Engineering of Linear Molecular Nanostructures by a Hydrogen-Bond-Mediated Modular and Flexible Host−Guest Assembly

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ABSTRACT The formation of a desired nanostructure with concomitant patterns and functions is of utmost importance in the field of surface molecular engineering and nanotechnology. We here present a flexible host−guest assembly, which steers the formation of linear molecular nanostructures on surfaces by a hydrogen-bond-mediated assembly process. A linear monodendron molecular template with periodic hydrogen-bond binding sites is shown to accommodate a variety of molecules with pyridylethynyl terminals. The unit cell parameters in the transverse direction of the linear pattern can be tuned from 3.4 to 7.3 nm in response to the packing of the guest molecules with different sizes, shapes, and aggregation number. The introduction of hydrogen-bonding partners into the host template and into guest molecules is responsible for the steering of the linear pattern of guest molecules. The modular approach could greatly facilitate the ordering of guest molecules with desired functional moieties.

KEYWORDS: hydrogen bond · self-assembly · molecular template · scanning tunneling microscopy · surface and interface

The design and fabrication of self-assembled structures on surfaces with controlled pattern and concomitant function have been widely explored in order to provide useful materials for the construction of molecular devices.[1−5] In the past years, with a detailed understanding of the weak interactions guiding the self-assembly process, it became possible to build up interesting nanostructures from organic compounds *via* chemical structure modification combined with external environment regulation.[6−10] From the viewpoint of molecular engineering, it is desirable to separate patterning and functionalization into independent steps to get a better control in the course of building up nanoarchitectures. One promising way to achieve stepped fabrication of nanoarchitectures is using molecular templates.[11−13] As an example, well-defined molecular networks with appropriate nanopatterns can serve as surface molecular templates to drive the selected molecular organization of guest molecules in precisely controlled position, orientation, and interdistance.[11−13] Until now, various two-dimensional (2D) molecular templates[14−19] as well as designed host−guest systems[20−38] have been constructed on solid supports and studied at the molecular scale by means of scanning tunneling microscopy (STM). Steered by 2D molecular templates, desired patterns of C_{60},[20−26] porphyrin, and phthalocyanine derivatives,[27−30] supramolecular metallacycles,[32−34] and many other functional molecules[36−38] have been accomplished. In many of these systems, the host templates are rigid 2D nanoporous networks,[14,18,20,23−25,29,31] while in few cases, they exhibit structural flexibility upon accommodation of different molecular aggregates.[11,28,36] The size and/or shape complement between the host cavity and the guest molecules is frequently proposed as a key factor responsible for the formation of the desired pattern assembly. The knowledge gained from these systems provides useful information for molecular nanostructure design, although the size and shape selectivity typically has limited scope.

We propose a new modular molecular template approach, as schematically shown in Figure 1a, to improve the versatility of surface template assembly. Ideally, a molecular template should have defined structures upon hosting different guest molecules and be versatile and flexible to incorporate a variety of guest molecules

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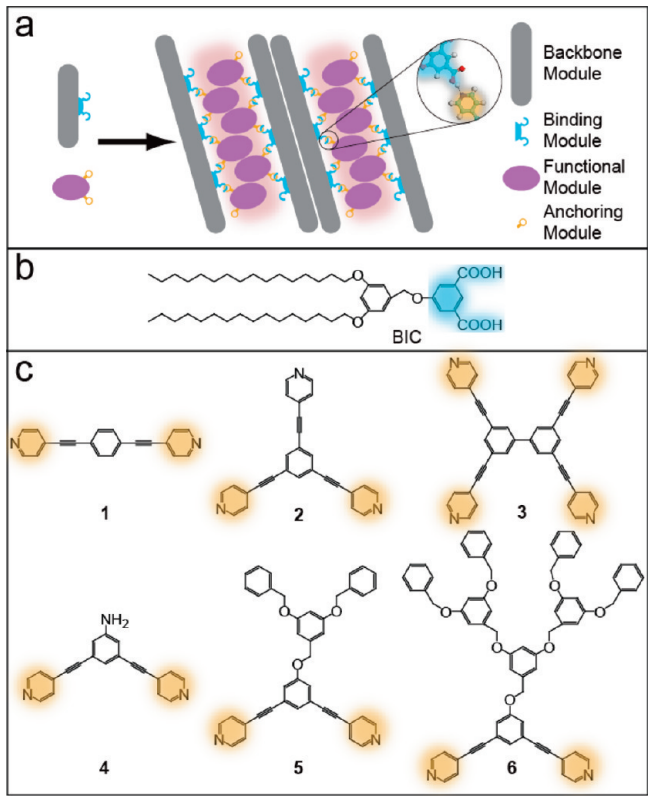


