

Letters

Supramolecular Ordering of Tripod Dyes at the Air/ Water Interface

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Received December 29, 2004. In Final Form: April 30, 2005

Monolayers of 2-(3,4,5-(trisdodecyloxy)phenyl)[1,3,4]oxadiazole based "tripod" dye, P2G, has been studied at the air/water interface with in situ X-ray reflectivity. Compression of the disordered Langmuir–Blodgett monolayer film induces a transition to a unique ordered phase, representing a supramolecular assembly with a unique spatial distribution and orientation of the molecules. At low pressure, the molecules having face-on orientation are interdigitated by the three arms. After first transition in the π -A isotherm, the molecular conformation is turned into an edge-on orientation, where the molecules are self-assembled into supramolecular structures.

Organic molecular layers and ultrathin films of insoluble long-chain amphiphilic molecules at the air/water interface have been investigated intensively due to their potential applications in photoconductors¹ and display devices.² The Langmuir–Blodgett (LB) technique enables fabrication of ordered monolayers and organized molecular assemblies with well-defined molecular orientation³ on desired substrates. Molecular ordering or supramolecular assemblies with a unique spatial distribution and orientation of molecules⁴ in Langmuir monolayer were used to be achieved simply upon compression of area per molecule.

As an example, dye molecules modified with terminal hydrophobic groups were spread on water and formed aggregated or ordered monolayers such as columnar liquid crystals (LCs) at the air/water interface at high surface pressure.⁵ These monolayer assemblies of the dye molecules on substrate or on water displayed optical properties different from that in their bulk state.⁶ Recently, circular peptide derivatives were designed that form side-by-side supramolecular assemblies in solution,⁷ which is stabilized by intermolecular hydrogen bonding. Similar concepts could be applied to molecules spread at the air/water

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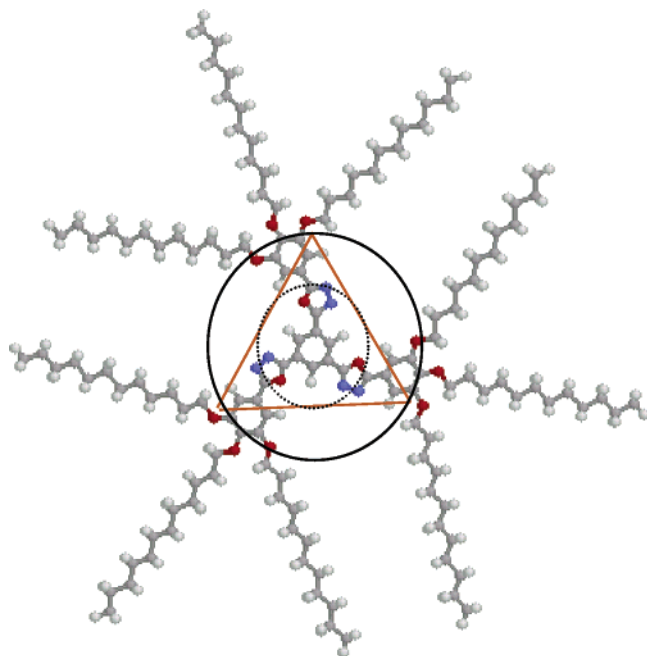


Figure 1. Structure of the novel star-shaped molecule, 1,3,5-tribenzene 2-(3,4,5-(tridodecyloxy)phenyl)oxadiazol-5-yl. The triangle is a guide for the tripod structure.

interface. Well-ordered supramolecular assemblies of Langmuir monolayers can be obtained by chemical modification of the molecules which enables noncovalent intermolecular interaction in the assembly.

Here we designed a novel star-shaped tripod molecule, P2G, composed of a 1,3,5-trisubstituted benzene core and 2-(3,4,5-(tridodecyloxy)phenyl)oxadiazol-5-yl arms.⁸ A molecular model of the molecule is shown in Figure 1. This molecule is composed of an oxadiazole center as a chromophore for potential applications in photonic and organic semiconducting materials along with nine hydrophobic dodecane side chains to enhance supramolecular assembly or stacking to form columnar mesophases via van der Waals interaction on the water. This molecule can be spread on the water due to six hydrophilic parts (three oxyl groups of tridodecyloxyphenyl and three oxadiazole groups) in the center.

Surface pressure versus area (π - A) isotherms of the monolayer were measured at 20 °C on a KSV3000 equipped with a Wilhelmy balance. The P2G solutions in 3–5 mg/mL CHCl_3 were spread on the water subphase obtained from Milli Q (resistivity ca. 18 M Ω cm), and compression of the monolayer was started 30 min after spreading in order to allow CHCl_3 to evaporate completely. Initial trough area was 772 cm², and the compression rate was 10.5 cm²/min. The monolayers were transferred via the Langmuir–Blodgett vertical dipping technique onto quartz slides. The quartz slides were cleaned prior to use by a solution of 30% H_2O_2 /concentrated H_2SO_4 (1/3) for 20 min and rinsing with Milli Q water.

