Nanotrains and Self-Assembled Two-Dimensional Arrays Built from Carboranes Linked by Hydrogen Bonding of Dipyridones

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ABSTRACT

The strong hydrogen bonding ability of 2-pyridones were exploited to build nanotrains on surfaces. Carborane wheels on axles difunctionalized with 2-pyridone hydrogen bonding units were synthesized and displayed spontaneous formation of linear nanotrains by self-assembly on SiO₂ or mica surfaces. Imaging using atomic force microscopy confirmed linear formations with lengths up to 5 μ m and heights within the range of the molecular height of the carborane-tipped axles.

KEYWORDS

Nanovehicles, nanotrains, 2-pyridone, hydrogen bonding, self-assembly

Introduction

Supramolecular engineering through noncovalent interactions is a promising tool for nanotechnological advances [1–3], such as potential applications in bioactive systems, sensors, field-effect transistors, thermoplastic elastomers, and optoelectronic devices [4–13]. With the use of interactions such as hydrogen bonding, π - π stacking, van der Waals forces, hydrophobic/hydrophilic interactions, and Coulombic interactions, separately or in combinations, impressive structures including helices, cylindrical tubes, grids and cyclic assemblies [14–31] have been realized through specific molecular design. In particular, hydrogen bond interactions are attractive for obtaining well-defined supramolecular structures due to their spatial arrangement, selectivity and directionality [32].

Well-defined hydrogen-bonded structures have been realized through an understanding of biological systems [33]. Multiple binding sites seen in DNA nucleotide-like molecules offer increased binding strength and organization. However, simpler hydrogen bonding molecules should not be overlooked for generating self-assembled structures. Both 2-pyridone and its tautomer, hydroxypyridine, are well-documented for their ability to form hydrogen bonded dimeric structures in both solution and the solid phase [34, 35]. Although simple methods have been proposed to modify the bond strength of these dimers, such as cocrystallization between carboxylic acid units [36], there are few reports of imaging or the use of multiple 2-pyridone moieties to generate more complex assemblies [36–38].

There are two notable difficulties in imaging

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assembled structures of 2-pyridones. Firstly, imaging via scanning tunneling microscopy (STM), requires conductive substrates. The substrate-molecule interactions for 2-pyridones on metallic surfaces or metal atoms are stronger than the hydrogen bonds between 2-pyridone molecules [39–43], although there is one example of 2-pyridone species forming a dimeric 2-D adlayer imaged via STM on a modified, highly oriented pyrolytic graphite (HOPG) [38]. There are also atomically resolved STM images of other hydrogen bonding moieties that self-assemble into unique architectures but the substrate-molecule binding energies are usually lower [44, 45]. Despite the disadvantages of using STM as an imaging technique, its lateral resolution remains unparalleled. The second difficulty is that 2-pyridones form one molecule thin self-assembled structures that are difficult to image with good lateral resolution. To address these difficulties, in the present work, imaging using atomic force microscopy (AFM) allows for the use of a wide range of surfaces including non-conductive ones for imaging the self-assembly of 2-pyridones. The resolution in AFM imaging, however, depends upon both the in-plane (X – Y) and Z -axis effects. The tip effect results in geometrical broadening (the approximate molecular width + $2 \times$ tip diameter) of the molecules [46]. Although there are reports suggesting the use of a single molecule as a tip [47], the sharpest tips currently available are at best 1 nm in radius [48, 49], thus resolution at the atomic or small molecule scale is extremely difficult. Other factors in AFM resolution are shot noise in the cantilever deflection photo detector and thermal vibration noise of the cantilever that occurs in the Z -axis. The combination of the noise effects contributes from ~ 0.2 to 0.7 nm in lost resolution depending on probe type, optical detection technique, and surface roughness [46], and thus resolving a monolayer of planar molecules is very difficult.

Our research in recent years has generated a class of surface-rolling molecules termed nanocars [50–60]. Preferential rolling versus sliding motion was observed on surfaces with the incorporated wheels interacting strongly with the substrate. The wheels, fullerenes (1 nm in diameter) or *p*-carboranes (0.8 nm in diameter) [61], that have been used can potentially serve as height-enhancing units for AFM imaging to enable imaging despite noise and tip effects. As an extension to the nanocar work, the synthesis of Monomer **1** containing 2-pyridones and a resulting self-assembled structure, a nanotrain, imaged by AFM is reported. For control purposes, Monomer **2** without the wheels was also synthesized.

