Hydrogen-Bonded Donor-Acceptor Arrays at the Solution-Graphite Interface


Abstract: Controlling the nanoscale morphology of organic thin films represents a critical challenge in the fabrication of organic (opto)electronic devices. The morphology of the (multi-component) thin films in turn depends on the mutual orientation of the molecular components and their supramolecular packing on the surface. Here we show how the surface co-assembly of electron-donating and -accepting building blocks can be controlled via (supra)molecular design. Hexa-peri-hexabenzocoronene (HBC) derivatives with multiple hydrogen-bonding (H-bonding) sites were synthesized and their co-assembly with alkyl-substituted perylenetetracarboxy diimide (PDI) was studied using scanning tunneling microscopy (STM) at the solution-graphite interface. STM data shows that electron rich HBCs co-assemble laterally with electron deficient PDIs via pre-programmed H-bonding sites with high fidelity. The surface stoichiometry of the two components could be readily tuned by changing the number of H-bonding sites on the HBC derivatives via organic synthesis. This model study highlights the utility of (supra)molecular design in co-assembly of building blocks relevant for organic electronics.

Introduction

The presence of organic electronics in our day-to-day lives is rapidly increasing. The widespread use of organic materials in high-definition displays of smartphones and tablets, curved television screens and portable solar cells is a testimony of how deeply organic electronics has percolated our daily lives. Although still relatively inferior to their inorganic counterparts, semiconducting organic materials are rapidly gaining ground due to some of their unrivalled advantages such as lower production cost, compatibility with a wide range of substrates and tunability of properties via organic synthesis.[1]

An important aspect that distinguishes organic electronics from traditional silicon-based electronics is the ability to define functionality at the molecular level and the solution processability of the materials. The functional part of a typical electronic device consists of a thin film of a semiconducting organic material deposited on a dielectric surface. Precise control over supramolecular organization within such active layers is crucial for obtaining long range-ordered, crystalline films. However, predicting the organization and the resultant thin film morphology, in particular for films prepared via solution processing, has remained a challenge. Given that their internal structure, among other factors, controls the functional properties and thus the performance of the device, much effort has been directed towards engineering the morphology of organic thin films.[2]

The role of supramolecular organization is even more critical for organic optoelectronic devices, where the mutual arrangement of electron donating and accepting units dictates the efficiency of energy/electron transfer processes. Nanoscale phase separation between donor and acceptor units is highly desirable since it provides efficient pathways for charge percolation. Since the physical blending of donors and acceptors often fails to provide the desired control over supramolecular ordering, chemical design strategies have been implemented. One of the intensively explored strategies consists of linking the donor and acceptor units through a covalent bond. Dyads, triads and star-shaped molecules containing covalently connected donor-acceptor units have been synthesized and their energy/electron transfer behavior has been studied.[3]

An alternative approach is to employ supramolecular engineering, where the donor and the acceptor units are linked via non-covalent interactions. Typically, the self-assembly guidelines are encoded at the molecular level in the form of specific functional groups that ensure co-assembly of the donor-acceptor units in the blend. Nanostructured assemblies have been obtained using ionic self-assembly[4] and hydrogen-bonding (H-bonding) interactions.[5] Phase separation has also been promoted by using donor and acceptor molecules containing hydrophobic and fluorophilic groups which are known to hinder miscibility.[6]

A large percentage of donor-acceptor systems used to date employ discotic molecules since they have a propensity to assemble into columnar superstructures in bulk which act as charge transport pathways. Hexa-peri-hexabenzocoronene (HBC) and perylenetetracarboxy diimide (PDI) represent a promising donor-acceptor combination. HBC as well as PDI exhibit excellent charge carrier mobilities and rich self-assembly behavior.[7] Nanophase-separation between the donor (HBC) and...
Results and Discussion

Based on our previous experience with the synthesis and characterization of covalently bonded HBC-PDI dyads, a rigid p-phenyleneethylenel type linker was chosen to introduce H-bonding functionality to the HBC core. In order to increase the interaction strength between the donor and the acceptor units, multiple H-bonding points are desirable instead of single H-bonding contacts. One of the most extensively used structural motifs in supramolecular chemistry is based on the complementary hydrogen-bonding observed between melamine and cyanuric acid. Keeping in mind the melamine-cyanurate type H-bonding adducts, bis-amido pyridine units were appended to the HBC core. These units were equipped with propyl chains for solubility reasons. Each unit provides a donor-acceptor-donor (D-A-D) type H-bonding site which is complementary to the acceptor-donor-acceptor (A-D-A) H-bonding site on the PDI molecule (inset, Scheme 1). In order to tune the stoichiometry of the H-bonded donor-acceptor units, the number of peripherally substituted bis-amido pyridine units was varied. HBC1 possesses two bis-amido pyridine units and four dodecyl chains whereas HBC2 is equipped with six bis-amido pyridine units (Scheme 1). As mentioned above, monoalkylated PDI was chosen as the electron accepting unit since it offers A-D-A-type H-bonding site complementary to that on the HBC derivative. The alkyl substituents installed on the building blocks improve their solubility in organic solvents.