Figure 2 shows π - A isotherms of P2G molecules at the air/water interface. The onset area of 220 Å² indicated by (a) is comparable to 260 Å², which is calculated from the cross-sectional area of the terminal phenyl ring (solid circle) shown in Figure 1. This indicates that the core ring interactions are major contributors to the surface pressure, whereas intermolecular interaction between hydrocarbon

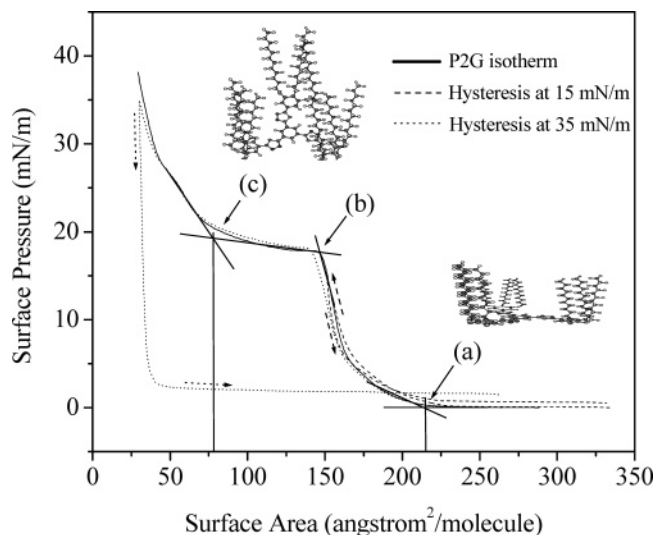


Figure 2. Surface pressure and surface area isotherms of P2G at the air/water interface, 25 °C (solid line). The dashed line represents the hysteresis at 15 mN/m, and the dotted line represents the hysteresis at 35 mN/m. Two schematic models show the planar shape at low surface pressure and vertically standing structure at high surface pressure.

side chains is very weak below the onset point. Therefore, at low pressure, it is intuitively accepted that the hydrocarbon side chains point upward and hydrophilic core faces down toward the water, called “face-on” orientation. After the onset area, the core rings start to interact with each other and partial interdigitation between hydrocarbon side chains might occur. Upon further compression, the surface pressure sharply increases and then reaches a plateau at a transition area of 150 Å² indicated by (b) in Figure 2. This area is slightly larger than the trisubstituted benzene core of 120 Å² (dashed circle) shown in Figure 1. It is assumed that P2G molecules have face-on orientation up to the transition area (b), confirmed by in situ X-ray reflectivity in Figure 3. Upon further compression, the surface pressure remains constant while the area is decreased from 150 to 80 Å² indicated by (c). This area is even less than the trisubstituted benzene core of 120 Å². After point (c), the surface pressure rises again sharply. Assuming the P2G molecules remain as a monolayer, this small area per molecule (80 Å²) is only allowed when the P2G molecule has an upright position, called “edge-on” orientation, even though hydrophobic hydrocarbon side chains are forced into the water surface in this orientation. Therefore, the plateau region corresponds to a transition in molecular orientation of P2G from face-on to edge-on.

The conformational transition of P2G molecules from face-on to edge-on orientation is further confirmed by the observation of hysteresis curves in the isotherm, i.e., differences in the π - A isotherm during compression and decompression. In Figure 2, below the transition point (b), there is no observed hysteresis as indicated by the arrows. On the other hand, after the transition point, a large hysteresis was observed (Supporting Information). Because of the high degree of symmetry in the edge-on conformation, attractive van der Waals interactions between the molecules are strong enough to keep the configuration even after the film is expanded. These edge-on packed molecules form nanosized tubelike structure as being observed by STM (scanning tunneling microscopy, Digital Instruments NanoScope E) on the LB film transferred at 0.88 and 7.0 mN/m (see Figure 3). Images were

