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COMMUNICATION

Molecular building blocks: chromophoric amphiphilic cyclodextrin derivatives

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The cyclodextrins, cyclic oligosaccharides, having two polar hydroxyl faces surrounding a somewhat hydrophobic cavity, have been used for the inclusion and transport of a wide variety of organic molecules.[3] Their low price and easy availability makes them attractive as '*off the shelf*' systems for the preparation of molecular assemblies.[4] The selective modification of one face is, now, relatively simple and in consequence a wide range of amphiphilic CD derivatives are available as molecular building blocks.[5–9] The use of such systems in 'molecular engineering' has involved inclusion of chromophores at the air-water interface.[10,11] Whilst successful, this method does not permit the introduction of large amounts of the chromophore into the layer and more importantly the geometry of the active material is non-variable.* In this communication we wish to describe the selective modification of the primary hydroxyl face of β-CD with *ortho-* (2), *meta-* (3), and *para-* (4) nitro-thiophenol groups, and the formation of monomolecular layers by these systems. The compression isotherms are modulated by the substituent stereochemistry, as, in consequence, must be the organisation at the interface.

The synthesis of 2, 3, and 4 is straightforward, given that heptakis-6-bromo-6-deoxy-β-CD (1) is readily available as a pure compound in multigram quantities,[8] and is given in Fig 1.

1 was reacted with 1.5 equivalents of the corresponding nitro-thiophenol, (prepared from the commercially available disulfides via reduction, with glucose in ethanol in the presence of NaOH,[12]) in dimethylformamide at room temperature for 12 h in the presence of triethylamine. The reaction was carefully followed by t.l.c., when the yield of the heptakis product was maximal the solvent was removed, and the product washed with methanol, acetone and water to give **2**, **3** and **4** in essentially quantitative yields, as yellow crystalline solids.

The UV-VIS spectra, in water, show maxima at 195 and 247 nm, **2**; 194 and 262 nm, **3**; and 190, 240 and 350 nm, **4**. In all cases there is apparent formation of molecular aggregates. Full NMR characterisation has been obtained via use of COSY and ^{1}H-^{13}C correlation spectra. In all cases H6 and H6′ are shifted upfield by *ca* 0.2 ppm as a result of the thio-phenol substitution.

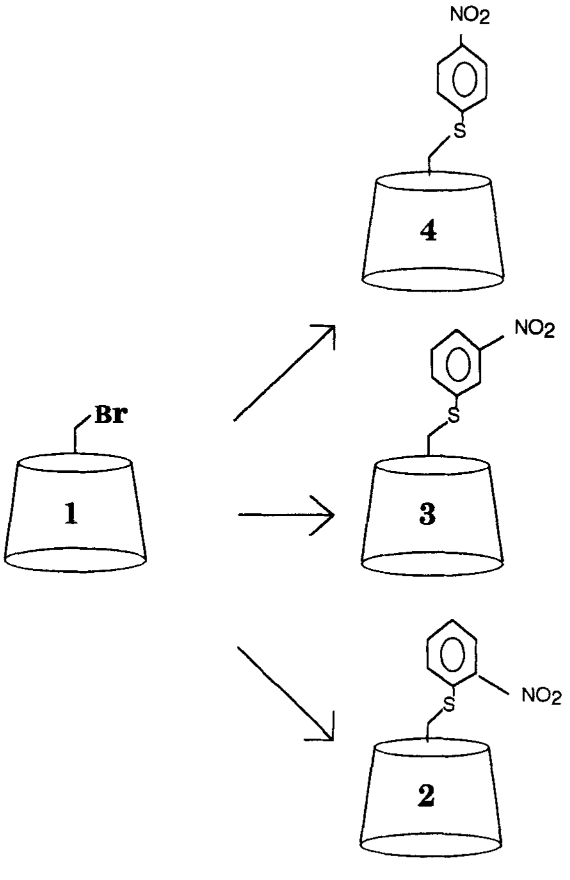

Figure 1 Synthetic route to amphiphilic cyclodextrins substituted with nitro-thiophenolate groups.

