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Structure of Intermolecular Donor–Acceptor Monolayers of *N*,*N*-Dimethyl-*p*-[15-(1-pyrenyl)pentadecanyl]aniline

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N,*N*-Dimethyl-*p*-[15-(1-pyrenyl)pentadecanyl]aniline (Py15DMA); 15-(*p*-*N*,*N*-dimethylaminophenyl)pentadecanyl pyrene-1-carboxylate (Py(COO)16 DMA); and 1,16-di(1-pyrene)hexadecane (Py16Py) monolayers sorbed at a liquid-solid interface were probed using an STM. High definition images were obtained of sufficient quality to determine the structural parameters of the monolayers.

A scanning tunneling microscope (STM) is a powerful tool that can be used to observe atomic resolution surface morphologies and electronic properties of materials. An STM can typically be used to image molecules under ultra high vacuum at extremely low temperature. However it can also be used in ambient laboratory conditions, proving useful for probing dynamic liquid-solid interfaces. Since the first STM report of a long chain alkane monolayer adsorbed on an atomically flat graphite substrate,[1] a variety of other organic physisorbed monolayers have been observed where the monolayer formation was assisted by various molecular interactions.[2–4] However, intermolecular donor–acceptor systems physisorbed at liquid-solid interfaces have been less well studied, despite their importance in photochemistry as intermediates as well in determining order in molecular assemblies.

In this report, we describe monolayer formation by *N*,*N*-dimethyl-*p*-[15-(1-pyrenyl)pentadecanyl]aniline (Py15DMA) adsorbed on an atomically flat graphite substrate and observed using an STM in order to determine its structure. 1,16-di(1-pyrenyl)hexadecane (Py16Py) and 15-(*p*-*N*,*N*-dimethylaminophenyl)pentadecanyl pyrene-1-carboxylate (Py(COO)16DMA) were also investigated for comparison.

The structures of these compounds are shown in Figure 1.[5] 1-Phenyloctane was selected as the solvent for all three molecules because it has a low conductivity and vapor pressure and a long alkyl chain which is compatible with the solute molecules. The optimal solute concentration used for observation of Py15DMA monolayers was 1.0×10^{-2} M (unsaturated). For Py16Py and Py(COO)16DMA concentrations of $\approx 1.0 \times 10^{-3}$ M (nearly saturated) were used.

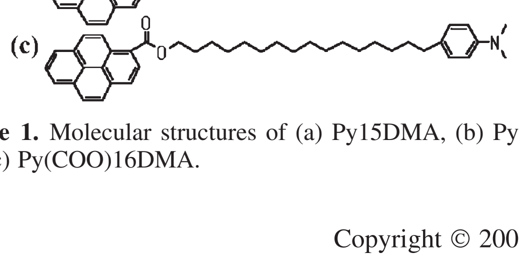

Figure 1. Molecular structures of (a) Py15DMA, (b) Py16Py, and (c) Py(COO)16DMA.

The STM images were obtained using a SOLVER P-47, NT-MDT fitted with mechanically clipped Pt/Ir (8/2) probe tips. After the highly oriented pyrolytic graphite (HOPG) substrate was cleaned and covered by a drop of the solutions under investigation, the STM tip was immersed into the drop and raster scanned at the liquid-solid interface in the constant current mode. The tunneling bias was changed in the range 0 to 0.9 V (sample negative). All measurements were carried out under ambient laboratory conditions.

An STM image of a Py15DMA physisorbed monolayer at the solution-HOPG interface is shown in Figure 2a. From this extremely high quality image the pyrene and DMA groups are individually recognizable. The pyrene and DMA groups are bright compared with the alkyl chain of the molecule, in agreement with similar reports on physisorbed monolayers formed by alkyl chains with aromatic rings and studied using STM.[2,6,7] In general, molecules with π-electrons are observed as brighter regions in the image than those with only σ-electrons. Figure 2b shows the most probable structure of the monolayer of Py15DMA, on the basis of the STM image. The pyrene groups of the Py15DMA adsorb on the HOPG substrate with the plane of the condensed aromatic rings parallel to the surface of the substrate. The DMA groups adsorb with the aromatic rings perpendicular to the substrate surface. The DMA groups are sandwiched between two pyrene rings. The alkyl chains are fully extended, lying flat on the graphite, with their long axes parallel to one of the symmetry axes of the graphite. The monolayer is formed by two unit cells (A and B) having the same sized rhomboids including two molecules in each unit as shown in Figure 2a. Unit B can be transposed to unit A by taking A's mirror image and turning it clockwise by 60 degrees. One unit cell is bordered by the other one with each contacting with a common vertex. From analysis based on the lattice constant of the HOPG substrate, the length of the short axis, long axis, and the angle between them (shown in Figure 2a and 2b as a, b and, γ, respectively) were estimated to be 1.22 ± 0.05 nm, 3.40 ± 0.05 nm, and $60 \pm 3^\circ$, respectively.

