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Dipolar Control of Monolayer Morphology: Spontaneous SAM Patterning

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Morphologies of self-assembled monolayers (SAM) are determined by adsorbate structure,[1] substrate surface structure,[2] and solvent.[3] A monolayer (ML) formed from multiple components can exhibit randomness associated with the relative placement of each component.[4] Here we demonstrate a strategy for controlling relative placements of molecules within multicomponent MLs at the solution−HOPG interface. The ML assembles from a complementary pair of 1,5-bis-alkyldiether-anthracenes bearing self-repelling side chains. Each diether side chain suffers repulsive dipolar interactions if it adsorbs next to an identical side chain in the ML morphology normally formed[5] by 1,5-bis-substituted-anthracenes (Figure 1c). Complementary side-chain pairs experience attractive dipolar interactions when adsorbed as neighbors in the normal ML morphology. These repulsive and attractive forces spontaneously drive formation of a patterned ML[4c,6] at the solution−HOPG interface. Each molecule adsorbs in its own row, sandwiched between two rows of the complementary anthracene. These studies demonstrate the viability of using weak dipolar interactions to control molecular placement and to pattern multicomponent MLs.[7]

1,5-Bis-substitued-anthracenes form interdigitated MLs at the solution−HOPG interface.[5] The anthracenes assemble in rows (Figure 1) with their side chains extending perpendicular to the row repeat. Neighboring side chains are connected to anthracenes in adjacent rows. 1,5-Bis-substituted-anthracenes are prochiral and adsorb to HOPG via enantiotopic faces. STM studies[5] reveal that anthracene rows separated by even length side chains, for example, hexadecyl, dodecyl, 3-thiatetradecyl, and 2-oxahexadecyl, adsorb via opposite enantiotopic faces and form MLs with *pg* plane group symmetry. Anthracene rows separated by odd length side chains, for example, 3-thiapentadecyl, 2-oxaundecyl, 2,9-dioxapenta-decyl, and 2-oxatridecyl adsorb via the same enantiotopic faces. These MLs exhibit *p2* plane group symmetry. Both the *pg* and *p2* morphology (i) align side chains such that a heavy atom (C, O, S) at position "n" is in registration with the $(\omega + 2 - n)^{\text{th}}$ position of neighboring side chains (ω is the side-chain length. The benzylic C is position 1); (ii) provide all side chain CH_2, except C-1, with van der Waals contacts to two adjacent chains; (iii) minimize steric repulsion between anthryl and methyl groups. The anthracene alignment in adjacent rows affords a visual, side-chain-length dependent test for the presence of a $(\omega + 2 - n)$ ML.

Two isomers of 1,5-bis-(dioxahexadecyl)-anthracene do not form the *pg*, $(\omega + 2 - n)$ ML expected for even length side chains. STM images of the ML from 1,5-bis-(2,15-dioxahexadecyl)-anthracene, **1**, display sets of six, "high tunneling" dots in a 2 × 3 array previously observed for anthracene[5] (Figure 2 and Figure S1, Supporting Information). Anthracenes in adjacent rows are aligned parallel, indicating a *p2* symmetry ML. The ML formed from 1,5-bis-(3,14-dioxahexadecyl)-anthracene, **2**, also exhibits *p2* symmetry, with parallel, high tunneling regions in adjacent rows (Figure 2). These high tunneling regions are roughly the size of an anthracene, although the tunneling pattern is more complex than a simple 2 × 3 dot array.

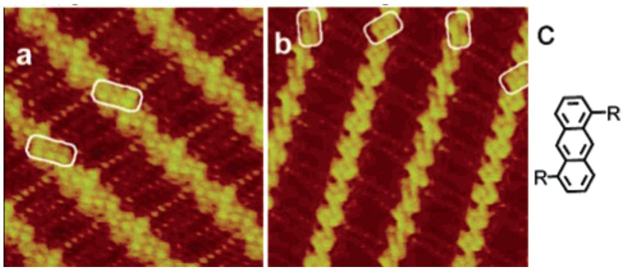


Figure 1. (a) 8 nm × 8 nm STM scan of the *p2*, $(\omega + 2 - n)$ ML from 1,5-bis-(2,9-dioxa-pentadecyl)-anthracene, **3**; (b) 10 nm × 10 nm STM scan of the *pg*, $(\omega + 2 - n)$ ML from 1,5-bis-(2-oxahexadecyl)-anthracene **4**. The white boxes outline individual anthracene groups. $V = 600$ mV; $I = 150$ pA.