Figure 1. Hydrogen-bond-mediated modular template assembly for linear molecular nanostructures. (a) Schematic diagram for the fabrication of linear pattern of guest molecules using modular template assembly. The hydrogen bond between the binding module and the anchoring module is shown in the inset. (b,c) Chemical structures of host BIC molecule and guest pyridylethylnyl derivatives 1−6 used in the present study. The binding module and anchoring module are highlighted with cyan and orange colors, respectively.

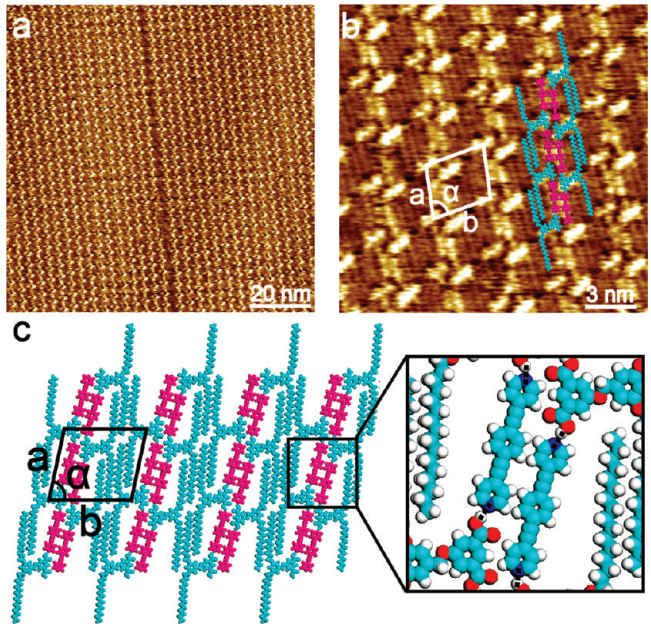


Figure 2. BIC-1 host−guest assembly. (a) STM image of BIC-1 host−guest structure on HOPG in 1-octanol. Sample bias voltage (V_B) = 480 mV, tunneling current (I_T) = 490 pA. (b) High resolution STM image of BIC-1 structure. V_B = 445 mV, I_T = 605 pA. (c) Molecular model for the BIC-1 structure. The cyan and red molecules correspond to BIC and 1, respectively. Hydrogen bonds are outlined by black dashed lines in the enlarged inset.

with different sizes, shapes, and functional groups. To improve the controllability of the template assembly process, appropriate chemical cues are introduced into the host template. In particular, a host template molecule consists of a backbone module to tune the pattern of the host−guest assembly and a binding module to interact with the guest molecules. Likewise, the guest molecules include an anchoring module to interact with the host template and a function module of interest. As schematically shown in Figure 1a, the assembly of guest molecules into a linear pattern mirroring the structure of the molecular template is mediated by, as one of many possibilities, the hydrogen-bonding interaction (inset of Figure 1a) between the binding modules and the anchoring modules. The significant feature of this strategy is that each module plays an independent role in the self-assembly process. Hence, the modular molecular template assembly will greatly facilitate the retro-design of guest molecules with desired properties and thus promote controllable fabrication of nanoarchitectures.

