Hydrogen-bonded donor–acceptor arrays at the solution–graphite interface

Citation for published version (APA):

Velpula, G., Li, M., Hu, Y., Zaganyarski, Y., Pisula, W., Müllen, K., Mali, K. S., & De Feyter, S. (2018). Hydrogen-bonded donor–acceptor arrays at the solution–graphite interface. *Chemistry : A European Journal*, 24(46), 12071-12077. <https://doi.org/10.1002/chem.201803115>

DOI:

[10.1002/chem.201803115](https://doi.org/10.1002/chem.201803115)

Document status and date:

Published: 14/08/2018

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

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

Gangamallai Velpula,^[a] Mengmeng Li,^{[b]#} Yunbin Hu,^[b] Yulian Zagranyski,^[b] Wojciech Pisula,^[b,c] Klaus Müllen,^{*,[b]} Kunal S. Mali,^{*,[a]} and Steven De Feyter^{*,[a]}

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 (multicomponent) 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 organic 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

- [a] Dr. G. Velpula, Dr. K. S. Mali, Prof. S. De Feyter
KU Leuven, Division of Molecular Imaging and Photonics,
Department of Chemistry, Celestijnenlaan 200F, B-3001 Leuven,
Belgium
E-mail: kunal.mali@kuleuven.be, steven.defeyter@kuleuven.be
- [b] Dr. M. Li, Dr. Y. Zagranyski, Dr. Y. Hu, Prof. W. Pisula, Prof. W. Pisula
Max Planck Institute for Polymer Research, Ackermannweg 10,
55128 Mainz, Germany
Email: muellen@mpip-mainz.mpg.de
- [c] Prof. Dr. W. Pisula
Department of Molecular Physics, Faculty of Chemistry, Lodz
University of Technology Zeromskiego 116, 90-924 Lodz, Poland
Email: pisula@mpip-mainz.mpg.de
- # Current address: Molecular Materials and Nanosystems, Institute for
Complex Molecular Systems, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands
Supporting information for this article is given via a link at the end of
the document.

Scheme 1. Molecular structures of **HBC1**, **HBC2** and **PDI**. The inset shows the anticipated H-bonding between the HBC and the PDI units.

the acceptor (PDI) units has been achieved using both covalent and non-covalent methods. Hybrid donor-acceptor molecules, where the HBC and the PDI units are covalently linked to each other, have been synthesized and the efficiency of electron transfer processes has been studied.^[8] Mixing behavior of an alkylated HBC with a PDI derivative containing perfluorinated chains has been studied where the demixing is driven by hydrophobic-fluorophilic interactions.^[6a]

In order to create donor-acceptor interfaces with well-defined internal structures, it is necessary to design and study them at the molecular scale. Direct probing of the internal structures however, is often challenging due to the “buried” nature of the interface. Bulk organization of such materials in the solid-state is usually studied using two-dimensional (2D) wide-angle X-ray scattering.^[9] Since X-ray based methods provide space-averaged information, it is crucial to complement the characterization of these materials using techniques that provide local information on supramolecular organization. Scanning probe microscopy, especially scanning tunneling microscopy (STM), has become a tool of choice for characterization of 2D nanostructured arrays of donor-acceptor systems.^[10] STM provides direct visual cue to the organization of molecules on solid surfaces. Typically, atomically flat conductive substrates are used, and under ideal conditions, sub-nanometer resolution on self-assembled (mono)layers can be obtained.^[11]

In this contribution, we report on the design and synthesis of two novel HBCs and their co-assembly with an alkyl-monosubstituted 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.