The synthesis of HBC1 and HBC2 is depicted in scheme 2, following a similar Sonogashira coupling synthetic approach used for previously reported alkynyl substituted HBC derivatives. The synthesis of HBC1 and HBC2 was conducted between 1 and 3, affording HBC1 in 67% yield. HBC2 was obtained by a six-fold Sonogashira-coupling between 2 and 3 with the yield of 89%.

In this contribution, we report on the design and synthesis of two novel HBCs and their co-assembly with an alkylmonosubstituted PDI derivative (Scheme 1) at the solution-solid interface. The HBC core is peripherally substituted with H-bonding units that are complementary to the monoalkylated PDI derivative. The self-assembly of the individual building blocks as well as their co-assembly was characterized at the 1,2,4-trichlorobenzene (TCB)/highly oriented pyrolytic graphite (HOPG) interface. STM reveals formation of long-range ordered, defect-free monolayers wherein the mutual arrangement of the donor and the acceptor molecules is defined by the H-bonding units as designed. Furthermore, the different number of H-bonding units on the two HBC derivatives provide a means to tune the on-surface stoichiometry. We show the potential of STM to serve as a complementary tool to test the outcome of design principles employed in the synthesis of organic semiconductors.
Figure 1. Self-assembly behavior of HBC1 at the TCB/HOPG interface (C_{HBC1} = 5.8 \times 10^{-6} \text{ M}). (a, b) Large- and small-scale STM images of HBC1 network, respectively. The graphite symmetry axes are displayed in the lower left corner of (b). Imaging parameters: I_{set} = 80 \text{ pA}, V_{bias} = -1.2 \text{ V}. (c) Proposed molecular model showing the arrangement of molecules in the row structure. (d, e) Large- and small-scale STM images of the Kagomé lattice formed by HBC1. Imaging parameters: I_{set} = 90 \text{ pA}, V_{bias} = -900 \text{ mV}. (f) Proposed molecular model for the Kagomé lattice. The alkyl substituents are not shown for the sake of clarity. For unit cell parameters see Table 1.

Before characterizing the surface co-assembly of the HBCs with PDI, the self-assembly of the individual components was studied at the TCB/HOPG interface. HBC1 forms disordered assemblies at relatively higher concentrations and ordered monolayers are obtained only when relatively dilute solutions are used (supporting information Figure S1). Two-types of ordered networks with drastically different symmetry were observed (Figure 1). The network that dominates the surface coverage consists of linear rows of HBC1 molecules. Figure 1 shows large- (a) and small-scale (b) STM images of the monolayer formed by HBC1. The bright circular features correspond to the HBC cores. Lack of submolecular resolution hindered the clear identification of the bis-amido pyridine units and the alkyl chains. A molecular model built using the unit cell parameters obtained from calibrated STM data is shown in Figure 1c. The molecules are possibly stabilized by H-bonding between the bis-amido pyridine units of adjacent molecules along unit cell vector ‘a’ whereas the van der Waals interactions between dodecyl chains stabilize it along the unit cell vector ‘b’. Thus, the darker regions separating the HBC cores can be assigned to the areas where the dodecyl chains are adsorbed. The distance between adjacent rows is not uniform which could be a result of different arrangement of dodecyl chains within the network as depicted in the model.

A second network, which exhibits a trinangular type tiling (Figure 1d, e), was found to co-exist with the row structure described above (Figure S2 in the supporting information). In contrast to the row structure, the surface coverage as well as the stability of this network was found to be relatively poor. Popularly known as the Kagomé lattice, such networks are characterized by two types of voids that differ in size and symmetry. They consist of equally spaced hexagonal voids that are separated from each other by triangular voids. Figure 1e shows a small-scale image of the Kagomé network. Although highly resolved STM data could not be obtained, the hexagonal voids clearly reveal additional bright spots which could be assigned to (a part) of the bis-amido pyridine units. This network is rather fragile and gets replaced by the row structure upon STM scanning. Figure 1f displays a tentative molecular model showing the proposed packing of HBC1 in the Kagomé network.

