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Direct Patterning of a Cyclotriveratrylene Derivative for Directed Self-assembly of C60

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Abstract

A novel apex-modified cyclotriveratrylene (CTV) derivative with an attached thiolane-containing lipoic acid linker was directly patterned onto gold substrates via dip-pen nanolithography (DPN). The addition of a dithiolane-containing linker to the apex of CTV provides a molecule that can adhere to a gold surface with its bowl-shaped cavity directed away from the surface, thereby providing a surface-bound CTV host that can be used for the directed assembly of guest molecules. Subsequent exposure of these CTV microarrays to C_{60} in toluene resulted in the directed assembly of predesigned, spatially controlled, high-density microarrays of C_{60}. The molecular

recognition capabilities of this CTV template toward C_{60} provides proof-of-concept that supramolecular CTV scaffolds can be directly patterned onto surfaces providing a foundation for the development of organic electronic and optoelectronic materials.

Introduction

With its unique structure, physical, and electronic properties, C_{60} (buckminsterfullerene) has been shown to possess great potential for the development of organic electrical and optical devices [1–4]. For example, C_{60} is an excellent electrical conductor at the nanoscale, nearly as good as copper metal. C_{60} is also a good thermal conductor and is one of the strongest materials known, being 100 times stronger than steel but one-sixth the weight [5–7]. Moreover, the ability of C_{60} to be a potent electron acceptor has led to its utilization in donor–chromophore–acceptor based molecular triads that are capable of intramolecular photoinduced electron transfer (PET) [8]. While C_{60} thin films on metal surfaces have been widely studied [3, 9–14], many challenges remain for the directed self-assembly of organic optoelectronic materials such as C_{60} into two-dimensional surface structures. Therefore, developing methods to pattern and immobilize organic electronic or optoelectronic materials with nanometer-scale control will provide a simple, robust, and flexible approach for the preparation of predetermined two-dimensional organic materials. By controlling the spatial distribution of organic molecules on a surface by directed molecular binding, these materials will potentially allow for the development of new nano-optical, nanoelectronic, and/or nanoelectrochemical systems (NEMS) [3, 8–12].

One way to pattern and immobilize organic electronic or optoelectronic materials with nanometer-scale control is to utilize a bottom-up, layer-by-layer approach based on host–guest chemistry [3]. Host–guest chemistry involves complementary binding between two different molecules that can involve electrostatic, hydrogen bonding, π–π stacking interactions, inductive and dispersion forces, as well as hydrophobic or solvatophobic effects [15]. Over the past decade, host–guest chemistry involving synthetic receptor molecules has received increasing interest partly due to the ever-advancing ability to synthesize complex molecular scaffolds to serve as host structures. One such receptor, cyclotriveratrylene (CTV) [16–18], has been extensively employed in host–guest chemistry as a supramolecular scaffold [19–21]. Enabled by its rigid bowl-shaped structure, CTV has been shown to act as a host molecule for a variety of small molecules including neutral or ionic polyhedral C_{60} and *o*-carborane derivatives [22, 23]. In 1994, Atwood *et al* [24] showed that the bowl-shaped crown conformer of CTV forms inclusion complexes with C_{60} in the ratio of $(C_{60})_{1.5}$(CTV)(toluene)$_{0.5}$ referred to as a 'ball-and-socket' structure. Zhang *et al* [25–28] utilized this ball-and-socket structure to prepare C_{60} self-assembled monolayers (SAMs) on gold utilizing CTV, however the CTV was derivatized on its perimeter resulting in the concave shape of the CTV molecule facing toward the gold surface, thus irreversibly trapping C_{60} against the surface and isolating it from neighboring CTV guests. This orientation of CTV prohibits its ability to function as a template for a layer-by-layer approach to building organic electronic or optoelectronic materials.

Herein we describe a robust and reliable method to produce predesigned, spatially controlled, high-density microarrays of C_{60}. We have designed and synthesized an apex-modified CTV derivative providing a surface-bound CTV template with its bowl-shaped cavity directed away from the surface. By utilizing a layer-by-layer approach and dip-pen nanolithography (DPN), which provides a flexible nanolithographic method capable of positioning molecules on a substrate with 10 nm resolution [29, 30], predesigned, spatially controlled microarrays of this modified CTV derivative were prepared on gold surfaces. The molecular recognition capabilities of this CTV template toward C_{60} provides proof-of-concept that supramolecular CTV scaffolds can be directly patterned on surfaces and through host–guest interactions provide a template for the development of organic electronic or optoelectronic materials.