Results and Discussion

Based on our previous experience with the synthesis and characterization of covalently bonded **HBC-PDI** dyads,^[8] a rigid p-phenylethylene 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.^[12] 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.¹³

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.^[8, 14] 2,11-dibromo-5,8,14,17-tetradodecylhexabenzocoronene (**1**)^[15] and 2,5,8,11,14,17-hexaiodo-5,8,14,17-tetradodecylhexabenzocoronene (**2**)^[16] were prepared according to the reported procedures, while *N,N'*-(4-ethynylpyridine-2,6-diyl)dibutylamide (**3**) was achieved by a facile three-step synthesis protocol with a total yield of 65% (see supporting information for details). A two-fold Sonogashira-coupling reaction 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%.

Scheme 2. Synthesis of **HBC1** and **HBC2**.

Figure 1. Self-assembly behavior of **HBC1** at the TCB/HOPG interface ($C_{\text{HBC1}} = 5.8 \times 10^{-6}$ 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: $I_{\text{set}} = 80$ pA, $V_{\text{bias}} = -1.2$ 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: $I_{\text{set}} = 90$ pA, $V_{\text{bias}} = -900$ 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 trihexagonal 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 1. Structural parameters of the self-assembled systems.

System	Unit cell parameters			N ^[b]
	a	b	γ	
HBC1 (linear)	2.5 ± 0.1	5.4 ± 0.1	72 ± 1	2
HBC1 (Kagomé)	4.0 ± 0.1	4.0 ± 0.1	59 ± 1	3
HBC2	-	-	-	-
PDI	1.2 ± 0.1	3.2 ± 0.1	78 ± 1	2
HBC1-PDI	5.3 ± 0.1	4.7 ± 0.1	85 ± 1	2 HBC1 , 4 PDI
HBC2-PDI	5.4 ± 0.3	5.3 ± 0.2	63 ± 2	1 HBC2 , 6 PDI

[b] Number of molecules per unit cell.

Figure 2. (a) Representative STM image of PDI network self-assembled at the TCB/HOPG interface ($C_{\text{PDI}} = 1.7 \times 10^{-4}$ M). The yellow arrow highlights a kink in the molecular row. The aromatic cores are highlighted by white ovals at a kink site. The graphite symmetry axes are shown in the lower left corner. Imaging parameters: $I_{\text{set}} = 100$ pA, $V_{\text{bias}} = -400$ mV. Unit cell parameters are provided in Table 1. (b) Molecular model showing the arrangement of PDI molecules in the self-assembled monolayer. The molecules are shown with only the octyl chain for the sake of clarity. For large scale STM images, see Figure S3 in the supporting information.

shaped structures which can be assigned to the aromatic backbone of **PDI**. Their pairwise appearance indicates presence of H-bonded dimers on the surface as anticipated from the H-bonding sites on **PDI**. Adjacent dimers are shifted by almost half a molecule with respect to each other. This shift indicates that pairs of adjacent dimers (along the same row) also interact with each other *via* weak $\text{C}=\text{O} \cdots \text{H}-\text{C}(\text{Aromatic})$ interactions (see Figure S4 in supporting information). Molecular models indicate that there is not enough space in between adjacent molecules for the adsorption of both alkyl chains per molecule. The chains that are not adsorbed on the surface are possibly back-folded in the supernatant solution phase. A peculiar feature of the **PDI** monolayer is 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 $\text{N}-\text{H} \cdots \text{O}=\text{C}-$ 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 supramolecular 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** ($C_{\text{HBC1}} = 3.4 \times 10^{-6}$ M) and **PDI** ($C_{\text{PDI}} = 6.8 \times 10^{-6}$ 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 $\text{C}=\text{O} \cdots \text{H}-\text{C}(\text{Aromatic})$ 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 units *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 network.^[17] 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

