Alkyl Chain Length Effects on Double-Deck Assembly at a Liquid/Solid Interface

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Controlled double-deck packing is an appealing means to expand upon conventional 2D self-assembly which is critical in crystal engineering, yet it is rare and poorly understood. Herein, we report the first systematic study of double-deck assembly in a series of alkylated aminoquinone derivatives at the liquid-solid interface. The competition between the fraction of alkyl chains adsorbed on the surface and the optimal conformation of the alkyl chains near the head group leads to a stepwise structural transformation ranging from complete double-deck packing to complete monolayer packing. Alkyl chains on the bottom or top layer of the double-deck assemblies were selectively visualized by carefully tuning the scanning tunneling microscopy settings. A method to easily identify mirror image domains was discovered based on the coincidence of domain boundaries with a graphite main axis. The effect of molecular symmetry and metal complexation on the formation of the double-deck assembly was also explored. Based on 2D crystal engineering principles, this bottom-up double-deck assembly can potentially provide an essential toehold for constructing precise 3D hierarchical structures.

Introduction

Molecular self-assembly has long been recognized as a powerful means towards bottom-up fabrication of functional surface-based nanostructures.¹ This approach enables the construction of well-ordered nanostructures on solid surfaces using small molecular building blocks.² Such functionalized surfaces can be used as templates or as functional elements in applications including crystal growth, catalysis, sensing, and organic electronic devices.^{3–5} The assembly of molecules in a programmed manner is a highly attractive and sought after goal to enhance molecular engineering. However, even in two-dimensions, it remains difficult to predict the outcome of molecular self-assembly solely on the basis of the chemical structure of the building blocks, due to the crucial role played by the competitive influence of non-covalent interactions (van der Waals interactions, hydrogen bonds, π - π stacking, electrostatic and dipole-dipole intermolecular forces). A better

understanding of such interactions continues to improve our ability to foresee and control the outcome of surface-supported supramolecular assemblies, which are, in turn, valuable for the construction of molecular nanostructures and nanodevices.

Alkyl chains have been demonstrated to play important roles in intermolecular interactions and hence affect supramolecular self-assembly.^{6, 7} Generally, alkyl side chains are attached onto molecular building blocks to tailor the molecular packing and thin-film morphology.^{8–11} More importantly, these structural effects induce alterations of chemical, physical, and surface/interfacial properties such as chemical reactivity, tribology, and electronic/electrochemical properties.^{6–8, 12, 13} For example, Yiu *et al.* revealed that long linear alkyl side-chains promote nanostructural order in thin-film solar cells, enhancing power conversion efficiencies from 5% to 6.5%.¹⁴ While Ghosh *et al.* demonstrated blue-shifted or red-shifted fluorescence properties of perylene bisimides with longer or bulkier side chains, respectively.¹⁵

Scanning tunneling microscopy (STM) is a very powerful tool to visualize molecular organization at the 'buried' and often inaccessible liquid/solid interfaces.¹⁶ It provides direct evidence of molecular structure with sub-molecular resolution. The gathered knowledge regarding alkyl chain behavior could not have been obtained otherwise^{17–21} For example, the direct visualization of chiral recognition and chirality transfer based on alkyl chain interactions *via* van der Waals forces.^{17, 21}

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Previously, studying charge-assisted hydrogen bonding (CAHB) assembly of *p*-quinonemonoimine, C18*m*, we discovered an unexploited aspect of alkyl chain packing behavior (Figure 1d & h).²² In particular, we found that only 3/4 of the alkyl chains in interdigitated C18*m* lamellae are visualized by STM. This type of ‘missing alkyl chain phenomenon’ in self-assembled molecular systems is quite prevalent.^{10, 11, 20, 23–68} Some researchers oversimplify and assume all the alkyl chains have adsorbed on the surface; while others rationalize that the alkyl chains are pointing out of the plane of the monolayer into the liquid phase (*a.k.a.*, ‘flying alkyl chains’) or air.^{10, 11, 20, 29, 30, 39–68} Correctly assigned packing models are essential for future developments in surface molecular engineering, since their location could significantly alter the interfacial properties and impact the hierarchical 3D growth. A fundamental understanding of the assembly process provides a starting point to tune the supramolecular assembly on surfaces and to ultimately fabricate functional devices.