As a proof of concept, we report a unique flexible molecular template which can direct the linear assembly of a series of pyridylethynyl derivatives with different sizes and shapes. The monodendron molecule, 5-(benzyloxy) isophthalic acid derivative (BIC, $C_{47}H_{76}O_7$, Figure 1b) is employed to build the host template. Our previous results have established that BIC molecules show polymorphism on highly oriented pyrolytic graphite (HOPG) in different solvents or at different concentrations.[39,40] In particular, it shows a linear ribbon structure in 1-octanoic acid, where the ribbons are stabilized *via* the close-packed alkyl chains, with isophthalic acid groups periodically located along the molecular ribbon (see Supporting Information, SI).[39] Upon introducing guest molecules with terminal pyridyl groups, as shown in Figure 1c, these pyridylethynyl derivatives are pegged onto the BIC ribbons through O−H···N hydrogen bonds[41] and confined into linear patterns on the surface by the BIC molecular template. It is of considerable interest that such a template process is flexible to accommodate various guest molecules with different sizes, shapes, and aggregation number by tuning the spacing between the neighboring ribbons. The versatility of this molecular template can be ascribed to the modular assembly mode between the template and the guest molecules. These results demonstrate the ability to construct patterned molecular nanostructures *via* a rationally designed molecular engineering strategy.

RESULTS

BIC-1 Host−Guest Structure. Compound **1** is a typical linear pyridylethynyl derivative molecule. After the deposition of a solution containing **1** onto the BIC adlayer, a ribbon featured structure is observed after several minutes. Figure 2a displays a large-scale STM image

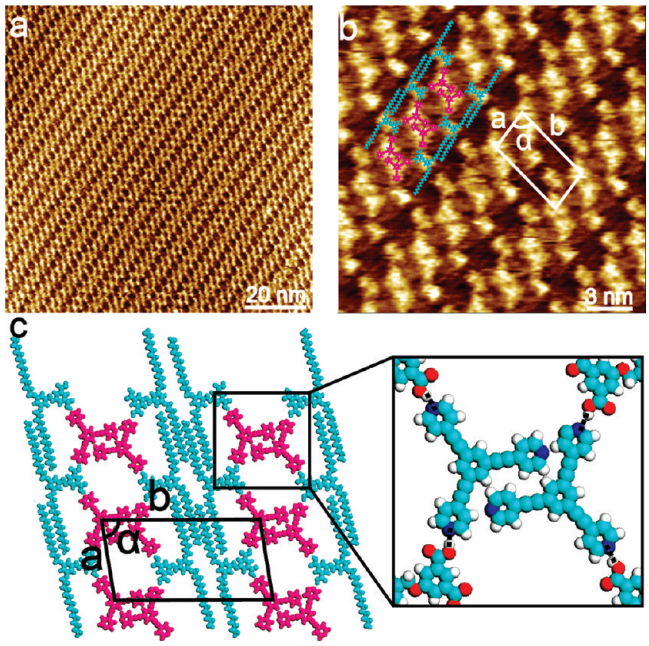


Figure 3. BIC-2 host−guest assembly. (a) Large scale STM image of BIC-2 host−guest structure on HOPG. V_B = 400 mV, I_T = 399 pA. (b) High resolution STM image of BIC-2 structure. V_B = 560 mV, I_T = 572 pA. (c) Proposed model for the BIC-2 structure. The cyan and red molecules correspond to BIC and 2, respectively. Hydrogen bonds are illustrated by black dashed lines in the enlarged inset.

of the ribbonlike structure on HOPG. A highly ordered adlayer with domain size over 100 nm can be clearly resolved. The detailed pattern structure of the assembly can be observed in the high resolution STM image in Figure 2b, which is composed of dark alkyl chains, bright rods transverse to the ribbon direction, and less bright but longer rods parallel to the alkyl chains. Owing to the size and shape of the molecules, the bright rods are attributed to the BIC aromatic cores, whereas the less bright but longer rods are attributed to compound **1**. The length of the alkyl chains is measured to be 1.9 ± 0.2 nm, consistent with the length of a hexadecyl chain. The two hexadecyl chains of each BIC molecule orient oppositely, and pack with other BIC hexadecyl chains interdigitally. Owing to this packing mode of hexadecyl chains the neighboring BIC distance along the ribbon is fixed at 3.0 ± 0.2 nm. Every two BIC rows in a ribbon take a head-to-head orientation and present a slight offset along the ribbon direction, extending on the surface to form a host template structure similar to the linear adlayer of BIC in 1-octanoic acid.[39] Two linear molecules of **1** are immobilized as guests and pack side-by-side in each pore of the template. The molecular ratio of BIC and **1** is determined to be 1:1.

