Modification of graphite surfaces for the adsorption of molecular motors

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To develop functional two-dimensional structures it is desirable to have access to many versatile building blocks for self-assembly at the liquid-solid interface. Here we report a new type of molecular template to adsorb small alkoxy-pyrene derivatives. The results in this chapter demonstrate that building blocks which could not be adsorbed on the bare graphite surface can be absorbed with our template in a remarkable zipper array.

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Chapter 5

5.1 Introduction

Self-assembly is a powerful tool for the bottom-up fabrication of well-defined and long-range ordered two-dimensional (2D) architectures at surfaces.\(^1\) Nanostructures constructed from multiple building blocks add to the versatility of the adlayer in terms of both spatial arrangement and function of the molecules. Precisely controlling the two-dimensional (2D) organization of functional molecules on surfaces is of great importance for the formation of functional supramolecular architectures.\(^2\) The designs of such architectures is limited to the use of building blocks which either have enough affinity with the underlying surface and/or strong interadsorbate interactions.\(^3,4\) New strategies must be developed to get access to a broader scope of building blocks. Several strategies for the fabrication of supramolecular multicomponent adsorbed systems at the liquid/solid interface have been reported including multiple host-guest strategies e.g. via the formation of porous networks\(^5-10\), core-shell systems\(^11\) or through a metal-ligand coordination on a porphyrin template.\(^12\) Where most multicomponent assemblies are based on host-guest interactions an alternative system was reported Zimmt et. al. where the four-component assembly was driven by complementary shapes and lengths of different alkadiyne side chains.\(^13\) An improvement to the field will be the fabrication of templates to facilitate the adsorption of new building blocks with insufficient affinity with the surface.

![Figure 5.1](image)

**Figure 5.1** Schematic representation of the template strategy for the adsorption of alkoxy-pyrene derivatives on HOPG.

Here we investigate the possibility of using an self-assembled monolayer of alkylated naphthalenediimide (NDI) on highly oriented pyrolytic graphite (HOPG) as adsorption template for alkoxy-pyrene derivatives (Figure 5.1). Exemplifying the necessity of this approach, any attempt to adsorb the alkoxy-pyrenes presented in Scheme 5.1 (except for 1-butoxypyrene) did not succeed under our experimental conditions. The use of
Templated Alkoxy-Pyrene Adsorption within an Alkylated NDI Adlayer on Graphite

NDI adlayers to trap these alkoxy-pyrene moieties was intuitively promising because of the electron-accepting nature of the NDI-cores and the electron-donating nature of the alkoxy-pyrenes.

**Scheme 5.1** Chemical structures of the used pyrene-derivatives, 1-methoxypyrene (PyrOMe), methyl 1-pyrenyl sulfide (PyrSMe), 1-ethoxypyrene (PyrOEt), 1-propoxypyrene (PyrOPr), 1-butoxypyrene (PyrOBu) and the chemical structure of uC33-NDI-uC33 with an internal double bond between carbon 11 and 12 in both alkyl chains. The compounds were synthesized using reported procedures.14–20

Alkylated NDI molecules have been proven to be good candidates for 2D surface engineering.21,22 The self-assembly of these molecules was previously investigated and showed the presence of lamellar structures at the solvent/HOPG interface for symmetrical NDIs functionalized with linear alkyl chains with a number of carbons ≥18.21–23 Moreover, there was a paramount role for the internal double bond i.e. the long-range order increased by the insertion of an internal double bond in the alkyl chains. The uC33-NDI-uC33 molecules form robust adlayers with large domains (see Chapter 3) and are therefore our template of choice.21 Furthermore, in this chapter, we investigate the possible use of the uC33-NDI-uC33 template as surface-infrastructure for third-generation molecular motors with alkoxy-pyrene linkers. We envision that the alkoxy-pyrene moieties can be used to anchor the molecular motor on the uC33-NDI-uC33 adlayer.

5.2 **Results and discussion**

5.2.1 **Alkoxy-pyrene adsorption**

By the use of a molecular template we envision to get access to a larger variety of adsorbates. The first molecule we attempted to adsorb via this molecular template was 1-methoxypyrene (PyrOMe), a small pyrene-derivative from which previous attempts to adsorb this compound at the bare n-octanoic acid/HOPG interface failed. Adlayers of uC33-NDI-uC33 molecules were prepared in the same way as reported in chapters 3 and 4.21,22 The solution of uC33-NDI-uC33 in 1-phenyloctane (0.4 mg/mL) was drop casted at 100 °C onto a freshly cleaved HOPG substrate. Prior to the deposition of the PyrOMe solution, the substrate with the uC33-NDI-uC33 adlayer was vigorously rinsed with n-octanoic acid to remove the excess of NDIs. It was confirmed by STM measurements that the adlayer was still intact after the rinsing step (Appendix 5A).
Chapter 5