Previously, we proposed another packing model to explain this mysterious ‘missing alkyl chain’ phenomenon where the missing alkyl chain is adsorbed on top an underlying chain. We coined this packing as double-deck assembly (Figure 1d & j). This double-deck assembly is related to self-assembly of double-deck cyclophane derivatives^{69–73} as both form layers two molecules thick where parts of a given molecule are located in the two planes. However, our system has an advantage of a dramatically simpler building blocks, readily synthesised by a one pot transamination reaction.

To gain full understanding of this missing alkyl chain phenomenon, we now explore the influence of alkyl chain length and molecular symmetry on double-deck packing by performing a systematic study of an expanded molecular repertoire of six zwitterionic *p*-quinonemonoimines. These are referred herein as *meta* quinones, C12*m*, C14*m*, C16*m* and, C22*m*, which differ in aliphatic chain length, a metal coordinated dimer of C18*m*, (C18*m*)₂Ni and an isomer of C18*m*, 2,5-bis(octadecylamino)1,4-quinone, with *para* orientation of the octadecylamino groups, C18*p* (Scheme 1).

Results and discussion

Zwitterionic *meta* quinones spontaneously self-assemble into ordered networks immediately after deposition of saturated solutions (trichlorobenzene; TCB) onto the HOPG surface. The surface is covered with a lamellar pattern of alternating bright and dark stripes. The quinone head groups appear as the bright regions while the alkyl chains are darker (Figure 1 a-f). The unit cell information is provided in Table 1. Strong charge-assisted hydrogen bonding (CAHB) locks the head groups of *meta* derivatives with a fixed separation. This is corroborated by the fact that the unit cell ‘*a*’ distances are constant for all the *meta* quinones (1.48 ± 0.04 nm), which provides an ideal terrain to explore alkyl chain length effects on 2D self-assembly. As expected, the unit cell ‘*b*’ distances increase as alkyl chain length increases (Table 1). The measured unit cell dimensions indicate that the alkyl chains of *meta* quinones are fully

Table 1. Unit cell dimensions for aminoquinone derivatives, where 'a' is the unit cell vector along the head-group row, 'b' is the unit cell vector connecting adjacent head-group rows, and 'γ' is the unit cell angle. '⊥ d' is the alkyl chain perpendicular separation and 'β' is the alkyl chain to head group row intersecting angle.

Name	a (nm)	b (nm)	γ	⊥ d (nm)	β
C12m	1.48 ± 0.02	1.94 ± 0.05	75 ± 1°	0.52 ± 0.01	46 ± 1°
C14m	1.49 ± 0.02	2.25 ± 0.05	70 ± 1°	0.52 ± 0.01	45 ± 1°
C16m	1.48 ± 0.02	2.36 ± 0.05	69 ± 1°	0.51 ± 0.01	45 ± 1°
C18m	1.48 ± 0.02	2.94 ± 0.05	79 ± 1°	0.43 ± 0.01	60 ± 1°
C22m type 1	1.48 ± 0.02	3.41 ± 0.08	75 ± 1°	0.43 ± 0.01	60 ± 1°
C22m type 2	2.99 ± 0.01	3.66 ± 0.06	76 ± 1°	0.43 ± 0.01	86 ± 1°
C22m type 3	1.50 ± 0.03	3.4 or 6.8 ± 0.1	36 ± 1°	0.42 ± 0.01	34 ± 1°
(C18m)₂Ni	1.51 ± 0.02	3.07 ± 0.05	66 ± 1°	0.46 ± 0.01	66 ± 1°
C18p	0.74 ± 0.04	3.69 ± 0.09	86 ± 1°	0.50 ± 0.03	43 ± 1°

