Engineering Long-Range Order in Supramolecular Assemblies on Surfaces: The Paramount Role of Internal Double Bonds in Discrete Long-Chain Naphthalenediimides

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ABSTRACT: Achieving long-range order with surface-supported supramolecular assemblies is one of the pressing challenges in the prospering field of non-covalent surface functionalization. Having access to defect-free on-surface molecular assemblies will pave the way for various nanotechnology applications. Here we report the synthesis of two libraries of naphthalenediimides (NDIs) symmetrically functionalized with long aliphatic chains (C_{28} and C_{33}) and their self-assembly at the 1-phenyloctane/highly oriented pyrolytic graphite (1-PO/HOPG) interface. The two NDI libraries differ by the presence/absence of an internal double bond in each aliphatic chain (unsaturated and saturated compounds, respectively). All molecules assemble into lamellar arrangements, with the NDI cores lying flat and forming 1D rows on the surface, while the carbon chains separate the 1D rows from each other. Importantly, the presence of the unsaturation plays a dominant role in the arrangement of the aliphatic chains, as it exclusively favors interdigitation. The fully saturated tails, instead, self-assemble into a combination of either interdigitated or non-interdigitated diagonal arrangements. This difference in packing is spectacularly amplified at the whole surface level and results in almost defect-free self-assembled monolayers for the unsaturated compounds. In contrast, the monolayers of the saturated counterparts are globally disordered, even though they locally preserve the lamellar arrangements. The experimental observations are supported by computational studies and are rationalized in terms of stronger van der Waals interactions in the case of the unsaturated compounds. Our investigation reveals the paramount role played by internal double bonds on the self-assembly of discrete large molecules at the liquid/solid interface.

INTRODUCTION

The non-covalent functionalization of surfaces has become one of the pillars of nanotechnology in the past 20 years. Achieving exact control over the formation of monolayers allows scientists to modulate the properties of surfaces in a predictable manner, which holds promise for relevant technological breakthroughs. For instance, controlling the density of nitrogen-based n-dopants on graphene via monolayer formation has proved to play a pivotal role in tuning the charge carrier concentration of the modified 2D material.

Surface-supported supramolecular assemblies rely on stabilizing interactions between the adsorbed molecules and the surface, as well as favorable intermolecular interactions between the adsorbed compounds. Given the significant epitaxial stabilization of 64 meV (1.5 kcal/mol) per methylene unit that highly oriented pyrolytic graphite (HOPG) exerts at the liquid/HOPG interface, the molecular designs typically adopted in the field feature long alkyl chains—usually up to 18 carbon atoms—to favor adsorption to the substrate. Previous work on long-chain alkanes highlighted the tendency of long aliphatic tails to form thermodynamically stable self-assembled monolayers. Moreover, a number of studies have highlighted the role played by the alkyl chains in the 2D structure. While a favorable interaction between the molecules and the substrate is certainly necessary, the structure and extent of order of the assemblies generated are mostly the manifestation of the intermolecular interactions between the adsorbed molecules. On-surface supramolecular assemblies are typically created by resorting to non-covalent forces, such as van der Waals (vdW) interactions, hydrogen bonding (HB), coordination chemistries, and halogen bonding. So far, various approaches focused on limiting the number of domain boundaries and/or molecular defects to improve the organization and quality of the 2D architectures gen-