Multiple attempts to visualize the self-assembled monolayer of HBC2 at the TCB/HOPG interface were unsuccessful. The lack of self-assembly could stem from the non-planar nature of HBC2. The peripheral bis-amido pyridine units are forced out-of-plane due to steric hindrance that arises from overcrowding. We also note that the solubility of HBC2 in TCB is lower than that of HBC1. PDI self-assembles readily at the TCB/HOPG interface. Large-scale STM images show wavy features covering the HOPG surface (Figure S3 in the supporting information). Smaller scale images reveal that the wavy features are made up of rows of oval

<table>
<thead>
<tr>
<th>System</th>
<th>Unit cell parameters</th>
<th>N [^{\text{[b]}}]</th>
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</thead>
<tbody>
<tr>
<td>HBC1(linear)</td>
<td>a: 2.5 ± 0.1, b: 5.4 ± 0.1, γ: 72 ± 1</td>
<td>2</td>
</tr>
<tr>
<td>HBC1(Kagomé)</td>
<td>a: 4.0 ± 0.1, b: 4.0 ± 0.1, γ: 59 ± 1</td>
<td>3</td>
</tr>
<tr>
<td>HBC2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDI</td>
<td>a: 1.2 ± 0.1, b: 3.2 ± 0.1, γ: 78 ± 1</td>
<td>2</td>
</tr>
<tr>
<td>HBC1-PDI</td>
<td>a: 5.3 ± 0.1, b: 4.7 ± 0.1, γ: 85 ± 1</td>
<td>2HBC1, 4PDI</td>
</tr>
<tr>
<td>HBC2-PDI</td>
<td>a: 5.4 ± 0.3, b: 5.3 ± 0.2, γ: 63 ± 2</td>
<td>1HBC2, 6PDI</td>
</tr>
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</table>

[^{[b]}]: Number of molecules per unit cell.
The co-assembly of organic building blocks in ordered networks often is a challenging task as it involves recognition between two molecules, we now focus on their co-assembly to test if the different molecules and thus well-ordered co-assembled networks are obtained only when their formation is preferred over the self-assembly of individual building blocks. In other words, the self-assembly of the individual components results in the presence of kinks (yellow arrow, Figure 2a) along the molecular rows. Inspection of the high-resolution STM images indicates that these defects do not interrupt the -C=O····H- C(Aromatic) hydrogen bonding between individual PDI molecules (dashed ovals, Figure 2a). The kinks are aperiodic and are not removed upon using dilute solutions and even upon annealing the sample at 80°C (Figure S5 in the supporting information).

Having described the self-assembly of the individual building blocks, we now focus on their co-assembly to test if the supermolecular design works well under these model conditions. The co-assembly of organic building blocks in ordered networks is often a challenging task as it involves recognition between two different molecules and thus well-ordered co-assembled networks are obtained only when their formation is preferred over the self-assembly of individual building blocks. In other words, the formation of a regular two-component network is favored only when the resulting structure is lower in energy compared to the native structures of the individual components.

Given the relatively straightforward self-assembly of HBC1, its surface co-assembly was first attempted with PDI. Based on the design, two molecules of PDI are expected to ‘bind’ to one molecule of HBC1. When a solution prepared by mixing equal volumes of HBC (C_{HBC1} = 3.4 \times 10^{-6} M) and PDI (C_{PDI} = 6.8 \times 10^{-6} M) was drop-cast on HOPG surface, a self-assembled monolayer that appears fundamentally different than that observed for either of the two single components was obtained. Figure 3a shows a representative large-scale STM image that reveals the HBC cores arranged in a zig-zag fashion. This packing is different than the ‘double-row’ structure observed for HBC1 (see Figure 1a) as well as the wavy self-assembly of PDI (see Figure 2a). High-resolution STM images (Figure 3b) clearly show presence of relatively less bright features in between the bright HBC cores. We assign these features to co-adsorbed PDI units. A molecular model (Figure 3c) built on the basis of calibrated STM data indicates a possibility of co-adsorption of two PDI molecules per HBC1 molecule and suggest that the binding could be mediated by H-bonding interactions with the bis-amido pyridine units of HBC1. Besides these heteromolecular H-bonding interactions, based on the relative orientation of the PDI units, homomolecular –C=O····H- C(Aromatic) H-bonding is also possibly involved in the stabilization of the networks (see Figure S6 in the supporting information). The alkyl substituents on the two molecules are adsorbed in the darker regions of STM image and in part control the intermolecular distances, at least along unit cell vector ‘b’. We concede that the arrangement of alkyl substituents proposed in the molecular model is rather tentative and they are possibly mobile on the time-scale of STM measurements or some of them are even back-folded in the solution phase. The co-assembled system is robust and survives annealing up to 80°C at the solution-solid interface.