extended and interdigitating within the lamellae. Interestingly, although all our *meta* derivatives pack in a lamellar fashion, they show a different ratio of the number of observed alkyl chains with respect to the number of head groups. In the high-resolution images (Figure 1a-c), the number of head groups and corresponding alkyl chains can be clearly viewed. For C12m, C14m and C16m the head group to alkyl chain ratio is 1:1 as opposed to the expected 1:2 ratio of the actual molecular structure. The intersection angles between the head group rows and chain-orientation (referred to hereafter as the β angle) are all 45° ± 1°. The missing alkyl chains are adsorbed on top of the lower layer of alkyl chains forming complete double-deck assembly (Figure 1g & j), *vide infra*.²²

When the alkyl chain length increases to 18 carbons (C18m) the head group-to-alkyl chain ratio changes to 4:3 (Figure 1d).²² In other words, 3 out of 4 alkyl chains are adsorbed on the HOPG and every 4th alkyl chain is proposed to be adsorbed on top of another alkyl chain (Figure 1h). In this case, the β angle is 60° ± 1°. Figure 2 is a simplified packing model of this partial double-deck assembly (top view) highlighting the β angle. The β angle can be measured directly from high-resolution STM images or indirectly obtained from domain orientation with respect to the underlying HOPG. The β angle and unit cell dimensions are the two essential parameters for modeling molecular packing, where the former indicates the alkyl chain orientation and the latter provides the building block-to-building block distance (*vide infra*).

C22m, bearing longer alkyl chains, not only shows two polymorphs (Figure 1e & f), but also displays two characteristic domain boundary transition structures (Figure 3). Besides the type 1 morphology, C18m-like, with 60° β angle and 3 out of 4 alkyl chains adsorbed on the HOPG (Figure 1e), C22m also forms another morphology (type 2) where the β angle is 86° ± 1° (Figure 1f). This type 2 morphology is more prominent and covers ca. 70% of the imaged graphite surface. In contrast to the type 1 morphology, there are 7 out of 8 alkyl chains adsorbed on the HOPG in this type 2 morphology (Figure 1i). Furthermore, two types of boundary transition structures of C22m (type 3) can be found between the two type 2 domains (Figure 3). Depending on the given separation at the boundaries, both non-interdigitated (type 3A; highlighted region in Figure 3a) and interdigitated (type 3B; highlighted region in Figure 3b)

Figure 2. Schematic representation of molecular packing. Head groups and alkyl chains are indicated by green disks and blue lines, respectively. A unit cell is highlighted by a dotted parallelogram. 'a' is the unit cell vector along the head-group row, 'b' is the unit cell vector connecting adjacent head-group rows. Note that the β angle is different from the unit cell γ angle. β is the angle intersecting the head group row (dark blue line) and alkyl chain direction (red line). $d_{\perp total}$ is the total perpendicular distance available to accommodate alkyl chain adsorption per unit cell.

arrangements can be found. For the non-interdigitated arrangement, *all* of the alkyl chains are adsorbed, while for the interdigitated arrangement only *half* of the alkyl chains are adsorbed on the surface. In the latter case, the other half of the alkyl chains are overlapping on top, forming a complete double-deck assembly similar to the shorter chain *meta* compounds (C12m, C14m and C16m). Both types of boundary transition structures share the same β angle of 34° ± 1°.

A possible reason for the rich and varied surface structures observed for C22m is attributed to the longer alkyl chains, which increase the adsorption energy. For every additional CH₂ group, the molecule-to-substrate affinity is expected to increase by 12.1 or 10.4 kJ mol⁻¹ in the flat or vertical orientations, respectively.⁷⁴ When the interaction between molecules and substrate is strong, molecules are more likely to get kinetically trapped in metastable structures. At initial nucleation sites, when molecules attach to the surface, strong affinity will decrease a molecule's mobility, thus hinder the system from reaching the global minimum structure. As a result, more metastable self-assemblies are observed for C22m.