Upon deposition of **PyrOMe** in *n*-octanoic acid on top of the NDI adlayer new protrusions appeared alongside the NDI cores in a zipper-like fashion (Figure 5.2a). This was not expected since we envisioned a stacked donor-acceptor complex. From the experimental observations we concluded the presence of a nucleation process. Isolated pyrenes were seldom observed, while domains with adsorbed pyrenes did grow over time (Appendix 5A). To investigate the adaptivity of the template, we substituted the oxygen atom in **PyrOMe** for a larger sulfur atom i.e. methyl 1-pyrenyl sulfide (PyrSMe). A similar assembly, as for **PyrOMe**, was observed after depositing a **PyrSMe** solution in *n*-octanoic acid on top of the *uC*₃₃-NDI-*uC*₃₃ adlayer (Figure 5.2b). This demonstrated that possible interactions were not affected and that the system is reproducible. It should be emphasized that both molecules, **PyrOMe** and **PyrSMe** could not be adsorbed on a bare HOPG surface while these compounds can now be trapped with the use of a molecular template (Figure 5.2a-b).

**Figure 5.2** STM topography images after the deposition of **PyrOMe** and **PyrSMe**, using different solvents, on top of the *uC*₃₃-NDI-*uC*₃₃ adlayer. a) Adsorption of PyrOMe within the *uC*₃₃-NDI-*uC*₃₃ template in *n*-octanoic acid (25 nm × 25 nm, *V*<sub>tip</sub> = 1 V, *I*<sub>set</sub> = 50 pA). b) Adsorption of PyrSMe within the *uC*₃₃-NDI-*uC*₃₃ template in *n*-octanoic acid (35 nm × 35 nm, *V*<sub>tip</sub> = 1 V, *I*<sub>set</sub> = 100 pA). c) Adsorption of PyrOMe within the *uC*₃₃-NDI-*uC*₃₃ template in 1-phenyloctane (35 nm × 35 nm, *V*<sub>tip</sub> = 1 V, *I*<sub>set</sub> = 60 pA). d) Adsorption of PyrSMe within the *uC*₃₃-NDI-*uC*₃₃ template in *n*-tetradecane (35 nm × 35 nm, *V*<sub>tip</sub> = 1 V, *I*<sub>set</sub> = 100 pA).
5.2.2 Influence of solvent molecules
To get more insight in the working mechanism of this template we examined the possible influence of the solvent. Several studies have shown that solvent molecules can influence the 2D-assembly. By varying the solvent we change the solubilizing nature of the solvent and study if there is any co-adsorption of solvent molecules promoting the adsorption of the pyrene-derivatives. We investigated three different solvents; n-octanoic acid which can possibly co-adsorb on the surface via hydrogen-bond interactions with either the NDI-core or the alkoxy-pyrene, 1-phenyloctane and n-tetradecane on the other hand would not be able to interact via hydrogen bonds. Furthermore, n-tetradecane is a rather large solvent molecule, it is therefore likely that if there is any co-adsorption of n-tetradecane it will be revealed by STM. PyrOMe and PyrSMe were dissolved in 1-phenyloctane and n-tetradecane, respectively, and deposited on the uC\textsubscript{33}-NDI-uC\textsubscript{33} template after the template was rinsed with the respective solvent. Figure 5.2c-d shows that the adsorption behavior in 1-phenyloctane and n-tetradecane is similar to that of the systems in n-octanoic acid (Figure 5.2a-b). We therefore conclude that the solvent molecules do not play a significant role in the adsorption of PyrOMe and PyrSMe. The high rigidity and reproducibility of this molecular NDI-template was demonstrated in three different solvents.

5.2.3 Size dependence of alkoxy-pyrenes
To extend the scope for this adsorption template we studied alkoxy-pyrenes with longer alkyl chains i.e. 1-ethoxy-pyrene (PyrOEt) and 1-propoxy-pyrene (PyrOPr). Like PyrOMe and PyrSMe, we could not adsorb PyrOEt and PyrOPr at the bare n-octanoic acid/HOPG interface under ambient conditions. Upon deposition of PyrOEt from n-octanoic acid on top of the uC\textsubscript{33}-NDI-uC\textsubscript{33} template, the same zipper-like adsorption pattern was visible in the STM images (Figure 5.3a) as was observed for PyrOMe and PyrSMe (Figure 5.2).

Figure 5.3 STM topography images after the deposition of PyrOEt and PyrOPr on top of the uC\textsubscript{33}-NDI-uC\textsubscript{33} adlayer in n-octanoic acid. a) Adsorption of PyrOEt (25 nm × 25 nm, V\textsubscript{tip} = 1 V, I\textsubscript{set} = 10 pA). b) Adsorption of PyrOPr (25 nm × 25 nm, V\textsubscript{tip} = 1.4 V, I\textsubscript{set} = 15 pA).
The overall coverage of alkoxy-pyrene derivatives decreased upon increasing the alkyl chain length. The last compound we examined was 1-butoxy-pyrene (pyrOBu). PyrOBu could still be trapped on the surface via the NDI-template, however, the coverage was rather low. Increasing the concentration of the PyrOBu resulted in an adlayer entirely consisting of PyrOBu (Appendix 5B). This indicates that the pockets formed upon adsorption are of a distinct size or that the alkyl chain is interfering with the interaction of the pyrene with either the NDI-core or the internal double bond of the alkyl chain.

