

## Monitoring conformational diversity in self-organised monolayers with scanning tunnelling microscopy at near atomic resolution

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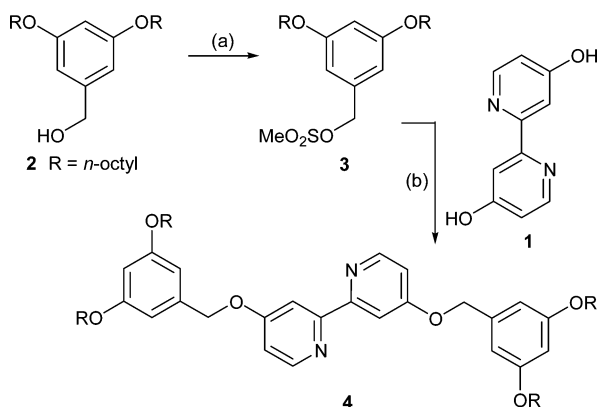
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The evaporation of solutions of dendron-functionalised 2,2'-bipyridines on a graphite surface gives highly ordered monolayers; near atomic resolution STM imaging has allowed a detailed conformational analysis to be made.

The direct imaging of chemical species at molecular and sub-molecular levels using tunnelling and force microscopy has revolutionised the visualisation and control of nanostructures.<sup>1</sup> It is now possible to probe self-assembled structures using scanning tunnelling microscopy (STM),<sup>2</sup> and interest in nano-assemblies has grown.<sup>3</sup> Although static and dynamic systems have been investigated, there is scope for addressing structural questions. Conventional 3D-methods (single-crystal X-ray crystallography or NMR spectroscopy) of determining molecular conformation give structures averaged over some 10<sup>15</sup> molecules. Analysis of the surface molecular conformation of 2D-arrays averaged over hundreds of molecules can be performed by analysing submolecular resolved STM images. Here, we report a system that exhibits multiple conformations on a graphite surface. We have chosen a bipy-based ligand because the coordination chemistry of such ligands is well understood,<sup>4</sup> and the coordination to a metal centre results in a loss of conformational freedom, locking the ligand in a *cis* conformation. This contrasts with a time-averaged *trans* conformation in the free ligand.<sup>5,6</sup>

Aromatic-rich Fréchet-type dendrimers<sup>7</sup> are ideally suited to visualisation by tunnelling methods.<sup>8</sup> In addition, these dendrimers provide a significant mechanical barrier to rotation about the bipy interannular C–C bond when the conjugate is in a conformationally restricted environment, e.g. a lattice or on a surface. In this paper, we discuss the consequences of forming monolayers of such conjugate structures on surfaces and show that not only the global minimum, but a range of conformations, can be found in surface-bound domains.

Compound **4** was synthesised by the reaction of **1**<sup>9</sup> with an electrophilic dendritic wedge (Scheme 1). The first-generation mesylate wedge **3**<sup>10</sup> was prepared from benzylic alcohol **2**.<sup>7,11</sup> This



**Scheme 1** Reagents and conditions: (a) methanesulfonyl chloride, NEt<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, –15 °C, 1 h; (b) <sup>n</sup>Bu<sub>4</sub>NI, EtOAc/H<sub>2</sub>O, 60 °C, 16 h.

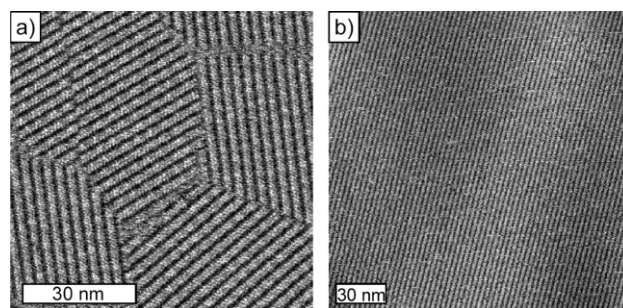
dendritic wedge was coupled with **1** under phase-transfer conditions to give **4** in 74% yield.<sup>†</sup> A related ligand with a spacer between the bipy unit and the wedge has been reported by Vögtle.<sup>12</sup>

Compound **4** contains two peripheral first-generation dendritic wedges. One drop of a 0.2 mM CH<sub>2</sub>Cl<sub>2</sub> or hexane solution of **4** was allowed to evaporate on a freshly cleaved highly-oriented pyrolytic graphite (HOPG) surface. The formation of monolayers was immediately detected (Fig. 1) by low-current STM measurements<sup>‡</sup> under ambient conditions. The results were fully reproducible.

