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Synthesis of self-orienting triptycene adsorbates for STM investigations

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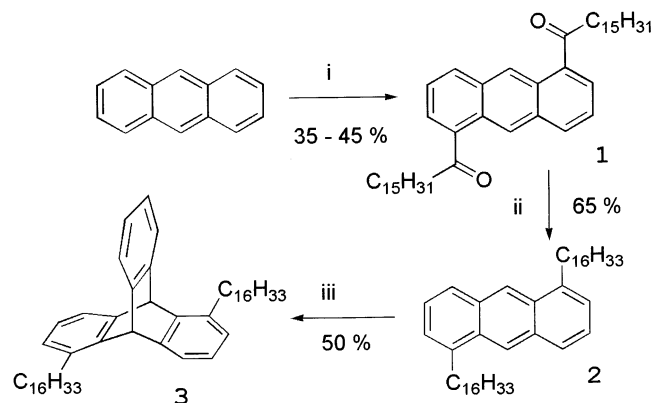
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Abstract—The syntheses of three C_2 symmetric triptycenes containing two pendant groups are described. The pendant groups are designed to promote oriented adsorption to graphite or gold electrodes such that the unfunctionalized aryl group extends perpendicular to the surface. Initial STM studies are consistent with oriented adsorption on graphite.
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Self-assembled monolayers (SAMs) are of considerable interest for tailoring the mechanical,¹ biological² and electronic properties³ of solid surfaces. SAMs are also used frequently in molecular electronics investigations.⁴ SAMs provide some control of molecular orientation at flat surfaces. Adsorbate–surface and adsorbate–adsorbate interactions determine adsorbate orientation and monolayer morphology.⁵ Molecules that spontaneously orient on surfaces in the absence of adsorbate–adsorbate contacts are of potential use in surface sensor and molecular electronics applications. Tripodal⁶ molecules constitute one class of self-orienting adsorbates. We are investigating the ability of C_2 symmetric triptycene derivatives⁷ to spontaneously orient on noble metal and graphite surfaces. A single adsorption orientation may be realized using a C_2 symmetric triptycene with a ‘surface adsorbing element’ (SAE) on two of the molecule’s three aromatic rings. Simultaneous interaction of the two SAEs with the surface should bring their attached aryl rings into contact with the surface and extend the third aryl ring (the ‘upspoke’) roughly perpendicular to the surface. Extensive homo-conjugation among the three aryl rings should engender large electronic coupling between the upspoke and the underlying surface.⁸ Ultimately, elaboration of the upspoke will provide electronic function to these self-orienting molecules.

Racemic mixtures of triptycenes with C_2 symmetry may be prepared by Diels–Alder reactions of benzynes with C_{2h} symmetric anthracene derivatives.⁹ A 1,5-substitution pattern for the triptycene SAEs (rather than 2,6-) was chosen to avoid impeding electronic overlap of the two aryl π systems with surface electronic states. Two facile routes to 1,5-disubstituted anthracenes are nucleophilic aromatic substitution reactions of 1,5-dichloroanthraquinone¹⁰ and Friedel–Crafts bis-acylations of anthracene.¹¹ The latter route was employed for these syntheses.

van der Waals interactions between long alkyl chains of adjacent adsorbates provide significant driving force for SAM formation on highly oriented pyrolytic graphite (HOPG).¹² In a 1,5-bis-alkyl-triptycene, chain–chain and chain–HOPG interactions should promote the



Scheme 1. Reagents and conditions: (i) $C_{15}H_{31}COCl$, $AlCl_3$, rt; (ii) $AlCl_3$, $LiAlH_4$, THF, reflux; (iii) anthranilic acid, i - $C_5H_{11}ONO$, reflux.

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desired adsorption orientation for each molecule in the monolayer. Consequently, *n*-hexadecyl chains were selected as the surface adsorbing elements for triptycene studies on graphite electrodes. Friedel–Crafts acylation of anthracene with palmitoyl chloride yielded an approximately 1:1 mixture of 1,5- and 1,8-bis-palmitoyl-anthracene (Scheme 1).¹¹ Recrystallization and chromatography provided 35–45% yields of the 1,5-isomer **1**. Reduction with lithium aluminum hydride in the presence of AlCl_3 produced 1,5-bis-hexadecyl-anthracene (**2**).¹³ Diels–Alder reaction with benzyne, formed in situ by diazotization of anthranilic acid,⁹ generated a racemic mixture of the desired 1,5-bis-hexadecyl-triptycene (**3**).