5.2.4 NDI core separation
To investigate why there is a limit in terms of alkyl chain length for the adsorption of alkoxy-pyrenes, we compared the assemblies of the adlayer with and without the presence of the pyrene-derivatives. Figure 5.4 shows two profile plots, one of the assembly after the adsorption of PyrSMe in n-octanoic acid on top of the NDI adlayer (top profile plot), and one plot of an area after the deposition but without adsorbed pyrenes near the NDI cores (bottom plot). The profile plots cover a length of approximately 42 nm and show that there are seven repetitive units in the first case and eight in the latter. Which illustrates, that upon adsorption of the pyrene-derivatives, the lamellae have broadened.

![Profile plot over about 42 nm, showing seven columns after adsorption (top) and eight columns of NDI cores in the original (bottom) adlayer. This indicates that the pyrene molecules do take up more space. STM topography image of PyrSMe adsorption within the uC33-NDI-uC33 adlayer in n-octanoic acid (V_tip = 1 V, I_set = 50 pA).](image-url)
Previously the unit cell of the $\text{uC}_{33}$-$\text{NDI}$-$\text{uC}_{33}$ at the 1-phenyloctane/HOPG interface was reported as $a=5.27 \pm 0.08$ nm, $b=0.94 \pm 0.06$ nm, $\gamma=84.93 \pm 1.80^\circ$ (see Chapter 3). After the deposition of PyrOMe on the $\text{uC}_{33}$-$\text{NDI}$-$\text{uC}_{33}$ adlayer, the unit cell changed substantially. The distance $a_{\text{PyrOMe}}$ (indicated in Figure 5.5) is estimated to be $6.05 \pm 0.15$ nm (average value for the assemblies in 1-phenyloctane and $n$-octanoic acid). The increased value of $a_{\text{PyrOMe}}$ compared to $a$, which represents the distance between the NDI-cores in two different columns, indicates that the adsorption of the pyrenes occurs next to the NDI-cores rather than on top.

### 5.2.5 Adsorption motif

The exact adsorption motif of the alkoxy-pyrene derivatives is not yet understood. High-resolution STM images confirmed the presence of the NDI’s alkyl-chains, it is therefore likely to assume that also the cores are still present in a similar assembly as in the original adlayer. Based on the experimental data we hypothesize that the alkoxy-pyrenes push the NDI-cores apart upon adsorption, creating small pockets of distinct size next to the NDI-cores within the adlayer. However, from the experimental data it was not possible to assign the exact position and orientation of the alkoxy-pyrenes and the NDI’s. In Figure 5.5 we propose a schematic representation of the possible zig-zag assembly.

![Figure 5.1 Schematic representation of possible molecular model of PyrOMe molecules within the $\text{uC}_{33}$-$\text{NDI}$-$\text{uC}_{33}$ adlayer. Values $a_{\text{PyrOMe}}$ and $b_{\text{PyrOMe}}$ are measured to be $6.05 \pm 0.15$ nm and $1.84 \pm 0.22$ nm, respectively.](image)

The sensitivity of the molecular template made from $\text{uC}_{33}$-$\text{NDI}$-$\text{uC}_{33}$ was illustrated when similar molecules were used to serve as a template. None of the following molecules, $\text{uC}_{28}$-$\text{NDI}$-$\text{uC}_{28}$, $\text{C}_{33}$-$\text{NDI}$-$\text{C}_{33}$, $\text{u}_{2}\text{C}_{44}$-$\text{NDI}$-$\text{u}_{2}\text{C}_{44}$, and $\text{u}_{3}\text{C}_{50}$-$\text{NDI}$-$\text{u}_{3}\text{C}_{50}$ (see Chapters 3 and 4) was able to significantly assist the adsorption of alkoxy-pyrene derivatives (Appendix 5B). The presence and the position of the internal double bond is presumable playing an important role which is not yet understood.
5.2.6 Third-generation molecular motor

In the previous paragraphs we have demonstrated that PyrOMe can be adsorbed via the template of uC33-NDI-uC33 molecules. The exact binding motif of this system is not yet understood, however, the system is attractive for further applications. Our ambition is to create molecular surface-infrastructures to guide molecular motors along a trajectory. It was demonstrated that the uC33-NDI-uC33 molecules form robust and long-range ordered adlayers (Chapter 3) and that we can adsorb alkoxy-pyrene derivatives on top of this molecular infrastructure. Based on these findings a third-generation molecular motor was designed with two methoxypyrene linkers to be adsorbed on the molecular ‘high-way’ of uC33-NDI-uC33 molecules.