Figure 3. STM images with molecular models showing characteristic boundary transition structures of C22m at the TCB/HOPG interface. a) Non-interdigitated packing (type 3A) and b) complete double-deck assembly (type 3B). The three main axes of graphite are highlighted with black lines. Tunneling parameters: a) $I_t = 20.0$ pA, $V_b = -856.0$ mV; b) $I_t = 25.0$ pA, $V_b = -313.0$ mV; c) $I_t = 22.0$ pA, $V_b = -47.0$ mV.

Figure 4. a) High-resolution STM image (left) and model (right) of (C18m)₂Ni at the TCB/HOPG interface. One (C18m)₂Ni molecule is colored in yellow. Note that one of the alkyl chains is underneath an alkyl chain from a molecule on the other side. $I_t = 26.0$ pA, $V_b = -800.0$ mV. b) A zoomed-in image of the head group region in (a). The shape of the head groups of the quinone is outlined in black and the position of the Ni atoms is highlighted. c) Molecular model of head groups of (C18m)₂Ni, where Ni is coloured in green. d) High-resolution STM image (lower) and model (upper) of C18p. The parallelogram indicates the unit cell. Unit cell dimensions are given in Table 1. The three axes of graphite are highlighted with black lines. $I_t = 16.0$ pA, $V_b = -200.0$ mV.

(C18m)₂Ni, homemade *via* a solvent-free mechanosynthesis⁷⁵, is a metal coordination complex formed from two C18m units and a nickel(II) ion (Scheme 1). Since all the *meta* quinones have the same head to head distance (unit cell *a* distance) due to the strong CAHB, the intention of inserting a metal ion was to increase the molecule to molecule distance and observe its effect on double-deck packing. Another consequence of forming the Ni complex was to change from CAHB to normal HB (*i.e.* metal complexation removes one proton from each quinone and the resulting (C18m)₂Ni is no longer zwitterionic). From high resolution images (Figure 4a), (C18m)₂Ni still forms double-deck packing, where 3 out of 4 alkyl chains are adsorbed on the HOPG, analogous to the self-assembly of C18m.²² In this case, the β angle is $66^\circ \pm 1^\circ$. As expected, the measured unit cell vector '*a*' increased to 1.51 nm (Table 1), which is slightly longer than that of C18m (1.48 nm). This distance increase is probably due to a decrease in hydrogen bonding strength from the CAHB to the normal HB. Ni(II), with a filled d_{z^2} orbital, cannot be visualized by STM,⁷⁶ however the position of Ni(II) can still be deduced from the head group arrangement (Figure 4b & c). Since the CAHB interaction has a zigzag motif, the Ni ion is expected to be located between two linearly aligned ligands.⁷⁷ Such high resolution STM images provide important evidence for determining the configuration of the metal complex, more specifically, the *trans*-geometry at the metal center.

Furthermore, C18p, which is a constitutional isomer of C18m, is designed to investigate the effect of building block symmetry on the alkyl chain packing. Though it is no longer zwitterionic, due to the partial charges on the nitrogen and oxygen, it can still form CAHBs (Scheme 1).⁷⁸ Different in the position of the alkyl chains attached to the quinone core, C18p has C_{2h} symmetry while C18m has C_{2v} symmetry. CAHB connects the head groups of C18p to form a string-of-pearl-like lamellar packing with non-interdigitated alkyl chains. Based on unit cell measurements, all alkyl chains are adsorbed on HOPG and are fully extended (Table 1 and Figure 4d).