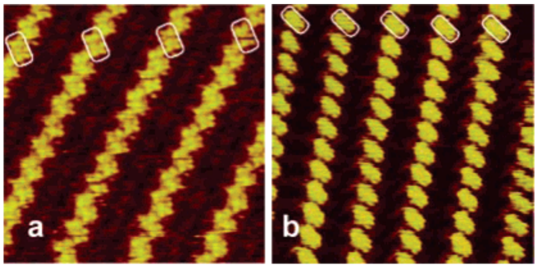
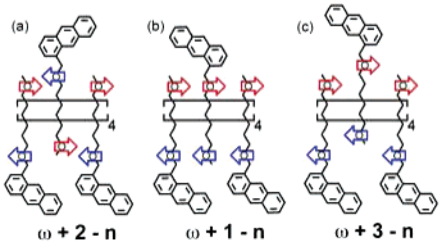


Figure 2. (a) 10 nm × 10 nm STM scan of the *p2* ML from **1**; (b) 12 nm × 12 nm STM scan of the *p2* ML from **2**. The white boxes outline individual anthracene units.

Chart 1. Side Chain Ether Dipole Alignments in *pg* $[(\omega + 2 - n)]$ and *P2* $[(\omega + 1 - n)$ or $(\omega + 3 - n)]$ Monolayers Formed from **1**



The failure of **1** and of **2** to form a *pg*, $(\omega + 2 - n)$ ML is not due, simply, to the presence of two ether groups in each side chain. 1,5-Bis-(2,9-dioxa-pentadecyl)-anthracene, **3**, has two ethers per side chain but exhibits the $(\omega + 2 - n)$ ML expected for odd length side chains (*p2* symmetry, Figure 1a). The placement and orientation of ether dipoles in neighboring side chains appear to control the ML morphology. Chart 1a reveals destabilizing, dipole alignments among nearest neighbor ether groups in a $(\omega + 2 - n)$ ML of **1**. The closest ether groups are one side-chain position out of registration, with antiparallel dipoles. Each side chain suffers four, repulsive ether dipole interactions with its nearest neighbors. Chart S1a (Supporting Information) predicts similar dipole repulsions between proximate ether dipoles within the side chains of **2** in a $(\omega + 2 - n)$ ML.

10.1021/ja065338t CCC: $33.50

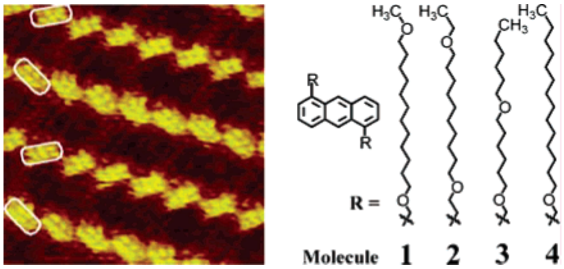


Figure 3. An 8 nm × 8 nm STM scan of the ML from a mixture of **1** and **2**. The 2 × 3 tunneling pattern characteristic of anthracene is visible.

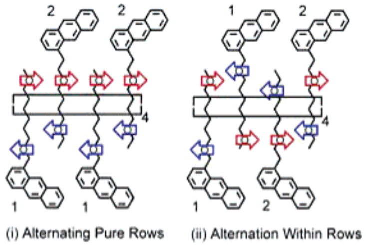
Repulsive, ether dipole interactions for **1** and **2** are specific to the $(\omega + 2 - n)$ ML. A $(\omega + 1 - n)$ ML positions anthracenes in adjacent rows one side-chain position closer and affords stabilizing, collinear dipoles for all proximate ether groups within adjacent chains of **1** (Chart 1b). A $(\omega + 1 - n)$ ML of **1** (or **2**) exhibits *p2* symmetry: anthracenes in adjacent rows adsorb via the same enantiotopic face. A $(\omega + 3 - n)$ ML (Chart 1c, Chart S1c for **2**) also yields stabilizing dipole interactions among proximate ethers and forms a *p2* symmetry ML. Anthracenes in this ML are separated by one more side-chain CH_2 compared to a $(\omega + 2 - n)$ ML. Nearby ether dipoles are parallel and offset by two side-chain positions. Prior STM studies of alkyl ethers on HOPG confirm that ether group dipoles prefer to be offset by two side-chain positions (Chart 1c) or in registration (Chart 1b).[8] Image resolution and hysteresis in our STM data preclude accurate evaluation of row separations and, thus, identification of the *p2* ML of structures **1** and **2** as $(\omega + 1 - n)$ or $(\omega + 3 - n)$.