On the basis of the above analysis, a structural model is proposed for BIC-**1** adlayer in Figure 2c. The BIC template and molecules **1** are colored with cyan and red in the model, respectively. According to the adlayer symmetry, a unit cell is outlined in Figure 2 panels b and c, with the constants measured to be a = 3.0 ± 0.2 nm, b = 3.4 ± 0.2 nm, and α = 78 ± 3°. The O−H···N hydrogen bonds exist between the pyridyl groups of compound **1** and the carboxyl groups of BIC,[41] as illustrated in the enlarged inset in Figure 2c. Clearly, the hydrogen bonds between molecules **1** and the BIC template play an important role in the host−guest assembly.

BIC-2 Host−Guest Structure. The BIC template is capable of capturing pyridylethynyl derivative molecules of different shapes and sizes. A similar BIC structural formation of linear molecular template can be induced by the triangular shaped molecule **2**. Figure 3a displays a typical large scale STM image exhibiting a ribbon feature, which was obtained after adding a solution containing molecules **2** onto the sample initially covered with pure BIC structures. The width of the neighboring ribbon in such a structure is markedly wider than that in the BIC-**1** host−guest structure, indicating that the BIC template is flexible in the dimension transverse to the ribbon direction. More detailed structural information can be obtained from the high resolution STM image in Figure 3b. The bright ribbons are clearly decorated with regularly outward facing rods, while the dark troughs are composed of interdigitally packed alkyl chains. The neighboring BIC distance along the ribbon is measured to be 2.9 ± 0.2 nm, almost the same as that in the BIC-**1** adlayer. Two triangular shaped spots

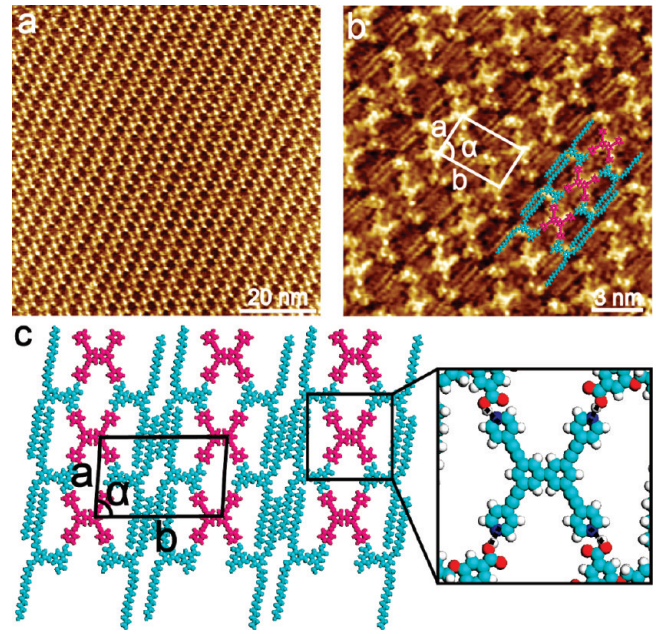


Figure 4. BIC-3 host−guest assembly. (a) Large scale STM image of BIC-3 host−guest structure on HOPG. V_B = 466 mV, I_T = 395 pA. (b) High resolution STM image of BIC-3 host−guest structure. V_B = 452 mV, I_T = 359 pA. (c) Structural model of BIC-3 host−guest structure. The BIC and molecules 3 are colored with cyan and red, respectively. Hydrogen bonds are shown in the enlarged inset with black dashed lines.