All the molecules studied herein are prochiral. Prochiral molecules can adopt a chiral conformation when adsorbed on a surface and, as such, chiral domains are often observed.⁷⁹ A total of 6 domain orientations can be observed in cases where the unit cell vector *a* does not run parallel or perpendicular to one of the three main symmetry axes of graphite. That is, 3

Figure 5. Characteristic domain boundary transitions between mirror image chiral domains. STM images of the self-assembled networks of C18p (a), (C18m)₂Ni (b), C22m type 2 morphology (c), C16m (d), C14m (e) and C12m (f) at TCB/HOPG interface. Mirror image chiral domains are highlighted in yellow (Left) and red (Right). a) A 'fuzzy' domain boundary is circled by a dotted oval, while a straight smooth domain boundary which follows one of the axes of HOPG is circled by a solid oval. In a) Molecular models illustrate the origin of noisy (top) and smooth (bottom) domain boundary transitions. Black lines highlight the three main symmetry axes of HOPG. Tunneling parameters: a) $I_t = 20.0$ pA, $V_b = -856.0$ mV; b) $I_t = 22$ pA, $V_b = -47$ mV; c) $I_t = 17$ pA, $V_b = -300$ mV; d) $I_t = 13$ pA, $V_b = -293$ mV. Image sizes: a) 100×100 nm², b) 20×20 nm², c) 36×36 nm², d) 80×80 nm², e) 78×78 nm², f) 25×25 nm².

domains rotate clockwise and 3 domains rotate counterclockwise with respect to graphite's symmetry axes (*i.e.* there are 3 pairs of mirror image domains).⁸⁰ In the two exceptions, when the head group row (unit cell vector *a*) lies parallel or perpendicular to the main symmetry axes of HOPG, only 3 domain orientations are observed. For example, in the case of C18*m* and the type 1 morphology of C22*m*, only 3 domain orientations are observed since the head group rows (unit cell vector *a*) follow one of the main axes of graphite. The alkyl chains follow one of the two remaining graphite axes resulting in the formation of either a linear or herringbone structure.²²

Some interesting behavior at the domain boundaries between two mirror-image chiral domains was observed for all the molecules studied here (Figure 5), except for C18*m* (*vide infra*). From the large-scale STM images in Figure 5, sometimes the domain boundary appeared 'fuzzy' (Figure 5a upper); while other times we see a flawless transition (Figure 5 lower, b, c, d upper, e & f). We attribute this phenomenon to alkyl chain alignment. From the upper model in Figure 5a, when the alkyl chains in two different domains are not aligned, a high energy domain boundary is created where there are large areas where molecules cannot be fully adsorbed (black empty space). On the other hand, when alkyl chains from two different domains are aligned (following the same HOPG axis; lower inset in Figure 5a) a much smoother transition can result. After careful examination, three characteristic features of the domain boundaries of mirror image domains were found: (i) a smooth straight line, (ii) parallel to one of the main axes of HOPG and (iii) the alkyl chains in both domains are parallel to the domain boundary. A straight domain boundary following the direction of the alkyl chains is the most stable, since it creates the least amount of high energy pockets. The only possibility for the two domains, in which alkyl chains are parallel to each other, while head group rows are not, can occur when the two domains are mirror image chiral domains (identified arbitrarily as R and L in Figure 5). This is why such a phenomenon is not observed for C18*m* and C22*m* type 1 morphology, since the domains are achiral. One should observe such phenomenon in most small molecules carrying long alkyl chains that form lamellar chiral domains. One can thus take advantage of these generic rules to help identify mirror image chiral domains.