STM images of SAMs formed from **3** exhibit a series of nearly structureless, parallel ridges separated by 2 nm (Fig. 1). The length and width of **3** (projection onto the page of Scheme 1) are comparable to that of **2**. SAMs formed from **2** on HOPG display alternating lamellae containing ordered alkyl chains or anthracenes, with a 2 nm spatial repeat between the anthracene lamellae. Provided comparable alkyl chain interactions drive SAM formation for both molecules, the monolayer formed from **3** will also exhibit a 2 nm spatial repeat and the triangular ridges in Figure 1 are due to the triptycene groups. The poor spatial resolution in the figure likely results from the inability of the STM tip to resolve the highly corrugated monolayer. In addition, tip-surface tunneling may be mediated by the upspokes even when the tip lies directly above the alkyl chain regions.

Isolated molecules of **3** on HOPG (i.e. at sub-monolayer coverages) will not experience intermolecular chain–chain van der Waals interactions. The interaction between the alkyl chains of a single molecule and HOPG may be insufficient to ensure adsorption in the desired orientation. A stronger, more directing molecule–surface interaction is required to achieve oriented adsorption at sub-monolayer coverages. Thiols form strong bonds to gold and other noble metal surfaces. Incorporating thiols at the SAE terminus should enhance the propensity for oriented adsorption

of an individual triptycene molecule, provided the SAEs are not too long. The 2'-thioethyl group was chosen as the initial SAE target to provide a limited amount of orientational flexibility upon adsorption.

Friedel–Crafts acylation of anthracene using acetyl chloride/ AlCl_3 in CH_2Cl_2 followed by chromatography afforded 1,5-bis-acetyl-anthracene (Scheme 2). Diels–Alder reaction with benzyne produced 1,5-bis-acetyl-triptycene (**4**) in 50–60% yield along with 30–40% of unreacted anthracene. Diels–Alder reaction of 1,5-bis-acetyl-anthracene with 2,3-dehydronaphthalene gave 1,15-bis-acetyl-benzotriptycene (**5**) in 40–45% yield. 2,3-Dehydronaphthalene was formed in situ from 3-amino-2-naphthalene carboxylic acid^{14,15} and *iso*-amyl nitrite in dimethoxyethane. Thallium nitrate adsorbed to K-10 montmorillonite clay¹⁶ effected oxidative rearrangement of the acetyl groups to methyl esters. Conversion of **4** to **6** was nearly quantitative whereas the rearrangement of **5** to **7** afforded a 50% yield and formation of a single unidentified side product.

The rearranged esters were reduced to alcohols, activated as mesylates and reacted with potassium thioacetate to generate the bis-acetyl thioesters of the C_2 symmetric triptycene dithiols, **8** and **9** (Scheme 3).¹⁷

The thioacetyl groups in **8** and **9** can be hydrolyzed¹⁸ to thiols in conjunction with dosing of a gold surface and collection of scanning tunneling microscope (STM) images. STM studies to evaluate the self-orientation proclivities of **3**, **8** and **9** at monolayer and sub-monolayer coverages are currently in progress.

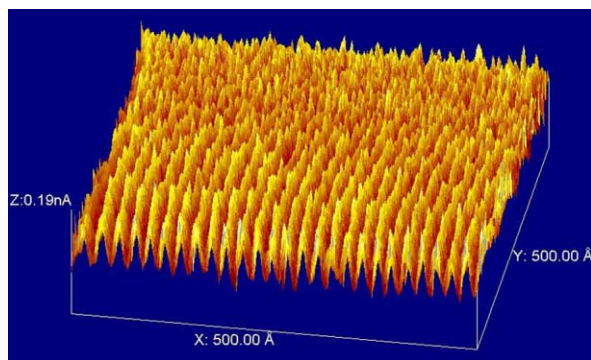
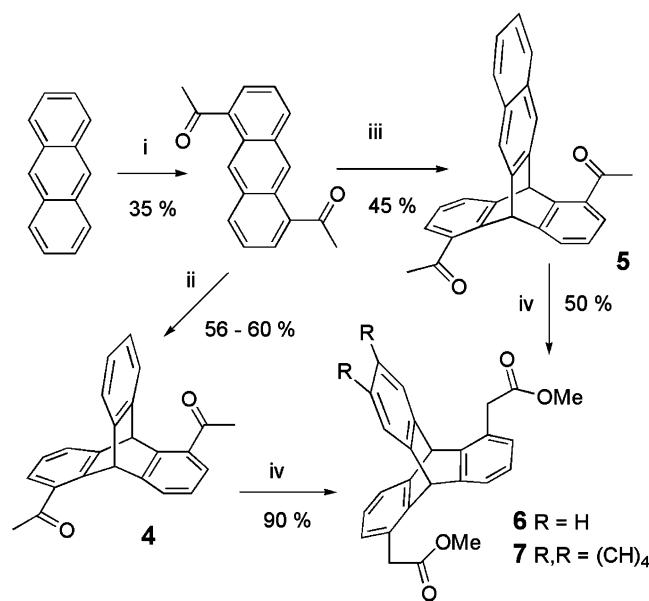
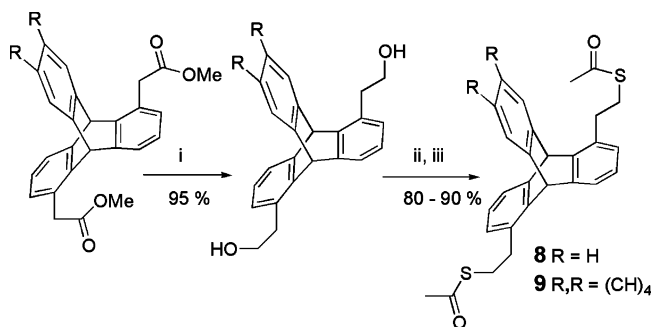


