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Self-assembly of microscale architectures with nanoscale inclusions

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We hypothesise that the recent discovery of nanodomains at the air–water interface can be leveraged to nano-functionalize surfaces through casting with incorporated functional species. The interfacial self-assembly of the amphiphilic molecules, 18-methyleicosanoic acid 18-MEA and 4-(tetradecyl)benzene diazonium tetrafluoroborate TDDS, at the air–water interface and cast on silicon wafer has been investigated using Langmuir–Blodgett (LB) techniques and atomic force microscopy. The impact of composition and surface pressure (SP) on the formation of nanodomains and microstructures was examined. TDDS (which can be used to modify the electronic structure of graphene) behaves as a co-surfactant in the 18-MEA film at low concentrations, facilitating the formation of homogeneous nanodomains with functional capacity. At higher TDDS concentrations, there is evidence for phase separation in the domains, and the TDDS furthermore partitions to

New concepts

We demonstrate a simple strategy to create functional nanostructures at the air–water interface by co-assembling an amphiphilic fatty acid (18-MEA) with a diazonium compound (TDDS), and transferring the resulting films onto solid substrates. This work shows that nanodomains emerging spontaneously at the interface can be tuned by adjusting the molecular composition and surface pressure, offering a route to controlled nano-patterning without the need for lithography. The use of TDDS, which can covalently modify carbon-based materials such as graphene and MoS₂, adds a chemical functionality to the nanodomains, enabling further modification after film transfer. Unlike most studies that rely on single-component films or post-assembly patterning, our approach exploits co-surfactant behaviour and interfacial dynamics to guide structure formation directly during film assembly. We also observe a transition from regular nanodomains to complex, periodic 2D patterns resembling 3D water-in-oil-in-water systems (“cookie structures”), suggesting new possibilities for designing hybrid interfacial architectures. This work provides mechanistic insight into interfacial phase behaviour in mixed amphiphilic films and opens up new pathways for creating chemically functionalised nanostructures with potential use in soft patterning, sensing, or surface engineering of 2D materials.



Emilio M. Pérez

Congratulations to Nanoscale Horizons for completing ten turns around the sun! In its role as the flagship journal of the Nanoscale family, it continues to provide a perfect venue for publication of results at the forefront of nanoscience. It is always a pleasure to contribute to the journal, both as an author and as a referee. For this special issue, we joined forces with Mark Rutland to bring some nano-cookies to the party. Here's to many more to come!

the aqueous phase at higher pressures. By manipulating the 18-MEA:TDDS ratio and SP, regular nano-patterns can be transitioned into novel 2D structures reminiscent of 3D water-in-oil-in-water (W/O/W) analogues (“cookie systems”), offering a versatile strategy for designing nanoarchitectures with potential applications in graphene patterning.

Introduction

The air–water interface is ideal for systematic investigations of the self-assembly of insoluble, amphiphilic molecules.¹ The dual nature of these compounds—containing both hydrophilic

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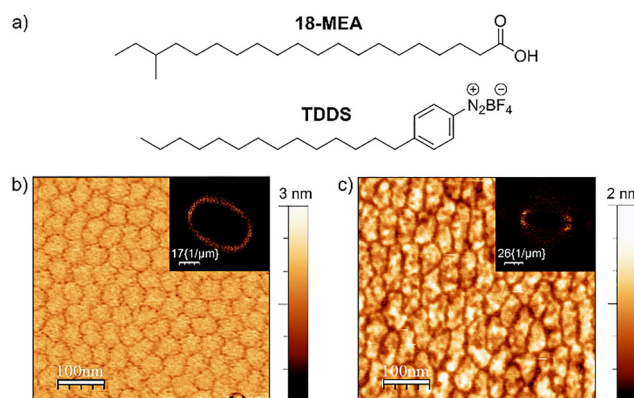
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Although functionalization of materials like graphene^{18,19} represents a long-term motivation—given its unique physicochemical properties^{20–22} and emerging role in nanotechnology—the current study is focused on understanding the interfacial organization and structural properties of these hybrid monolayers.