Below, we delve deeper into the adsorption behaviour of *meta* quinones (C12*m*, C14*m*, C16*m*, C18*m* and C22*m*) as well as the closely related metal complex (C18*m*)₂Ni and isomeric aminoquinone derivative C18*p*, focusing on the role of alkyl chain length. As discussed above, a series of double-deck assembly structures with different numbers of alkyl chains adsorbed on the surface is proposed, except for C18*p*. Every second alkyl chain in C12*m*, C14*m* and C16*m* is in the upper layer, thus forming a complete double-deck assembly structure (Figure 1a-c). The packing of C22*m*, bearing longer alkyl chains, ranges from complete monolayer packing to complete double-deck assembly. The type 1 morphology, C18*m*-like, has 1 of 4 alkyl chains adsorbed on top of the first layer (Figure 1e), while

the type 2 morphology has 1 of 8 alkyl chains adsorbed on top of the first layer (Figure 1f). In Figure 1f & i, the yellow colored molecules do not have another molecule lying on top of them; while the green colored molecules are lying on top of yellow colored molecules. The type 3 morphology of C22*m* has a complete monolayer structure (Type 3A; Figure 3a) or a complete double-deck assembly (Type 3B; Figure 3b).

In response to changes in alkyl chain length, a systemic quantized change in the double-deck assembly of aminoquinone derivatives is observed. For *meta* quinones, the β angles and the fraction of unaccounted alkyl chains (*i.e.* missing alkyl chains) were plotted against the alkyl chain length (Figure 6). The fraction here refers to the number of alkyl chains that are not adsorbed on the surface divided by the total number of alkyl chains in a unit cell. From the graph, one can notice that the β angles and the fraction of unaccounted alkyl chains are coupled with each other. The fraction remains the same for the shorter alkyl chain *meta* quinones (C12*m*, C14*m* & C16*m* fraction equals to 1/2), which form complete double-deck assembly (*i.e.* they all have the same $45 \pm 1^\circ$ β angle). A sudden decrease in the fraction from 1/2 to 1/4 occurs when the alkyl chain length increases to C18. The 1/4 partial double-deck assembly of C18*m* and the type 1 packing of C22*m* both have a $60 \pm 1^\circ$ β angle. The next sudden decrease in the fraction from 1/4 to 1/8 occurred for the C22*m* type 2 polymorph, which is the major polymorph. The β angle increases to $86 \pm 1^\circ$ for the 1/8 partial double-deck assembly. This trend of decreasing the fraction of unaccounted alkyl chains as a function of alkyl chain length is due to the competition between van der Waals interactions and alkyl chain bending propensity. The molecular mechanics (MM+) optimized structure of an isolated *meta* quinone derivative has both alkyl chains naturally open at 45° away from the central axis of the molecule (Figure S2). When the alkyl chains are short, the tendency for the chains to bend away from an optimal geometry is low. However, *when the alkyl chains get longer, the adsorption energy increases, and as a result, more alkyl chains will adsorb on the surface at the expense of the β angle*. Increasing the number of alkyl chains adsorbed to the HOPG is realized by an increase in the total perpendicular distance assigned to the alkyl chains in a unit cell ($d_{\perp tot}$, highlighted in Figure 2). Measuring $d_{\perp tot}$ can also allow

Figure 6. A plot of alkyl chain length vs. fraction of unaccounted missing alkyl chains for the *meta* quinones.

us to estimate the number of alkyl chains adsorbed directly to the substrate. Given that the alkyl chain separation is typically about 4.5 nm,⁸¹ one can estimate that there are *ca.* 2, 2, 2, 3, 3, 7 and 2 alkyl chains adsorbed on the substrate (per unit cell) for C12*m*, C14*m*, C16*m*, C18*m*, (C18*m*)₂Ni, C22*m* and C18*p*, respectively.

The *missing alkyl chain phenomenon* has been observed in high-resolution STM images for all the *meta* quinone derivatives and (C18*m*)₂Ni. Generally, it is important to determine the location of the missing alkyl chains (whether extended into the solution or adsorbed on the surface), since their location fundamentally affects 3D hierarchical growth of the film and the resulting properties (*e.g.*, hydrophobicity). Several observations presented below validate that for our systems, the alkyl chains are overlapping. First, in many high-resolution images, every 4th or 7th alkyl chain appears higher than its neighbors for C18*m* and C22*m*, respectively (Figure 7a & b). These periodic patterns match exactly with the observed ratio of unaccounted alkyl chains. The contrast variation cannot be attributed to Moiré effect because split images in Figure 8 (obtained by suddenly changing the bias voltage from a molecular setting to an HOPG setting) clearly show that the alkyl chains are fully commensurate with the HOPG lattice.

