatic molecules bearing 'middle-size' aliphatic chains on the periphery are excellent building blocks for making in-plane orientated LB films, owing to the anisotropic columnar aggregates that they form at the air–water interface.[6] Indeed, peripherally substituted phthalocyanines and triphenylene derivatives form stable Langmuir monolayers with an 'edge-on' organization of the macrocycles. Well-controlled built-up films exhibit a high in-plane linear dichroism which is observed in both the UV–VIS and IR spectral regions and by polarizing microscopy, that can be explained by some orientational order in the plane of the LB multilayers.[7–9] However, symmetrically alkyl-chain substituted Pcs are not ideal molecules for LB formation since they do not exhibit amphiphilic characteristics. It has been demonstrated that the introduction of amphiphilic character in the Pc macrocycles facilitates the ordering of the macrocycles at the air–water interface, and the monolayers can be deposited as highly ordered LB films.[10]

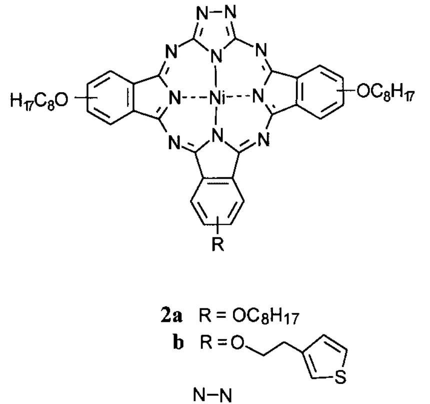
Triazolephthalocyanines[11] are a novel family of non-symmetric disk-like molecules with particularly appropriate characteristics for Langmuir film formation. They possess both the excellent ability exhibited by phthalocyanines to form columnar aggregates and the amphiphilic structure of classical LB molecules, provided by replacement of one of the isoindole subunits of the phthalocyanine macrocycle by the polar 1,2,4-triazole moiety. In addition, the 1,2,4-triazole unit can coordinate transition metal ions[12] that can be eventually incorporated in the aqueous subphase. Recently, we have reported on the use of a Ni^{II} acetate subphase to induce in-plane orientation in LB films of nickel(II)-triazolephthalocyanines.[13]

The ultimate goal of preparing in-plane orientated LB films of rod-like molecules or columnar aggregates is to use them for inducing an anisotropic organization of monomer precursors of conjugated conducting polymers, for instance thiophene units, which could form well orientated molecular wires after their polymerization in the condensed LB phase. An enhancement in the conductivity of the final conducting polymers has been predicted starting from anisotropically preorientated monomers.[14] Roncali and co-workers have attempted the electropolymerization of a thiophene derivative bearing a mesogenic substituent.[15] However, to our knowledge, thiophene derivatives have not been organized by means of the LB technique, using a columnar polymer or aggregate as template.

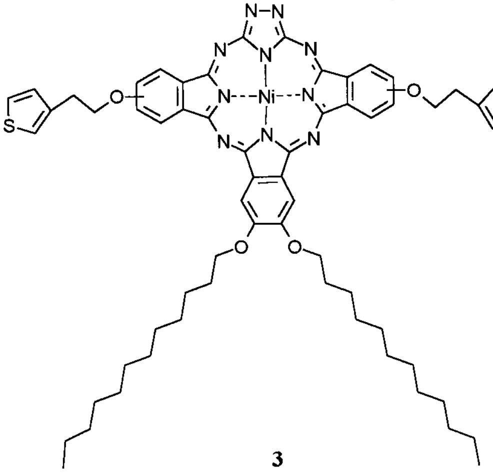
In this paper, we report the monolayer formation behaviour of representative examples of this new class of phthalocyanine analogues **1–4** and the use of the Ni^{2+} cation to increase the ability of the aromatic macrocycles to form columnar stacks at the air–water interface by complexation of the 1,2,4-triazole subunit. The use of such a method to organize triazolephthalocyanines having covalently linked thiophene units may represent a new way towards the formation of anisotropically orientated LB films of thiophene monomeric units, this being a big challenge in the synthesis of polythiophenes with enhanced conducting properties.