Figure 1. STM image (current mode, 0.5 V, 600 pA) of a SAM formed from triptycene **3** on HOPG.



Scheme 2. Reagents and conditions: (i) CH_3COCl , AlCl_3 , rt; (ii) anthranilic acid, *i*- $\text{C}_5\text{H}_{11}\text{ONO}$, reflux; (iii) 3-amino-2-naphthalenecarboxylic acid, *i*- $\text{C}_5\text{H}_{11}\text{ONO}$, reflux; (iv) $\text{Ti}(\text{NO}_3)_3/\text{K-10}$, CH_2Cl_2 , rt, 6 days.



Scheme 3. Reagents and conditions: (i) LiAlH_4 , 0°C ; (ii) $(\text{MeSO}_2)_2\text{O}$, pyridine, 2 h; (iii) KSC(O)CH_3 , acetone, 4 days.

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- A SmithCreator microwave reactor from Personal Chemistry was used in place of an autoclave to prepare 3-amino-2-naphthalene carboxylic acid from 3-hydroxy-2-naphthalene carboxylic acid. A 5 mL Smith reaction vial containing concentrated NH_4OH was slowly charged with ZnCl_2 and 3-hydroxy-2-naphthalenecarboxylic acid. After sealing, the tube was heated to 140°C for 120 s. This dissolves all material and prevents excessive pressure build up in the next step. The tube contents were heated to 210°C for 16 h and worked up as in Ref. 14.
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- Spectral data of selected new triptycene compounds are provided (^1H and ^{13}C NMR were recorded in CDCl_3 at 300 and 75 MHz, respectively, in δ ppm). Compound 3: ^1H NMR: 7.37–7.34 (m, 2H), 7.21 (d, 2H, $J=7.3$ Hz), 6.99–6.96 (m, 2H), 6.88 (t, 2H, $J=7.5$ Hz), 6.80 (d, 2H, $J=7.4$ Hz), 5.62 (s, 2H), 2.80 (t, 4H, $J=7.8$ Hz), 1.61 (m, 4H), 1.26 (m, 52 H), 0.88 (t, 6H, $J=6.6$ Hz); ^{13}C NMR: 145.6, 145.1, 143.5, 136.9, 126.0, 125.0, 124.6, 123.5, 121.5, 50.5, 33.0, 31.9, 31.8, 29.7 (m), 29.4, 22.7, 14.1. Compound 8: ^1H NMR: 7.52–7.49 (m, 2H), 7.41 (dd, 2H, $J=7.4$ Hz, $J=1.0$ Hz), 7.02–6.99 (m, 2H), 6.93 (t, 2H, $J=7.5$ Hz), 6.83 (dd, 2H, $J=7.4$ Hz, 1.0 Hz), 5.99 (s, 2H), 3.11–2.98 (m, 8H), 2.44 (s, 6H); ^{13}C NMR: 196.2, 145.7, 145.4, 144.1, 134.1, 126.0, 125.2, 125.1, 123.8, 122.7, 50.0, 33.9, 30.8, 30.4. Compound 9: ^1H NMR: 7.90 (s, 2H), 7.73–7.70 (m, 2H), 7.46 (dd, 2H, $J=7.2$ Hz, 1.0 Hz), 7.37–7.34 (m, 2H), 6.96 (t, 2H, $J=7.4$ Hz), 6.87 (dd, 2H, $J=7.5$ Hz, 1.0 Hz), 3.13–3.03 (m, 8H), 2.47 (s, 6H); ^{13}C NMR: 196.3, 145.0, 143.4, 142.1, 134.2, 131.8, 127.5, 126.4, 125.6, 125.5, 122.8, 121.8, 49.7, 34.0, 30.9, 30.5.
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