Edge-on Adsorption of Multi-Chain Functional Alkanes Stabilizes Noncovalent Monolayers on MoS2

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Modified long-chain alkanes are often used to functionalize graphene and MoS_2 noncovalently, with the goal of controlling substrate electronic structure or interactions with the environment. Alkyl chain adsorption enthalpy is lower on MoS_2 than on graphite; the decreased molecule–substrate interaction strength suggests utility for monolayer structures that increase stability through other means. Previously, we have found that diyne phospholipid monolayers on HOPG are more stable toward solution processing than monolayers of single-chain amphiphiles. Here, we show that this is also true for assembly on MoS_2, but that the additional stability appears to arise from edge-on adsorption, producing monolayers in which alkyl chains form two stacked layers on the substrate.

Introduction

Surface chemistry of 2D materials is key in controlling not only substrate electronic structure, but interactions with the environment. Significant effort has been directed toward controlling the surface chemistry of graphene.[1-3] Developing routine control over the surface chemistry of other 2D materials such as MoS_2,[4-5] which have useful electronic properties (*e.g.* native band gaps), would facilitate application in devices.

Many routes to noncovalent functionalization of 2D materials[1-3] such as graphene and highly oriented pyrolytic graphite (HOPG) utilize epitaxial matching between the zig-zag alkyl backbone and the hexagonal graphitic lattice (Fig. 1a, 1b), both to strengthen molecule–substrate interactions and to order other functional groups. For example, long chain alkanes (*e.g.* 10,12-pentacosadiynoic acid, PCDA) assemble into striped lamellar phases on HOPG and graphene,[6-7] with alkyl chains orienting along the <11$\underline{2}$0> lattice direction. Lamellar phases of diynes can be photopolymerized to produce conjugated ene-yne polymer backbones, useful both as molecular wires[8] and to stabilize the noncovalent monolayer toward further processing.[1,9-11]

Differences in surface structure reduce stability of such monolayers on MoS_2 in comparison with HOPG; previous calorimetry measurements of adsorption of *n*-dotriacontane from *n*-heptane indicate a 3-fold larger adsorption enthalpy for alkyl chains on HOPG vs. MoS_2.[12] Thus, in spite of the increasing interest in controlling MoS_2 surface chemistry, and the fact that lying-down phases on MoS_2 have been visualized by scanning probe microscopy for nearly as long as those on HOPG,[13-14] relatively few reports demonstrate control of lying-down phases on MoS_2.[5,15-18]

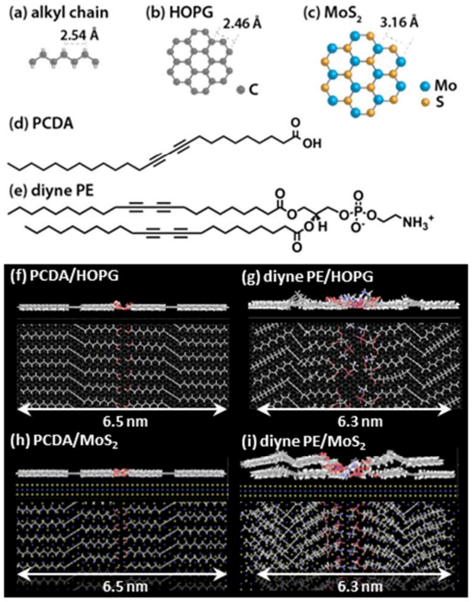

Fig. 1. (a) Periodicity of alkyl carbon backbone, and lattice structures of (b) HOPG and (c) MoS_2. Molecular structures of (d) PCDA and (e) diyne PE, and minimized models of lamellar phases of these molecules on (f,g) HOPG and (h,i) MoS_2.