The HBC1-PDI domains extend several hundred square nm. The network shows high-fidelity in the binding of the donor and the acceptor via the pre-programmed H-bonding thus indicating that the design principles implemented in the synthesis step work reasonably well. The monolayer shows scattered defects in the form of missing PDI units (see Figure S7 in the supporting information). No phase segregation was detected at this solution composition. We note that the perfect match between anticipated surface stoichiometry (HBC1:PDI = 1:2) and the experimentally used solution stoichiometry is rather serendipitous. It is readily expected that the adsorption energy of HBC1 is higher than that of PDI. For experiments targeting multicomponent systems, the difference in the adsorption energies is typically compensated by adjusting the solution mole ratio. As a consequence, the solution composition which leads to formation of a given multicomponent system, is rarely the same as expected from the stoichiometry deduced from an ideal surface-adsorbed system. Besides the adsorption energy, the relative solubility and intermolecular interactions are also at play in multicomponent co-adsorption experiments. In the present case, when equimolar quantities of the two components were used, only phase separated patches of HBC1 and PDI were observed at the TCB/HOPG interface (see Figure S8 supporting information).

Experiments targeting the on-surface co-assembly of HBC2 with PDI were carried out despite the lack of self-assembly of the former. We reasoned that successful formation of H-bonding between the donor and acceptor units will alleviate the non-planarity issue. Furthermore, changing the number of bis-amido pyridine units on the HBC core will also allow to establish whether or not the H-bonding interactions indeed drive the co-assembly with PDI since the surface stoichiometry for this system is...
expected to be HBC2:PDI = 1:6. Given the poor solubility of HBC2 in TCB, the co-assembly experiments were carried out using a mixture of TCB and octanoic acid. Stock solution of HBC2 (1mg/mL) was prepared in octanoic acid and then further diluted to arrive at different mole ratios. When a premixed TCB solution containing HBC2:PDI mole ratio of 1:6 was deposited on the HOPG surface, preferential adsorption of PDI was observed. No co-assembled domains were formed. HBC2 co-assembles with PDI only when the mole ratio is HBC2:PDI = 1:3. At this solution composition, long-range ordered monolayer that consists of star-shaped features is formed at the solution/HOPG interface (Figure 3d) together with phase-separated domains of PDI (See Figure S10 in the supporting information). Each star-shaped feature is composed of a central bright disc that is surrounded by six bright features (Figure 3e).

We assign the central disc to the HBC2 core which is peripherally H-bonded to six PDI units. Lattice parameters obtained from calibrated STM images were used to build a molecular model provided in Figure 3f. The molecular model accurately reproduces the observed matrix and the symmetry of the co-assembled network. In accordance with the supramolecular design, the two molecules interact via H-bonding between D-A-D sites of HBC2 with A-D-A sites of PDI. The co-assembled monolayer shows long-range order, with few missing molecule defects (Figure S11 in the supporting information). The HBC2-PDI system was also found to survive annealing up to 80°C at the solution-solid interface. We note that similar solvent combination (TCB + octanoic acid) when used for self-assembly of HBC2 alone did not yield fruitful results. An interesting aspect of the HBC2-PDI co-assembled system is that long-range ordered arrays are obtained despite the lack of ordered network formation by any of the individual components.

Both co-assembled systems (HBC1-PDI and HBC2-PDI) are relatively challenging for STM imaging. A plausible reason could be formation of multilayers in the vicinity of the solution-solid interface given the anticipated tendency of the building blocks to aggregate in solution via π-stacking. The scanning STM tip removes the higher layers and as a consequence, maintaining stable imaging conditions was found to be challenging. Both co-assembled monolayers are prochiral and opposite handed domains were found to co-exist (see Figure S12 and S13 in the supporting information) on the surface of HOPG. While the STM data clearly reveal successful formation of H-bonded donor-acceptor complexes, it remains to be seen if such organization extends into the bulk. Nevertheless, given the relatively weak molecule-substrate interactions between graphite and aromatic molecules, it is not unreasonable to assume that the H-bonding which dictates self-assembly on surface will also prevail in the solid state. Lastly, the fact that both the bicomponent networks survive annealing to 80°C indicate that the donor-acceptor complexes are not merely kinetically trapped structures. Under the specific experimental conditions used, their formation appears to be driven by thermodynamic considerations.