Figure 3. Co-assembly of HBCs and PDI at the TCB/HOPG interface. (a, b) Large- and small-scale STM images of **HBC1-PDI** co-assembled network, respectively. ($C_{\text{HBC1}} = 3.4 \times 10^{-6}$ M and $C_{\text{PDI}} = 6.8 \times 10^{-6}$ M) Imaging parameters: $I_{\text{set}} = 80$ pA, $V_{\text{bias}} = -1.35$ V (c) Proposed molecular model for the **HBC1-PDI** co-assembled network. **HBC1** is shown with only two alkyl chains whereas the **PDI** is shown with only an octyl chain for the sake of clarity. (d, e) Large- and small-scale STM images of **HBC2-PDI** co-assembled network, respectively. Imaging parameters: $I_{\text{set}} = 60$ pA, $V_{\text{bias}} = -1.0$ V. ($C_{\text{HBC2}} = 4.0 \times 10^{-6}$ M and $C_{\text{PDI}} = 1.2 \times 10^{-5}$ M). (e) Proposed molecular model for the co-assembly of **HBC2-PDI**. **HBC2** is shown without any alkyl substituents whereas **PDI** is shown with only an octyl chain for the sake of clarity. For additional STM images, see Figure S9 in the supporting information.

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 using TCB to make a series of concentrations. These solutions were then mixed with appropriate quantities of TCB solutions of **PDI** 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)s (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^[3b] 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

lack of crystallinity in the OPV-PDI and OPV-NDI systems could originate from the relatively flexible nature of the OPV building blocks. In comparison to the covalent HBC-PDI dyads reported earlier^[8], the present system shows better solution processability. In the case of former, only isolated single molecules were 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 SiO₂ 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 ($C_{\text{HBC1}} = 2.9 \times 10^{-4}$ 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 $\geq 99\%$). 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 Pt/Ir 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 ZYB, 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_{set}), and sample bias (V_{bias}). The molecular models were built using HyperchemTM 7.0 program.

Acknowledgements

G. V. acknowledges award of Marie Skłodowska-Curie individual fellowship (number 706314, GRAPHIL). This work is supported by the Fund of Scientific Research–Flanders (FWO), KU Leuven –Internal Funds, Belgian Federal Science Policy Office (IAP-7/05), and European Research Council under the European Union's Seventh Framework Programme (FP7/2007–2013)/ERC Grant Agreement No. 340324. M. L. acknowledges the funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 747422.

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

- [1] J. Yang, D. Yan and T. S. Jones, *Chem. Rev.* 2015, 115, 5570–5603.
- [2] M. Hong, Y. Hin - Lap, H. Fei and J. A. K. - Y., *Adv. Funct. Mater.* 2010, 20, 1371–1388.
- [3] a) M. Wang and F. Wudl, *J. Mater. Chem.* 2012, 22, 24297–24314; b) A. Miura, Z. Chen, H. Uji-i, S. De Feyter, M. Zdanowska, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, F. Würthner and F. C. De Schryver, *J. Am. Chem. Soc.* 2003, 125, 14968–14969.
- [4] J. López-Andarias, M. J. Rodríguez, C. Atienza, J. L. López, T. Mikié, S. Casado, S. Seki, J. L. Carrascosa and N. Martín, *J. Am. Chem. Soc.* 2015, 137, 893–897.
- [5] a) B. H. T. and P. D. F., *Angew. Chem. Int. Ed.* 2014, 53, 2138–2142; b) B. Feringán, P. Romero, J. L. Serrano, C. L. Folcia, J. Etxebarria, J. Ortega, R. Termine, A. Golemme, R. Giménez and T. Sierra, *J. Am. Chem. Soc.* 2016, 138, 12511–12518; c) F. Würthner, Z. Chen, F. J. M. Hoeben, P. Osswald, C.-C. You, P. Jonkheijm, J. v. Herrikhuizen, A. P. H. J. Schenning, P. P. A. M. van der Schoot, E. W. Meijer, E. H. A. Beckers, S. C. J. Meskers and R. A. J. Janssen, *J. Am. Chem. Soc.* 2004, 126, 10611–10618.
- [6] a) G. De Luca, A. Liscio, M. Melucci, T. Schnitzler, W. Pisula, C. G. Clark, L. M. Scolaro, V. Palermo, K. Mullen and P. Samori, *J. Mater. Chem.* 2010, 20, 71–82; b) H. Y. Li, C. Wei, L. Hui, M. Jing, P. Jens and W. A. T. Shen, *Small* 2010, 6, 70–75.
- [7] a) C. Zhijian, D. M. G., D. Tony, O. Peter and W. Frank, *Chemphyschem* 2004, 5, 137–140; b) K. Daniel, B. Asif, D. Xi, W. Gregor, M. Klaus and W. Christof, *Adv. Mater.* 2010, 22, 384–388.
- [8] L. F. Dössel, V. Kamm, I. A. Howard, F. Laquai, W. Pisula, X. Feng, C. Li, M. Takase, T. Kudernac, S. De Feyter and K. Müllen, *J. Am. Chem. Soc.* 2012, 134, 5876–5886.
- [9] a) X. Feng, W. Pisula, M. Takase, X. Dou, V. Enkelmann, M. Wagner, N. Ding and K. Müllen, *Chem. Mater.* 2008, 20, 2872–2874; b) L. Chen, K. S. Mali, S. R. Puniredd, M. Baumgarten, K. Parvez, W. Pisula, S. De Feyter and K. Müllen, *J. Am. Chem. Soc.* 2013, 135, 13531–13537.
- [10] J. L. Zhang, S. Zhong, J. Q. Zhong, T. C. Niu, W. P. Hu, A. T. S. Wee and W. Chen, *Nanoscale* 2015, 7, 4306–4324.
- [11] J. A. A. W. Elemans, S. Lei and S. De Feyter, *Angew. Chem. Int. Ed.* 2009, 48, 7298–7332.
- [12] A. G. Slater, L. M. A. Perdigão, P. H. Beton and N. R. Champness, *Acc. Chem. Res.* 2014, 47, 3417–3427.

