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### Discotic Liquid Crystals as Self Assembled Monolayers

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## DISCOTIC LIQUID CRYSTALS AS SELF ASSEMBLED MONOLAYERS

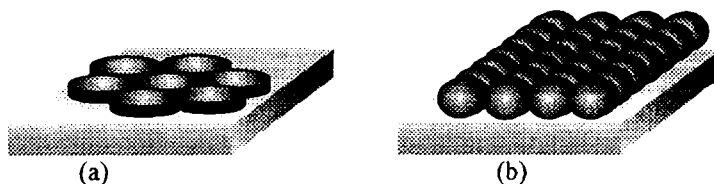
H. ALLINSON, N. BODEN, R.J. BUSHBY, S.D. EVANS and P.S. MARTIN  
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**Abstract** A derivative of a triphenylene based discotic liquid crystal incorporating an ethyleneoxy-thiol side chain was bound to an “ultra-clean” gold surface to form a self-assembled monolayer (SAM). Initial characterisation indicates that the molecules on the surface are oriented in an “edge on” manner.

### INTRODUCTION

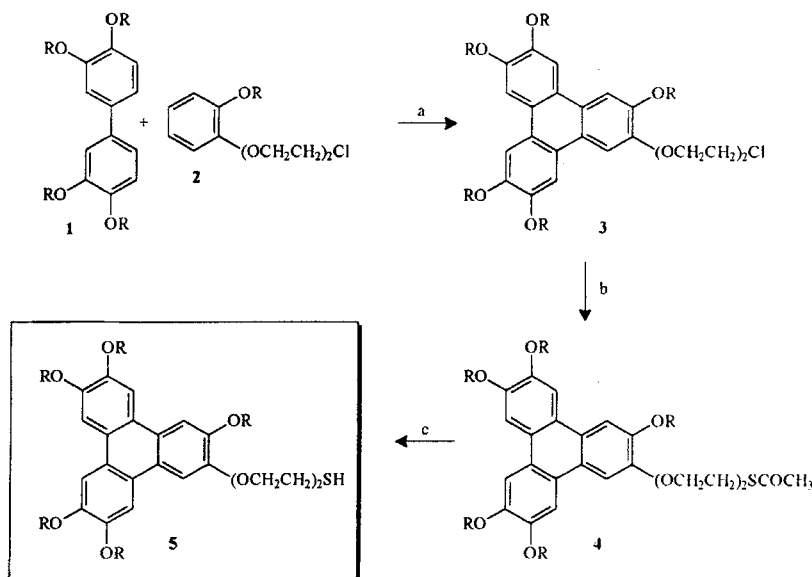
Self assembled monolayers (SAMs) can be viewed as the successors to Langmuir-Blodgett films, but they possess fewer surface defects and are covalently bound to the interface. These systems have found application in molecular switches<sup>1</sup> and photoresist devices.<sup>2</sup> Preferred linkages for SAMs are either of the silicon-oxygen or sulphur-gold type. Recently alkyl-thiol SAMs have been used to orient calamitic liquid crystals, by varying the hydro-philic/phobic nature of the terminal groupings.<sup>3</sup>

Attention has now turned to exploiting SAM technology for aligning discotic liquid crystals, with the director oriented parallel to the organic-support interface. To this end an attempt was made to form a SAM that mirrored this alignment at the surface.



**Figure 1** Schematic representation of discoidal self assembling monolayers, with the director (a) perpendicular and (b) parallel to the surface.

In this paper we describe the synthesis of a thiol functionalised triphenylene and subsequent characterisation of the formation of a self assembled monolayer.



**Scheme 1** Synthetic route to ethyleneoxythiol substituted triphenylene **5**, R=hexyl, (a) (i) FeCl<sub>3</sub>/(ii) MeOH/34%, (b) NaSCOCH<sub>3</sub>/EtOH/67%, (c) NaOH/THF/H<sub>2</sub>O/98%.

## DISCUSSION

A synthetic route for the production of the triphenylene thiol **5** is outlined in Scheme 1.