To comprehensively investigate the joint behaviour of these two organic compounds, a systematic series of isotherms at the



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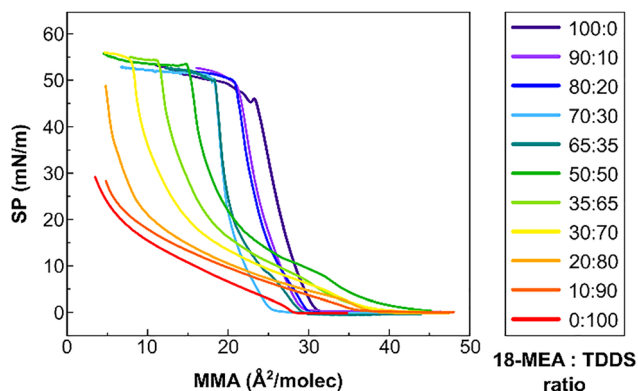


Fig. 2 Isotherm trend for different 18-MEA:TDDS molar ratios. Surface pressure is plotted against the mean molecular area, assuming a 2D interface.

water–air interface were recorded for different 18-MEA:TDDS molar ratios (Fig. 2): 100:0, 90:10, 80:20, 70:30, 65:35, 50:50, 35:65, 30:70, 20:80, and 0:100. A clear trend emerges, allowing for the identification of three distinct regimes based on the shape of the isotherms: (i) fatty acid-like behaviour (100:0 to 70:30), (ii) a phase transition regime (65:35 to 30:70), and (iii) a regime dominated by solubilization of TDDS molecules (20:80 to 0:100). The rationale behind these assignments is discussed in detail below.

In the fatty acid-like regime (100:0 to 70:30 mol%) the lift-off of the surface pressure (SP) occurred at a mean molecular area (MMA) of approximately $25\text{--}32\text{ Å}^2$. It is important to note that MMA is classically calculated under the assumption of a flat interface defined by the barrier positions and therefore does not accurately reflect the true molecular area within the curved nanodomains $SP > 0\text{ mN m}^{-1}$.²³ The MMA decreases slightly with increasing TDDS concentration within this regime, which is consistent with the absence of branching. However, caution should be exercised in interpreting these changes, as minor variations—on the order of a few Å^2 —may also arise from experimental uncertainties in the estimation of the number of molecules deposited (see Materials and methods). The isotherm subsequently increases until film collapse, occurring at a nearly constant pressure of $46\text{--}52\text{ mN m}^{-1}$. This behaviour aligns well with previously reported isotherms of pure fatty acids, suggesting a single-component system exhibiting characteristic nanodomain formation.^{15,16,23} Within this regime, TDDS appears to behave as a dilute additive within the surface film.

At intermediate TDDS mole fractions (65:35 to 30:70 mol%), a distinct behaviour emerges—referred to here as the phase transition regime. This regime is characterized by the appearance of a shoulder in the isotherms at approximately 10 mN m^{-1} . As the TDDS content increases, the lift-off area shifts to significantly larger values (*ca.* $35\text{--}40\text{ Å}^2$), which are indicative of a liquid-expanded phase. Although these samples collapse at the same pressure as those in the fatty acid-like regime, the observed MMA at collapse is unrealistically low if all molecules are assumed to remain in the film. However, the collapse areas are consistent with the amounts of fatty acids in the original films, or at least

with a low concentration of TDDS. These observations suggest that, at low surface pressures, the film behaves as a mixed monolayer of TDDS and 18-MEA, but as the pressure increases, the more soluble TDDS is progressively excluded. Ultimately, the film collapses at a composition and area characteristic of the fatty acid-dominated regime.

Finally, the third regime, referred to as “solubilized molecules” (20:80 to 0:100 mol%), is characterized by the absence of collapse and an extremely low slope in the isotherm. This regime can be considered as an extension of the pressure-induced exclusion behaviour observed in the second regime, but with a sufficiently diluted fatty acid composition such that there is not enough barrier range to reach collapse pressure. Pure TDDS, on the other hand, can achieve a pressure of approximately 30 mN m^{-1} ; however, the molecular area per molecule suggests that less than a quarter of the molecules remain on the surface (assuming a cross-sectional area of 20 Å^2 per molecule and a flat surface).