![Figure 5.2 Schematic representation of, a) the molecular high-way from uC33-NDI-uC33 molecules, b) adsorbed alkoxy-pyrene molecules on top of the molecular high-way and c) third-generation molecular motor with alkoxy-pyrene linkers on top of the molecular high-way. This graphical abstract was illustrated by Mathijs Mabesoone.](image)

The target motor (Figure 5.7) has two distinct groups attached at the pseudo-asymmetric carbon atom of the core i.e. phenyl and methyl, which makes the rotation of the motor unidirectional.29,30 At the other side of the core, a o-terphenyl bridge separates the two legs of the motor. The two legs with the alkoxy-pyrene linkers are connected to the bridge with a C5-chain. The alkyl chain induces some flexibility in the system which ideally induces a paddling motion of the motor. We envisioned that the linkers adsorb on both side of the NDI core and upon rotation one linker detached and will attach again at a new position.

The molecular surface infrastructures of uC33-NDI-uC33 molecules were prepared in the same way as described before i.e. the solution of uC33-NDI-uC33 in 1-phenyloctane (0.4 mg/mL) was drop casted at 100 °C onto a freshly cleaved HOPG substrate. Prior to the deposition of the third-generation molecular motors with alkoxy-pyrene linkers, the substrate with the adlayer was vigorously rinsed with the solvent which was used to dissolve the motor. The first experiments were performed in 1-phenyloctane, solutions of 7.7×10⁻⁴M or saturated solutions have been deposited on top of the adlayer at room temperature or at 150°C. In none of the cases molecular motors were observed on the surface. The second set of experiments was carried out in n-octanoic acid. Solutions of 4×10⁻⁵M and saturated solutions (approximately 8×10⁻⁵
were deposited at the adlayer at room temperature or 150°C. The subsequent STM measurements did likewise not reveal any adsorption of molecular motors on the surface. The molecular motor could also not be adsorbed using pre-mixed solutions (uC₃₃-NDI-uC₃₃/motor) or on bare HOPG.

**Figure 5.3** Third-generation molecular motor with alkoxy-pyrene linkers. a) Chemical structure of the target motor (synthesized by José Berrocal). Molecular model of the target motor b) sight view and c) top view.

### 5.3 Conclusion

In conclusion, we demonstrated that the uC₃₃-NDI-uC₃₃ adlayer can serve as a trapping template for the adsorption of small alkoxy-pyrene derivatives. These alkoxy-pyrenes i.e. PyrOMe, PyrSMe, PyrOEt and PyrOPr could not be adsorbed on a bare HOPG substrate, where they can be adsorbed if supported by an uC₃₃-NDI-uC₃₃ template. We demonstrated that this strategy is reproducible and suitable for different alkoxy-pyrene derivatives in various solvents. This research allows for a larger variety of building blocks for surface assembly and paves the path towards engineering complex 2D-crystals. Furthermore, we investigated the possible use of this uC₃₃-NDI-uC₃₃ template for the adsorption of third-generation molecular motors with alkoxy-pyrene linkers. Unfortunately, it was, so far, not possible to adsorb the molecular motors on the uC₃₃-NDI-uC₃₃ adlayer.

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José Berrocal and professor Bert Meijer are thankfully acknowledged for the fruitful collaboration on this project. José was responsible for the synthesis of uC₃₃-NDI-uC₃₃ (see Chapter 3), C₁-NDI-C₁ and the third-generation molecular motor with pyrene linkers. Mathijs Mabesoone is greatly acknowledged for the illustrations (Figure 5.2).

### 5.4 Experimental

STM measurements: All experiments were performed at room temperature (21-25 °C) using a Molecular Imaging STM operating in constant-current mode at the solvent/HOPG interface. STM tips were prepared by mechanical cutting of Pt/Ir wire (90/10, diameter 0.25 mm, Goodfellow). The solution of the template molecules was prepared by dissolving uC₃₃-NDI-uC₃₃ (0.4 mg/ml) in 1-phenyloctane (>98.0%,
The NDI solution was heated to 100 °C and subsequently drop casted onto a freshly cleaved HOPG surface (ZYB grade, Bruker AFM probes). Next, the \textit{uC}_{33}-NDI-\textit{uC}_{33} layer was vigorously rinsed with the solvent used in the pyrene adsorption experiments (1-phenyloctane, \textit{n}-octanoic acid or \textit{n}-tetradecane) and imaged with the STM before the deposition of the pyrene-derivatives. In order to perform the STM measurements it was required that the adsorbates were as pure as possible. \textit{PyrOMe} (1.9×10^{-1} mbar at 130°C) and \textit{PyrOPr} (4.0×10^{-2} mbar at 155°C) were purified by sublimation prior to the STM experiments. \textit{PyrOEt} and \textit{PyrSMe} were recrystallized from MeOH prior to the STM experiments. \textit{PyrOBu} was further purified by another flash column chromatography (pentane/DCM(0-10%)) in order to obtain a white solid. The purified alkoxy-pyrene derivatives were dissolved in 1-phenyloctane (>98.0%, purchased by TCI), \textit{n}-octanoic acid (>98.0%, purchased by TCI) or \textit{n}-tetradecane (>99.5%, purchased by TCI) and drop casted on top of \textit{uC}_{33}-NDI-\textit{uC}_{33} at room temperature. All STM images were analyzed and processed using WSxM 5.0. All bias values are given with respect to a grounded tip.