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



2a R = OC_8H_{17}
b R =



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Experimental Procedure

Materials and methods

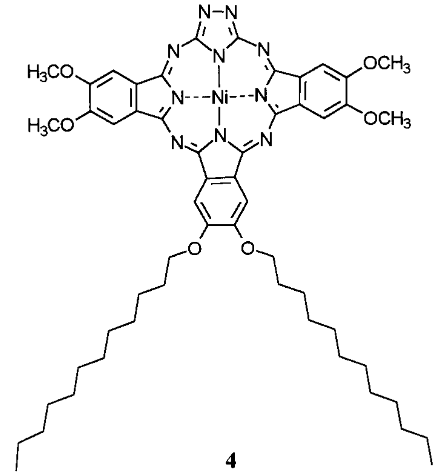
4-Nitro-1,2-dicyanobenzene[16] was prepared as described. Compounds **1a–c**,[11b] **1d**[17] and **2a**[13] were prepared following literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. UV–VIS and IR spectra were recorded on Perkin-Elmer Model Lambda 6 and PU 9716 Philips spectrometers, respectively. Melting points were determined on a Büchi melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker WM-200-SY spectrometer with either the solvent as reference or tetramethylsilane as the internal standard. All chemical shifts are quoted on the δ scale. All coupling constants are expressed in Hz. Fast atom bombardment mass spectra (FABMS) were obtained from a MAT 900 (Finnigan-MAT GmbH, Bremen Instruments) spectrometer. Samples of the molecules were dissolved in a small volume of *m*-nitrobenzyl alcohol and loaded on to a stainless steel probe tip. Microanalyses were performed by the University Microanalytical Service.

Synthesis of 4-[2-(3′-thienyl)ethoxy]-1,2-dicyanobenzene 5

4-Nitrophthalonitrile (2.00 g, 14.5 mmol), 2-(3′-thienyl)ethanol (3.70 g, 28.9 mmol) and K_2CO_3 (3.99 g, 28.9 mmol) were stirred in dry dimethylformamide (DMF) (10 ml), at 40 °C under an argon atmosphere for 24 h. The crude reaction mixture was poured into H_2O and then extracted with CH_2Cl_2. After removing the organic solvent, **5** was purified by column chromatography (SiO_2, CH_2Cl_2–hexane, 2:1), to yield 2.38 g of a colourless solid (81% yield); mp > 250 °C. δ_H ($CDCl_3$) 7.70 (d, *J* 8.8, 1H; benz.), 7.31 (dd, *J* 4.9, 2.9, 1H; thiophene), 7.26 (d, *J* 2.5, 1H; benz.), 7.17 (dd, *J* 8.8, 2.5, 1H; benz.), 7.10 (m, 1H; thiophene), 7.01 (dd, *J* 4.9, 1.2, 1H; thiophene), 4.26 (t, 2H; OCH_2), 3.18 (t, 2H; CH_2); δ_H [$(CD_3)_2SO$] 8.24 (m, 1H; arom.), 7.79 (m, 1H; arom.), 7.45 (m, 2H; arom.), 7.31 (m, 1H; arom.), 7.09 (m, 1H; arom.), 4.35 (t, 2H; OCH_2), 3.33 (t, 2H; CH_2).

Synthesis of 5-[2-(3′-thienyl)ethoxy]-1,3-diiminoisoindoline 6a

Compound **5** (1.06 g, 4.2 mmol) was suspended in dry MeOH (25 ml) containing NaOMe (0.07 g, 1.3 mmol). NH_3(g) was bubbled through the suspension at room temperature for 30 min. The mixture was heated at reflux temperature for 8 h whilst maintaining the NH_3(g) flow. After cooling the suspension, a greenish powder was filtered off and washed with MeOH to give **6a** in quantitative yield; mp > 250 °C; ν/cm^{-1} (KBr) 3400–2900 (NH), 1620, 1540 (C=N), 1490, 1450, 1315, 1270, 1230, 1145, 1070, 1025, 860, 840, 780; δ_H [$(CD_3)_2SO$] 8.4 (m, 1H; arom.), 7.7 (m, 1H; arom.), 7.5 (m, 1H; arom.), 7.3 (m, 1H; arom.), 7.1 (m, 2H; arom.), 4.3 (t, 2H; OCH_2), 3.1 (t, 2H; CH_2).