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oleic acid and Z-impressive results in terms of order. However, the defect-blies on uncon electron poor and have a pronounced tendency to be which both the long carbon chains and aromatic cores lie (C functionalized with fully hydrogenated, linear alkyl chains storage of the modiﬁed HOPG interface. Particularly relevant for the present work, the morphology of the obtained lattice was created (almost exclusively) by one stereoisomer. Moreover, to answer the key question about the role of the internal double bonds, we envisioned a system based on long carbon molecular assemblies at the liquid/solid interface allows for evaluation of the self-assembly (Chart 1). We discover that the self-assembled monolayers obtained at the 1-PO/HOPG interface from the saturated compounds are characterized by a signiﬁcantly higher degree of organization compared to their saturated counterparts, with a size difference for ordered domains corresponding to thousands of squared nanometers. The experimental results are supported by computational studies. Our results point to the establishment of the internal double bond as a counter-intuitive yet key structural element for obtaining long-range order in self-assembled monolayers at the liquid/solid interface. Finally, the highly adaptive character of supramolecular assemblies at the liquid/solid interface allows for the use of mixtures of EE, EZ, and ZZ isomers of the unsaturated NDIs, as the system selects the most stable pattern created (almost exclusively) by one stereoisomer.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization.** Compounds uC28-NH2 and uC33-NH2 (Chart 1) were the key intermediates in the preparation of the target NDIs. They were synthesized from building blocks 1, 2, and 3 in 67% and 40% yield, respectively, applying a strategy based on Wittig olefination (Scheme 1). Details on the preparation of 2 and 3 are presented in the Supporting Information (SI). The amines were obtained as an ~84:16 mixture of non-separable Z and E isomers, respectively (assigned by integration of the 13C NMR spectra, see SI). The preference for the Z-configuration of the feature either 28 or 33 carbon atoms in the linear chain (C28 and C33, respectively) and only differ by the presence/absence of one unsaturation in each carbon chain. The unsaturation (when present) is highlighted by the letter u. The key synthetic intermediates in the preparation of the ﬁnal compounds were the unsaturated amines uC28-NH2 and uC33-NH2, also shown in Chart 1. We discover that the self-assembled monolayers obtained at the 1-PO/HOPG interface from the unsaturated monolayers were characterized by a signiﬁcantly higher degree of organization compared to their saturated counterparts, with a size difference for ordered domains corresponding to thousands of squared nanometers. The experimental results are supported by computational studies. Our results point to the establishment of the internal double bond as a counter-intuitive yet key structural element for obtaining long-range order in self-assembled monolayers at the liquid/solid interface. Finally, the highly adaptive character of supramolecular assemblies at the liquid/solid interface allows for the use of mixtures of EE, EZ, and ZZ isomers of the unsaturated NDIs, as the system selects the most stable pattern created (almost exclusively) by one stereoisomer.

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The double bond is in line with the Wittig olefination conditions adopted, especially with the use of non-stabilized phosphonium ylides. The position of the unsaturation along the two carbon chains (between C6 and C7 in uC28, and C11 and C12 in uC33) was exactly engineered, as will be corroborated by our STM study (vide infra). The choice of the base-induced Wittig reaction for the elongation step implied a careful choice of protecting groups for the amino moieties on the phosphonium salts. We opted for tert-butyloxycarbonyl- (Boc) and phthalimide- (Phth) protected 2 and 3 for uC28-NH2 and uC33-NH2, respectively, after an initial screening of the reaction conditions. A related approach for obtaining discrete oligoethylenes (Cn ≤ 400) was previously reported in the effort to build model compounds to study the crystallization of polyethylene. Being complementary, our synthesis allows for the introduction of functional groups in the linear moieties, expanding the applicability of these long aliphatic chains. The cleavage of the -Boc and -Phth protecting groups was carried out with trifluoroacetic acid (TFA) and methylamine solution in ethanol (33 wt%), respectively (experimental details in SI).

The unsaturated amines were subsequently coupled to commercially available naphthalenedianhydride (NDA) via a modified microwave assisted protocol (Scheme 2). The unsaturated NDIs uC28-NDI-uC28 and uC33-NDI-uC33 were obtained in 71% and 80% yield, respectively, as non-resolvable mixtures of ZZ:ZE:EE isomers (∼70.5:27:2.5, based on the possible combinations of the two reacting amines) after chromatographic purification. The fully saturated analogs C28-NDI-C28 and C33-NDI-C33 were prepared from their alkenyl counterparts by palladium-on-carbon (Pd/C)-catalyzed hydrogenation in ethyl valerate at 100 °C (Scheme 1) and purified by Soxhlet extraction (see SI).

**Self-Assembly on HOPG.** We started our investigation by studying the self-assembly of saturated C28-NDI-C28 and C33-NDI-C33 at the 1-PO/HOPG interface. Solutions of the two NDIs (0.4 mg/mL in 1-PO) were drop-cast at 100 °C onto freshly cleaved HOPG substrates and subsequently imaged. The saturated compounds spontaneously self-assembled into ordered lamellae immediately after deposition. In the STM images, the aromatic cores appear as bright protrusions and the alkylic chains as dark regions (Figure 1a–d). The lamellar packings are consistent with the aromatic cores lying flat and next to each other on the surface, while the alkylic chains are straight and parallel to each other and modulate the distance between the NDI cores (Figure 1a,c). The arrangement of the individual alkylic chains was determined from high-resolution STM images. We could identify two different
packing modes for the aliphatic chains of C_{28}-NDI-C_{28} (Figure 1b) and C_{33}-NDI-C_{33} (Figure 1d): an interdigitated mode, hereby defined as "lamellar phase A", and a non-interdigitated diagonal mode, denominated "lamellar phase B". A pictorial representation of both lamellar phases A and B is given in Figure 1e. The lamellae are rotated by 60° with respect to each other. The observation of the two different packing modes of the aliphatic chains is in line with previous reports on C_{n}-NDI-C_{n} with 13 ≤ n ≤ 18.\textsuperscript{17} In this respect, extending the length of the aliphatic chains did not result in significant differences compared to previous studies.