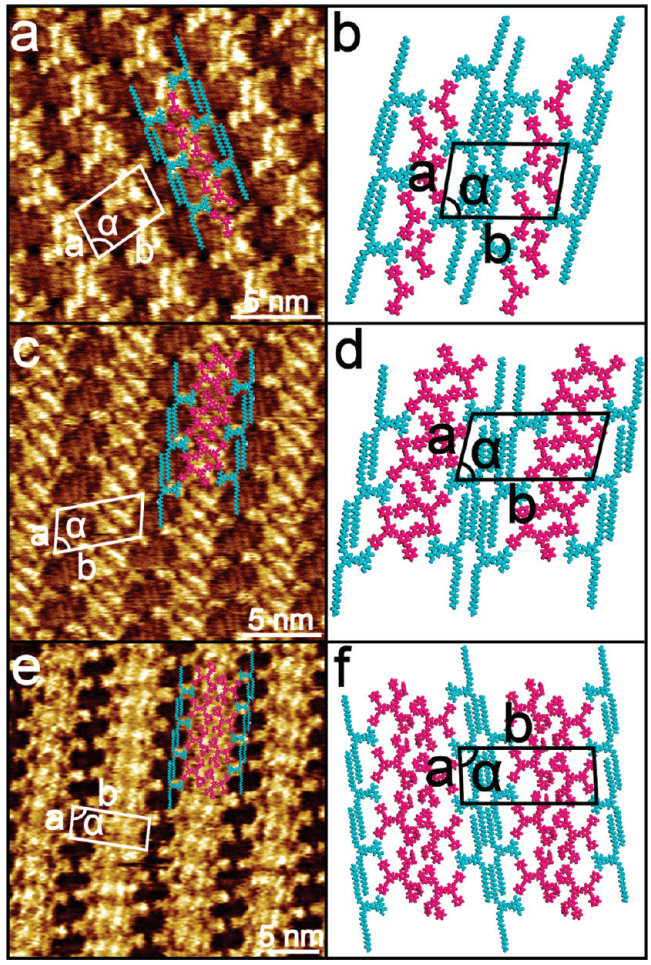


Figure 5. Linear assembly of other pyridylethynyl derivatives 4−6 by BIC template. (a) High resolution STM image of the BIC-4 host−guest structure. V_B = 452 mV, I_T = 359 pA. (b) The structural model for the BIC-4 adlayer. (c) High resolution STM image of the BIC-5 host−guest structure. V_B = 605 mV, I_T = 661 pA. (d) A tentative structural model based on the STM image. (e) High resolution STM image of the BIC-6 host−guest structure. V_B = 539 mV, I_T = 493 pA. (f) A tentative structural model based on the STM image. Large scale STM images of the structures are provided in the SI.

with an inverse orientation are trapped in a template pore formed by the neighboring four rods. On the basis of the molecular shape and size, the small rods are attributed to the BIC aromatic cores, and the triangular shaped spots are attributed to molecules **2**. The BIC molecules therefore self-organize into a host template, immobilizing **2** as guest molecules to form a 1:1 BIC-**2** composite structure on HOPG.