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General procedure for the preparation of 7,10:19,24-diimino-5,26:12,17-dinitrilotribenzo[*f,g,p*][1,2,4,9,14,19]hexaazaeicosinato(2−)-*N*^{27},*N*^{28},*N*^{29},*N*^{30}-nickel(II) complexes 2b, 3 and 4

A mixture of the appropriate 1,3-bis[(3′-imino-1′-isoindolinylidene)amino]-1,2,4-triazole **7a–c**[18] (1.1 mmol) and nickel(II) acetate tetrahydrate (0.28 g, 1.1 mmol) in 2-ethoxyethanol (40 ml) was stirred at 80 °C for 2 h. The mixture was cooled to 50 °C and then the 1,3-diiminoisoindoline **6a** or **6b** (1.1 mmol) in 2-ethoxyethanol (10 ml) was added. The reaction mixture was stirred at 50 °C for 48 h. The mixture was filtered and the resulting solid was triturated with hot MeOH several times. Finally, the solid was purified by column chromatography (SiO_2, CH_2Cl_2–MeOH, 15:1).

Data for **2b**: brown solid; yield 30%; mp > 250 °C; ν/cm^{-1} (KBr) 3600–3300 (OH), 1600, 1490, 1470, 1450 (C=N), 1370, 1340, 1290, 1250, 1070, 1020, 770; UV–VIS ($CHCl_3$): λ_{max}/nm (log ε) = 274 (4.72), 363 (4.42), 421 (4.28), 516 (4.11), 529 (4.02), 637 (4.08); FABMS: *m*/*z* = 905, 907 [$(M+H)^+$, 100], 793, 795 [$([M-C_8H_{16}]+H)^+$, 28], 571, 573 [$([M-2\times C_8H_{16}-C_6H_6S]+H)^+$, 31]; δ_H ($CDCl_3$) 7.2 (m, 2H), 7.1 (m, 2H), 6.8 (m, 4H), 6.3 (m, 4H), 3.9 (m, 2H), 3.6 (m, 4H), 2.9 (m, 2H), 1.7 (m, 4H), 1.6–1.2 (m, 12H), 0.9 (m, 6H); δ_C ($CDCl_3$) 137.4, 128.6, 125.1, 121.6, 31.7, 29.0, 25.6, 23.0, 14.1 (Found: C, 61.77; H, 5.82; N, 15.38; S, 3.30. Calc. for $C_{48}H_{50}N_{10}O_3SNi \cdot 1.5H_2O$: C, 61.81; H, 5.73; N, 15.02; S, 3.44%).

Data for **3**: brown solid; yield 13%; mp > 250 °C; ν/cm^{-1} (KBr) 3600–3100 (OH), 1600, 1465 (C=N), 1385, 1330, 1280, 1240, 1225, 1080, 965, 860, 825, 775; UV–VIS ($CHCl_3$): λ_{max}/nm (log ε)=292 (4.68), 367 (4.34), 475 (sh), 572 (sh), 636 (3.83); FABMS: m/z=1143, 1145 $[(M+H)^+$, 100]; δ_H ($CDCl_3$) 7.3 (m, 6H), 7.1 (m, 6H), 6.7 (m, 2H), 4.1 (m, 8H), 3.1 (m, 4H), 1.9 (m, 4H), 1.6–1.2 (m, 40H), 0.9 (m, 6H); δ_C ($CDCl_3$) 128.4, 125.7, 121.8, 32.0, 30.9, 29.9, 29.7, 29.6, 26.2, 22.8, 14.1 (Found: C, 62.07; H, 6.84; N, 10.96; S, 5.18. Calc. for $C_{62}H_{72}N_{10}O_4S_2Ni \cdot 3H_2O$: C, 62.15; H, 6.56; N, 11.69; S, 5.35%).

Data for **4**: brown solid; yield 35%; mp>250 °C; ν/cm^{-1} 3600–3300 (OH), 1600, 1500, 1460, 1440 (C=N), 1365, 1290, 1220, 1070, 870, 760; UV–VIS ($CHCl_3$): λ_{max}/nm (log ε)=290 (4.94), 365 (4.62), 430 (4.43), 534 (4.18), 575 (4.12), 632 (4.20); FABMS: m/z=1011, 1013 $[(M+H)^+$, 100], 843, 845 $[([M-C_{12}H_{24}]+H)^+$, 18], 675, 677 $[([M-2\times C_{12}H_{24}]+H)^+$, 34]; δ_H ($CDCl_3$) 7.2 (m, 6H), 4.0 (m, 12H), 3.6 (m, 4H), 1.3 (m, 40H), 0.9 (m, 6H) (Found: C, 62.55; H, 6.84; N, 13.04. Calc. for $C_{54}H_{68}N_{10}O_6Ni \cdot H_2O$: C, 62.98; H, 6.85; N, 13.60%).