The unit cell parameters determined for C_{28}-NDI-C_{28} and C_{33}-NDI-C_{33} are listed in Table 1, while for a visualization of the unit cell we refer to Figure 5 and the discussion further on. Although the two lamellar assemblies differ in the orientation of the aliphatic chains, the unit cell parameters do not differ for a fixed alkyl chain length. The measured value are a = 4.45 ± 0.24 nm, b = 0.88 ± 0.08 nm, and γ = 85.21 ± 3.39° for C_{28}-NDI-C_{28}, and a = 5.29 ± 0.49 nm, b = 0.99 ± 0.10 nm, and γ = 84.10 ± 5.28° for C_{33}-NDI-C_{33}.

Next, we focused on unsaturated uC_{28}-NDI-uC_{28} and uC_{33}-NDI-uC_{33} at the 1-PO/HOPG interface under similar experimental conditions. Exemplary images are shown in Figure 2. Assemblies similar to the ones obtained for the saturated NDIs were observed with uC_{28}-NDI-uC_{28} and uC_{33}-NDI-uC_{33}. The lamellar arrangements correspond to parallel NDIs at the surface (bright protrusions) and the interdigitating aliphatic chains that tune the distance between them (dark regions) (Figure 2a for uC_{28}-NDI-uC_{28} and Figure 2b for uC_{33}-NDI-uC_{33}). In stark contrast with the saturated NDIs, additional bright protrusions were observed in the STM images of uC_{28}-NDI-uC_{28} and uC_{33}-NDI-uC_{33} (orange arrows in Figure 2a,b). They appeared symmetrically with respect to the aromatic cores, and their distance to the aromatic cores changed upon extending the chain length. These features were less evident in the case of uC_{33}-NDI-uC_{33} (Figure 2a), while they appeared more separated and resolved in the case of uC_{33}-NDI-uC_{33} (Figure 2b). We attribute these additional bright protrusions to the double bonds present in the unsaturated chains. As a general remark, the imaging of the double bonds was in general easier for uC_{33}-NDI-uC_{33} than uC_{28}-NDI-uC_{28}. Such behavior is attributed to the structural differences between the two molecules and corroborates the remote position of the double bond with respect to the NDI core in uC_{33}-NDI-uC_{33} (between C_{11} and C_{12}) compared to uC_{28}-NDI-uC_{28} (between C_{6} and C_{7}).

The determined unit cell parameters for uC_{28}-NDI-uC_{28} and uC_{33}-NDI-uC_{33} are reported in Table 1. The values are very similar to those obtained for the saturated counterparts, pointing to an apparent similarity between the assemblies of saturated and unsaturated NDIs. The close resemblance of the unit cell parameters of the NDIs with the same chain length (C_{28} or C_{33}) strongly suggests that the self-assembled monolayers are mostly formed by all-E-configured molecules. The E-configured carbon chains are expected to assume zigzag conformations on HOPG in a similar fashion to alkyl chains and hence cover distances comparable to their saturated counterparts (C_{28} and C_{33}). The Z-configured chains, instead, should differ in distance, as the Z-configuration forces a bending of the carbon which cannot be compensated by a rotation around the double bond (forbidden in this case). As an indicative example, the carbon chain of Z-oleylamine shows this bending as a consequence of the fixed configuration of the double bond.\textsuperscript{44} The deposition of mainly EE-isomer is remarkable, since this isomer is calculated to be roughly 2.5% of the whole population of unsaturated NDIs (based on the \textsuperscript{13}C NMR analysis of uC_{28}NH_{2} and uC_{33}NH_{2} and the binomial distributions of the two amines). The remaining 97.5% of the material, which accounts for the EZ- and ZZ-isomers, remains in the overlying liquid phase and is not imaged. We conclude that our long-chain NDIs system at the 1-PO/HOPG interface is highly dynamic and adaptive. Such characteristic allows for the use of EE-, EZ-, and ZZ-isomers mixtures because the system autonomously selects the isomer that forms the most stable pattern on the surface—the EE-isomer in this case. A similar concept has been recently reported by Samori, Lehn, et al. with on-surface bisimine formation.\textsuperscript{17} It should be noted that some Z-configured double bonds were present in the monolayer and we speculate that these are responsible for the tiny defects and irregularities observed in the monolayers.

