JOURNAL OF Materials CHEMISTRY

Supramolecular organization of subphthalocyanines in Langmuir and Langmuir–Blodgett films

M. Victoria Martínez-Díaz,[a] Belén del Rey,[a] Tomás Torres,*[a] Beatrice Agricole,[b] Christophe Mingotaud,*[b] Nicolas Cuvillier,[b] Gema Rojo[c] and Fernando Agulló-López*[c]

[a]*Departamento de Química Orgánica (C-I), Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain. E-mail: tomas.torres@uam.es*
[b]*Centre de Recherche Paul Pascal, Chateau Brivazac, Avenue A. Schweitzer, F-33600 Pessac, France*
[c]*Department of Physics of Materials, (C-IV), Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain*

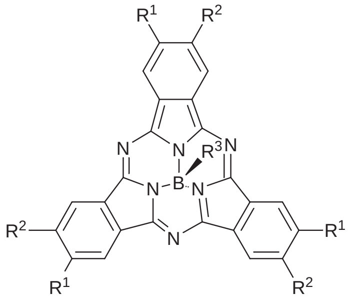
Received 15th March 1999, Accepted 13th May 1999

Interfacial studies of a series of subphthalocyanine (SubPc) macrocycles **1**–**3**, **5** and **6**, differently substituted either in the periphery (with polar and donor groups) or in the axial position of the macrocycle (with a chlorine atom or a trihexylsiloxy group), have been carried out. Remarkable changes in the orientation of the macrocycles at the air/water interface have been observed by varying the number of polar groups in the periphery or adding a bulky group in the axial position. The morphology of the monolayers has been carefully studied by Brewster angle microscopy. Monolayers made of compounds **1**–**3** could be efficiently transferred onto hydrophobic substrates. LB films of SubPc **1** were characterized in detail by UV–VIS and IR spectroscopies, and X-ray diffraction and ellipsometry experiments. These studies indicate that the LB films of SubPc **1** are surely Y-type, formed by layers of a well-defined average thickness of *ca.* 16 Å. Preliminary studies on the nonlinear optical (NLO) properties of these materials have been carried out. In particular, second harmonic generation (SHG) experiments have been performed on LB films of SubPc **1**.

Phthalocyanines (Pcs)[1] are compounds presenting fascinating properties. They have been largely studied either in solution or in various organized systems.[2] In order to design new practical devices from such derivatives, the relationship between the supramolecular architecture and the physical behavior of the material should be perfectly understood.[3] The Langmuir–Blodgett (LB) technique[4] for depositing organized thin organic films has been widely used with amphiphilic phthalocyanines and related analogues for this goal.[5] A variety of technological applications of phthalocyanine thin films such as photovoltaics, electrochromism, and gas sensors, among others have been actively investigated.

Subphthalocyanines (SubPcs)[6] (**1**–**6**) are the lowest-sized analogues of phthalocyanines composed of three coupled isoindole moieties arranged around a boron atom having a delocalized 14 π-electron system. Unlike the related planar phthalocyanines, SubPcs have a cone-shaped structure, which does not prevent them from having an aromatic character. Recently, SubPcs have received considerable attention as excellent building blocks to synthesize unsymmetrical functionalised phthalocyanines[6b] and as materials for nonlinear optics.[7–9] They present an excellent second harmonic generation (SHG) response in solution.[8] Our interest in studying the nonlinear properties of these systems in condensed phases and in establishing the relationship between the microscopic and the macroscopic levels prompted us to analyze the organization of these molecules in evaporated and spin-coated films.[9]

We report in this paper on the organization of subphthalocyanines **1**–**3**, **5** and **6** (see structures in Fig. 1) in Langmuir monolayers, and in Langmuir–Blodgett films when they can be transferred onto solid substrates. To the best of our knowledge, this is the first time that a subphthalocyanine has been organized in this kind of condensed phase. Preliminary studies on the second order NLO responses of these films are also discussed.



1 $R^1 = H, R^2 = SO_2C_8H_{17}, R^3 = Cl$
2 $R^1 = H, R^2 = Bu^t, R^3 = Cl$
3 $R^1 = H, R^2 = SC_8H_{17}, R^3 = Cl$
4 $R^1 = H, R^2 = SC_8H_{17}, R^3 = OH$
5 $R^1 = H, R^2 = SC_8H_{17}, R^3 = OSi(C_6H_{13})_3$
6 $R^1 = R^2 = SO_2C_8H_{17}, R^3 = Cl$

Fig. 1 Structural formulae of subphthalocyanines **1**–**6**.

Experimental

Subphthalocyanines **1**, **3** and **6** have been previously described.[8b] Compound **2** was obtained according to a method reported by us[6a] and purified by column chromatography on silica gel (CH_2Cl_2) in 43% yield.