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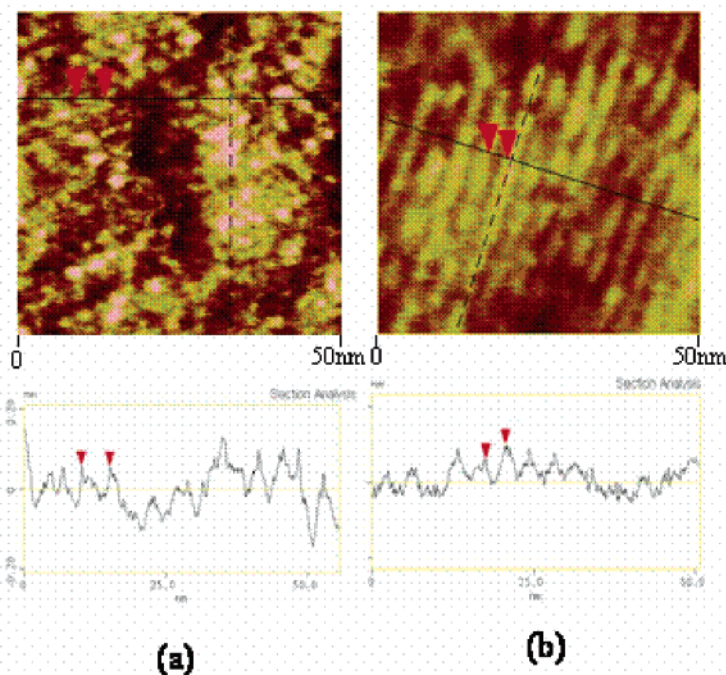


Figure 3. STM image of P2G monolayer transferred onto a polished ITO surface at (a) 0.88 and (b) 7.0 mN/m, 25 °C.

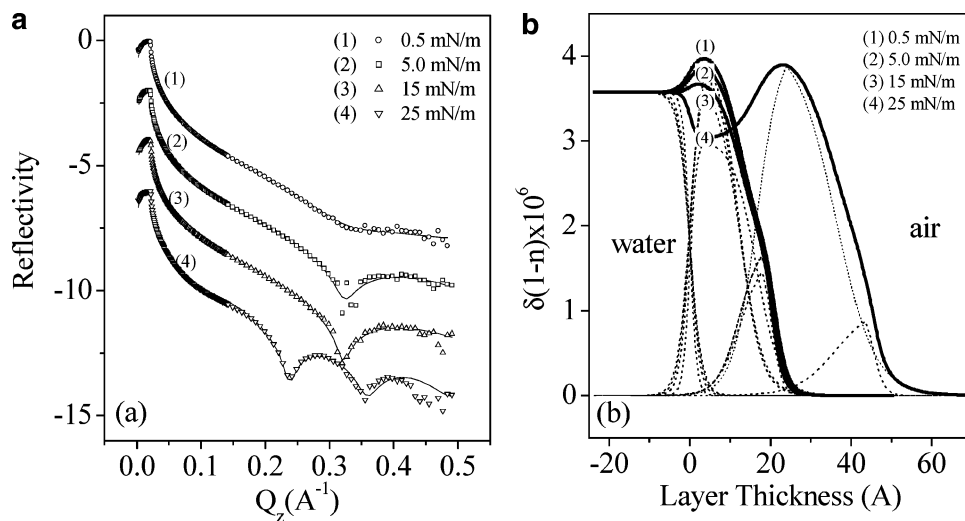


Figure 4. (a) X-ray reflectivity profiles of a P2G monolayer at the air/water interface at 20 °C (symbol) and the corresponding fit (line). (b) Electron density depth profiles of the monolayer at different surface pressures. Solid line is the integrated layer profile and its layer component is in dotted line. The curves are shifted in the y-direction for clarity.

acquired at constant current mode by a Pt/Ir tip. Bias voltage between 150 and 380 mV and tunneling currents from 400 to 500 pA were applied between the tip and sample. Linear packing was observed at a relatively high surface pressure, 7.0 mN/m, which was compared with the image at 0.88 mN/m.

In situ, X-ray reflectivity studies were performed to prove the face-on to edge-on transition of the P2G molecules at the air/water interface. The reflectivity studies used a horizontal liquid reflectometer with a tilting Cu K α anode tube (Bruker, Co.). P2G molecules were spread on a KSV minitrough enclosed in a homemade Plexiglass box on an antivibration table. Reflectivity profiles were obtained as a function of the scattering wave-vector transfer, $q_z = (4\pi/\lambda) \sin(\theta)$, where λ is the wavelength and θ is the reflected angle which equals the incident angle.

Figure 4a shows the X-ray reflectivity profiles of the P2G at the air/water interface at different surface pressures, where the solid lines are best fitted to electron density depth profiles of the monolayers to the z direction shown in Figure 4b. In Figure 4b, the individual and total layer electron density profiles are displayed as dotted and solid lines, respectively. Electron density of the molecule, ρ_{el} , has a relation to refractive index of the molecule, $n = 1 - \delta$ where $\delta = \lambda^2 \rho_{el} r_0 / 2\pi$ with the classical electron radius, r_0 .