Note that by changing the bias voltage, one can selectively observe the bottom layer or the double layer (Figure 7c). Clearly at 328 mV or 437 mV, no molecules are removed from the surface. Such reversible appearance/disappearance of structures on the STM images at respectively high/low voltages is known as the “tunneling transparency”.^{82–84}

In order for *meta* quinones to densely pack either in a crystalline form or on the surface, the two *meta* related alkyl chains have to bend to be parallel to each other. To avoid repulsion energy the head groups will bend away from the plane of the alkyl chains, as has been shown in the corresponding crystal structures.^{22, 75} Due to the CAHB, quinone head groups self-assemble into zigzag backbone axes (Figure 1). The out-of-plane bending of the head groups causes the alkyl chains at either side to be at different levels (Figure 1j). In other words, when one side of the alkyl chains is adsorbed on a surface, the head groups

Figure 7. STM topography image of C18*m* and C22*m* adsorbed at the TCB/HOPG interface, where periodic bright alkyl chains were observed. For C18*m* every 4th alkyl chain is bright, while for C22*m* every 7th alkyl chain is bright, in agreement with the proposed model. (a) $I_t = 19.8$ pA, $V_b = 259.40$ mV; (b) $I_t = 8.8$ pA, $V_b = 393.7$ mV. Green arrows highlight alkyl chains and the longer green arrows highlight the brighter alkyl chains. (c) Visualization of the alkyl chains can be influenced by the imaging parameters: upper: $I_t = 6$ pA, $V_b = 328.3$ mV; lower: $I_t = 6$ pA, $V_b = 437.0$ mV.

lift the alkyl chains on the other side upwards, which allows optimal stacking on top of the neighboring row, *i.e.* double-deck assembly. This hypothesis has been verified with both C18*p* and (C18*m*)₂Ni self-assemblies. When the alkyl chains are in the *para* position, the molecule lies flat on the HOPG and cannot form double-deck assembly. On the other hand, Ni complexation increased building-block to building-block distance, however, since the intrinsic bending near the head group region is still present, double-deck assembly can and does occur.

In addition, this quasi-three-dimensional interdigitated structure of alkyl chain lamellae features multiple attractive van der Waals interactions. In fact, the parallel alignment of alkyl chains adsorbed on another layer of alkyl chains is the preferred orientation in 3D crystals.²²

There is great interest in the controlled formation of multilayered supramolecular structures. For example, Beton *et al.* have reported the guest-induced growth⁸⁵ and the sequential epitaxial deposition of supramolecular multilayers.⁸⁶

The facile growth of ordered multilayers described herein further supports the proposed neatly packed double-deck lamellae. Multilayer growth in both a criss-crossed (Figure 9) and parallel fashion (Figure S3) have been observed for quinone derivatives with alkyl chains equal or longer than 18 carbons. We ascribe this phenomenon to strong intermolecular interactions which ‘link’ them to pack into stripe-like fibers that can stack on top of

Figure 8. Split image of C18*m* (a) and C22*m* (b & d) at the TCB/HOPG interface, where the bias voltages were changed during scanning, revealing graphite lattice underneath. The alkyl chain separations are indicated by blue lines, all of which have the same separation. (c) Schematic diagram indicated the blue lines separation and orientation. (d) Zoomed-in image of (b). It can be easily noticed that the alkyl chain separation of both C18*m* and C22*m* matches exactly with the HOPG periodicity along $\langle -1\ 1\ 0\ 0 \rangle$ direction that is 4.26 Å as indicated in (c). (a) $I_t = 16$ pA, $V_b = -300.0$ mV (SAMN) and 39.0 mV (HOPG), (b) $I_t = 18$ pA, $V_b = -350.0$ mV (SAMN) and 40.0 mV.