Synthesis of SubPc 4

A suspension of SubPc **3** (862 mg, 1 mmol) in water was heated with vigorous stirring under reflux for 24 h. After cooling, the reaction mixture was filtered and the solid purified further by column chromatography (aluminium oxide deactivated with 10% water; CH_2Cl_2–hexane (1:1)) leading to the pure product **4** as a sticky violet solid (820 mg, 97%). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) δ 8.5 (m, 6H), 7.5 (m, 3H), 3.2 (m, 6H), 1.9–1.1 (m, 36H), 0.8 (m, 9H). MS (FAB, NOBA) *m/z* 844 $(M+H)^+$. UV–VIS ($CDCl_3$, nm (log ε/dm^3 mol^{-1} cm^{-1})) λ_{max} 574 (4.2), 540 (sh), 353 (4.2), 287 (4.4). IR (KBr, cm^{-1}) ν 2922, 2853, 1741 (C=N), 1464, 1425 (B–N), 1353 (B–O), 740. Anal. Calc. For $C_{48}H_{61}N_6S_3BO$: C, 68.23; H, 7.27; N, 9.94; S, 11.38. Found: C, 60.54; H, 7.42; N, 9.58; S, 10.95%.

Synthesis of SubPc 5

To a solution of SubPc **4** (843 mg, 1 mmol) in dry chlorobenzene (40 mL) under argon atmosphere trihexylchlorosilane (350 mg, 1.1 mmol) was slowly added. Then the mixture was vigorously stirred for 2 h at reflux temperature. After cooling the reaction mixture, the crude product was purified by flash chromatography (aluminium oxide deactivated with 10% water–hexane and then CH_2Cl_2) to yield **5** as a sticky violet solid (270 mg, 28%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.67 (d, 3H), 8.66 (d, 3H), 7.75 (dd, 3H), 3.2 (m, 6H), 1.8–0.6 (m, 78H), −0.4 (m, 6H). MS (FAB, NOBA) *m/z* 1127 $(M+H)^+$. UV–VIS ($CHCl_3$, nm (log ε/dm^3 mol^{-1} cm^{-1})) λ_{max} 288 (4.4), 361 (4.0), 540 (sh), 580 (4.5). IR (KBr, cm^{-1}) ν 2956, 2922, 2854, 1606 (C=N), 1465 (B–O), 1185 (Si–O), 756 (C–S), 669 (Si–C). HRMS calcd. for $C_{66}H_{99}N_6BOSi$: 1126.6887. Found: 1126.6888.

Physical measurements and instrumentation

The UV–VIS and IR measurements were carried out respectively on Perkin Elmer Model Lambda 6 and Bruker IFS66V instruments. MS spectra were determined on a VG AutoSpec instrument. ^{1}H-NMR and ^{13}C-NMR were recorded with a Bruker AC-200 spectrometer (200 and 50 MHz respectively).

Preparation of Langmuir and Langmuir–Blodgett films. Chloroform (HPLC grade from Prolabo) was used as spreading solvent. The water of the subphase was Millipore Q-grade with a resistivity higher than 18 MΩ cm^{-1}. Compression isotherms and built-up films (vertical lifting method) have been obtained using a laboratory-made LB trough working at room temperature under a continuous dried nitrogen flow. After each increase of the surface pressure (steps of 2 mN m^{-1} were usually chosen), a waiting time allowed the system to reach its equilibrium. The films were transferred (at 10, 5 and 4 mN m^{-1} respectively for **1**, **2** and **3**) on to optically polished calcium fluoride or zinc selenide for infrared measurements and on to silanized glass for ellipsometry and X-ray diffraction experiments.

Alternated monolayers of SubPc **1** and behenic acid were transferred using a KSV 5000 trough.

Infrared (IR) spectra were recorded on an FTIR 750 Nicolet spectrometer. Linear dichroism in IR spectrometry was used to determine the orientation of the molecules in LB films. Two different IR spectra were recorded using polarized light. The substrate normal is respectively parallel and tilted by an angle of 60° *versus* the polarized incident beam. The out-of-plane dichroic ratio β for each band is then defined as:

$$\beta(60°)=A(60°)/A(0°)$$

where A is the absorbance of the IR band.

This ratio leads to an estimation of the mean angle between the normal to the substrate and the dipole moment of a particular vibration with an accuracy of a few degrees. Furthermore, the in-plane dichroic ratio, ρ, is defined for a particular IR peak by the relation:

$$\rho=A_{\perp}/A_{\parallel}$$

where $A_{\perp}$ and $A_{\parallel}$ are respectively the absorption of the LB films when the light polarization is set perpendicular or parallel to the dipping direction. Using this dichroic ratio, one can define an order parameter, P_2, as:

$$P_2=(1-\rho)/(1+\rho).$$

This parameter is equal to the average of $\cos(2\theta)$ over the distribution of molecular orientation, where θ is the angle of the dipole moment associated with the analyzed peak and the dipping direction.