- [13] J. Wu, W. Pisula, and Klaus Müllen, *Chem. Rev.* 2007, 107, 718–747.
- [14] H. Yunbin, D. L. F., W. Xiao - Ye, M. Sankarapillai, P. Wojciech, D. F. Steven, F. Xinliang, M. Klaus and N. Akimitsu, *ChemPlusChem* 2017, 82, 1030-1033.
- [15] Y. Xiaoyin, D. Xi and M. Klaus, *Chem. Asian J.* 2008, 3, 759-766.
- [16] J. Wu, M. Baumgarten, M. G. Debije, J. M. Warman and K. Müllen, *Angew. Chem. Int. Ed.* 2004, 43, 5331-5335.
- [17] G. Velpula, T. Takeda, J. Adisojoso, K. Inukai, K. Tahara, K. S. Mali, Y. Tobe and S. De Feyter, *Chem. Commun.* 2017, 53, 1108-1111.
- [18] a) J. Teyssandier, N. Battaglini, M. Seydou, G. Anquetin, B. Diawara, X. Sun, F. Maurel and P. Lang, *J. Phys. Chem. C* 2013, 117, 8737-8745; b) J. A. Gardener, O. Y. Shvarova, G. A. D. Briggs and M. R. Castell, *J. Phys. Chem. C* 2010, 114, 5859-5866.
- [19] a) F. J. M. Hoebe, J. Zhang, C. C. Lee., M. J. Pouderoijen, M. Wolffs, F. Würthner, A. P. H. J. Schenning, E. W. Meijer, and S. De Feyter, *Chem. Eur. J.* 2008, 14, 8579-8589; b) I. De Cat, C. Roger, C. C. Lee, F. J. M. Hoebe, M. J. Pouderoijen, A. P. H. J. Schenning, F. Würthner and S. De Feyter, *Chem. Commun.* 2008, 5496-549

FULL PAPER

Entry for the Table of Contents

FULL PAPER

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.

Gangamallai Velpula, Mengmeng Li, Yunbin Hu, Yulian Zagaryarski, Wojciech Pisula, Klaus Müllen, Kunal S. Mali,* and Steven De Feyter**

Page No. – Page No.

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