**General remarks synthesis:** Chemicals were purchased from Sigma-Aldrich or TCI Europe. Column chromatography was performed on silica gel (SiO\textsubscript{2}) purchased from Merck (230-400 mesh) or on an auto column (Büchi Reveleris system with Büchi cartridges). Melting points (mp) were determined using a Büchi-B545 capillary melting point apparatus. The \textit{\textsuperscript{1}}H and \textit{\textsuperscript{13}}C NMR spectra were acquired on a Varian Mercury-Plus 400 MHz at 298K. Chemical shifts are denoted in \textit{δ} values (ppm) relative to the residual solvent signal (for CHCl\textsubscript{3} \textit{\textsuperscript{1}}H: \textit{δ} = 7.26 and \textit{\textsuperscript{13}}C: \textit{δ} = 77.16, for DMSO \textit{\textsuperscript{1}}H: \textit{δ} = 2.50). For \textit{\textsuperscript{1}}H NMR the splitting parameters are designated as follows: s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). High resolution mass spectroscopy (HRMS) was performed on a Thermo Fischer Scientific LTQ Orbitrap XL with ESI or APCI ionization sources.

**1-methoxypyrene (PyrOMe):** 1-hydroxypyrene (501 mg, 2.3 mmol) was added to a mixture of Na\textsubscript{2}CO\textsubscript{3} (900 mg, 8.4 mmol) and MeI (540 mg, 3.8 mmol) in DMF (15 mL) under nitrogen atmosphere. The reaction mixture was heated to 60°C and stirred overnight. The mixture was diluted in ether (100 mL) after cooling to rt and washed with brine (2× 150 ml). The aqueous phases were combined and extracted with ether (150 mL). The organic layer was subsequently washed with brine and dried over MgSO\textsubscript{4} prior to the evaporation of the solvent under reduced pressure. The residue was purified by flash column chromatography (pentane/DCM(0-20%)) to yield 1-methoxypyrene (475 mg, 2.0 mmol, 89% yield) as a white solid. mp: 88-89°C. \textit{\textsuperscript{1}}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{δ} (ppm) 8.46 (d, \textit{J} = 9.2 Hz, 1H), 8.13 – 8.04 (m, 4H), 7.98 – 7.94 (m, 2H), 7.89 (d, \textit{J} = 8.9 Hz, 1H), 7.76 (d, \textit{J} = 8.4 Hz, 1H), 4.18 (s, 3H). \textit{\textsuperscript{13}}C NMR (101 MHz, CDCl\textsubscript{3}): \textit{δ} (ppm) 153.8, 131.9, 131.8, 127.4, 126.5, 126.2, 126.0, 125.6, 125.4, 125.1, 124.4, 124.3, 121.3, 120.4, 108.2, 56.3. HRMS (ESI+, m/z): Calcd for C\textsubscript{17}H\textsubscript{13}O [M+H\textsuperscript{+}]: 233.0966, found: 233.0959. These results match with previously reported data on 1-methoxypyrene.\textsuperscript{14-17}
1-ethoxypyrene (PyrOEt): 1-hydroxypyrene (500 mg, 2.3 mmol) was added to a mixture of Na₂CO₃ (600 mg, 5.6 mmol) and ethyl iodide (430 mg, 2.8 mmol) in DMF (15 ml) under nitrogen atmosphere. The reaction mixture was stirred at 60°C overnight. To push the reaction to full conversion, excess Na₂CO₃ (200 mg, 1.9 mmol) and ethyl iodide (978 mg, 6.3 mmol) was added and the reaction mixture was allowed to cool down to rt after 4 h. The mixture was dissolved in EtOAc (50 ml) and washed with H₂O (50 ml). The organic layer was subsequently washed with H₂O (50 ml) and brine (50 ml) and dried over MgSO₄. The volatiles were removed in vacuo and the residue was recrystallized from MeOH* prior to purification by flash column chromatography (pentane/DCM(0-10%)) yielding an off white solid. The solid was recrystallized twice in MeOH and EtOH to yield a white solid (271 mg, 1.1 mmol, 49%). mp: 71 °C (lit. 72-73 °C).¹⁸ ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.50 (d, J = 9.1 Hz, 1H), 8.13 – 8.04 (m, 4H), 7.98 – 7.94 (m, 2H), 7.89 (d, J = 8.9 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 4.40 (q, J = 6.9 Hz, 2H), 1.64 (t, J = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 153.3, 131.9, 131.9, 127.4, 126.4, 126.2, 126.0, 125.6, 125.3, 125.1, 125.1, 124.3, 124.2, 121.5, 120.6, 109.3, 77.5, 77.2, 76.8, 64.7, 15.2. HRMS (ESI+, m/z): Calcd for C₁₈H₁₅O [M+H⁺]: 247.1123, found: 247.1128.

*Compound was pure by ¹H NMR after the first recrystallization but was further purified for the use in the STM experiments.