UV–visible spectra were recorded with a 330 Perkin Elmer spectrometer.

Ellipsometry was done with a Plasmos ellipsometer working at 632.8 nm.

X-Ray diffraction experiments (θ–2θ scans) were performed with an apparatus described previously.[10]

Brewster angle microscopy developed by Hénon and Meunier[11] enables the observation of the monolayer morphology. The instrument used in this work has been already fully described.[12]

NLO measurements of the LB films. The SHG intensity was detected as a function of the incidence angle of the laser beam, which is changed by tilting the sample with regard to an axis in the film plane and perpendicular to the incident fundamental beam. A Q-switched Nd^{3+}: yttrium–aluminium–garnet (YAG), with a 10 ns pulse duration and a repetition rate of 10 Hz, operating at 1.064 μm was used as fundamental light source.

In front of the sample, a linear polarizer and a half-wave plate are used in order to obtain the s- and p-polarizations of the incident beam. We also used a polarizer behind the sample to measure only the p-polarization component of the second-harmonic signal which is detected by a photomultiplier tube, averaged by a boxcar integrator and stored in a computer.

Results and discussion

Synthesis and spectroscopic characterization

Syntheses of SubPcs **1**–**3** and **6** were carried out in moderate yield by boron trichloride-induced cyclotrimerization of the appropriately substituted phthalonitrile derivatives in 1-chloronaphthalene, following a procedure reported by Meller and Ossko.[13] Compounds **1**–**5** were in fact a mixture of two isomers with symmetries C_1 and C_3 in a 3:1 ratio.[8] The synthesis of subphthalocyanine **5** bearing a siloxy group in the axial position was accomplished in two steps involving replacement of the chlorine atom in **3** by a hydroxy group to give **4**, which was further reacted with trihexylchlorosilane to yield **5**. The transformation of compound **3** into **4** was monitored by IR spectroscopy, observing the disappearance of the B–Cl band centered at 968 cm^{-1} and simultaneous appearance of a new band at 1353 cm^{-1} assigned to a B–O vibration. The IR spectrum of compound **5** shows new bands around 1000 and 1400 cm^{-1} for the Si–O and B–O bonds, respectively.

The ^{1}H-NMR spectrum in $CDCl_3$ of subphthalocyanine **5** shows characteristic resonances at high field (1.8 to −0.4 ppm) for the methylene and methyl groups of the hexylsiloxy chains in the axial position of the boron SubPc.

The UV–visible spectra of subphthalocyanines **1**–**6** in $CHCl_3$ are dominated typically by two intense bands: the Q band around 560 nm and the Soret (B) transition in the UV-region of the spectrum around 300 nm. The bands are blue shifted compared to those of metallophthalocyanines owing to the smaller conjugated system (14 *vs.* 18 π electrons). Unlike many phthalocyanines, we have not observed any concentration dependence either in the wavelength or in the shape of the absorption maxima. This result indicates that SubPcs remain monomeric in the range of concentration studied.

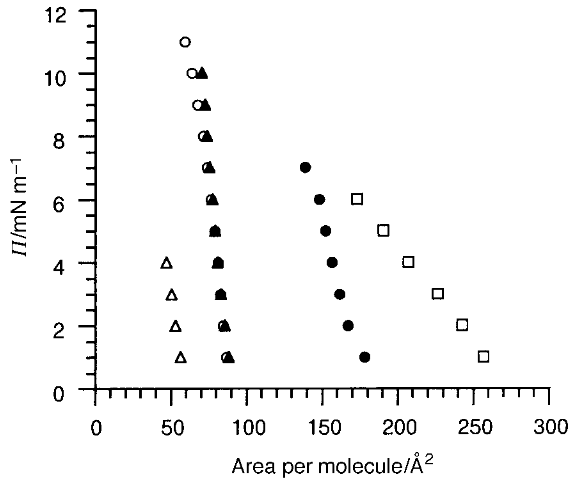


Fig. 2 Step-by-step compression isotherm of subphthalocyanine derivatives on pure water (room temperature). Full triangles: SubPc **1**. Open circles: SubPc **2**. Open triangles: SubPc **3**. Full circles: SubPc **6**. Open squares: SubPc **5**.