Here, we illustrate a structural design principle for increasing ordering and stability of monolayers with weak molecule–substrate interactions, comparing assembly of two

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Electronic Supplementary Information (ESI) available: Experimental details, Fig S1-S12. See DOI: 10.1039/x0xx00000x polymerizable amphiphiles on HOPG and MoS_2. PCDA, a single-chain amphiphile (Fig. 1d), has been broadly used in noncovalent functionalization of HOPG, and also forms lamellar phases on MoS_2. Diyne phosphoethanolamine (diyne PE, Fig. 1e), a dual-chain amphiphile, has also recently been shown to form lamellar phases on HOPG.[9,11,19-20] In monolayers on HOPG, both chains typically contact the graphitic lattice (Fig. 1g). However, in principle such molecules could also adsorb in an edge-on packing in which only one chain interacts with the substrate (Fig. 1i), an orientation observed for dialkylquinones and alkylated tetrathiafulvalenes at solid–liquid interfaces with HOPG.[21-22] This geometry would become increasingly favourable on substrates to which the molecules adsorb weakly, as molecule–molecule interaction strength becomes a more important driver of monolayer formation. Edge-on packing enables chain–chain interactions in two layers, allowing formation of two layers of polymer chains (Fig. S1); both factors potentially increase monolayer stability. Here, we find diyne PE on MoS_2 forms domain structures consistent with edge-on assembly.

Results and discussion

Structure of monolayers on MoS_2. To compare structural and physical properties, monolayers of PCDA and diyne PE were assembled on MoS_2 (Fig. 2) using Langmuir-Schaefer transfer with a custom transfer stage that maintained an elevated substrate temperature.[11] Optimal transfer was observed at substrate temperatures of 50–70°C, consistent with our previous observations on HOPG,[11] and are used for comparisons here. (A range of assembly conditions were screened for both molecules to compare their assembly properties. The ESI shows experiments comparing drop-casting, dip-coating, and a range of thermally controlled transfer conditions; overall, diyne PE improved ordering vs PCDA under most conditions tested.) Line scans acquired from AFM images of diyne PE on MoS_2 (Fig. 2e, blue trace) illustrate two topographic heights associated with the domains. The larger domains visible in Fig. 2d have heights of ~0.8 nm, while the smaller domains have average heights of ~0.4 nm (see Fig. S2–6 for larger-area images). Because 0.8 nm is approximately twice the thickness of diyne PE monolayers on HOPG (red trace) in which both alkyl chains adsorb to the HOPG surface, we propose that this domain structure arises from edge-on adsorption (Fig. 1i), and that the 0.4 nm high domains represent face-on adsorption.

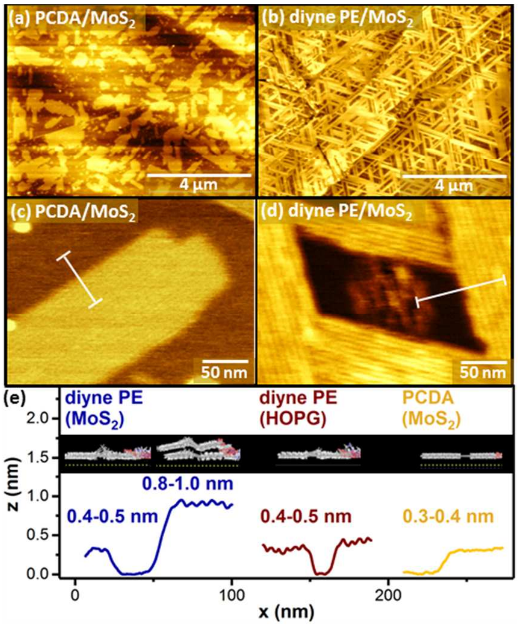

Fig. 2. AFM images of (a,c) PCDA and (b,d) diyne PE on MoS_2. (e) Line scans extracted over domains of diyne PE on MoS_2 (blue), HOPG (red), and PCDA on MoS_2 (gold). Figs. S2-5 show larger versions of images in (b,d) and image for diyne PE/HOPG line scan.