1-propoxypyrene (PyrOPr): 1-hydroxypyrene (507 mg, 2.3 mmol) was added to a mixture of Na₂CO₃ (728 mg, 6.8 mmol) and propyl iodide (590 mg, 3.4 mmol) in DMF (15 mL) under nitrogen atmosphere. The reaction mixture was stirred at 60°C overnight. To push the reaction to full conversion, excess of Na₂CO₃ (150 mg, 1.4 mmol) and propyl iodide (100 mg, 0.6 mmol) was added and the reaction mixture was allowed to cool down to rt after 4 h. The mixture was diluted in ether (100 mL) and washed with half saturated brine (2× 150 ml). The combined aqueous phases were extracted with ether and the volatiles were removed in vacuo. The residue was purified by flash column chromatography (pentane/DCM(0-20%)) to yield 1-propoxypyrene (469 mg, 1.8 mmol, 78% yield) as a white solid. mp: 81 °C (lit. 78-79 °C).¹⁸ ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.51 (d, J = 9.2 Hz, 1H), 8.13 – 8.04 (m, 4H), 7.98 – 7.95 (m, 2H), 7.89 (d, J = 9.0 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 4.29 (t, J = 6.4 Hz, 2H), 2.05 (m, 2H), 1.22 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 153.4, 131.9, 131.9, 127.4, 126.4, 126.2, 126.0, 125.6, 125.3, 125.1, 125.0, 124.3, 124.2, 121.4, 120.6, 109.3, 70.6, 23.0, 11.0. HRMS (ESI+, m/z): Calcd for C₁₉H₁₇O [M+H⁺]: 261.1279, found: 261.1274. These results match with previously reported data on 1-propoxypyrene.¹⁹

1-butoxypyrene (PyrOBU): 1-hydroxypyrene (500 mg, 2.3 mmol) was added to a mixture of Na₂CO₃ (610 mg, 5.7 mmol) and 1-bromobutane (381 mg, 2.8 mmol) in DMF (75 ml) under nitrogen atmosphere. The reaction mixture was stirred at 60°C for
Chapter 5

48 h. The mixture was diluted in ether and washed with H₂O. The organic layer was washed with brine (2×) and dried over MgSO₄. The volatiles were removed in vacuo and the residue was purified by flash column chromatography (pentane/EtOAc (0-10%) to yield 1-butoxypyrene (440 mg, 1.6 mmol, 70% yield) as an off white solid. mp: 87-88 °C (lit. 87 °C).

1H NMR (400 MHz, CDCl₃): δ (ppm) 8.48 (d, J = 9.2 Hz, 1H), 8.12-8.08 (m, 3H), 8.03 (d, J = 9.2 Hz, 1H), 7.97 - 7.93 (m, 2H), 7.87 - 7.83 (m, 2H), 7.55 (d, J = 8.4 Hz, 1H), 4.34 (t, J = 6.4 Hz, 2H), 2.05 - 1.97 (m, 2H), 1.73 - 1.63 (m, 2H), 1.08 (t, J = 7.4 Hz, 3H).

13C NMR (101 MHz, CDCl₃): δ (ppm) 153.4, 131.9, 131.9, 127.4, 126.4, 126.2, 126.0, 125.6, 125.3, 125.2, 125.0, 124.3, 124.2, 121.5, 120.6, 109.3, 68.84, 31.8, 19.7, 14.1. HRMS (ESI+, m/z): Calcd for C₂₀H₁₉O [M+H⁺]: 275.1436, found: 275.1430.

methyl 1-pyrenyl sulfide (PyrSMe) A solution of 1-bromopyrene (500 mg, 2.3 mmol) in dry THF (25 mL) was cooled down to -78°C. n-Buli (1 ml, 2.5 mmol, 2.5 M in hexane) was added to the solution. The solution was stirred for 30 min, then dimethyl disulfide (237 mg, 2.5 mmol) was added and the solution was stirred for other 15 min. The reaction mixture was allowed to warm up to rt, followed by quenching with 2 mL MeOH. The volatiles were removed in vacuo and the residue was dissolved in DCM (50 mL) and washed with brine (2× 50 mL). The organic layer was dried over MgSO₄ and the volatiles were removed in vacuo. The residue was purified using flash column chromatography (pentane/DCM (0-20%) to yield methyl 1-pyrenyl sulfide (315 mg, 1.3 mmol, 55% yield) as an off white solid. mp: 73-74 °C. 1H NMR (400 MHz, CDCl₃): δ (ppm) 8.56 (d, J = 9.2 Hz, 1H), 8.19 - 8.10 (m, 4H), 8.03 - 7.98 (m, 4H), 2.71 (s, 3H).

13C NMR (101 MHz, CDCl₃): δ (ppm) 133.2, 131.6, 131.1, 129.5, 129.4, 127.7, 127.4, 127.0, 126.2, 125.4, 125.2, 125.1, 124.6, 123.8, 17.4. HRMS (ESI+, m/z): Calcd for C₁₇H₁₂S [M⁺]: 248.0660, found: 248.0651. Synthesis was adapted from literature.