Interfacial studies

Step-by-step compression isotherms of compounds **1**–**3**, **5** and **6** spread on pure water are given in Fig. 2. As described above, compounds **1**–**5** are a mixture of two isomers and the compression isotherms may then depend on the relative proportion of those isomers. In such curves, the last points are those recorded before the collapse which appears at a surface pressure of a few mN m^{-1}. For higher values, the system is slightly unstable *versus* time indicating a slow collapse or crystallization process. These collapse pressures are therefore very low, especially when comparing the subphthalocyanine films with those obtained with phthalocyanine derivatives.[14] For phthalocyanines, the somewhat high collapse pressure should be related to the strong π–π interactions occurring between molecules at the gas/water interface. The 'conical' shape of the SubPc derivatives with the B–R^3 group pointing out of the macrocycle may prevent or at least reduce those interactions and therefore the stability of the Langmuir film. The areas per molecule are found to be either around 50–100 Å^2 per molecule for SubPcs **1**–**3** or above 150 Å^2 per molecule for SubPcs **5** and **6**. Evaluations of the molecular dimension can be done using CPK models. Then, the subphthalocyanine macrocycle should occupy an area of *ca.* 50 Å^2 (or 225 Å^2) when standing on its edge at the gas/water interface (or lying along the interface, respectively). Therefore, an edge-on disposition may be assumed from the compression isotherm for the subphthalocyanines **1**–**3** (see Fig. 3a). On the contrary, derivative **5** presents a π–A curve which is strongly shifted towards the large areas per molecule. The alkyl substituent linked directly to the boron atom clearly prevents the edge-on orientation and forces the subphthalocyanine to lie more flat on the water surface (see Fig. 3b). Similarly, SubPc **6** bearing six alkylsulfonyl groups adopts the same organization within the monolayers. This orientation maximizes the interactions between polar groups and water. These results suggest that the orientation of subphthalocyanines at the air/water interface can be chemically modulated; by increasing the number of polar groups in the periphery (**1** compared to **6**) or adding a bulky group in the axial position (**3** compared to **5**) we can achieve respectively a somewhat edge-on or side-on disposition.

The morphology of the monolayers was then studied by Brewster angle microscopy (BAM) in the particular cases of compounds **1** and **5**. The monolayer of **1** presents at low surface pressures the expected transition from a gaseous state to a liquid phase (not shown). Similar results were found for SubPc **5** which forms a foam at large areas per molecule (see Fig. 4), the size of the gaseous bubbles decreasing during the compression and leading to a homogeneous Langmuir film in a liquid phase. However, and on the contrary to SubPc **1**, inhomogeneities in the compound **5** film appear for surface pressure higher than a few mN m^{-1} (see Fig. 5). Those bright indefinite islands should correspond to multilayers or 3D crystallites suggesting that the monolayer undergoes a slow but irreversible crystallization during the compression. In fact, the lower slope of the compression isotherm of **5** compared to the other monolayers may be related to this process. Finally, these BAM experiments as well as the extrapolated area at zero pressure of the π–A curve suggest that SubPc **5** forms a real monolayer only at null surface pressure and that crystallization occurs when the surface pressure increases. For this reason, transfer onto solid substrate was not attempted with this derivative.

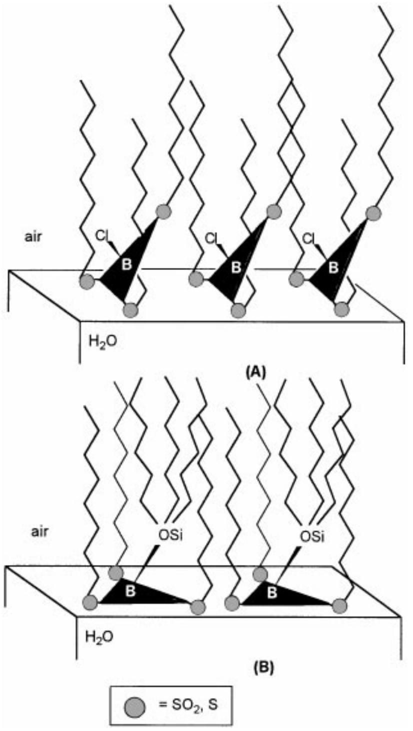


Fig. 3 Schematic representation of A) an edge-on and B) a side-on disposition for subphthalocyanines at the air/water interface.

Langmuir–Blodgett films

Transfers of the SubPcs **1**–**3** monolayers onto hydrophobic substrates were performed at a surface pressure below the collapse (see Experimental section) with a dipping speed of 1 cm min^{-1} (transfer ratios close to 0.8–0.9). On the contrary, no efficient transfer has been obtained with compound **6**, presumably because of the too expanded state of the monolayer. The Y-type LB films are optically defect-free. The UV–visible spectra of the LB films show bands comparable to those recorded in solution (*vide supra*): 580 nm and a shoulder at *ca.* 520 nm for the derivative **1**, 575 nm and a shoulder at *ca.* 535 nm for **2**, 600 nm and a shoulder at *ca.* 550 nm for compound **3**. Further structural characterizations were done in the case of SubPc **1**.