Polymerization of monolayers on MoS_2. During UV photopolymerization, we find that monolayers of diyne PE retain lamellar structure longer than monolayers of PCDA; polymerization of both molecules is more rapid on MoS_2 than on HOPG, consistent with earlier studies of PCDA on MoS_2 by STM.[16] AFM images (Fig. 3) illustrate the progression of PCDA polymerization on MoS_2, for comparison with diyne PE below. Prior to UV irradiation, lamellar domains with edge lengths of ~100 nm are visible (Fig. 3a); after 10 min (Fig. 3b) and 20 min (Fig. 3c) of irradiation, lamellar areas become patchy, largely disappearing at longer irradiation times, although lamellar domain structures are still visible by SEM (Fig. 3e,f).

Polymerization of diyne PE on MoS_2 also proceeds rapidly, with lamellar roughening within the first 10 min. Unlike PCDA, lamellar structures remain clearly visible throughout the first 30 min of UV exposure (Fig. 4a–c), with substantial changes in monolayer structure between 30 and 60 min (Fig. 4d) producing features with topographic variations of ~0.6 nm

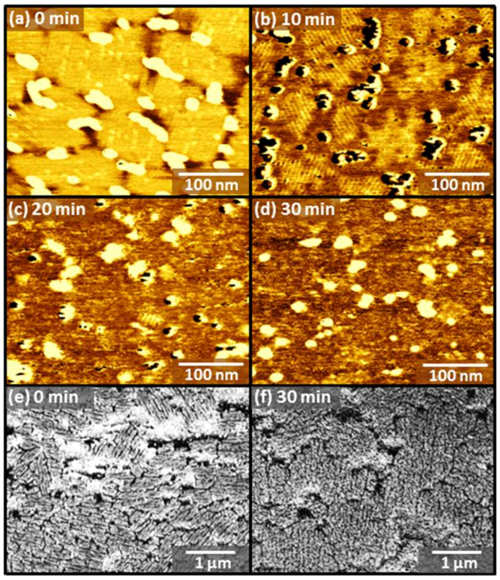

Fig. 3. AFM images of PCDA on MoS_2: (a) unpolymerized, and polymerized by UV irradiation for (b) 10 min, (c) 20 min, and (d) 30 min. SEM images of PCDA on MoS_2: (e) unpolymerized, and (f) polymerized for 30 min.

along domain surfaces, in contrast with 0.1–0.2 nm variations prior to polymerization (Fig. 4g). Domain edges remain visible by SEM after roughening (Fig. 4f). Similar roughening occurs at longer UV exposure for diyne PE on HOPG (0–6 h, Fig. S7).

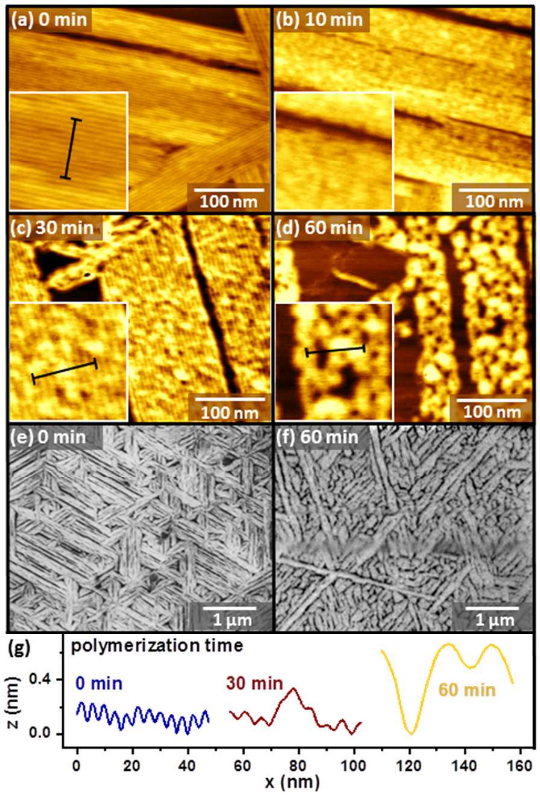

Fig. 4. AFM images of diyne PE on MoS_2: (a) unpolymerized, and polymerized by UV irradiation for (b) 10 min, (c) 30 min, and (d) 60 min. SEM images of diyne PE on MoS_2: (e) unpolymerized and (f) polymerized for 60 min. (g) AFM line profiles from a, c, and d.