Langmuir–Blodgett film formation and characterization

Chloroform solutions (spectroscopic grade) of **1a–d**, **2a–b**, **3** and **4** (10^{-4} M) were spread at the surface of pure Millipore water purified by reverse osmosis and deionization. The Langmuir trough, made of special non-porous PTFE (ATEMETA trough, model LB 105), was 0.4 m^2 in size.

For IR and UV studies, Langmuir monolayers were deposited on CaF_2 hydrophilic substrates which were made hydrophobic by predeposition of three fatty acid monolayers.

Results and Discussion

Synthesis

The 1,3-diiminoisoindoline **6a** was prepared in a two-step procedure by nucleophilic substitution of the nitro group[19] of 4-nitro-1,2-dicyanobenzene[16] with 2-(3′-thienyl)ethanol yielding the dicyanobenzene **5**. Compound **5** was subsequently treated with ammonia gas in the presence of a catalytic amount of sodium methoxide[20] to afford the target compound **6a** (Scheme 1).

Nickel(II) triazolephthalocyanines **2b**, **3** and **4** were synthesized in a two-step, one-pot reaction by treatment of the corresponding 1,3-bis[(3′-imino-1′-isoindolinylidene)amino]-1,2,4-triazole **7**,[18] with nickel(II) acetate in 2-ethoxyethanol at 80 °C followed by addition of the appropriate 1,3-diiminoisoindoline **6** at 50 °C (Scheme 2). Compounds **2b**, **3** and **4**, bearing aliphatic chains on some of the isoindole rings are readily soluble in apolar organic solvents. They were purified by column chromatography and fully characterized by elemental analysis and NMR, FABMS, IR and UV–VIS techniques.

A typical UV–VIS spectrum in $CHCl_3$ of this kind of compounds, represented by **1d**, is depicted in Fig. 1. It shows the presence of several absorption peaks at 632, 574, 529, 507, 371 and 260 nm as a consequence of the lack of symmetry of the molecule. Furthermore, the spectrum does not exhibit strong changes in either the absorbance values or the wave-

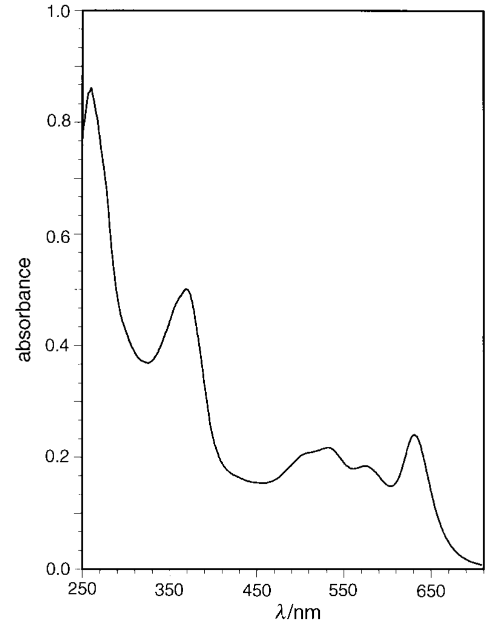
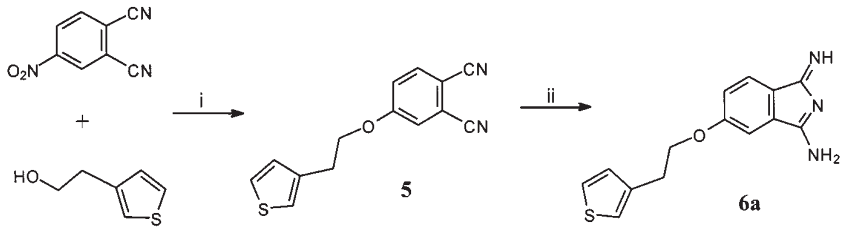
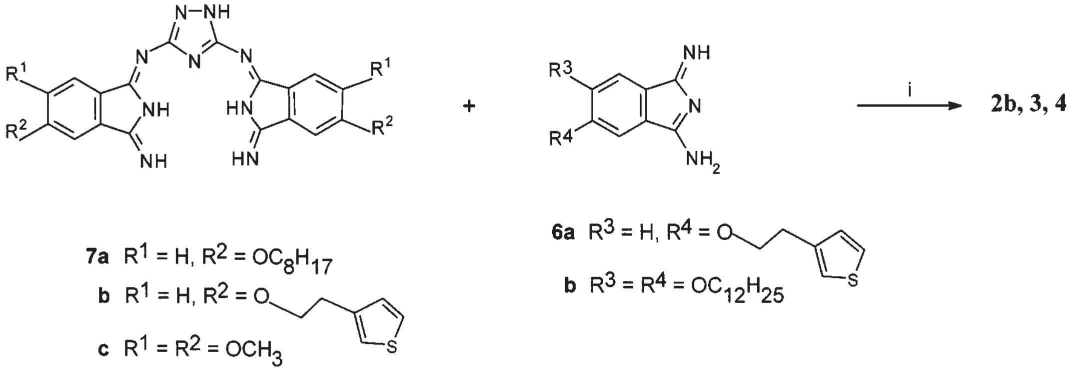