Infrared spectroscopy allows one to probe the molecular orientation within the LB films. In particular, a slight in-plane dichroism (see Fig. 6a) is observed suggesting some ordering during the LB transfer. Vibrations corresponding to wavenumbers in the range 1600–1700 cm^{-1} are assigned to the C=C and C=N bonds of the macrocycle. Therefore, the dichroism of those peaks indicates that this subphthalocyanine presents a very small preferential alignment with respect to

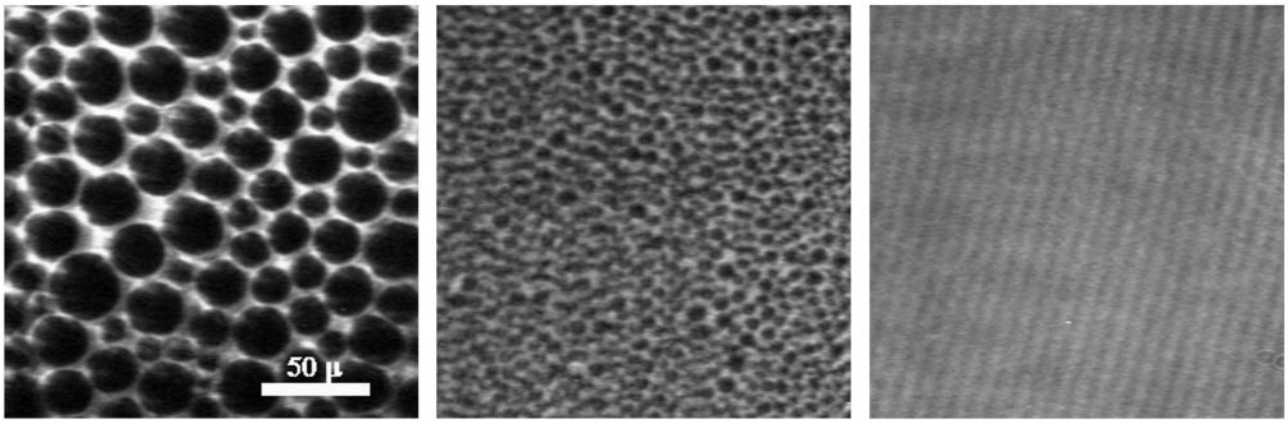


Fig. 4 BAM images of the monolayer of SubPc **5** during compression. Null surface pressure. From left to right: 640 Å^2 per molecule to 400 Å^2 per molecule.

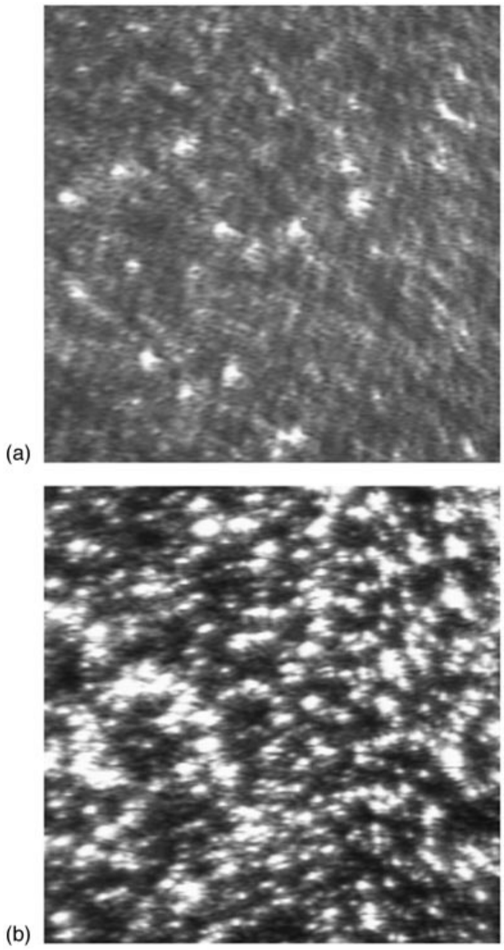


Fig. 5 BAM images of a monolayer of SubPc **5** during compression. Surface pressure (a) *ca.* 3 and (b) 6 mN m^{-1}.