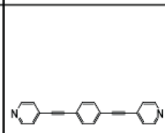
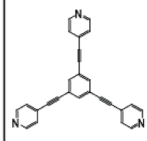
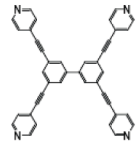
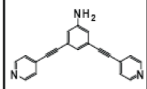
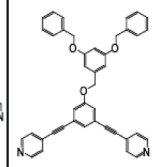
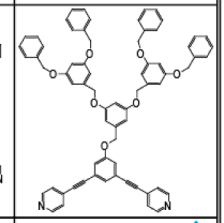
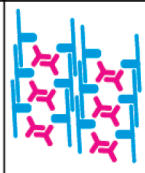
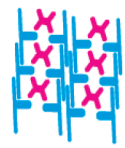
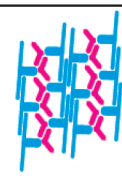
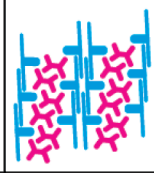
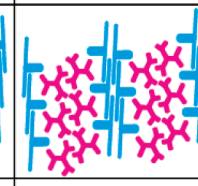
Figure 3c illustrates the structural model of the BIC-**2** adlayer structure, in which BIC and molecule **2** are marked with cyan and red color, respectively. The BIC template accommodates **2** by tuning the dimension in the *b* lattice orientation, which is measured to be 5.4 ± 0.2 nm. Similar to the case in the BIC-**1** system, the O−H···N hydrogen bonds could be formed between BIC and **2** as shown in the enlarged inset in Figure 3c by black dashed lines, which serve as the driving force for the host−guest assembly. The constants of the unit cell in Figure 3b,c are determined to be a = 2.9 ± 0.2 nm, b = 5.4 ± 0.2 nm, and α = 81 ± 3°. The structural model is in good agreement with the STM results.

BIC-3 Host−Guest Structure. The host−guest structure formed by BIC and the four-pointed star shaped molecule **3** with four pyridyl groups has also been investigated. The experimental procedure is the same as for those of **1** and **2**. A large scale and well-ordered adlayer exhibiting a ribbon feature can be clearly seen in the STM image in Figure 4a. This ribbonlike structure is similar to the BIC-**1** and BIC-**2** host−guest structures, although possessing a different spacing of 4.6 ± 0.2 nm along *b* lattice direction of the assembly. The molecular morphology and the self-assembled pattern can be clearly distinguished in the high resolution STM image in Figure 4b. BIC hexadecyl chains are found adsorbed interdigitally on the HOPG surface, with the neighboring BIC distance of 2.9 ± 0.2 nm along the ribbon direction, almost the same as that of **1** and **2**. The molecules **3** can be clearly observed in the image, exhibiting a characteristic four-pointed star shape. The pyridyl groups of **3** are pointed to the BIC carboxyl groups, making it feasible to form O−H···N hydrogen bond between the two compounds. Interestingly, only one molecule can be trapped inside each pore of the BIC template, leading to a 2:1 BIC-**3** host−guest molecular ratio on the surface. This result demonstrates that the BIC template is flexible in one dimension to accommodate guest molecules of different aggregation numbers as well as different sizes and shapes.

A structural model for the BIC-**3** structure is deduced from the high resolution STM image in Figure 4b and illustrated in Figure 4c. By coloring BIC with cyan and **3** with red color, the BIC template is clearly distinguished in the model. Each guest molecule is precisely immobilized inside one template pore and donates four pyridyl groups as hydrogen-bond acceptors to interact with the carboxyl groups, resulting in a 2:1 BIC-**3** host−guest structure. The enlarged inset image of the model illustrates the existing O−H···N hydrogen bonds by black dashed lines. A unit cell is superimposed on Figure 4 panels b and c. The lattice constants are a = 2.9 ± 0.2 nm, b = 4.6 ± 0.2 nm, and α = 86 ± 3°.

Host−Guest Structures of BIC and Other Pyridylethynyl Derivatives. The BIC template is further found adjustable in response to other pyridylethynyl derivatives including molecules **4**−**6**. These molecules have the same hydrogen-bond acceptor groups but distinct attached moieties. It was found that each template pore can immobilize two guest molecules with four hydrogen-bond acceptors in total to satisfy the four carboxyl groups in one pore, leading to 1:1 host−guest structures. Figure 5 panels a, c, and e display high resolution STM images of BIC-**4**, BIC-**5**, and BIC-**6** host−guest adlayers, respectively. All the images exhibit a similar ribbon feature, with different widths between the neighboring ribbons. The hexadecyl chains are adsorbed interdigitally and

TABLE 1. Summary of Structures and Parameters of the Host−Guest Adlayers Formed by BIC and Pyridylethynyl Derivatives 1−6