Fig. 1 UV–VIS Spectra of compound **1d** in $CHCl_3$ (1.3×10^{-5} M)



Scheme 1 *Reagents and conditions*: i, K_2CO_3, DMF; ii, NH_3 (g), NaOMe, MeOH



Scheme 2 *Reagents and conditions*: i, $Ni(CH_3CO_2)_2 \cdot 4H_2O$, $EtOCH_2CH_2OH$, 50 °C

length upon variation of the concentration. Therefore, it seems that no strong aggregates are formed in solution in the concentration range 3×10^{-4} to 5×10^{-5} M.

Monolayer formation

Chloroform solutions of compounds **1a–d**, **2a–b**, **3** and **4** 10^{-4} M were spread at the surface of pure Millipore water. Pressure–area isotherms (π–A curve) at 20 °C represented in Figs. 2 and 3 were reproducible and Langmuir films were stable until 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 in an 'edge-on' configuration on the aqueous subphase with the polar 1,2,4-triazole in contact with the water. This result suggests the formation of well-packed monolayers. Monosubstituted triazolephthalocyanines **1b,c** presented similar isotherms with a reproducible molecular area of *ca.* 34 Å^2 for the solid phase. This result tends to indicate the formation of a bilayer-like structure at the air–water interface. For compound **1d**, a slow phase transition was observed at surface pressures from 15 to 20 mN m^{-1}. At low pressures, the pressure–area isotherm is similar to that of **1b** but for high pressures, the film is composed of multilayers.

In the case of the trisubstituted macrocycle **2a**, the CPK models give a theoretical molecular cross section of *ca.* 75 Å^2. Therefore, the first part of the π–A curve is clearly compatible with an 'edge-on' orientation of the macrocycle at the air–water interface. However, at a pressure of *ca.* 16 mN m^{-1}, a phase transition occurs with a decrease of the molecular area to half its value. This step in the curve is probably due to the formation of a double layer at the air–water interface. Such behaviour has also been observed for other aliphatic chain substituted macrocycles.[8e]