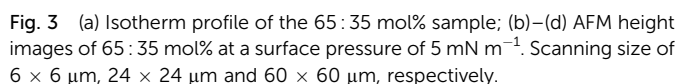
Based on the behaviour observed in the different isotherms, two new samples were selected for a more detailed study and comparison with the 90:10 mol% sample (chosen due to its similarity to previous studies). These samples were deposited at different surface pressures to investigate domain formation and packing. The selected samples were 65:35 mol% and 35:65 mol%, both within the phase transition regime, with the latter being very close to the behaviour of “solubilized molecules”. Given the initial goal of this project, which was to achieve nanopatterns containing an active component, mixtures with a higher fraction of TDDS (which is partially soluble in water) were not considered viable.

Surprisingly, no nanodomains were obtained for the 65:35 mol% mixture when deposition was performed at 20 mN m^{-1} or higher (including 35 mN m^{-1} , close to collapse). Instead, circular particles with varying lateral sizes were observed across the surface, which were transferred onto the silicon substrate (see SI, Fig. S4 for images). The particles, with a height of $16 \pm 8\text{ nm}$, appeared to be systematically distributed, with some vestigial hexagonal packing remaining, except in areas where larger particles ($83 \pm 17\text{ nm}$ in height) were surrounded by bare regions—suggesting aggregation. This observation implies that, in the presence of higher amounts of TDDS, when high surface pressure is applied, molecules tend to partially dissolve in the subphase and coalesce into circular macrodomains, probably during deposition onto the substrate.

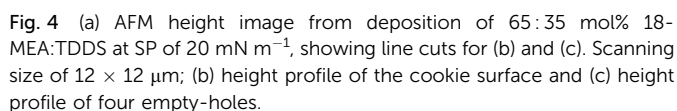
However, experiments performed at low surface pressure, below the shoulder observed in Fig. 3a) at around 10 mN m^{-1} , showed very different, novel morphologies. Such a shoulder is not observed for pure 18-MEA (Fig. 3a) or low fractions of TDDS (Fig. 2). This change in slope indicates that different structures can be expected on either side of it, with expulsion and possibly coalescence at higher SP.

Deposition at 5 mN m^{-1} , resulted in novel morphologies of the deposited films: microdomains containing nanodomains. As shown in Fig. 3b, rounded domains encapsulating circular holes were observed after deposition, reminiscent of a chocolate-chip cookie structure. Fig. 3c and d show zoomed-out





To further confirm this behaviour, depositions immediately below (7.5 mN m^{-1}) and above (10 mN m^{-1}) the shoulder pressure were also performed. At 7.5 mN m^{-1} , the cookie-like architecture was maintained, with the appearance of a mesh-like network between the rounded domains. This suggested that 18-MEA molecules could reaggregate into monodispersed, ellipse-like domains. At 10 mN m^{-1} , the domains began to deform, with some collapsing into neighbouring domains, and smaller circular particles appeared at the junction points. This behaviour indicated that as the transition phase approached, TDDS may have been released from the 18-MEA moiety, promoting the crystallization of smaller circular TDDS droplets. At 12.5 mN m^{-1} , the architecture was completely lost, and a continuous amorphous monolayer with circular particles was



In the concentration regime where TDDS is highest and is expelled from the film at the water air interface (regime (iii) in Fig. 2), the deposited films have rather interesting morphologies involving circular particles but are difficult to interpret and are unlikely to attain any practical applications. This regime is thus fully addressed only in the SI (Fig. S10, S11 and Fig. S12).

Reagents and solvents

Low roughness Si/SiO₂ wafers were purchased from Sil'Tronix ST and used after washes: through immersion in 5% chromosulfuric acid for 5 minutes followed by thorough rinsing with Milli-Q and drying with N₂ flow. Graphene substrates (supported on Si/SiO₂) were purchased from Graphenea and used as received.

Synthesis of 4-(tetradecyl) benzene diazonium tetrafluoroborate

The formation of the diazonium salt was performed as previously reported²⁴ by our group. Briefly, 4-tetradecylaniline (500 mg, 1.73 mmol, 1 eq.) and nitrosonium tetrafluoroborate (301 mg, 2.59 mmol, 1.5 eq.) were dissolved in 10 mL in two different Schlenk flasks under a nitrogen atmosphere and cooled to $-40\text{ }^{\circ}\text{C}$. Then, 4-tetradecylaniline was slowly cannulated into the second solution and the mixture was stirred for 1 h. After that, the solutions were gradually warmed up to $0\text{ }^{\circ}\text{C}$ during 2 h, while stirring. Finally, it was poured into cold Et_2O , and the yellow precipitate was then filtered, washed with Et_2O and dried under vacuum (89% yield). The solid was stored at $-4\text{ }^{\circ}\text{C}$.