Molecular domain orientations. Edge-on adsorption of diyne PE can occur with the NH_3^+ group oriented toward the substrate (down) or the environment (up), leading to three possible lamellar median symmetries (down|down, down|up, or up|up). Energy-minimized models (Fig. S8,9) suggest NH_3^+-up adsorption is preferred, bringing the glycerol backbone into contact with the substrate. However, the down|up median structure produces lamella with similar calculated energies, by allowing lamellar edges to interdigitate (Fig. 5c).

In monolayers of diyne PE, we observe two distinct classes of domains with differences in angular orientation and linear defects (Fig. 5a,b).[23] A 5–10° rotational offset is observed (wind rose plot, Fig. 5a) between domains with long linear defects (blue) and those with smaller defects (gold). Large linear vacancies (in blue domains) are visible in AFM images of both polymerized and unpolymerized monolayers, suggesting defects in assembly. Smaller linear vacancies in gold domains are visible only in SEM images, and are similar to polymerization-related restructuring observed previously by SEM when lamellae narrow during polymerization.[23] Domains exhibiting rotational offsets have lamellar widths ~0.2 nm greater than the majority domains (Fig S6).

A majority (blue) domain structure with an antisymmetric lamellar median (Fig. 5c) would create interlocked lamellar edges, consistent with lamellae that are narrower by ~0.2 nm. The small overlap at lamellar edges could also reasonably minimize the appearance of cracking during polymerization.

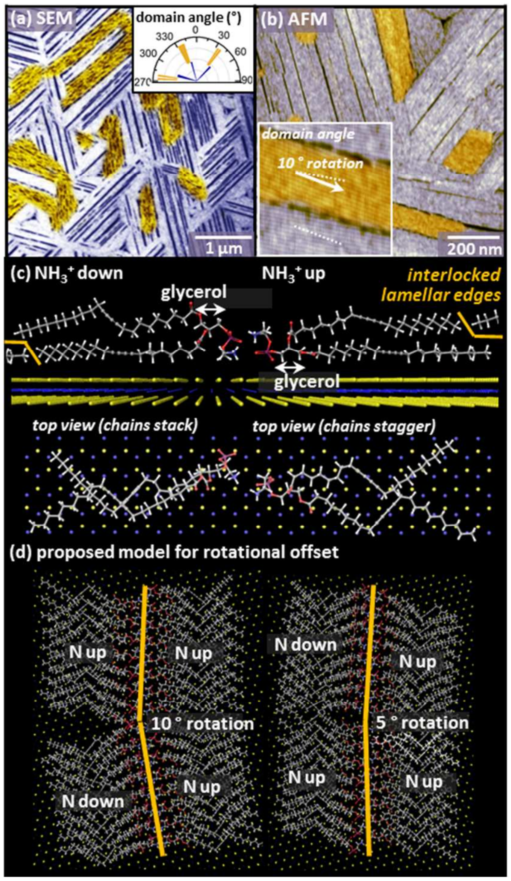

Fig. 5. Diyne PE on MoS_2: (a) SEM after 20 min UV irradiation (b) AFM prior to UV irradiation, illustrating two classes of rotational angles (minority domain orientation highlighted in gold). (c) Molecular models of edge-on adsorption of diyne PE with terminal NH_3^+ oriented down (left), and up (right) in proposed majority lamellar structure. (d) Proposed model for rotational offset in lamellar transition from up|down to up|up orientation.