1. Materials and methods

1.1. Materials

All solvents and reagents used were purchased from Sigma-Aldrich (Milwaukee, WI) and were used as received without further purification.

1.2. Synthesis of 10,15-dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]-cyclononen-O-[5-(1,2-dithiolan-3-yl)pentanoyl]-5-oxime (2a/b)

CTV ketone and CTV oxime were prepared by a modification of the previously published procedure [31]. For the synthesis of the crown and saddle CTV-oxime–lipoic-acid derivatives, lipoic acid (283 mg, 1.37 mmol), hydroxybenzotriazole (HOBT) (200 mg, 1.48 mmol), N, N'-dicyclohexylcarbodiimide (DCC) (330 mg, 1.60 mmol), and 3.0 ml of dry tetrahydrofuran (THF) were mixed in a round bottom flask and allowed to stir at room temperature for 1 h. A mixture of crown and saddle conformers of CTV oxime **1a/b** (545 mg, 1.14 mmol) in 2.7 ml of dry THF was then added to the round bottom flask drop-wise. The reaction was allowed to stir for ~ 24 h and was monitored via TLC using ethyl acetate/dichloromethane (EA/DCM, 1/9) as the eluent. Upon consumption of the starting material, the reaction was filtered over celite to remove the insoluble urea and washed with ~ 30 ml of DCM. The solvent was then removed under reduced pressure. The crude mixture was purified using flash chromatography with an RS-40 cartridge and an eluent gradient of EA/hexane (1/2 to 2/1, v/v). The crown/saddle (**2a/b**) fractions were combined and upon removal of the solvent a light brown solid was recovered (434 mg, yield: 57%). This product was characterized by ^{1}H NMR, ^{13}C NMR, and IR. ^{1}H NMR (300 MHz, CDCl$_3$, TMS as internal standard) δ7.33 (s, 1H), 6.94 (s, 1H), 6.93 (s, 1H), 6.91 (s, 1H), 6.83 (s, 1H), 6.80 (s, 1H), 6.78 (s, 1H), 6.68 (s, 1H), 6.65 (s, 1H), 6.64 (s, 1H), 6.58 (s, 1H), 6.54 (s, 1H).

1.3. Preparation of gold substrates

Silicon oxide substrates with 500 nm thermally evaporated oxide layers were purchased from WaferNet, Inc. (CA). Thin films of Cr and Au with thicknesses of 10 nm and 30 nm, respectively, were evaporated onto pre-cut, piranha (3:1 = H_2SO_4:H_2O_2) cleaned silicon pieces using an Edwards Auto 306 system. (Caution! Piranha solution should be handled carefully as it may cause serious burns.)

1.4. Fabrication of CTV microarrays

A NanoInk, Inc. Nscriptor™ was used to prepare DPN arrays under ambient conditions with temperatures ranging from 20 to 22 °C and humidity levels within the enclosed chamber between 25 and 35%. V-shaped, silicon nitride contact-mode tips (NanoInk, Inc.) with a spring constant of 0.5 N m^{-1} were used for DPN patterning. A 10 mM solution of **2a/b** was prepared in acetonitrile containing 1% polysorbate 20 for wettability. For DPN patterning, atomic force microscopy (AFM) tips were first dipped into inkwells filled with **2a/b**. The stationary diffusion constants were calculated based on the model developed by Jang *et al* [32] prior to each patterning process. Dot-shaped patterns were made by holding the tip stationary in contact with the surface. The samples with DPN arrays were allowed to stand at room temperature for ~ 10 min and rinsed with acetonitrile then ethanol and dried under a stream of nitrogen.

1.5. Modification of the DPN-patterned templates

Substrates with DPN generated patterns were incubated in a 1 mM solution of octadecanethiol (ODT) in ethanol for ~ 30 min to block any exposed gold surface from further unwanted contaminations or modifications. The samples were then rinsed with ethanol and dried under a stream of nitrogen. Regions coated with **2a/b** were then functionalized using a 1 mM solution of C$_{60}$ in toluene with deposition times ranging from 20 min to 1 h. Functionalized samples were rinsed with toluene and dried under a stream of nitrogen.