Characterization motor: 1H NMR (400 MHz, CHCl₃): δ (ppm) 8.58 (d, J = 8.0 Hz, 2H), 8.44 (d, J = 9.1 Hz, 2H), 8.25-8.15 (m, 3H), 8.12 - 8.04 (m, 7H), 8.00 (d, J = 9.2 Hz, 2H), 7.97 - 7.90 (m, 4H), 7.86 (m, 2H), 7.80-7.75 (m, 7H), 7.50 (m, 3H), 7.40 (m, 2H), 7.23 (m, 3H), 7.18 - 7.05 (m, 8H), 6.75 (d, J = 8.7 Hz, 4H), 4.31 (t, J = 6.3 Hz, 4H), 3.97 (t, J = 6.3 Hz, 4H), 2.43 (s, 3H), 2.05 (p, J = 6.5 Hz, 4H), 1.88 (q, J = 6.9, 6.4 Hz, 4H), 1.77 (p, J = 7.5, 6.9 Hz, 4H). HRMS; calcd for C₉₆H₇₃O₄⁺ [M + H⁺]: 1289.5503 found 1289.5471.

Appendix 5A

Additional data showing the time dependent adsorption studies of PyrOMe, PyrSMe and PyrOPr on the uC₃₃-NDI-uC₃₃ template. Figure 5A.1a shows that the adlayer is still intact after vigorously rinsing with 1-phenyloctane. The adsorption of PyrOMe in 1-phenyloctane on the molecular template took place within 7 min after the deposition.
Templated Alkoxy-Pyrene Adsorption within an Alkylated NDI Adlayer on Graphite

Figure 5A.1 STM topography images of PyrOMe adsorption experiments in 1-phenyloctane. a) $uC_{33}$-NDI-$uC_{33}$ template layer prior to the deposition of PyrOMe and after the rinsing step ($V_{\text{tip}} = 1 \, \text{V}, I_{\text{set}} = 100 \, \text{pA}$). b) Adsorbed PyrOMe (saturated solution 10× diluted) on the $uC_{33}$-NDI-$uC_{33}$ layer at the 1-phenyloctane/HOPG interface. Showing a small island of bare NDI molecules in the bottom right corner ($V_{\text{tip}} = 1 \, \text{V}, I_{\text{set}} = 50 \, \text{pA}$). c) Adsorbed PyrOMe (saturated solution 10× diluted) on the $uC_{33}$-NDI-$uC_{33}$ layer at the 1-phenyloctane/HOPG interface. Showing islands of bare NDI molecules in the top right corner ($V_{\text{tip}} = 1 \, \text{V}, I_{\text{set}} = 60 \, \text{pA}$).

Figure 5A.2 PyrSMe ($8 \times 10^{-3} \, \text{M in} \, n$-tetradecane) adsorption on $uC_{33}$-NDI-$uC_{33}$ template followed over time. The time underneath the images corresponds to the time lapsed after the deposition of the PyrSMe deposition. The turquoise marker is placed on all the images on the same spot of the surface. More PyrSMe molecules were adsorbed over time in the area indicated by the orange box. Imaging parameters a-c) $V_{\text{tip}} = 1 \, \text{V}, I_{\text{set}} = 100 \, \text{pA}$ and d) $V_{\text{tip}} = 1 \, \text{V}, I_{\text{set}} = 50 \, \text{pA}$.
Figure 5A.3 PyrOPr adsorption on uC₃₃-NDI-uC₃₃ template followed over time (solution: saturated solution in n-octanoic acid 2 to 3 times diluted). The time underneath the images corresponds to the time lapsed after the deposition of the PyrOPr deposition. a-d) Imaging parameters: 300 nm × 300 nm, $V_{tip} = 0.8$ V, $I_{set} = 25$ pA.
Appendix 5B

Selectivity of the template

The adsorption of small alkoxy-pyrene derivatives i.e. PyrOMe, PyrSMe and PyrOEt, could successfully be facilitated with the use of the uC$_{33}$-NDI-uC$_{33}$ template. However, the adsorption of larger molecules (for example PyrOPr), was more difficult i.e. less NDI molecules could be covered with PyrOPr molecules and it was difficult to resolve the structures due to the deteriorated resolution upon adsorption. We studied the adsorption behavior of several other molecules (Figure 5B.1 and Figure 5B.2) in order to get more insight in the limits of the uC$_{33}$-NDI-uC$_{33}$ template, including PyrOBu as described in the main text. The adsorption of PyrOBu via the molecular template was expected quite difficult, only small island of trapped PyrOBu were observed (Figure 5B.1a, designated areas). The fuzzy protrusions in Figure 5B.1b show, similar to PyrOPr, that it was difficult to resolve PyrOBu within the uC$_{33}$-NDI-uC$_{33}$ adlayer.