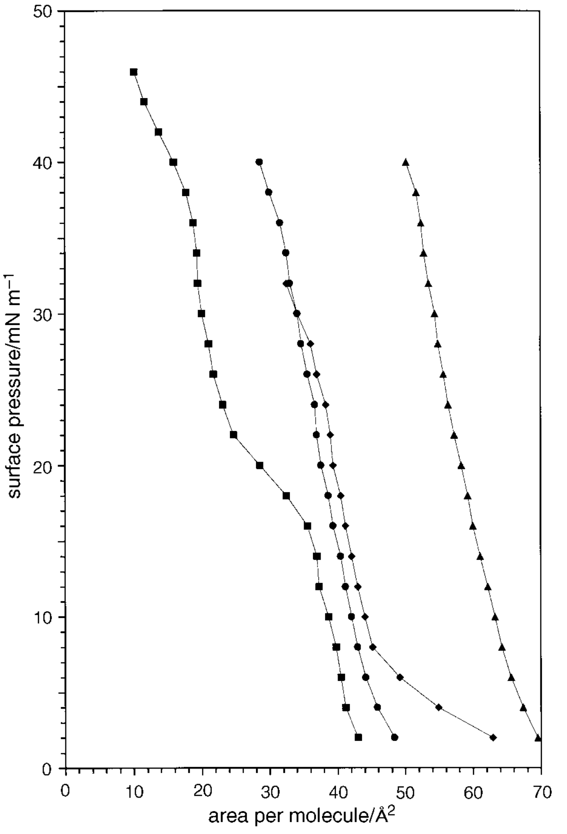


Fig. 2 Pressure–area isotherms at 20 °C for molecules **1a–d**: (▲) **1a**, (◆) **1b**, (●) **1c** and (■) **1d**

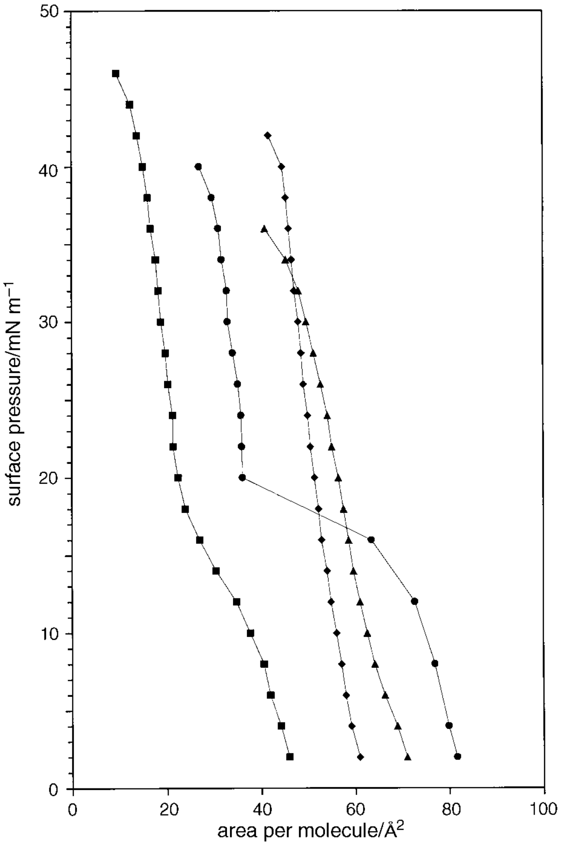


Fig. 3 Pressure–area isotherms at 20 °C for molecules **2a**, **b**, **3** and **4**: (●) **2a**, (■) **2b**, (▲) **3** and (◆) **4**

The π–A curve for compound **2b** is very similar to that of compound **1d**. This result suggests that the organization of these macrocycles at the air–water interface is driven by the presence of a 3-(2′-ethoxy)thiophene substituent on the isoindole ring situated opposite to the 1,2,4-triazole ring rather than by the octyloxy chains positioned in the horizontal axis of the macrocycle.

Compounds **3** and **4** show similar monolayer behaviour to compound **1a**. Again, the two dodecyloxy substituents on the isoindole ring opposite to the triazole subunit seem to be an important structural feature in the organization of triazolephthalocyanines in Langmuir films. The pressure–area isotherm of compound **3** displays a reproducible molecular area of *ca.* 56 Å^2. This result suggests a highly packed monolayer considering the theoretical cross section calculated by CPK models (75 Å^2) (Fig. 4). The same behaviour is exhibited by compound **4**. In this case, a molecular area of *ca.* 52 Å^2 is obtained from the pressure–area curve while a theoretical cross section of *ca.* 70 Å^2 is estimated.

In summary, compounds with long aliphatic substituents on the isoindole opposite to the triazole (**1a**, **2a**, **3** and **4**) form monomolecular films at the air–water interface with the molecules standing vertically at the interface. This result is expected since, according to their chemical structure, **1a**, **2a**, **3** and **4** do present an 'adequate' balance between van der Waals and π–π interactions. Within this group of triazolephthalocyanines, macrocycle **2a** shows a different Langmuir behaviour—a collapse of the monolayer is observed at very low pressure (16 mN m^{-1}). Obviously, substitution of the side isoindole groups by large groups (octyloxy) is not a favourable molecular structure for Langmuir film formation. This is confirmed if one compares the results for **1d** (clear solid phase at low surface pressure) with **2b** (unclear π–A curve).