1.6. Imaging and surface characterization

Fabricated microarrays were characterized by AFM. A NanoInk, Inc. Nscriptor™ was employed to acquire topography, phase and frictional force images. A v-shaped, silicon nitride contact-mode cantilever tip (model MSCT-AUNM-10 purchased from Veeco, Inc.) with a spring constant of 0.05 N m^{-1} was used for lateral force microscopy (LFM) images while a beam-shaped, silicon tapping-mode tip with a spring constant of 40 N m^{-1}, from Pacific Nanotechnology, was used for Tapping-Mode AFM (TMAFM) imaging. All the AFM images were acquired with resolutions of 512 pixels × 512 pixels. Self-assembled monolayers for matrix assisted laser desorption ionization mass spectrometry (SAMDI-TOF MS) spectra were obtained using a 4800 MALDI-TOF/TOF (Applied Biosystems, Farmingham, MA) with a 335 nm Nd:YAG laser as a desorption/ionization source using a matrix of 2,4,6-trihydroxyacetophenone, 25 mg ml^{-1} in acetonitrile. All spectra were acquired with 20 kV accelerating voltage using a positive reflector mode. The extraction delay was 450 ns, 1200 laser shots were applied, and the entire surface of the circle was sampled. Each spectrum was calibrated using the EG3–EG3 disulfide background as an internal standard.

2. Results and discussion

We hypothesized that derivatizing the apex of the CTV bowl would provide a supramolecular scaffold with the concave bowl receptor pointing away from the surface, enabling CTV to function as a surface-bound host molecule. To accomplish this, CTV was oxidized to the monoketone and converted to the oxime in high yield as an equilibrium mixture of the crown **1a** and the saddle **1b** conformers (figure 1) [31]. The CTV oxime was coupled to (±)-α-lipoic acid affording a mixture of the coupled crown (**2a**) and saddle (**2b**) conformers in 52% yield (figure 1). The resulting CTV–lipoic-acid derivatives (**2a/b**) contain a dithiolane-terminated linker for coordination to gold, thus enabling the bowl of CTV to face away from the surface.
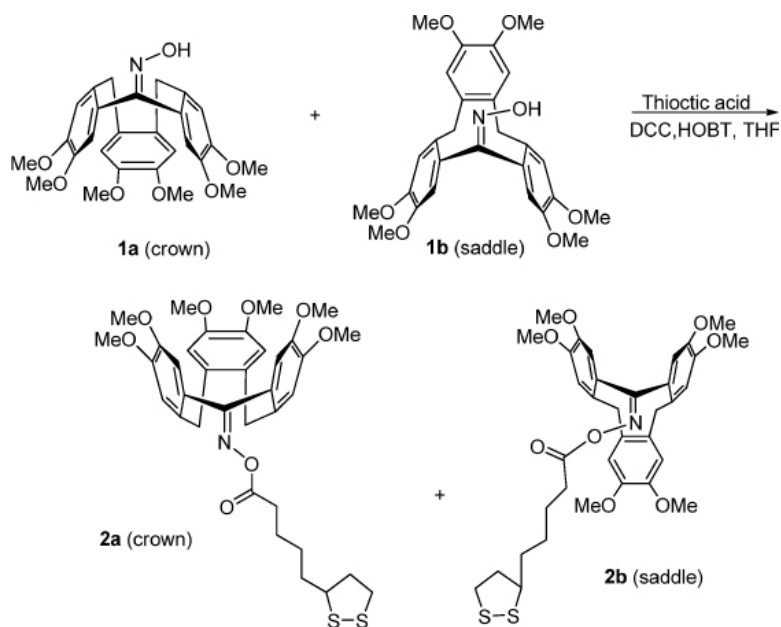

Figure 1. Synthetic scheme for the synthesis of the apex-modified dithiol CTV oxime (**1**).