As mentioned before, the design of H-bonding sites employed here closely resembles (a part of) melamine-cyanuric acid complex which has been intensively studied in self-assembled systems,[12, 18] Similar type of H-bonding moieties have been used in the past in the design of donor-acceptor arrays. Donor-acceptor systems based on oligo(p-phenylene vinylene) (OPVs) as electron donors are the closest to the design presented here.[5c, 19] A melamine derivative with two OPV substituents was synthesized and its co-assembly behaviour with bay-substituted PDI[20] and naphthalene diimide (NDI)[19b] derivatives was studied at the solution-solid interface. While both systems exhibit co-assembly based on H-bonding interactions, the stoichiometry of the donor and acceptors was ill-defined. Furthermore, no long-range order was observed in the co-assembled networks. The
solution processability, long-range order and high-fidelity in the HBC-PDI observed at the solution-Au(111) interface. On the contrary, the HBC-PDI systems described above exhibits relatively better solution processability, long-range order and high-fidelity in the donor-acceptor binding allowing precise control over surface stoichiometry.

Conclusions

Molecularly organized materials which possess well-defined internal structures hold a key towards development of efficient organic (opto)electronic devices. In the work described above, we have illustrated how the surface co-assembly of electron-donating and -accepting building blocks can be controlled via (supra)molecular design. STM revealed that the design strategy implemented in the synthesis of the HBC derivatives works well, at least at the level of single layered films formed at the solution-graphite interface. The monolayers show long-range order with well-defined internal structures. The molecular design approach imparts tunability to the co-assembly wherein the relative number of donor and acceptor units in the film could be defined by the available H-bonding sites on the donor molecule.

Considering the original goal of controlling the surface organization of donor and acceptor molecules via supramolecular design, the results obtained are very promising. It must be noted however, that the present study tests the design principles from a reductionist’s approach and the use of such films for practical applications necessitates further optimization of the film structure. At a very fundamental level, how the morphology of multi-layered films compares to those observed here for monolayers, needs to be investigated. Furthermore, while this study employed graphite as a model substrate to suit the characterization method, namely STM, most organic electronic devices use dielectric surfaces such as SiO$_2$ which are drastically different than graphite. How the surface organization proceeds on such dielectric surface remains to be seen and some of the outstanding issues mentioned above are the subject of ongoing investigation.

Experimental Section

Stock solution of HBC1 (C$_{46}H_{61}N_{12}O_{4}S$; 2.9 × 10$^{-4}$ M) and PDI (8.3 × 10$^{-4}$ M) was prepared by dissolving appropriate amount of solid in 1,2,4-trichlorobenzene (TCB) (Sigma-Aldrich, >99%). Stock solution of HBC2 was prepared by dissolving appropriate amount of solid in octanoic acid (Sigma ≥ 99%). The stock solution was diluted further with TCB to make concentration series. All STM experiments were performed at room temperature (21–23 °C) using a PicoLE (Agilent) machine operating in constant-current mode with the tip immersed in the supernatant liquid. STM tips were prepared by mechanically cutting a PtIr wire (80%/20%, diameter 0.2 mm). Prior to imaging, a drop of solution was placed onto a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG, grade 2YB, Advanced Ceramics Inc., Cleveland, USA). The experiments were repeated in 2-3 sessions using different tips to check for reproducibility and to avoid experimental artefacts, if any. For analysis purposes, recording of a monolayer image was followed by imaging the graphite substrate underneath it under the same experimental conditions, except for increasing the current and lowering the bias. The images were corrected for drift via Scanning Probe Image Processor (SPIP) software (Image Metrology ApS), using the recorded graphite images for calibration purposes, allowing a more accurate unit cell determination. The unit cell parameters were determined by examining at least 4 images and only the average values are reported. The images are Gaussian filtered. The imaging parameters are indicated in the figure caption: tunneling current (I$_{tun}$), and sample bias (V$_{bias}$). The molecular models were built using HyperChem™ 7.0 program.

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Keywords: donor-acceptor • self-assembly • STM • organic electronics • hydrogen-bonding

Self-assembled monolayers formed by hydrogen-bonded donor-acceptor complexes are described. Here we show how the surface co-assembly of electron-donating and -accepting building blocks can be controlled via (supra)molecular design.

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