	1	2	3	4	5	6
Guest molecular structure						
Structural model						
a (nm)	3.0 ± 0.2	2.9 ± 0.2	2.9 ± 0.2	2.9 ± 0.2	2.9 ± 0.2	3.0 ± 0.2
b (nm)	3.4 ± 0.2	5.4 ± 0.2	4.6 ± 0.2	4.4 ± 0.2	5.7 ± 0.2	7.3 ± 0.2
α (°)	78 ± 3	81 ± 3	86 ± 3	81 ± 3	76 ± 3	87 ± 3

packed densely on the surface to maximize the van der Waals forces. The neighboring BIC distance along the ribbon maintains a constant distance and allows for a good steric match between the hydrogen-bond donor and acceptor groups from host and guest molecules, respectively, to form hydrogen bonds. On the other hand, the two face-to-face oriented BIC rows in one ribbon change their distance and offset in order to accommodate different guest molecules. The constants of *a* in the unit cells are almost constant at about 2.9 nm, while the constants of *b* in the unit cells are determined to be 4.4 ± 0.2, 5.7 ± 0.2, and 7.3 ± 0.2 nm for BIC-**4**, BIC-**5**, and BIC-**6** structures, respectively. The corresponding structural models for the BIC-**4**, BIC-**5**, and BIC-**6** are shown in Figure 5 panels b, d, and f, respectively. The host template is highlighted by cyan color, while the guest molecules are colored red in these models. The superimposed structural models match the STM images well. The hydrogen bonds between the BIC and guest molecules are crucial in forming these host−guest structures.

DISCUSSION

Table 1 summarizes the structural models as well as the unit cell parameters of the composite structures formed by BIC and the pyridylethynyl derivatives **1**−**6**. A ribbon featured BIC template is formed on the surface in response to all the guest pyridylethynyl compounds **1**−**6**. The BIC template shows great flexibility in order to accommodate guest molecules with different sizes, shapes, and aggregation number by adjusting its inter-ribbon spacing. We note that varying the concentration of guest molecules in the solution phase has no significant effect on the formation of this featured linear pattern, further highlighting the structure-direction role of the BIC molecular template.

The template process of BIC toward the pyridylethynyl guest molecules can be analyzed using a molecule engineering method. First, each BIC molecule can be divided into two parts, the alkyl chains as the backbone module and isophthalic acid as the binding module. In all the structures, two oppositely orientated hexadecyl chains of each BIC molecule adsorb along the close-packing direction of graphite (see SI) and are packed interdigitally with the neighboring BIC hexadecyl chains to form a ribbon structure by maximizing the van der Waals interactions. As a result, the isophthalic acid moieties are located periodically along the alkyl chain ribbons and serve as "hooks" for the guest molecules. Likewise, the guest molecules may also be partitioned into two different parts, although they possess a variety of sizes and shapes. The anchoring modules of the guest molecules are two pyridyl terminals with rigid ethynyl spaces. The terminal pyridyl groups interact with the carboxylic acid moieties of the BIC template to build up the composite adlayer. The functional module can be attached to the anchoring module *via* synthesis. It has been demonstrated in solid state crystal engineering that the carboxylic acid moiety prefers interacting with pyridyl as hydrogen partner rather than with itself,[41] which is the driving force for the structural transformation of monocomponent BIC assembly into linear composite structures upon introduction of the guest molecules **1**−**6**. After the BIC molecular template directed

assembly, the guest molecules are brought into close proximity and form linear patterns on the surface. For example, the dendrons in **5** and **6** are aligned into a linear pattern by this approach. It is reasonable to expect that the BIC template could be used to build linear structures of other moieties of interest as well, simply by changing the attached functional moieties of the guest molecules, as long as the functional moieties do not interfere with the hydrogen-bonding reorganization between the molecular template and the anchoring modules of the guest molecules. The assembly of functional guest molecules with interesting electronic properties using the approach demonstrated here is currently under investigation.