With the successful design and synthesis of an apex-modified CTV supramolecular scaffold head group with a dithiolane tail, microarrays of **2a/b** were prepared via DPN by direct patterning using a NanoInk, Inc. Nscriptor™ system [29, 30]. DPN is a particularly important nanolithographic method for patterning molecular inks since DPN is capable of positioning molecules on a substrate with 10 nm resolution in predesigned, spatially controlled arrays [29]. As previously reported, the addition of 1% polysorbate 20 to a 10 mM solution of **2a/b** in

acetonitrile enhanced the diffusion of **2a/b** during the DPN process by making the solvent more wettable [33]. DPN generated patterns of **2a/b** were prepared at 20 °C with humidity levels between 25 and 35% [34]. To assess the adsorption of the **2a/b** molecular ink, surface topography changes were measured by atomic force microscopy (lateral force microscopy (LFM) and tapping-mode atomic force microscopy (TMAFM)) after curing in air at room temperature for ~ 10 min, followed by rinsing with acetonitrile and ethanol and drying under a stream of nitrogen.

Typical AFM images of DPN generated **2a/b** patterns are shown in figure 2. Surface-bound **2a/b**, which is more hydrophilic than gold, is observed as the light contrast areas in the TMAFM image (figure 2(a)) and a darker contrast in the LFM image (figure 2(b)). The height of DPN generated patterns of **2a/b**, measured from randomly placed height profiles using TMAFM revealed a height of 1.2 ± 0.3 nm every 1.5 µm with a width of 0.5 µm (figure 2(c)). The calculated height of a **2a/b** monolayer is 1.5 nm, consistent with the experimentally observed height values obtained for **2a/b**, indicating the formation of a **2a/b** SAM. Gold substrates containing **2a/b** SAMs were immersed in a 1 mM solution of ODT in ethanol for ~ 30 min, rinsed with ethanol, and dried under a stream of nitrogen. A TMAFM topography image after passivation with ODT was recorded and the corresponding height profiles are shown in figure 3(a). TMAFM images demonstrate that the heights of **2a/b** SAM and the surrounding ODT backfilled resist layers are similar due to the nearly identical heights of their SAMs (about 1.5 nm versus 1.8 nm, respectively) [35]. However, microarrays of **2a/b** backfilled with ODT can be clearly differentiated by LFM due to the greater frictional force represented as the darker contrast in comparison to the ODT resist layer between the AFM tip and the **2a/b** SAM (figure 3(b)). The height profile (figure 3(c)) confirmed the relatively constant height of the ODT backfilled surface.
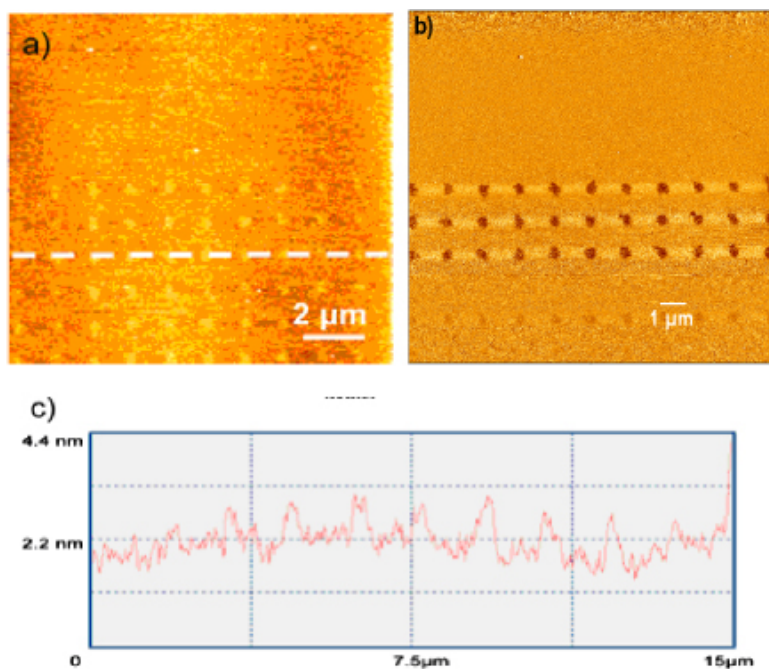