1. Results and discussion

Compound **1** was synthesized using a known procedure [56], starting with the installation of the *p*-carborane wheels with the alkynyl bromide **3**, to give **4** (Scheme 1). This was followed by the deprotection of the triisopropylsilylacetylene (TIPS-acetylene) groups to give **5**. Finally, Pd-catalyzed coupling of the 2-pyridone moieties gave nanotrain Monomer **1** (Fig. 1). Similarly, the dialkynyl benzene precursor **6** [62] was coupled via a simple Sonogashira protocol to obtain control Monomer **2** (Scheme 2). In some cases, the NMR analyses do not give first order spectra. We assume that there is

Figure 1 Target monomer molecules for hydrogen bonded self-assembled structures. Monomer **1** contains *p*-carborane moieties to produce heightened images for AFM analysis. Monomer **2** serves as a control. The carborane has a B–H at each vertex except the darkened positions that have C–H para and C ipso to the alkyne

Scheme 1 Synthesis of Compound 1

¹ Images taken by the AFM were processed using Nanoscope 5.30r1. Nanotrain formation was unaffected when switching the substrate from SiO_2 to mica.

² In an attempt to avoid possible π -stacking interactions, drop-casting was also attempted using benzene and toluene as solvent but no trains were observed, presumably due to the low solubility of the molecules.

some degree of hydrogen bonding and/or tautomerization detected in the NMR analyses, and that causes peak broadening as well as the presence/absence of peaks.

To study the self-assembling nature of these 2-pyridone derivatives, a $10\text{ }\mu\text{mol/L}$ solution of the monomer in tetrahydrofuran (THF) was drop-cast onto a SiO_2 or a freshly cleaved mica surface, vacuum dried (in the case of the samples on SiO_2 ; vacuum drying the mica samples did not produce good results), and observed by AFM¹. Conventional tapping-mode etched silicon probes (TESP) with tip sizes of approximately 25 nm in diameter were used in ambient atmosphere. For superior lateral resolution, high resolution (MikroMasch HI-RES) tips of diameter 1 nm were also used under similar conditions. Without the height-enhancing carborane structures, Monomer 2 showed no recognizable self-assembled structures anywhere on the SiO_2 surface (Fig. 2(a)) whereas Monomer 1 self-assembled into linear structures (Figs. 2(b)–(d)) with lengths as long as $\sim 5\text{ }\mu\text{m}$. Heights were in the range of $0.7\text{--}1.6\text{ nm}$, within the range of the molecular height of carboranes or carboranes with axles [61]. Although imaging of the nanotrain using MikroMasch HI-RES tips on mica surfaces indeed provided sharper images than their conventional counterparts, (Fig. S-1 in the Electronic Supplementary Material (ESM)), the data from Figs. 2 and S-1 are in agreement that intra- or interchain interactions arising from folding, or multiple chains bound side-to-side, are quite possible due to the widths of the observed formations. Unfortunately, in an effort to obtain images of single nanotrains, AFM using the HI-RES tip of samples deposited from toluene or toluene/THF on mica did not produce usable images².

There are three possible combinations of hydrogen bonding patterns through rotation about the alkyne bond linking the 2-pyridone to the rigid core (Fig. 3). In Fig. 3(a), with an assembly of the monomer in the *cis* conformation only, where both of the 2-pyridones are facing the same side, a linear chain is produced. In Fig. 3(b), a linear chain is again produced with all the monomers in the *trans* conformation and the pyridones facing the opposite directions. In Fig. 3(c), the combination of both the *cis* and the *trans* confirmations of 1 linking randomly can result

Scheme 2 Synthesis of Compound 2

Figure 2 (a)–(d) Four AFM images of drop-cast nanotrain 1 and control 2 in THF (1×10^{-5} mol / L) on SiO_2 , scan rate 1.30 Hz, sample resolution 512. (a) 2, $20.0 \mu\text{m} \times 20.0 \mu\text{m}$; (b) 1, $0.90 \mu\text{m} \times 0.90 \mu\text{m}$; (c) 1, $2.5 \mu\text{m} \times 2.5 \mu\text{m}$; (d) 1, $6.5 \mu\text{m} \times 6.5 \mu\text{m}$; (e) typical height profile of the self-assembled nanotrain

in a curved structure. We are not able to resolve the individual moieties responsible for hydrogen bonding, and all three structures could co-exist. In a report of similar hydrogen bonding via bis-pyridone structures linked by alkynes to a rigid core, X-ray crystallography showed a preferential planar polymeric motif based on the *trans* pattern [36].

Figure 3 Nanotrain configurations from Monomer 1. Three possible patterns of 2-pyridone self-assembly: (a) *cis* only, linear assembly; (b) *trans* only, linear diagonal assembly; (c) combination of *cis* and *trans* in random fashion, which can result in curvature

This result is based on a closely packed crystalline structure, whereas the diluted condition on the surface presents a different environment, and thus the exact hydrogen bonding scheme is unknown.