Figure 9. Evidence for multilayer formation; a) $I_t = 12$ pA, $V_b = 686$ mV. b) $I_t = 26$ pA, $V_b = 528$ mV. c) $I_t = 20$ pA, $V_b = 600$ mV. d) $I_t = 30$ pA, $V_b = -1753$ mV. Parallel double layer see Figure S3.

each other, forming multilayers, while the orientations are governed by the underlying layer. The favorable inter-layer interactions are probably promoted by electrostatics and may also involve alkyl chain/alkyl chain van der Waals interactions.^{87, 88} The second layer often extends over domain boundaries leading to misaligned bilayers easily visualized as a characteristic rhomboidal grid. Note that these motifs are not due to a double-tip effect sometimes observed in STM imaging since: (i) monolayers and multilayers can be identified in the same image and (ii) the phenomenon of multilayer formation is reproducible in several experimental sessions. In short, evidence of multilayer growth supports the hypothesis of double-deck assembly, where high-density multilayers can be formed. On the other hand, if these missing alkyl chains point out of the plane of the monolayer, they are expected to perturb the assembly of the second layer.

Experimental

Materials and methods: STM measurements were carried out under ambient conditions (20–22°C) with a Bruker Nanoscope MultiMode Scanning Probe Microscope equipped with a low-current STM head or an RHK STM (SPM1000) running under ambient conditions. *In situ* STM imaging was performed at the liquid/solid interface; the substrate was freshly cleaved highly oriented pyrolytic graphite (HOPG; ZYB quality; NT-MDT Castletroy, Limerick, Ireland). Mechanically sharpened Pt/Ir (80/20; NanoScience Instruments, Phoenix, AZ) tips were tested by obtaining atomic resolution images of graphite and subsequently a drop (*ca.* 4 μ L) of sample solutions in 1,2,4-trichlorobenzene (Aldrich, 99%) was added. Self-assembled monolayers (SAMs) were observed immediately after the tip was

engaged. Solutions of C18m, C22m and (C18m)₂Ni were heated prior to deposition to improve the solubility. For other derivatives, saturated solutions were used. The specific tunneling conditions are given in the figure captions. All the images were corrected for drift by WSxM software⁸⁹, using the recorded graphite images for calibration purposes. A detailed and useful tutorial showing how images were calibrated can be found in the ESI. For the synthesis of the alkylated aminoquinone derivatives that were employed in this study, see the Supporting Information.

Conclusions

We reported a systematic STM study of double-deck assembly at the liquid-solid interface. Exploring self-assembly of zwitterionic *p*-quinoneimine derivatives as a function of alkyl chain length, we demonstrate that the occupation of the upper deck decreases as the alkyl chain length increases. The associated structural transformation from full double-deck assembly (*i.e.* C12m – C16m) to complete monolayer packing (*i.e.* type 3A packing of C22m) is quantized (Figure 6). This is rationalized in terms of competition between maximizing the alkyl chains adsorption on a surface and minimizing their conformational distortion near the head group (β angle). With regard to chiral domain formation, mirror image domain boundaries are ideal (*i.e.* linear and not ‘fuzzy’) and coincide with a graphite main axis due to alkyl chain epitaxial alignment. This study provides definitive evidence of double-deck assembly as a general behavior of polyalkylated molecules which can now be used to promote the *selective* formation of hierarchical supramolecular films. Such double-deck assembly should generally occur when molecules have two competing interactions with mismatching periodicities. The ability to control the density of the second layer with precise periodicity paves the way towards the bottom-up construction of hierarchical structures with long range periodicities. In the future, a dynamic transamination of these zwitterionic *p*-quinoneimines⁹⁰ may open the possibility of *in situ* functionalization of the second layer electronically decoupled from the surface.

Conflicts of interest

There are no conflicts to declare

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