The data in Figure 4b suggest that at low surface pressure the hydrophilic core (i.e., higher ρ_{el}) is in contact with the water surface while the hydrocarbon side chains sit at the air interface. As the monolayer is compressed, the electron density contrast between the layers becomes more pronounced until the transition point (b) in Figure 2 is reached. At 15 dyn/cm, just below the transition point

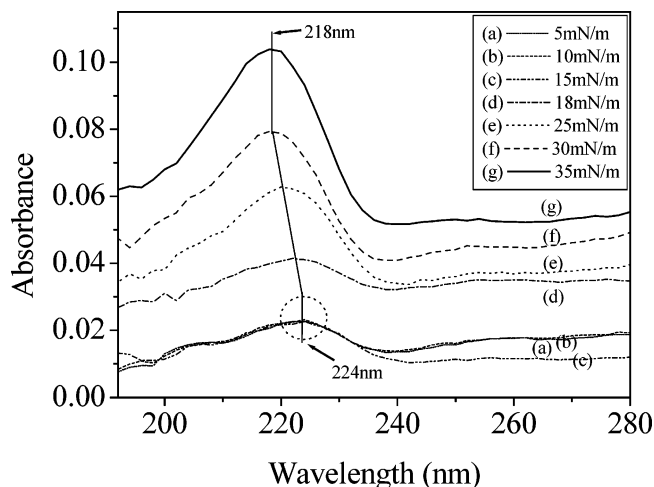


Figure 5. UV spectra of a P2G monolayer transferred onto quartz slides at different surface pressures.

(b), the higher density layer thickness is up to 12.3 Å, which corresponds to the height of the hydrophilic core and the lower density layer thickness of the hydrocarbon chains is the same significant figures (i.e., 10 Å). Prior to the transition point, the P2G molecules form a close-packed face-on orientation. For the monolayer at 25 dyn/cm, i.e., on the plateau, the electron density profile is best described by a trilayer model, where the lower density layer faces the water surface, a higher density layer is in the middle, and another lower density layer is at the air interface, as shown in Figure 4b. The thickness of the higher density middle layer is found to be 19.6 Å, which corresponds to the size of the core ring. This density profile strongly indicates that P2G molecules have an edge-on conformation. As seen in the STM observations, consequently, the edge-on molecules form a highly packed structure, i.e., tubelike structure, even though lateral morphology of the monolayer has not been fully confirmed yet. In edge-on conformations, unfavorable enthalpic interaction of hydrocarbon side chains with the water surface is overcome by a strong van der Waals interaction between the stacked molecules forming the tube conformation. For more than 35 mN/m, reflectivity profiles reveal that the molecules form multilayer or irregular aggregates.

Tubelike conformations of P2G molecules exhibit changes in optical properties since UV-vis spectra of aggregated monolayer films show a blue shift in contrast to the solution spectrum.¹⁰ Figure 5 shows UV-vis spectra

on the LB films as a function of surface pressure. A Perkin-Elmer Lambda 35 spectrometer was used with 152 scans at 1 nm resolution. The quartz slides were used as the substrate for the film deposition. The absorption intensity increases due to incremental increases in area per molecule. In the spectrum, λ_{\max} shifts from 224 to 218 nm with an increase in surface pressure from 5 to 30 mN/m and is relatively constant up to 35 mN/m. Up to the transition point (b) shown in Figure 2, λ_{\max} remains constant at 224 nm, indicating that there is no intermolecular edge-on stacking prior to the plateau region. The magnitude of blue shift, $\Delta\lambda_{\max}$, has been shown to be a function of the degree of stacking of P2G molecules.⁹ $\Delta\lambda_{\max}$ is maximized to 218 nm at 30 dyn/cm, and the λ_{\max} peak becomes sharper with increasing surface pressure, indicating that the stacking is saturated at 30 dyn/cm. Similar behaviors have been reported for dye molecules known to be an H-aggregate of the monolayers.¹⁰

In summary, a tripod dye molecule, P2G, was designed for obtaining supramolecular self-assembly stabilized by van der Waals interaction between hydrocarbon side chains at the air/water interface. P2G monolayers showed a conformational change from face-on to edge-on as the monolayer was compressed at the air/water interface, validated by π -A isotherms analysis as well as in situ X-ray reflectivity. Moreover, a high degree of stacking of the edge-on molecules at high surface pressures was confirmed using STM and UV adsorption experiments. Highly symmetric nine hydrocarbon chains in the P2G molecule favor strong van der Waals interaction between the edge-on molecules, leading to the formation of tubelike conformations even though an unfavorable enthalpic interaction of the hydrophobic chains to the water is involved.

Acknowledgment. This work was supported by the ABR program (Grant No. R-14-2002-004-01002-0), and S.-G. Youm was supported by the National R & D project for Nano Science and Technology in Korea. S.Y.P. acknowledges NRL project support.

Supporting Information Available: Hysteresis measurements of P2G. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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