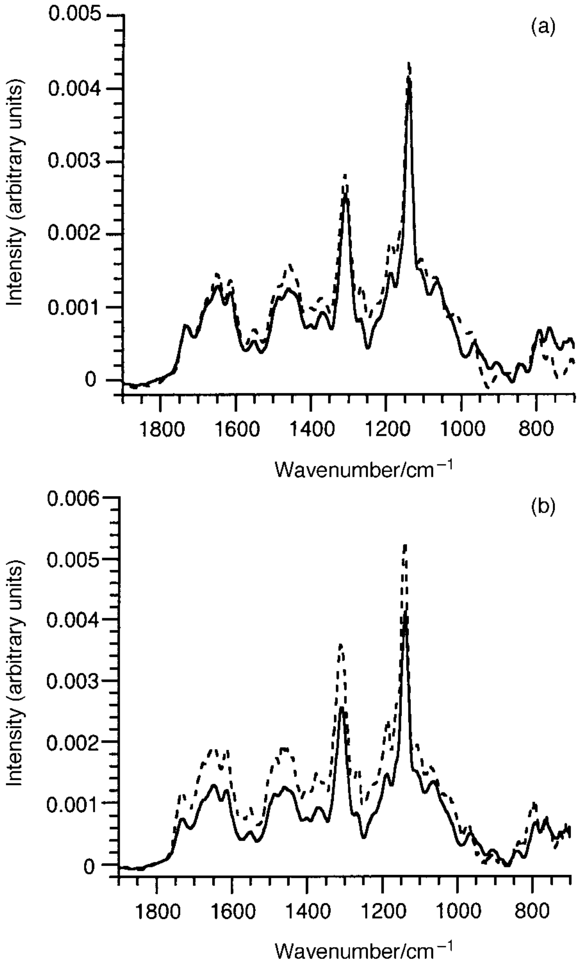


Fig. 6 (a) Infrared spectra of 20 layers of SubPc **1** deposited onto a zinc selenide substrate. In-plane dichroism: E vector parallel (solid line) or perpendicular (dashed line) to the dipping direction. (b) Infrared spectra of 20 layers of SubPc **1** deposited onto a zinc selenide substrate. Out-of-plane dichroism: the angle between the E vector and the normal to the substrate is 0° (solid line) or 60° (dashed line).

the dipping direction. Indeed, the corresponding order parameter P_2 (*ca.* 0.04) is one order of magnitude smaller than that found for some phthalocyanine derivatives in LB films.[5c,14,15] Finally, the peaks at 2930 and 2860 cm^{-1} associated with the alkyl chains present no in-plane dichroism, demonstrating that the macrocycle only presents a slight in-plane orientation. The positions and the linewidth of those antisymmetric and symmetric stretching bands of the CH$_2$ groups show that a large portion of the C–C bonds in the alkyl chains should have a gauche conformation. Therefore, the alkyl chains are poorly organized in those LB films. The average tilt angle of the alkyl groups (*ca.* 25°) deduced from the out-of-plane dichroism of the 2930 and 2860 cm^{-1} peaks is then purely indicative. The other IR peaks show some out-of-plane dichroism, related in particular to an out-of-plane organization of the macrocycle ring of SubPc **1** (Fig. 6b). The analysis of such a dichroism suggests that various transition dipoles of SubPc are tilted *versus* the normal to the substrate with an angle of *ca.* 60°. Even if the exact peak assignment is currently unknown, this result clearly indicates that the macrocycle is tilted in the LB

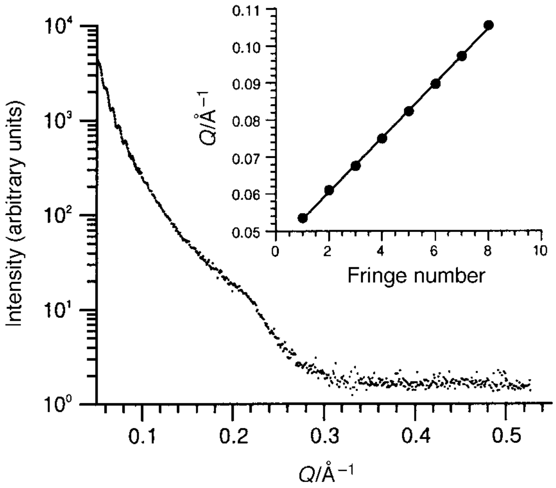


Fig. 7 X-Ray diffractogram of an LB film (50 layers deposited on glass) of SubPc **1**. Insert: the *Q* positions of the Kiessig fringes.

film. This tilting process during the transfer should be similar to the one observed for phthalocyanines.[5]