Solutions

Solutions of 1 mg mL 18-MEA and TDDS were prepared through dissolution in CHCl_3 at room temperature, and stored at $-8\text{ }^{\circ}\text{C}$. The subphase was prepared by mixing 5 mL of 0.18 mM NaCl and 5 mL of 0.1 mM NaHCO_3 and buffered to pH = 10.0 with the addition of NaOH.

Langmuir–Blodgett isotherm and deposition

A KSV NIMA 5000 system (Biolin Scientific, Sweden) was used for isotherms and depositions. It was equipped with a PTFE (polytetrafluoroethylene) trough with hydrophilic POM (polyoxymethylene) barriers. Wilhelmy plates from lint free paper (Biolin Scientific) were used to monitor surface pressure to a certainty of $\pm 0.01\text{ mN m}^{-1}$. The temperature of the subphase was set to $22.0 \pm 0.1\text{ }^{\circ}\text{C}$. Monolayers were spreading on top of the subphase and CHCl_3 was allowed to evaporate for 10–15 minutes before starting the experiments. The barriers were then compressed by 3 mm/min for both isotherm and deposition experiments. Isotherms were analyzed in terms of surface pressure keeping the movement of the barriers constant. Depositions were performed on silicon wafers keeping the surface pressure constant at a different value (from 5 to 35 mN m^{-1}).

AFM

A Multimode Microscope LN (Bruker, United States) was used in tapping mode for imaging of deposited monolayers. Silicon cantilevers (HQ:NSC35/AL BS, MikroMasch, Switzerland) with a nominal radius of 8 nm were used. The nominal resonance frequency and force constant of the cantilevers were 150 kHz and 5.4 N m^{-1} , respectively. AFM images were analysed using the WsXM 5.0 software.

Conclusions

A range of well-defined self-assembled micropatterns with nano-sized inclusions can be achieved at the air–water interface and transferred onto silicon substrates using mixtures of TDDS and 18-MEA in water. The morphology of the patterns can be controlled through variations of the film composition and surface pressure.

TDDS appears to behave as a cosurfactant within the insoluble 18-MEA monolayer, particularly at low concentrations

where it remains in the nanodomains. Thus, under these conditions, regular nanopatterns containing small amounts of the functionalizing agent can be systematically and reproducibly deposited on a substrate where the 3D self-assembly nanodomains at the water surface are deposited intact.¹⁴ This results in the homogeneous spatial arrangement of the functionalizing species. These complex and homogeneous structured films could in principle be reacted with a graphene substrate, achieving the goal of patterned covalent decoration.

As the TDDS proportion increases, the ability of TDDS to solubilize within the monolayer decreases. This reduction leads to two phenomena: Firstly, TDDS appears to be increasingly expelled from the interfacial film at higher pressures. Secondly TDDS appears to phase separate within domains in the interfacial film, which leads to the formation of micro-sized circular domains on the surface, containing circular holes of nanoscale dimensions. At even higher concentrations of TDDS, the domain structure becomes poorly defined.

At the intermediate TDDS levels, novel, apparently 2D microemulsion structures can be obtained. The formation of a W/O/W-like structure (cookie system), where TDDS remains incorporated as domains within the 18-MEA film is a novel observation which could be leveraged for other systems to deposit well defined 2D droplets of a lipid matrix incompatible species.

The approach provides a flexible strategy for patterning and creating diverse nanoarchitectures, as well as for delivering a functionalizing agent with regular spatial control. This approach thus shows particular promise for graphene patterning, where diazonium salts could be delivered at will and subsequently covalently anchored.

Author contributions

A. N. performed the experimental work, and contributed to data analysis, figure preparation, and manuscript writing. M. B. contributed to the experimental work. E. M. P. and M. W. R. conceived the idea, supervised the project and contributed to interpretation, manuscript writing and revision. All authors discussed the results and contributed to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article, including AFM and Langmuir isotherm data, are available at IMDEA Nanociencia Repository (<https://repositorio.imdeananociencia.org/home>) at <https://hdl.handle.net/20.500.12614/3978>.

Supplementary information (SI): synthetic and characterization details and supporting figures. See DOI: <https://doi.org/10.1039/d5nh00356c>.



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