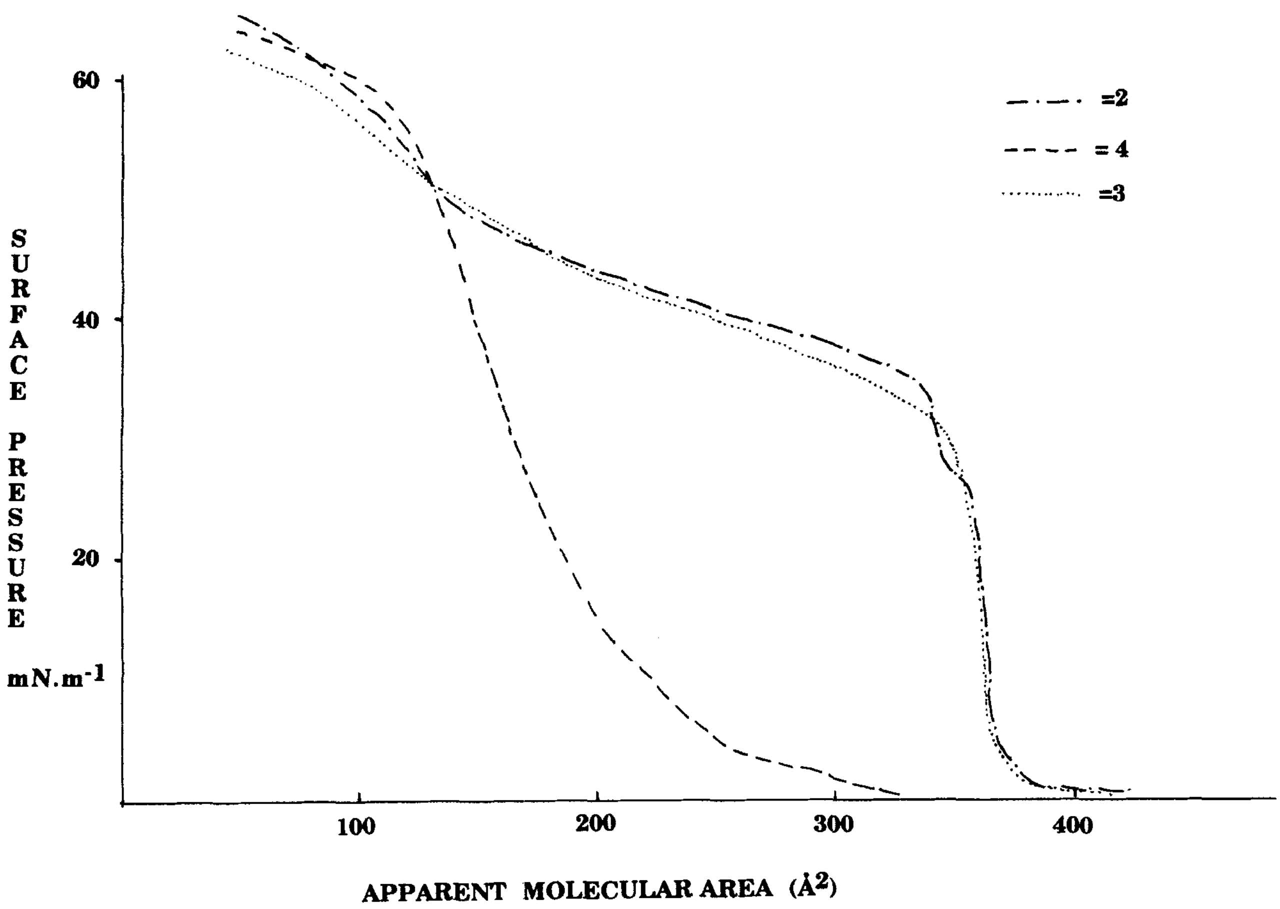

Figure 1 Synthetic route to amphiphilic cyclodextrins substituted with nitro-thiophenolate groups.

As expected, **2**, **3**, and **4** form stable monolayers at the air-water interface. The Langmuir compression isotherms are given in Fig 2. The isotherms for **2** and **3** differ radically from that observed for **4**. Apparent A_0 values[13] are 362 Å^2, 364 Å^2, and 325 Å^2, respectively.[13] A_0 values correspond to the largest observed molecular area.

Inspection of the isotherm for **4** allows via extrapolation of the steepest descent in the isotherm proposition of an apparent molecular area (A) of *ca.* 230 Å^2. In **4** the nitro group is in the para-position and is, therefore, sterically non-demanding. The second A value is close to that area observed for the β-CD moiety in the crystal structure of **1**, 225 Å^2.[13] The compression isotherm of **4** may be interpreted as a fluid (low energy) folding of the para-nitrothiophenol groups into a perpendicular geometry in the region 320–230 Å^2. There exists a collapse at a pressure of 60 mNm^{-1} and an apparent area of 120 Å^2 which may correspond to a molecular bilayer.

For compounds **2** and **3** the observed isotherms resemble each other strongly. The observed A_0 value of 360 Å^2 gives a molecular diameter of 19 Å, implying that each nitro group contributes *ca.* 2 Å, fitting closely with the value expected from bond lengths. The steep rise in the compression isotherm is evidence for a highly rigid assembly at the interface, suggesting that the nitro groups are strongly sterically demanding and block rearrangement of the phenyl groups. For **2** there is a small but reproducible rearrangement observed at a pressure of 28 mN^{-1}. Collapse of the monolayer occurs at 37 mNM^{-1} for **2** and 35 mNm^{-1} for **3**. For **2** the inflection in the isotherm suggests stabilisation at an area of 120 Å^2. That this corresponds to the A/2 for the parent β-CD system implies that here the nitro groups are sterically non-demanding.

From the above it is evident that we have been able to construct a series of molecular building blocks in which a rigid alignment of chromophoric groups may be obtained at the air-water interface. The combination of these systems with other amphiphilic molecules may allow the construction of molecular devices containing multiple functions.

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