When measured with a negative bias voltage, the HOMOs of the molecule are visualised in the STM image.<sup>13</sup> Semi-empirical calculations at the PM3 level<sup>§</sup> confirmed the expected ordering of orbitals with a cluster of filled orbitals of the benzyl substituents close to the HOMO–LUMO gap, and filled bipy orbitals lying at lower energy. The images were obtained at submolecular resolution showing the extension of the HOMO over the oxygen atoms of the octyloxy chains, allowing us to interpret them in terms of molecular structure. Conformational analysis was made by measuring the distances between the two peripheral benzyl groups which appeared on the STM image as regions of highest intensity.

Multiple domains were observed in the monolayers; those from hexane were typically larger than those from CH<sub>2</sub>Cl<sub>2</sub> (Fig. 1), consistent with a slower rate of evaporation of hexane ( $\Delta H_{\text{vap}}^{\circ} = 31.56 \text{ kJ mol}^{-1}$ ) than of CH<sub>2</sub>Cl<sub>2</sub> ( $\Delta H_{\text{vap}}^{\circ} = 28.82 \text{ kJ mol}^{-1}$ ). We normally observed two sets of three domains, with an angular relationship between the sets of 6.5°. Within each set, three domains reflect the 3-fold symmetry of the graphite surface.<sup>14</sup> The two sets of domains arise from different conformations of **4**. In most images, domains corresponding to two conformers were observed. Although previously documented,<sup>15</sup> this is unusual because one would expect only the lowest energy conformer to be present in a thermodynamically stable self-assembled monolayer (Scheme 2). The domains were very stable; no blebbing or migration was observed in response to the STM tip.

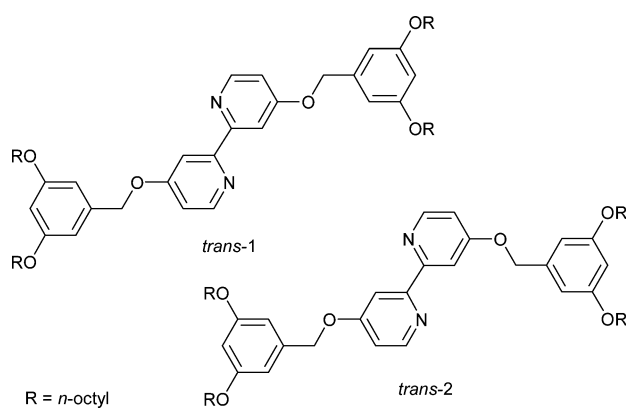
Compound **4** possesses many degrees of conformational freedom (*cis*–*trans* at bipy; *syn*–*anti* at ArOCH<sub>2</sub>Ar). We assumed (and subsequently confirmed) that the bipy-unit would always adopt the



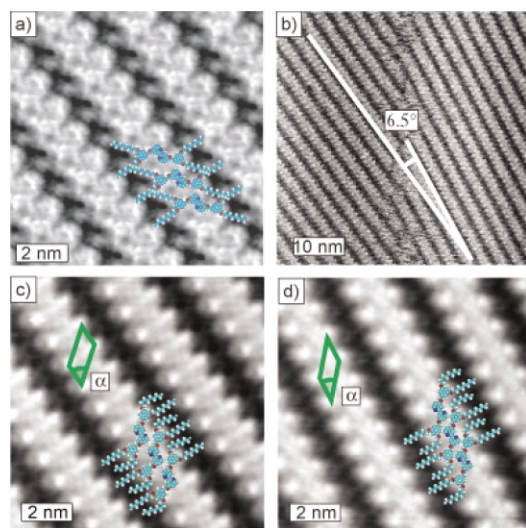
**Fig. 1** STM image of a monolayer formed from (a) CH<sub>2</sub>Cl<sub>2</sub> ( $U_t = -700 \text{ mV}$ ,  $I_t = 0.8 \text{ pA}$ ), and (b) hexane ( $U_t = -700 \text{ mV}$ ,  $I_t = 1 \text{ pA}$ ). Left: different small domains are seen. Right: the image shows part of a domain extending over  $>500 \text{ nm} \times 500 \text{ nm}$ .

lowest energy *trans*-conformation.<sup>16</sup> As the octyl chains are not expected to be imaged at high resolution, we limit the discussion to the *syn*- or *anti*-conformation between bipy and the wedge. Co-planar bipy and benzyl groups were assumed based on  $\pi$ -stacking interactions with the graphite and the known conformation of structurally characterised Fréchet dendrimers. In the two domains in Fig. 2(b), the difference in conformation can be shown by comparing the relative positions of the benzyl groups of two neighbouring molecules. Manual fitting of all possible conformers constrained to co-planar arrangements of the aromatic groups gave unique fits of the conformations to the STM images [Fig. 2(c) and 2(d)]. Conformer *trans*-2 (Scheme 2) occurred in two different packing arrangements [Fig. 2(a) and 2(c)]. These packing arrangements differ in the orientation of the molecules with respect to the surface, and in the inter- and intra-lamellar spacings. The 2D packing densities are similar for both arrangements.