Figure 2. AFM generated images of **2a/b** dot patterns patterned onto the bare gold surface. (a) TMAMF image showing height increase of **2a/b** dots patterned onto the bare gold surface via DPN. (b) LFM images of **2a/b** patterned on a base gold substrate utilizing DPN. (c) Step height profile from AFM of the sample represented in image a.
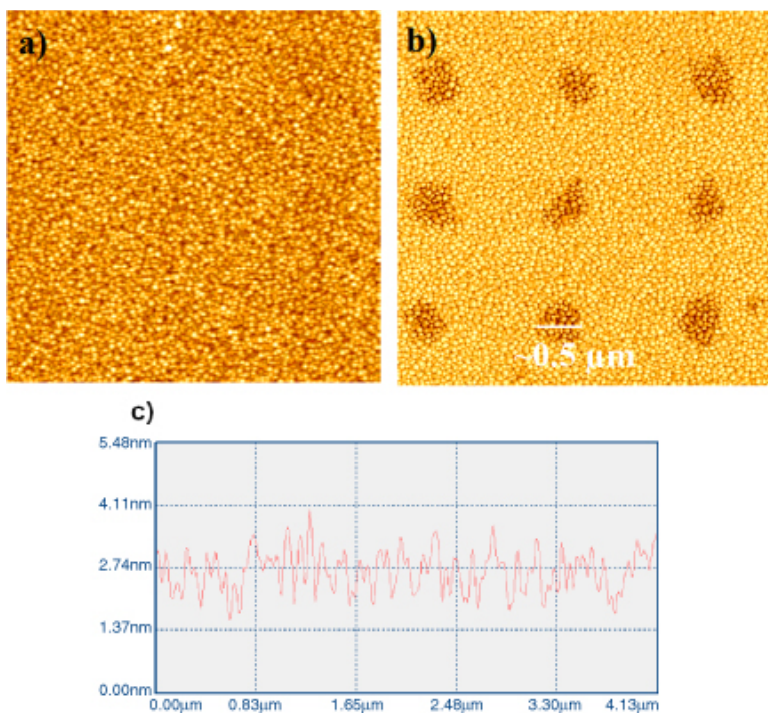
Figure 3. AFM generated images of **2a/b** dot patterns after backfilling the bare gold surface with ODT. (a) TMAFM and (b) LFM images of **2a/b** dot patterns. (c) Step height profile from AFM of the sample represented in image (a).

The molecular recognition capabilities of the DPN generated CTV-template microarrays toward C_{60} were also examined. Arrays of **2a/b**–ODT were immersed in a 1 mM solution of C_{60} in toluene for ~ 40 min and after extensive rinsing with toluene were dried with nitrogen and characterized via TMAFM. A typical TMAFM image showing C_{60} attached to the CTV template is presented in figure 4(a). The binding interaction of the **2a/b**–ODT SAMs with C_{60} is consistent with the observed TMAFM contrast (figure 4(a)) and a clearly visible contrast in the LFM image (figure 4(b)). These data are in good agreement with the hydrophobicity of C_{60}, which is somewhat more hydrophilic than ODT. C_{60} was observed bound to individual dots with little or no binding to the resist ODT monolayer. Additional confirmation for C_{60} binding to DPN generated **2a/b** templates was obtained from SAMDI-TOF mass spectroscopy. Mrksich and co-workers have shown that SAMDI-TOF MS is an excellent tool to directly detect organic molecules, such as synthetic intermediates, at surfaces [36]. Therefore, SAMDI-TOF MS spectra were collected on DPN generated SAMS of **2a/b** before and after exposure to C_{60} (supplementary material figures S1 and S2 available at stacks.iop.org/0957-4484/22/i=27/a=275611/mmedia). For SAMs of **2a/b**, a significant (74%) m/z peak at 462.27 was observed, which we assign to the cleavage product of **2a/b** at the N–O bond (figure 1). No parent peak was observed for **2a/b** and no peaks at larger masses were detected, indicating that the lipoic acid tail of **2a/b** was lost in the laser desorption process. Exposure of DPN generated SAMS of **2a/b** to C_{60} resulted in the observation of an m/z peak at 720.05 in the SAMDI-TOF mass spectrum indicating the presence of C_{60} bound to the **2a/b** monolayer. These data, taken together, provide proof-of-concept that supramolecular CTV scaffolds can be directly patterned on surfaces and retain their ability to bind host molecules such as C_{60}.
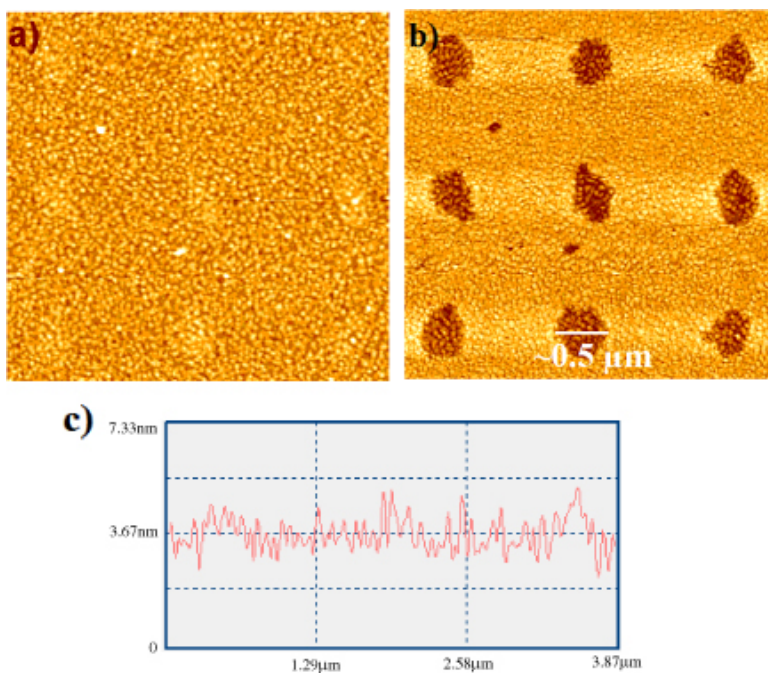
Figure 4. AFM images of the samples after C_{60} deposition. (a) TMAFM image showing that a height increase of ~ 1.0 nm is observed where the CTV-disulfide ink was patterned, but not on the surrounding ODT surface. (b) The frictional contrast between CTV-C_{60} is apparent relative to the backfilled ODT surface in the LFM image. (c) Cross-sectional step height profile from tapping-mode AFM shows the periodic height increase of ~ 1.0 nm on the sample.