X-Ray diffraction experiments performed on SubPc **1** multilayers show a broad reflection (see Fig. 7) around 0.2–0.21 Å^{-1} for the Q wave vector. The lack of strong Bragg peaks and the presence of such a broad reflection suggest that the lamellar structure is not perfectly well-defined. Presumably, this may be related to the poor organization of the alkyl chains which may induce interpenetration between successive deposited layers. The position of this broad reflection leads however to an estimated thickness of *ca.* 30–32 Å for the repeating unit of the LB film. Moreover, the diffractogram presents clear Kiessig fringes (see Fig. 7 and its insert). The total thickness of the LB film can then be calculated.[16] Knowing the number of deposited layers, the average thickness of each layer is then evaluated to *ca.* 17 Å. Therefore, the comparison of the thickness calculated from the broad reflection and the Kiessig fringes show that the LB film is surely Y-type with a layer thickness close to 15–17 Å. Such a value is confirmed by ellipsometry experiments. Indeed, Fig. 8 shows the total thickness of LB films for SubPc **1** evaluated by ellipsometry *versus* the number of deposited layers. The linear increase demonstrates the regular deposition onto the solid substrate and the slope of this line leads to an estimation of the layer thickness to *ca.* 16 Å. LB film of SubPc **1** is then formed of layers somewhat interpenetrated but having a well-defined average thickness of *ca.* 16 Å. Such a value is clearly compatible with the molecular structure, taking into account the tilting of the macrocycle as deduced from the dichroism experiments and the large number of gauche conformations in the alkyl chains suggested by the IR spectra.

In order to get more information concerning the influence of the organization within the LB film on the SHG response, we built up onto a glass substrate alternated multilayers using SubPc **1** and behenic acid. Monolayers of behenic acid were transferred during the upper stroke at a surface pressure of 28 mN m^{-1} with a dipping speed of 5 mm min^{-1}. On the other hand, in the down stroke the monolayer of SubPc **1** was transferred at a surface pressure of 15 mN m^{-1} with a dipping speed of 5 mm min^{-1}. Transfer ratios were close to unity for both behenic acid and SubPc **1** monolayers. This cycle was repeated 24 times leading to an alternated film of SubPc **1** and behenic acid made of 48 layers.

Non-linear optical properties of the LB films

Preliminary SHG experiments have been carried out at $\lambda = 1.064$ µm on LB films made of 100 layers of SubPc **1**. For an s-polarized fundamental beam the data show a small but appreciable SHG yield when the observation and illumination directions lie at an angle of ~50° with the normal to the film. The angular spread of the SHG signal is quite narrow (~10°). No significant yield could be measured for a p-polarized fundamental beam. These results are consistent with a non-centrosymmetric ordering that is restricted to the first layers on the glass substrate.[17] In other words, the molecular ordering of those first layers may be slightly different when compared to the other layers.

It is worth mentioning that complementary experiments have also been performed on alternated LB films of SubPc **1** and behenic acid. They have revealed a strong increase of the SHG response and much broader angular spectra. This is illustrated in Fig. 9 including the data for both s- and p-polarization (note also the interference fringes associated with multiple reflection inside the substrate). Therefore, it may be concluded, as expected, that layer alternation induces the non-centrosymmetric molecular ordering through the whole film thickness. Although these results are preliminary, they confirm the feasibility of achieving non-centrosymmetric ordering in LB films of SubPcs and its potentiality for second-order NLO applications.

We acknowledge financial support from CICYT and Comunidad de Madrid (Spain) through grants MAT-96-0654 and 07N/0020/1998 respectively.

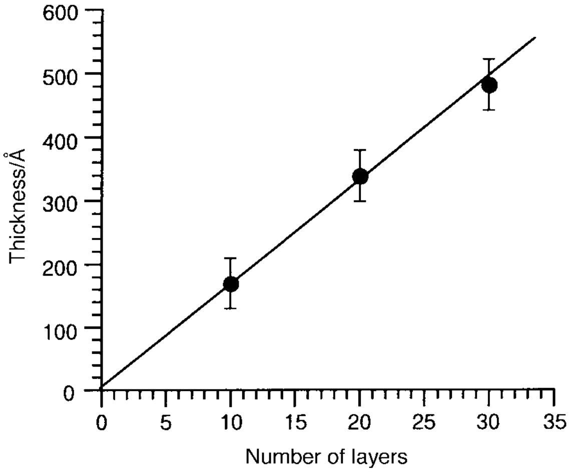


Fig. 8 Thickness of the LB films of SubPc **1** determined by ellipsometry *versus* the number of deposited layers.

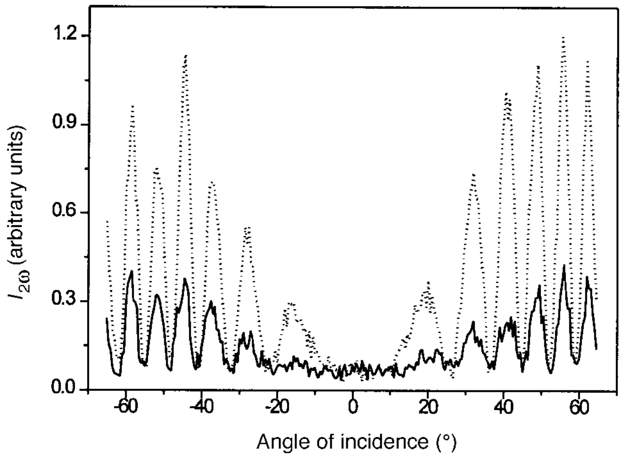


Fig. 9 SHG yield of an alternated LB film with 24 layers of SubPc **1** and 24 layers of behenic acid. Data for p-polarized (dotted line) and s-polarized (solid line) incident beams are included.