We have shown that deposition of a dendritic wedge-functionalised ligand on HOPG results in the formation of well-defined monolayers exhibiting different conformations of the molecule.



**Scheme 2** The two conformations of **4** observed in the STM study.



**Fig. 2** (a) STM image of a monolayer from hexane (10 nm  $\times$  10 nm,  $U_t = -900$  mV,  $I_t = 4$  pA). The benzyl groups have the highest intensity. (b) STM images of two domains; the angle between them is 6.5° (50 nm  $\times$  50 nm,  $U_t = -1111$  mV,  $I_t = 1.5$  pA). (c) and (d) Expanded images (10 nm  $\times$  10 nm) of the left and right domains, respectively, of (b). Angle  $\alpha$  in (c) and (d) is 55 and 38°, respectively. Overlaying the molecular structures confirms that (c) corresponds to conformation *trans*-2 and (d) to *trans*-1. Images (a), (c) and (d) were averaged. ‡

The near atomic resolution allows us to assign two conformers which spontaneously and rapidly form molecular domains under ambient conditions. Within a molecular domain, only one conformer is present and domains of different conformers are observed side by side. No preference for one conformer was observed. We aim to attach higher-generation dendrons to bipy and investigate self-assembly properties.

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## Notes and references

† MeSO<sub>2</sub>Cl (1.04 mL, 13.5 mmol) was added over 15 min at  $-15$  °C to **2** (1.23 g, 3.38 mmol) and NEt<sub>3</sub> (2.08 mL, 16.9 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL). After 1 h, the mixture was poured into crushed ice/conc. HCl (10 mL). The CH<sub>2</sub>Cl<sub>2</sub> layer was separated, washed with saturated NaHCO<sub>3</sub> solution, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to give **3** (1.80 g, 3.20 mmol) as an oil. Crude **3** (41.5 mg, ca. 75.0  $\mu$ mol), **1** (6.90 mg, 35.0  $\mu$ mol), K<sub>2</sub>CO<sub>3</sub> (50.0 mg, 362  $\mu$ mol) and <sup>63</sup>Ni (2 mg) were stirred in EtOAc (400  $\mu$ L) and H<sub>2</sub>O (400  $\mu$ L) (60 °C, 16 h). Water (20 mL) was added; the mixture was extracted with EtOAc (3  $\times$  20 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and evaporated. Preparative chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>:MeOH 10:1) gave **4** as a white powder (23.1 mg, 74%). For **4**: mp 61 °C;  $\delta_H$  (250 MHz, CDCl<sub>3</sub>): 8.49 [d,  $J = 6.0$  Hz, 2H, H<sup>6(bipy)</sup>], 8.11 [d,  $J = 2.3$  Hz, 2H, H<sup>3(bipy)</sup>], 6.91 [dd,  $J = 5.7, 2.7$  Hz, 2H, H<sup>5(bipy)</sup>], 6.58 [d,  $J = 2.2$  Hz, 4H, H<sup>2(Ar)</sup>], 6.42 [t,  $J = 2.3$  Hz, 2H, H<sup>4(Ar)</sup>], 5.15 [s, 4H, HOCH<sub>2</sub>Ar], 3.94 [t,  $J = 6.6$  Hz, 8H, HOCH<sub>2</sub>CH<sub>2</sub>], 1.80–1.72 [tt,  $J = 6.8, 6.5$  Hz, 8H, HOCH<sub>2</sub>CH<sub>2</sub>], 1.49–1.21 [m, 48H, H<sup>octyl-(CH<sub>2</sub>)s</sup>], 0.92–0.84 [t,  $J = 7.8$  Hz, 12H, H<sup>CH<sub>3</sub></sup>]. MS (ESI+):  $m/z$  903.5 ([M + Na]<sup>+</sup>), 881.6 ([M + H]<sup>+</sup>). Found: C, 76.10; H, 9.80; N, 2.78. C<sub>56</sub>H<sub>84</sub>N<sub>2</sub>O<sub>6</sub> requires: C, 76.32; H, 9.61; N, 3.18%.

‡ Experiments were carried out in constant-current mode using a NanoscopeIII and data were processed with SXM software (©Uni Basel). STM tips were mechanically formed from Pt/Ir (90%:10%) wire. The 10 nm  $\times$  10 nm images were processed by correlation averaging.

§ PM3 implementation, Spartan'04, ©Wavefunction Inc., 2003.

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