These results show that two or more sets of proximate, ether dipole repulsions per adjacent side-chain pair are *necessary* and *sufficient* to establish the self-repelling characteristic. **3** forms the normal, *p2*, $(\omega + 2 - n)$ ML (Figure 1a) as it has only one set of antiparallel, proximate ether dipoles per side-chain pair.[9] By contrast, the side chains of **1** (**2**), with two ether dipole repulsions per side-chain pair, are self-repelling: a row of **1** precludes self-assembly of an adjacent row of **1** in a $(\omega + 2 - n)$ morphology.

A solution of **1** *and* **2** on HOPG produces ML domains with apparent *pg* symmetry (Figure 3). As only *p2* MLs are formed from either pure **1** or **2**, the *pg* domains must contain both **1** and **2**. Similar amounts of **1** and **2** must be present to observe the *pg* domains: MLs formed from 10:1 or 1:10 solutions exhibit only *p2* domains. It appears that *pg* domains formed from the mixture contain similar amounts of **1** and **2**.

1 and **2** are indistinguishable in STM scans of the *pg* domains.[10] However, the fore mentioned dipole interaction model offers an explanation for *pg* ML formation from mixtures. Two limiting cases for a two-component, *pg* ML with $(\omega + 2 - n)$ morphology are (i) pure rows, alternately assembled from **1** or **2** or (ii) alternating adsorption of **1** and **2** within each row (Chart 2). All proximate ether dipole interactions are stabilizing for case i: the ether dipoles closest to the anthracenes of **2** are collinear. The ether dipoles closest to the anthracenes of **1** are parallel and offset by two side-chain positions.[8] By contrast, alternating placement of **1** and **2** in each row (case ii) affords an equal number of stabilizing and destabilizing dipole interactions, providing no net stabilization to a *pg*, $(\omega + 2 - n)$ ML. A random ML would suffer a mix of stabilizing and destabilizing ether interactions. Thus, case i ML has the lowest enthalpy. There is no entropic difference between case i and case ii.[11] A ML with randomly placed **1** and **2** has Rln2 higher entropy per position.

Chart 2. Side Chain Ether Dipole Alignments for Two Limiting Cases of *pg*, $(\omega + 2 - n)$ ML Formed from 1:1 Mixtures of **1** and **2**



The anthracene and side-chain placements in the *pg* domains of **1**/**2** mixed MLs are regular along and orthorogonal to the rows, on submolecular and domain (Figure S2) length scales. This uniformity is inconsistent with varying side-chain interactions for a case ii or random ML. Thus, the STM data and the dipole model support "patterned" ML formation from **1**/**2** mixtures.

STM studies of pure **1** or **2** on HOPG show that exchanging two sets of side-chain ether, dipole repulsions for attractions provides sufficient stabilization to override the normal preference for a $(\omega + 2 - n)$ ML. By contrast, use of complementary pairs of self-repelling molecules affords sufficient dipolar stabilization to spontaneously form a patterned $(\omega + 2 - n)$ ML at the solution−graphite interface: **1** and **2** adsorb as pure rows, sandwiched between two rows of complementary partner. These studies demonstrate that weak dipolar interactions can be used to control self-assembled ML morphology. Efforts to develop additional, complementary pairs for complex patterning of MLs are ongoing.

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Supporting Information Available: Dipole alignment chart for **1** and **2**; 50 nm constant current and height scans of mixed **1**/**2** ML; high-resolution image of anthracenes **1**, **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) In a $(\omega + 2 - n)$ monolayer, a dipole in the side-chain *n*th position repels an identical dipole in the $(\omega + 3 - n)$ or $(\omega + 1 - n)$ position of adjacent chains and attracts an identical dipole in the $(\omega - \mathrm{n})$, $(\omega + 2 - n)$, or $(\omega + 4 - n)$ position.
(10) Under optimal conditions, ether oxygens and CH_2 groups are discernible.[8]
(11) For case i and case ii, specifying the molecule at one position in a domain (**1** or **2**) fixes the identity of every other molecule in the domain.

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