References

1 *Phthalocyanines, Properties and Applications*, ed. C. C. Leznoff and A. B. P Lever, VCH, Cambridge, 1989, 1993, 1996, vol. 1–4.

2 (*a*) K. Ohta, L. Jacquemin, C. Sirlin and J. Simon, *New J. Chem.*, 1988, **12**, 751; (*b*) J. F. van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 615; (*c*) J. A. Duro, G. de la Torre and T. Torres, *Tetrahedron Lett.*, 1995, **36**, 8079; (*d*) M. J. Cook, *J. Mater. Chem.*, 1996, **6**, 677.

3 T. Verbiest, S. Van Elshocht, M. Kauranen, L. Hellemans, J. Sanauwaert, C. Nuckolls, T. J. Katz and A. Persoons, *Science*, 1998, **282**, 913.

4 *Langmuir-Blodgett Films*, ed. G. Roberts, Plenum, New York, 1990.

5 (*a*) S. Baker, M. C. Petty, G. G. Roberts and M. V. Twigg, *Thin Solid Films*, 1983, **99**, 53; (*b*) M. J. Cook, D. A. Mayes and R. H. Poynter, *J. Mater. Chem.*, 1995, **5**, 2233; (*c*) S. Peiffer, C. Mingotaud, C. Garrigou-Lagrange, P. Delhaes, A. Sastre and T. Torres, *Langmuir*, 1995, **11**, 2705; (*d*) F. Armand, M. V. Martínez-Díaz, B. Cabezón, P.-A. Albouy, A. Ruaudel-Texier and T. Torres, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1673.

6 (*a*) M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, A. Sastre and T. Torres, *Synthesis*, 1996, 1139; (*b*) A. Sastre, B. del Rey and T. Torres, *J. Org. Chem.*, 1996, **61**, 8591.

7 (*a*) G. de la Torre, T. Torres and F. Agulló-López, *Adv. Mater.*, 1997, **9**, 265; (*b*) G. de la Torre, P. Vázquez, F. Agulló-López and T. Torres, *J. Mater. Chem.*, 1998, **8**, 1671.

8 (*a*) A. Sastre, T. Torres, M. A. Díaz-García, F. Agulló-López, C. Dhenaut, S. Brasselet, I. Ledoux and J. Zyss, *J. Am. Chem. Soc.*, 1996, **118**, 2746; (*b*) B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux and J. Zyss, *J. Am. Chem. Soc.*, 1998, **120**, 12808.

9 (*a*) M. A. Díaz-García, F. Agulló-López, A. Sastre, T. Torres, W. E. Torruellas and G. I. Stegeman, *J. Phys. Chem.*, 1995, **99**, 14988; (*b*) G. Rojo, A. Hierro, M. A. Díaz-García, F. Agulló-López, B. del Rey, A. Sastre and T. Torres, *Appl. Phys. Lett.*, 1997, 1802; (*c*) G. Rojo, B. del Rey, F. Agulló-López and T. Torres, *J. Appl. Phys.*, 1998, **84**, 6507.

10 H. T. Nguyen, A. Bouchta, L. Navailles, P. Barois, N. Isaert, R. J. Twieg, A. Maaroufi and C. Destrade, *J. Phys. II*, 1992, **2**, 1889.

11 S. Hénon and J. Meunier, *Rev. Sci. Instrum.*, 1991, **62**, 936.

12 N. Cuvillier, R. Bernon, J.-C. Doux, P. Merzeau, C. Mingotaud and P. Delhaes, *Langmuir*, 1998, **14**, 5573.

13 A. Meller and A. Ossko, *Monatsh. Chem.*, 1972, **103**, 150.

14 P.-A. Albouy, *J. Phys. Chem.*, 1994, **98**, 8543.

15 J.-P. Bourgoin, F. Doublet, S. Palacin and M. Vandevyver, *Langmuir*, 1996, **12**, 6473.

16 J. Reiche, U. Pietsch, H.-P. Fink and H. Lemmetuinen, *Acta Polym.*, 1992, **43**, 206.

17 L. Werner, W. Hill, F. Marlow, A. Glismann and O. Hertz, *Thin Solid Films*, 1991, **205**, 58.

Paper 9/01986C