Given that the diameter of C_{60} is ~ 1 nm, a height increase for a SAM of **2a/b** after the addition of C_{60} is expected if C_{60} binds to the CTV macrocycle in a ball-and-socket fashion as observed by Atwood *et al* [24] in the solid state. AFM height profiles of the **2a/b**-C_{60} SAM after the addition of the ODT resist were found to be 1.0 ± 0.3 nm (figure 4(c)). Since **2a/b** and ODT have approximately the same height, the 1 nm height increase is evidence of C_{60} binding through π–π interactions (figure 5) similar to the binding mode reported for the solid state [24]. Previously we had shown that apex-modified CTV derivatives interconvert between two different conformers, crown **1a** and saddle **1b** [31]. The interconversion equilibrium between the two conformers was shown to be solvent dependent with the crown conformer being favored in non-polar solvents [37]. Given the nearly complete coverage of the CTV-surface-bound template, the equilibrium between the crown conformer **2a** and the saddle conformer **2b** must be shifted toward **2a** (figure 1) enabling a ball-and-socket interaction between the host CTV molecules and the C_{60} guest [37]. Therefore, the apex-bound lipoic-acid–CTV molecule (**2a**) resides on the surface with its bowl-shaped cavity directed away from the surface. The proposed conformation of the CTV bowl is consistent with other cyclophane SAMs, such as calix[n]arenes (*n* = 4, 6, 8) [26, 38].
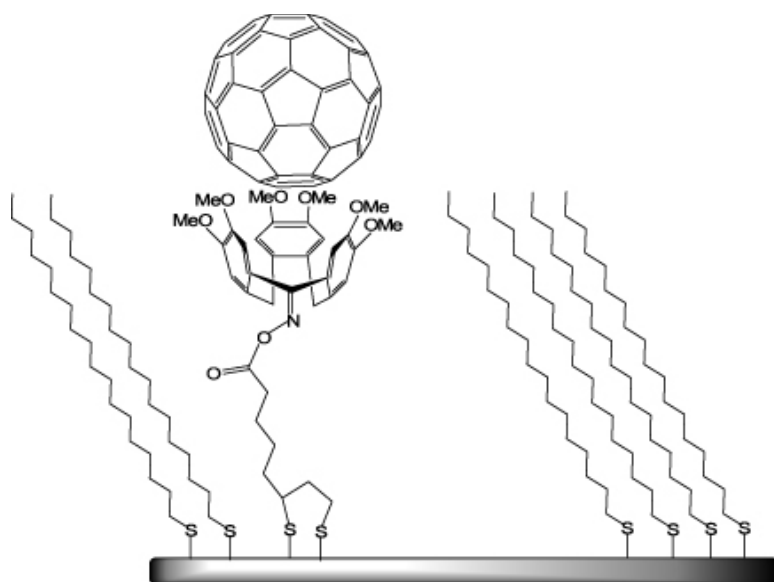
Figure 5. Proposed C_{60} binding to the apex-modified, surface-bound CTV.