Complexation of transition metal ions such as Ni^{2+} by the

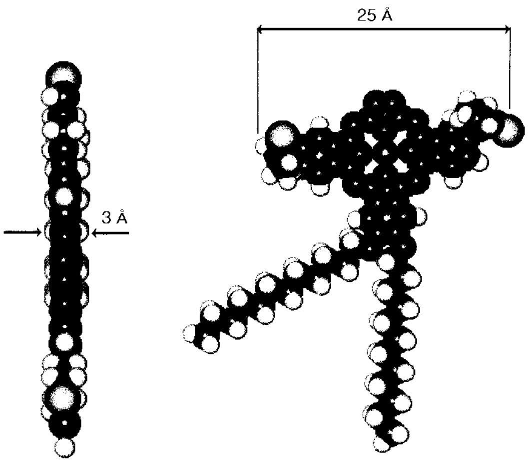


Fig. 4 Space-filling representation of compound **3**

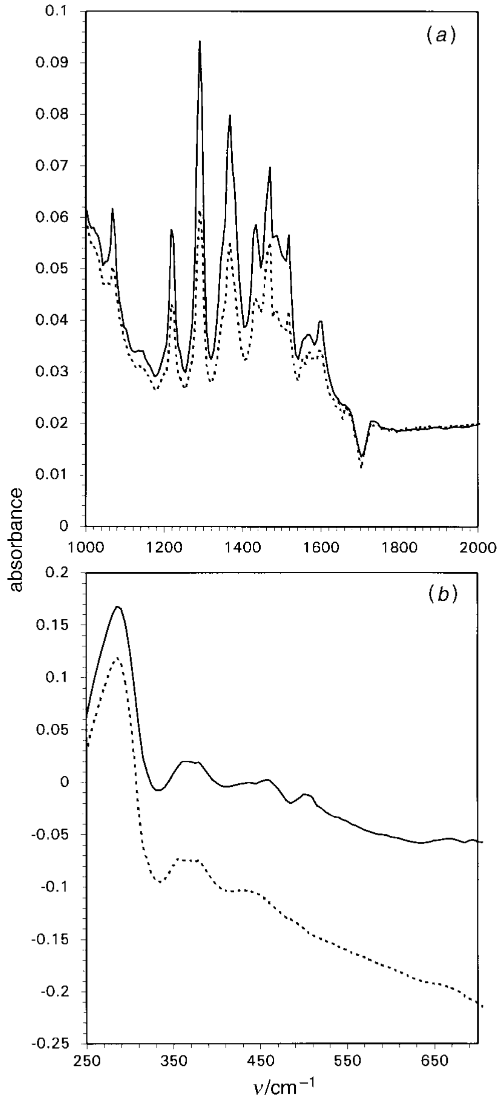


Fig. 5 (*a*) IR and (*b*) UV–VIS dichroism of an LB film of **4** on a CaF_2 substrate. The Langmuir film was realized on a 10^{-3} M nickel(II) acetate subphase. Solid line corresponds to a polarization perpendicular to the dipping direction and dotted line corresponds to a polarization parallel to the dipping direction.

1,2,4-triazole moiety of the triazolephthalocyanines was studied at the air–water interface. The pressure–area curves of compounds **1a**, **2a** and **4** showed hardly any change when nickel(II) acetate was introduced in a 10^{-3} M concentration in the water subphase. This result indicates that the orientation of the triazolephthalocyanines is not affected upon complexation of the Ni^{II} ions present in the aqueous subphase, and confirms the 'edge-on' orientation of the macrocycles with the 1,2,4-triazole moiety in contact with the water phase.

LB film formation

Using the vertical dipping method, macrocycles **1a**,**b**,**d**, **2a**,**b**, **3** and **4** were deposited onto CaF_2 hydrophilic substrates made hydrophobic by predeposition of three fatty acid monolayers. The surface pressure for deposition and transfer ratio of the Langmuir films are listed in Table 1. At their transfer pressure, the films of **1a**, **2a**, **3** and **4** were monolayer-like and gave 100% transfer. Compounds **1c** and **2b** gave poor results and were not investigated further.