Figure 5B.1 STM topography images after the adsorption of PyrOBu molecules. a-b) STM image after deposition of PyrOBu (6.5×10$^{-2}$M in n-octanoic acid) on the uC$_{33}$-NDI-uC$_{33}$ template. Imaging parameters: a) 220 nm × 220 nm, $V_{tip} = 1.4$ V, $I_{set} = 25$ pA and b) 60 nm × 60 nm, $V_{tip} = 1.4$ V, $I_{set} = 25$ pA. c) STM image after deposition of PyrOBu (1.6×10$^{-1}$M in n-octanoic acid) on the uC$_{33}$-NDI-uC$_{33}$ template, showing perfectly resolved PyrOBu, which indicates that the NDIs were probably replaced by PyrOBu (30 nm × 30 nm, $V_{tip} = 1.3$ V, $I_{set} = 15$ pA). d) STM image after the deposition of PyrOBu (1.6×10$^{-1}$M in n-octanoic acid) on bare HOPG, showing the same assembly as observed in image (c) (30 nm × 30 nm, $V_{tip} = 1.0$ V, $I_{set} = 25$ pA).
Chapter 5

Figure 5B.2 STM topography images from adsorption experiments on the uC33-NDI-uC33 template. Left) Small island of C1-NDI-C1 molecules (saturated solution in n-octanoic acid) within the uC33-NDI-uC33 adlayer (60 nm × 60 nm, V_{tip} = 1 V, I_{set} = 25 pA). Right) Images after the deposition of PyrOC9OPyr (9×10^{-4} M in n-octanoic acid) on top of the uC33-NDI-uC33 adlayer, showing the possible replacement of the adlayer molecules by PyrOC9OPyr (25 nm × 25 nm, V_{tip} = 1 V, I_{set} = 100 pA). Synthesis of PyrOC9OPyr courtesy of Andreas Rösch.

Pyrenes with a 5-methoxypentanoate linker (PyrOC4COOC) could not be observed upon the deposition of a saturated solution in n-octanoic acid on the uC33-NDI-uC33 adlayer. Adsorption of C1-NDI-C1 via the template was difficult, only seldom small islands of the characteristic zipper-like structures were observed (Figure 5B.2, left image). Lastly we observed that the self-assembly of PyrOC9OPyr on the HOPG surface (Figure 5B.2, right image) was so robust that these molecules probably have replaced the uC33-NDI-uC33 adlayer as previously observed for the PyrOBu molecules (Figure 5B.1c-d). Experiments with PyrOC9OPyr on bare HOPG supported this hypothesis since the same assembly was observed without the presence of uC33-NDI-uC33 in the solution.

Investigation of different templates

Various experiments with different molecular adlayers were performed in order to get more insight in the working mechanism of the uC33-NDI-uC33 template. The molecules used for this adlayers varied in alkyl chain length, number of unsaturations in the alkyl chain and/or the position of the unsaturations in the chain. None of the investigated templates could facilitate the adsorption of PyrOMe and PyrSMe as efficient as uC33-NDI-uC33. The presence of an unsaturation in the alkyl chain seemed to be crucial for the adsorption of the alkoxy-pyrenes. However, the exact binding motif is not yet understood.

All adlayers were prepared using reported procedures (0.4 mg/ml (u_i)C_n-NDI-(u_i)C_n in 1-phenyloctane deposited at 100 °C (150 °C for n ≥ 50) on a bare HOPG substrate) and either PyrOMe in n-octanoic acid or PyrSMe in n-tetradecane were used to test the different templates. Only traces of adsorbed pyrenes could be observed on the u2C39-NDI-u2C39 and u3C50-NDI-u3C50 adlayers (Figure 5B.3), while no pyrene derivatives were observed on the u(C6-C7)C28-NDI-u(C6-C7)C28 (Figure 5B.3), u(C11-C12)C28+NDI-u(C11-C12)C28, and C33-NDI-C33 adlayers.
Figure 5B.3 STM topography images after the adsorption experiments with **PyrOMe** in *n*-octanoic acid on a) the \( u_2C_{39}-NDI-u_2C_{39} \) adlayer and b) on the \( u_3C_{50}-NDI-u_3C_{50} \) adlayer showing small traces of adsorbed **PyrOMe**.

Figure 5B.3 Adsorption experiments with **PyrSMe** \( (8 \times 10^{-3} \text{ M in } n\text{-tetradecane}) \) on the \( uC_{28}-NDI-uC_{28} \) (double bond between carbon 6 and 7) adlayer. The time underneath the images corresponds to the time lapsed after the deposition of the **PyrSMe** solution. There were no significant changes of the adlayer overtime and therefore no signs of **PyrSMe** adsorption. a) 200 nm × 200 nm, \( V_{\text{tip}} = 1 \text{ V, } I_{\text{set}} = 100 \text{ pA} \), b) 500 nm × 500 nm, \( V_{\text{tip}} = 1 \text{ V, } I_{\text{set}} = 100 \text{ pA} \), c) 250 nm × 250 nm, \( V_{\text{tip}} = 1 \text{ V, } I_{\text{set}} = 100 \text{ pA} \).

5.5 References


Chapter 5


Templated Alkoxy-Pyrene Adsorption within an Alkylated NDI Adlayer on Graphite