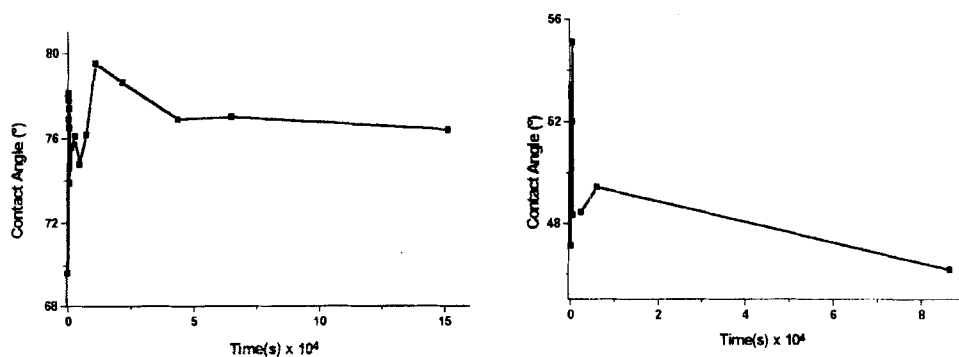
The initial step involved the oxidative coupling of 3,3',4,4'-tetrahexyloxybiphenyl **1** with the chloroethyleneoxy derivative **2** using ferric chloride<sup>4,5,6</sup> to produce the chloro precursor **3**. This was converted in high yield to the protected thiol derivative **4** by a simple S<sub>N</sub>2 reaction, and deprotected to give the free thiol **5** using mild base.

The SAM was formed by inserting a clean glass slide coated in 1000Å of gold into a

1 mM solution of the compound **5** in dichloromethane. After measured periods of time the slide was removed from solution, washed with dichloromethane and contact angle and fixed angle ellipsometric measurements were made.

## RESULTS

Initially, large fluctuations were observed in both contact angle (figure 2) and ellipsometric measurements (figure 3) indicating, a high degree of disorder within the SAM.



**Figure 2** Plot of (a) advancing and (b) receding contact angle for water as a function of time showing formation of the discotic SAM of compound **5** on a gold surface. The lines are included as an aid to the eye.

The steady behaviour observed after ~3h indicates that the surface is slightly less hydrophobic than for a normal alkyl-terminated SAM.

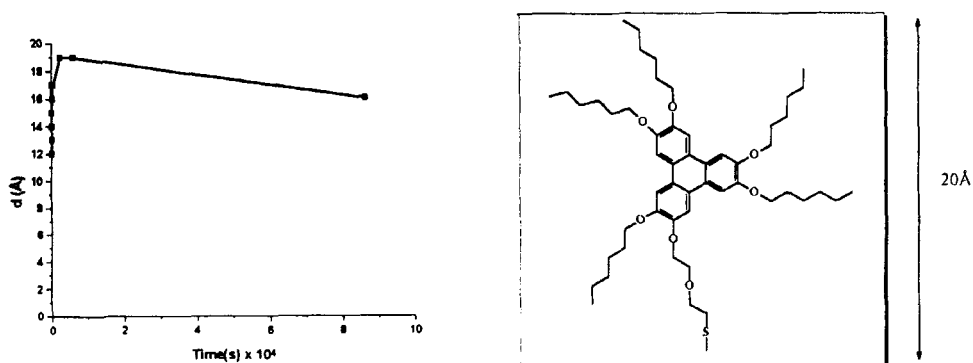


Figure 3 Thickness measurements for the formation of a Discotic SAM (Compound 5)

The ellipsometry results (figure 3) indicate that a monolayer is forming with an average thickness of 16-19 Å, which is slightly less than the diameter of the molecule (~20 Å).

### CONCLUSIONS

Preliminary investigations are consistent with the formation of a SAM from the mono-thiol functionalised discoidal molecule **5**, in which the molecules are arranged "edge-on" to the surface, however further detailed investigation is planned to confirm these findings.

### EXPERIMENTAL

#### 2-(2-(2-Chloroethoxy)ethoxy)-3,6,7,10,11-pentahexyloxytriphenylene

Anhydrous iron(III) chloride (2.60g) was added to a stirred mixture of 3,3',4,4'-tetrahexyloxybiphenyl (2.31g; 0.0042mol) and 2-(2-(2-chloroethoxy)ethoxy)-1-hexyloxybenzene (1.3g; 0.0043mol) in dichloromethane (50ml). The mixture was stirred