For low surface pressures, the Langmuir film of **1d** behaved similarly to that of molecule **1b**; the transfer results for both compounds are the same. However, for high surface pressures, the film of **1d** is made of multilayers that could not be transferred. UV–VIS and IR dichroism measurements were tried on films of **1a**, **b**, **d**, **2a**, **3** and **4** but they did not show any preferential orientation of the molecules. On the contrary, if nickel(II) acetate is introduced in a 10^{-3} M concentration in the water subphase, Langmuir–Blodgett films of **1a**, **2a** and **4** lead to in-plane orientated Langmuir–Blodgett layers. In the case of **1a**, the IR dichroism spectra clearly show that the molecular planes are preferentially orientated perpendicularly to the dipping direction. This result was confirmed by X-ray diffraction in a transmission geometry.[13] The same results were obtained for the structurally related triazolephthalocyanine **4**, as the IR and UV–VIS dichroism spectra, presented in Fig. 5(*a*) and (*b*), respectively, show. In this case, an increase of the band at 505 nm was observed in the UV spectrum when cross-polarized light was used. To some extent, this in-plane orientation induced by the introduction of nickel(II) acetate into the aqueous subphase was evident in Langmuir–Blodgett films of compound **3**.

The in-plane orientation could be explained considering the well-known complexation ability of the 1,2,4-triazole subunit towards Ni^{II} ions.[12] The Ni^{II} ions may certainly behave as bridges between triazolephthalocyanines leading to the formation of a pre-organized polymer-like structure at the air–water interface such as the one represented in Fig. 6. Upon deposition, this would induce a preferential in-plane orientation of the molecules. Using other transition metal cations, such as Fe^{II}, the induced orientation of the triazolephthalocyanines in multilayers was not observed.

Table 1 Characteristics of the transfer of molecules **1a–d**, **2a–b**, **3** and **4** onto CaF_2 substrates

	1a	**1b**	**1c**	**1d**	**2a**	**2b**	**3**	**4**
surface pressure for deposition/mN m^{-1}	25	20	25	10	10	8	25	25
transfer ratio	1 (up and down)	1 (up only)	no transfer	1 (up only)	1 (up and down)	<0.5 (after 2 layers)	1 (up and down)	1 (up and down)

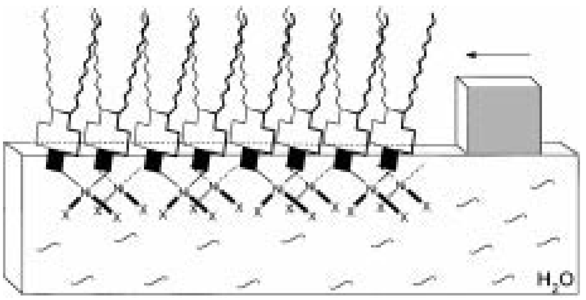


Fig. 6 Schematic representation (side view of the Langmuir trough) of the proposed organization for the Langmuir film of triazolephthalocyanine **1a**. The black square represents the triazole subunit and the wavy line the lipophilic chains.

One of the key results of this study is the potential for directly obtaining thin films of macrocycles bearing no aliphatic chains like **1b** and **1d**. The π–A curves suggest that **1b** and **1d** form multilayer-like structures at the air–water interface even at low pressures. However, the results were reproducible and good transfer has been realized as explained above. Obviously, the formal replacement of one of the isoindole moieties in a phthalocyanine by a triazole unit gives rise to a new type of amphiphilic molecules for LB studies in which the aliphatic chains are replaced by aromatic macrocycles. On the other hand, the asymmetry of triazolephthalocyanines and the organization found in LB films of these compounds suggest a great potential for their use as templates to orientate other molecules. The preliminary studies presented in this paper on macrocycles substituted with thiophene subunits gave poor results. This may be related to the perturbation induced by the thiophene on the arrangement of the macrocycles because of the short length of the spacer (two methylene groups only). Current work is focused on exploring further this kind of induced in-plane orientation on similar macrocycles with various substitution patterns in order to understand the influence of substitution on the orientational ability of the macrocycles.

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