Solvent-stability of diyne PE and PCDA monolayers. Monolayers of diyne PE exhibit increased stability toward further solution processing, in comparison with polymerized PCDA. Fig. 6 shows a monolayer of diyne PE polymerized for 15 min (Fig. 6a) then washed with 5 mL of ethanol (Fig. 6b). Although the lamellar surface roughens during washing, similar washing of PCDA monolayers (Fig 6c,d) produces rounded vacancies and an absence of obvious lamellar structure, consistent with more substantial monolayer restructuring.

Conclusions

Here, we examine the role of molecular structure in stabilizing monolayers on MoS_2, comparing structure and stability of two different amphiphiles assembled using an optimized LS transfer process at elevated temperature. Overall, we find that diyne PE is capable of forming ordered molecular domains with edge lengths of multiple µm on MoS_2, despite the relatively weak alkyl–MoS_2 adsorption enthalpy. Diyne PE domains are substantially larger than those observed for PCDA, and have a thickness of ~0.8 nm consistent with edge-on molecular assembly. Changes in monolayer structure during polymerization, examined over areas of several μm^2, illustrate that polymerization of diyne PE occurs ~4-fold faster on MoS_2 than on HOPG. Domains of diyne PE exhibit enhanced stability in comparison with PCDA, during polymerization and in subsequent solvent washing assays. These findings point more generally to the possibility of using edge-on adsorption as a strategy for stabilizing monolayers on layered materials such as MoS_2 to which alkyl chains adsorb relatively weakly.

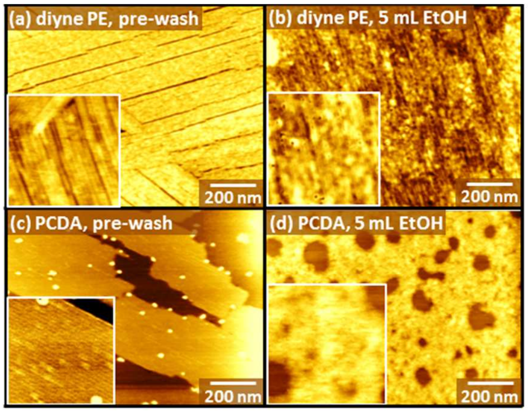

Fig. 6. AFM images of diyne PE on MoS2: (a) before and (b) after washing with 5 mL ethanol. PCDA on MoS2: (c) before and (d) after washing with 5 mL ethanol.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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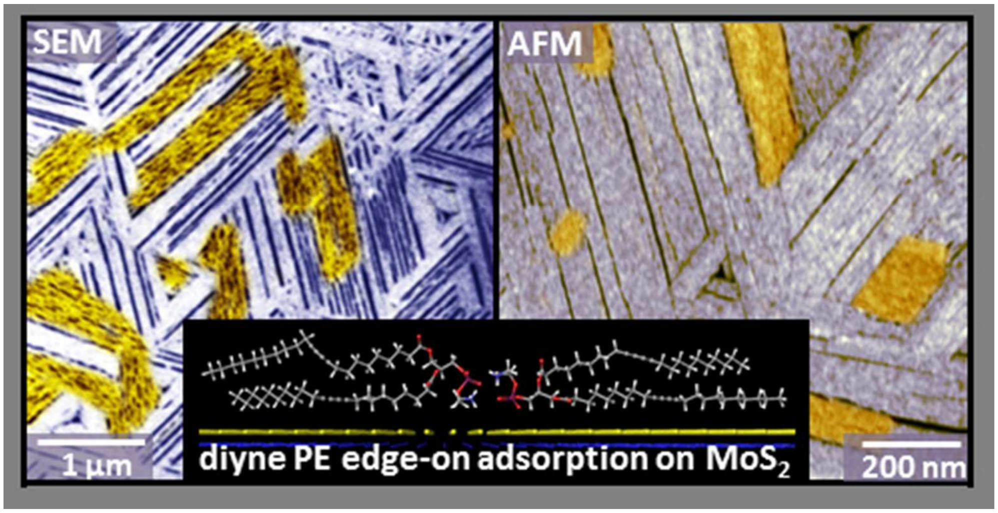
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