Molecular packing of Py16Py was quite different from that of Py15DMA. Figure 3a shows an STM image of a Py16Py physisorbed monolayer. The bright regions surrounded with white circles in Figure 3a correspond to pyrene and darker portion highlighted by the zigzag line between circles corresponds to the alkyl chain. It was found that pyrene groups adsorb with the condensed aromatic plane parallel to the HOPG surface as was the case of Py15DMA. The axis of the alkyl chain is arranged along the graphite main axis. A model structure of the monolayer of Py16Py is shown in Figure 3b. The same analysis as described above enabled us to determine the constants of the unit cell of α, β, and γ represented in Figure 3a and 3b to be

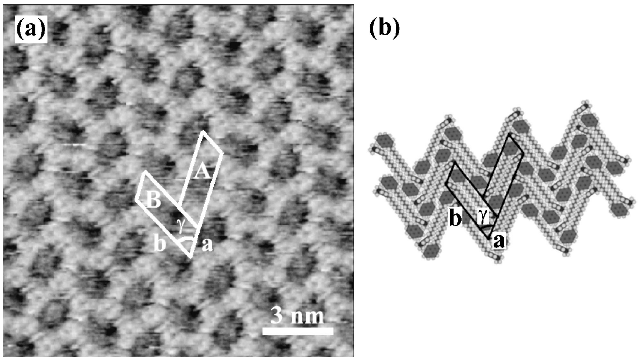

Figure 2. (a) STM image of a monolayer of Py15DMA physisorbed on an HOPG substrate in 1-phenyloctane solution at a bias voltage and a tunneling current of 0.9 V (sample negative) and 0.05 nA, respectively, and (b) a model structure of the monolayer based on the STM image.

1.31 ± 0.05 nm, 3.69 ± 0.07 nm, and 90 ± 3°, respectively.

In the case of Py(COO)16DMA dissolved in 1-phenyloctane, STM measurements at the interface between solution and the HOPG substrate were unsuccessful in that no images could be obtained. However this observation allowed us to conclude that Py(COO)16DMA dissolved in this solvent does not easily form a physisorbed monolayer on an HOPG substrate. In view of the structural similarity between Py(COO)16DMA and that of Py15DMA, Py(COO)16DMA including just an ester group and having a chain length just one carbon longer, this fact is interesting. Perhaps the presence of the ester group led to chain kinking leading to unfavorable packing, which inhibited the formation of a stable packing structure. We stress that various factors control physisorbed monolayers such as packing factors, inter- and intra- molecular interactions as well as those between the molecules and substrates.[8,9]

In summary, the structures of physisorbed monolayers of the donor-acceptor system Py15DMA and the linked π-system Py16Py physisorbed on an atomically flat HOPG substrate at the liquid-solid interface were observed using an STM. From the STM image structural parameters of the monolayers were determined. Notably the pyrene and DMA ring planes are orthogonal meaning that hydrogens on the pyrene are directed towards the DMA π-cloud. It is known that for some donor acceptor systems, between two orthogonal aromatic moieties, contacts between C–H bonds and π-clouds are important in determining the structure within a molecular assembly.[10] This also supports the structural analysis given here. Py16Py formed monolayers for which we obtained images with a similar resolution to that seen for similar systems.[7] Py(COO)16DMA did not form monolayers, which was unexpected since the ester group is electron withdrawing and hence increases the electron acceptor character of this group compared to the pyrene in Py15DMA. However, the finding may be due to a reduction in packing efficiency due to the presence of the ester group.

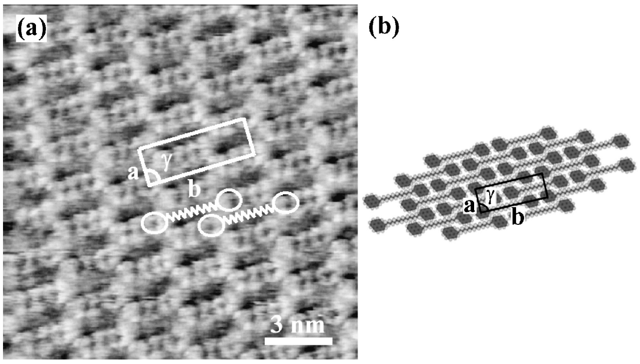

Figure 3. (a) STM image of a monolayer of Py16Py physisorbed on an HOPG substrate in 1-phenyloctane solution at a bias voltage and a tunneling current of 0.77 V (sample negative) and 0.06 nA, respectively, and (b) a model structure of the monolayer based on the STM image.

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