3. Conclusion

We have shown that an apex-modified CTV supramolecular scaffold can be patterned into pre-defined microarrays via DPN. Through host–guest interactions, these microarrays have been shown to form bottom-up, layer-by-layer complexes with C_{60} with potential toward advancing nanoelectronics and optoelectronics. Having the ability to directly pattern molecular host active surfaces via DPN opens the door to preparing a wide range of host–guest materials with reproducible, homogeneous features with high edge resolution, which will facilitate the fabrication of microcircuitry and optical electronics based on host–guest chemistry.

Acknowledgments

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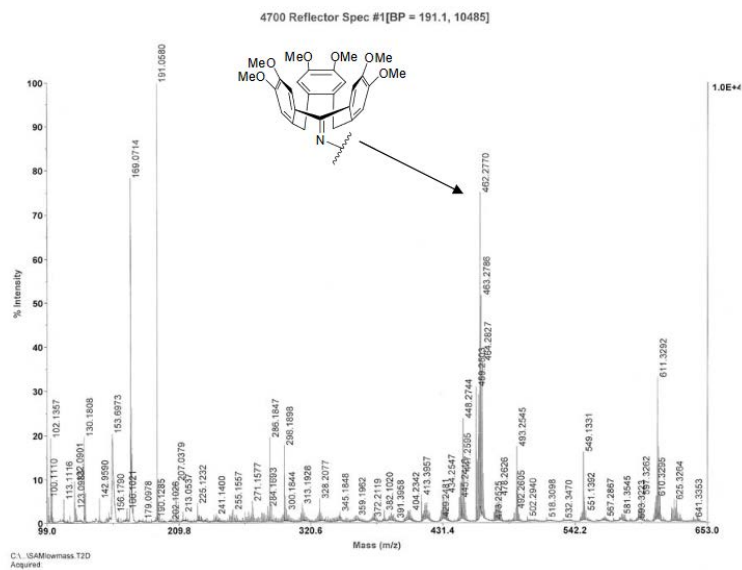
Supplementary Material

Figure S1: Low mass SAMDI-TOF MS of CTV-MHA on gold substrate
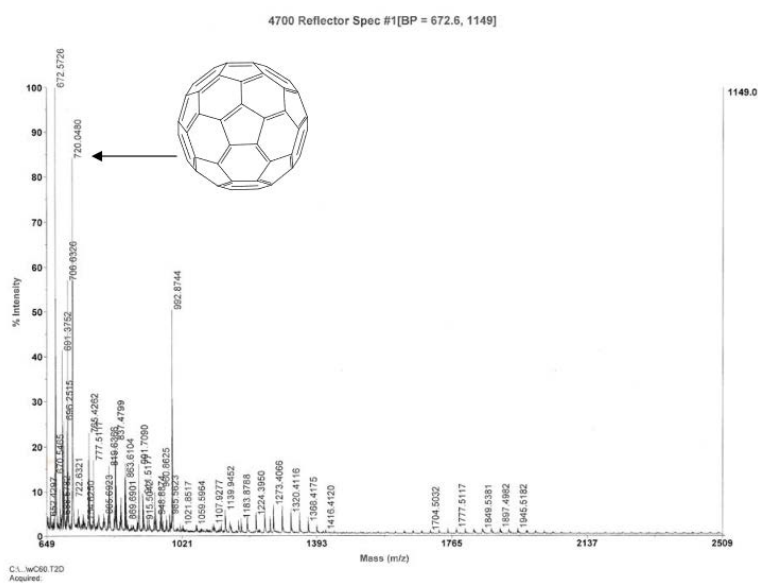

Figure S2: SAMDI-TOF MS of C$_{60}$ on the gold surface