The interdistance of the two pyridyl terminals of the guest molecules must match the interdistance of the carboxylic acid groups along the ribbon template in order to achieve a successful host guest assembly process. For example, our attempt to build a linear pattern of tetrapyridyl phorphyrin using this BIC molecular template failed, although it bears a similar shape to compound **3**. The distance between the two neighboring pyridyl groups of a tetrapyridyl phorphyrin molecule is measured to be 1.1 nm, which is too short to match the neighboring carboxylic acids with a distance of 1.9 nm in the BIC template. As the interdistance of the binding modules is determined by the length of the alkyl chains of the BIC molecules, it is predicted that a linear pattern of tetrapyridyl phorphyrin might be possible by using BIC template molecules with shorter alkyl chains.

Every two BIC rows in one ribbon taking a back-to-back configuration are separated from each other with different distances to accommodate the guest molecules of different shapes, sizes, and number. It can be seen from Table 1 that the constants are tunable from 3.4 to 7.3 nm in the lattice orientation *b*, while almost identical with a length of about 2.9 nm in the lattice orientation *a*. In the assembly process, it is found that the pyridylethynyl molecules **1**−**6** are able to serve as hydrogen-bond acceptors owing to their pyridyl rings, and interact with the hydrogen-bond donor carboxyl groups of the BIC molecules. Consequentially, the template is able to selectively immobilize guest molecules with pyridyl terminals of determined distances on a HOPG surface. The hydrogen bonds in the host−guest systems play a significant role in inducing the BIC template formation and thereby producing the resulting host−guest adlayers.

CONCLUSIONS

We have shown that a flexible linear template formed by BIC can accommodate a variety of guest molecules with pyridyl terminals with linear, triangular, and square shapes and different sizes. In all these composite assembly structures, the two hexadecyl chains of BIC molecules are closely packed to form the backbone of the linear structures. The carboxylic acid groups are periodically distributed along the molecular template and act as binding partners for the guest molecules. The guest molecules are accommodated by the BIC molecular template *via* O−H···N hydrogen bonds between the hydrogen-bond donor of the BIC carboxyl groups and the pyridyl terminals of the guest molecules. In response to the packing of the guest molecules with different shapes, sizes, and number into a linear pattern, the unit cell parameters along the transverse ribbon direction are effectively regulated from 3.4 to 7.3 nm. Analysis of these assemblies reveals a modular molecular engineering basis for the versatility of the BIC template. The BIC template may be employed to construct linear patterns of other desired moieties. Although the hydrogen bonding is employed to direct the template assembly process in the present study, the principle demonstrated here can be easily extended to the systems incorporating other intermolecular interaction partners, which is the subject of our further investigation. Finally, we expect that the molecular engineering principle demonstrated in the present system may be applied to the construction of other 2D nanoarchitectures.

EXPERIMENTAL SECTION

The molecule BIC and the guest pyridylethynyl molecules **1**−**6** were synthesized as described in the literature.[42−46] 1-Octanol from Acros Organics with HPLC grade was used as a solvent without further purification.

The self-assembled structures of pure BIC in 1-octanol were prepared by depositing a drop (~2 μL) of solution with a concentration lower than 1×10^{-3} M onto freshly cleaved HOPG with an atomically flat surface (quality ZYB, Digital Instruments, Santa Barbara, CA). After the featured structures were examined with STM,[40] a drop (~2 μL) of a solution containing the guest molecules was added onto the original sample to obtain the molecular template assembly structures.

STM experiments were carried out at the liquid−solid interface with a Nanoscope IIIa scanning probe microscope (Veeco, Santa Barbara, CA) at room temperature. The tunneling tips were prepared by mechanically cut Pt/Ir wires (90/10). All the images were recorded in the constant current mode and shown without further processing. The specific tunneling conditions of each STM image are provided in the corresponding figure caption.

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Supporting Information Available: The assembly structures of BIC in 1-octanol and 1-octanoic acid on HOPG, STM images showing the orientation relationship between the molecular ad-

layer of the BIC template and the graphite lattice, and large-scale STM images of the BIC-**4**, BIC-**5**, and BIC-**6** structures. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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