2. Experimental

General methods. All reactions were performed under an atmosphere of nitrogen unless otherwise stated. Reagent grade THF was distilled from sodium

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benzophenone ketyl. Triethylamine (TEA) was distilled over CaH_2 . Flash column chromatography was performed using 230–400 mesh silica gel from EM Science. TLC was performed using glass plates precoated with silica gel 40 F₂₅₄ purchased from EM Science. NMR analysis was done at 500 MHz with shifts reported relative to tetramethylsilane (TMS); s=singlet, d=doublet, m=multiplet, dd=doublet of doublets.

Compound 1 (Fig. 1(a)). To an oven-dried round-bottom flask equipped with a magnetic stirrer bar was added Compound 5 [56] (0.054 g, 0.118 mmol), 2-hydroxy-5-iodopyridine (0.057 g, 0.259 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.003 g, 0.004 mmol), and CuI (0.002 g, 0.011 mmol). THF (30 mL) and TEA (2 mL) were added and the mixture was stirred at rt overnight. Upon completion, the reaction was quenched with a saturated solution of NH_4Cl . The organic layer was diluted with ethyl acetate and was washed with water. The aqueous layers were extracted with ethyl acetate and CH_2Cl_2 (2×). The combined organic layers were dried over MgSO_4 , filtered, and the solvent was removed from the filtrate in vacuo to afford the crude product, which was purified by SiO_2 column chromatography using 10% MeOH in ethyl acetate. Removing the solvent in vacuo afforded a yellow-orange solid **1** (Fig. 1(a)) (0.037 g, 54%). FTIR 3050, 2947, 2860, 2621, 1725, 1654, 1595, 1529, 1437, 1176, 1122, 829 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , ppm) δ 7.61–7.68 (m, 2H), 7.60–7.51 (m, 1H), 7.57 (s, 2H), 7.49–7.42 (m, 2H), 6.42 (d, 1H, J = 10.23 Hz), 4.50–1.00 (m, 22H); ^1H NMR (500 MHz, MeOD ppm) δ 7.67 (dd, 1H, J = 2.55 Hz, J = 9.53 Hz), 7.63–7.56 (m, 4H), 7.54–7.48 (m, 2H), 6.33 (dd, 1H, J = 0.66 Hz, J = 9.53 Hz), 4.50–1.00 (m, 22H); ^{13}C NMR (125 MHz CDCl_3) δ 149.2, 140.1, 132.5, 132.1, 132.0, 132.0, 131.7, 128.6, 128.5, 122.1, 122.1, 103.7, 66.9, 66.1; EI-HRMS m/z calcd for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_2$ 644.79, found 644.78.

Compound 2 (Fig. 1(b)). To an oven-dried round-bottom flask equipped with a magnetic stirrer bar was added Compound 6 [62] (0.080 g, 0.634 mmol), 2-hydroxy-5-iodopyridine (0.308 g, 1.39 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.008 g, 0.011 mmol), and CuI (0.005 g, 0.026 mmol). THF (30 mL) and TEA (5 mL) were added and the mixture was stirred at rt overnight. Upon completion, the reaction was quenched with a

saturated solution of NH_4Cl . The organic layer was then diluted with ethyl acetate and was washed with water. The aqueous layers were extracted with ethyl acetate and CH_2Cl_2 (2×). The combined organic layers were dried over MgSO_4 , filtered, and the solvent was removed from the filtrate in vacuo to afford the crude product, which was purified by SiO_2 column chromatography using 10% MeOH in ethyl acetate. Removing the solvent in vacuo afforded a yellow orange solid **2** (Fig. 1(b)) (0.127 g, 64%). FTIR 2930, 2849, 1643, 1600, 1567, 1513, 1410, 1247, 992, 661 cm^{-1} ; ^1H NMR (500 MHz, MeOD, ppm) δ 7.65 (m, 4H), 7.46 (d, 2H, J = 8.73 Hz), 7.42 (s, 2H), 6.49 (d, 2H, J = 9.72 Hz); the solubility was too low for ^{13}C NMR analysis; EI-HRMS m/z calcd for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2$ 312.09, found 312.09.

3. Conclusions

In summary, self-assembled structures using simple but strong hydrogen bonding of 2-pyridone moieties have been designed, synthesized and imaged by AFM. A linear nanotrain was synthesized with two hydrogen bonding sites at opposite positions. Imaging of the nanotrain at the atomic level on modified substrates is underway with the eventual goal of imaging concerted rolling motion.

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Electronic Supplementary Material: Supplementary material including spectroscopic data (FTIR, ^1H NMR, ^{13}C NMR) for Compounds **1** and **2** and the AFM images of **1** on mica is available in the online version of this article at <http://dx.doi.org/10.1007/s12274-008-8041-4> and is accessible free of charge.

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