for 2h and poured carefully onto methanol (200ml). The resultant precipitate was filtered off and purified by column chromatography[silica, light petroleum-dichloromethane (1:1)] and recrystallised from ethanol to give 2-(2-(2-chloroethoxy)ethoxy)-3,6,7,10,11-pentahexyloxytriphenylene (1.2g, 34%) as a white solid. Micro. Anal., theoretical(C 73.4%; H 9.29%), observed(C 73.5%; H 9.49%)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.93(s, 1H, ArH), 7.84(s, 5H, ArH), 4.41(t, 2H,  $J=4.5\text{Hz}$ ,  $\text{ArOCH}_2$ ) 4.25(t, 10H,  $J=7\text{Hz}$ ,  $\text{ArOCH}_2$ ), 4.01 (t, 2H,  $J=4.5\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2$ ), 3.91(t, 2H,  $J=7\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2$ ), 3.71(t, 2H,  $J=7\text{Hz}$ ,  $\text{CH}_2\text{Cl}$ ), 1.81 (m, 2H,  $J=7\text{Hz}$ ,  $\text{OCH}_2\text{CH}_2\text{R}$ ), 1.33-1.49 (m, 6H,  $\text{CH}_2$ ), 0.97 (t, 3H,  $J=7\text{Hz}$ ,  $\text{CH}_3$ ).

2-(2-(2-Acetylthioethoxy)ethoxy)-3,6,7,10,11-pentahexyloxytriphenylene

Thioacetic acid (54mg) was added to a mixture of ethanol(50ml) and sodium ethoxide(48mg), and stirred for 1h. 2-(2-(2-Chloroethoxy)ethoxy)-3,6,7,10,11-pentahexyloxytriphenylene(0.5g; 0.0006mol) was added and the solution refluxed for 24h. The cooled mixture was poured carefully on to hydrochloric acid (50ml), extracted with dichloromethane, the solvent evaporated and the product purified by column chromatography [silica, dichloromethane] to give 2-(2-(2-acetylthioethoxy)ethoxy)-3,6,7,10,11-pentahexyloxytriphenylene (360mg, 67%) as a white solid. K(60.4)D(74.7)I. Micro. Anal., theoretical(C 72.8%; H 9.21%), observed(C 72.9%, H 9.3%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.93(s, 1H, ArH), 7.84(s, 5H, ArH), 4.39(t, 2H,  $J=4.5\text{Hz}$ ,  $\text{ArOCH}_2$ ) 4.25(t, 10H,  $J=7\text{Hz}$ ,  $\text{ArOCH}_2$ ), 3.96(t, 2H,  $J=4.5\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2$ ), 3.78(t, 2H,  $J=7\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2$ ), 3.28(t, 2H,  $J=7\text{Hz}$ ,  $\text{CH}_2\text{SCOCH}_3$ ), 2.32(s, 3H,  $\text{SCOCH}_3$ ), 1.81 (m, 2H,  $J=7\text{Hz}$ ,  $\text{OCH}_2\text{CH}_2$ ), 1.33-1.49 (m, 6H,  $\text{CH}_2$ ), 0.97 (t, 3H,  $J=7\text{Hz}$ ,  $\text{CH}_3$ ).

2-(2-(2-Thioethoxy)ethoxy)-3,6,7,10,11-pentahexyloxytriphenylene

Sodium hydroxide (1 pellet) was added to a vigorously stirred solution of 2-(2-(2-acetylthioethoxy)ethoxy)-3,6,7,10,11-pentahexyloxytriphenylene (330mg, 0.00037mol) in THF(50ml) and water(10ml) under a nitrogen atmosphere. The mixture was stirred for 24h, poured onto ammonium chloride(50ml) and extracted with chloroform. The solvent was evaporated under vacuum at room temperature, and the product purified by column chromatography [silica, dichloromethane] and reprecipitated from chloroform/methanol to give 2-(2-(2-thioethoxy)ethoxy)-3,6,7,10,11-pentahexyloxytriphenylene(310mg, 98%), K(75)D(90.4)I. Micro. Anal., theoretical(C 73.5%; H 9.49%), observed(C 73.4%; H 9.2%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.93(s, 1H, ArH), 7.84(s, 5H, ArH), 4.39(t, 2H,  $J=4.5\text{Hz}$ ,  $\text{ArOCH}_2$ ), 4.25(t, 10H,  $J=7\text{Hz}$ ,  $\text{ArOCH}_2$ ), 3.96(t, 2H,  $J=4.5\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2$ ), 3.78(t, 2H,  $J=7\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2$ ), 3.28(t, 2H,  $J=7\text{Hz}$ ,  $\text{CH}_2\text{SCOCH}_3$ ), 1.81 (m, 2H,  $J=7\text{Hz}$ ,  $\text{OCH}_2\text{CH}_2$ ), 1.33-1.49 (m, 6H,  $\text{CH}_2$ ), 0.97 (t, 3H,  $J=7\text{Hz}$ ,  $\text{CH}_3$ ).

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