### Table 1. Unit Cell Parameters for the Supramolecular Arrangements of C_{28}-NDI-C_{28}, uC_{28}-NDI-uC_{28}, C_{33}-NDI-C_{33}, and uC_{33}-NDI-uC_{33} at the 1-PO/HOPG Interface\textsuperscript{\textsuperscript{a}}

| Compound | a [nm] | b [nm] | γ [deg] | Lamellar Phase | Domain Size Average [nm²] | Domain Size Median [nm²] | Disordered Areas [%] |
|----------|--------|--------|---------|----------------|---------------------------|--------------------------|----------------------|
| C_{28}-NDI-C_{28} | 4.45 ± 0.24 | 0.88 ± 0.08 | 85.21 ± 3.39 | A and B | 949 | 737 | 26 ± 5 |
| uC_{28}-NDI-uC_{28} | 4.53 ± 0.08 | 0.86 ± 0.10 | 87.33 ± 1.78 | A | 6764 | 2923 | — |
| C_{33}-NDI-C_{33} | 5.29 ± 0.49 | 0.99 ± 0.10 | 84.10 ± 5.28 | A and B | 1268 | 540 | 24 ± 8 |
| uC_{33}-NDI-uC_{33} | 5.27 ± 0.08 | 0.94 ± 0.06 | 84.93 ± 1.80 | A | 8026 | 3684 | — |

\textsuperscript{a}The lengths of the unit cell vectors are labeled a and b, and the internal angle is specified by γ (see also Figure 5a,b).

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\[\text{Figure 2.} \text{Self-assembly of uC}_{28}\text{-NDI-uC}_{28} \text{and uC}_{33}\text{-NDI-uC}_{33} \text{at the 1-phenylcraht/HOPG interface. (a) STM image of uC}_{28}\text{-NDI-uC}_{28} (20 \text{nm × 20 nm}, V_{tip} = 1 \text{V}, I_{tip} = 100 \text{pA}). (b) STM image of uC}_{33}\text{-NDI-uC}_{33} (20 \text{nm × 20 nm}, V_{tip} = 1 \text{V}, I_{tip} = 90 \text{pA}). The double bonds appear as bright protrusions next to the bright NDI cores (orange arrows). Both unsaturated molecules assemble in an interdigitated fashion (phase A).}\]
saturated and unsaturated NDIs at the 1-PO/HOPG interface. However, a very important difference arises in the organization of the aliphatic chains: the fully saturated ones simultaneously arrange in either phase A or B, while the unsaturated chains only pack in the phase A fashion. This difference does not alter the local ordering of the self-assembled monolayer, but has dramatic repercussions on the global ordering of the 2D architectures. The presence of just one type of self-assembly arrangement (phase A) for the carbon chains of uC28-NDI-uC28 and uC33-NDI-uC33 results in considerably increased domain sizes and thus, in a reduction of the number of domains per area compared to those created by their saturated counterparts. The contrast is striking: for large-scale images, very large domains and significantly less defects are observed in the STM images of uC28-NDI-uC28 and uC33-NDI-uC33 (Figure 3b,d, respectively) compared to those of C28-NDI-C28 and C33-NDI-C33 (Figure 3a,c, respectively).

The different position of the double bonds in uC28-NDI-uC28 and uC33-NDI-uC33 does not seem to play a role, considering the very similar behavior (Figure 3b,d). Results obtained on a positional isomer of uC28-NDI-uC28 with the double bond located between carbon atoms 11 and 12 also rule out a positional influence of the unsaturation (see SI). In contrast, the overview STM images of the saturated NDIs are characterized by relatively small domains accompanied by disordered areas. The lack of a clear preference for either lamellar phase A or B arrangements seems to cause the existence of disordered regions and wüler areas (Figure 3a,c; see SI for the assignment of disordered areas).

We conducted a statistical analysis on the domain sizes for the different NDIs to support the qualitative observation on the dramatic influence of the internal double bonds. For a detailed description on the assignment of the domain size and further experimental observations upon scanning see the SI.

The results on the domain size distributions for C28-NDI-C28 and uC28-NDI-uC28, and C33-NDI-C33 and uC33-NDI-uC33, are summarized by the two histograms shown in Figure 4. The saturated NDIs mainly arrange in relatively small domains (≤1000 nm²) (Figure 4a and 4b, blue columns). Moreover, on roughly 24% of the surface, the molecules do not arrange in an ordered way resulting in disordered areas. On the other hand, the images of the unsaturated NDIs show only a marginal amount of disordered areas. The observed domains reach much larger extensions, with a significant population larger than 15000 nm² (Figure 4a,b, orange columns).

The experimental results were rationalized by means of a computational study (for computational details see SI). For consistency with our experimental observations on the self-assembled monolayers, we studied only alkenes with E-configurations. Our working hypothesis focused on the increasing strength of van der Waals interchain interactions upon introducing internal double bonds in the carbon chains. Initial studies on shorter carbon chains (C6) in the gas phase showed a promising trend in this respect (see SI). Periodic energy decomposition analysis (PEDA)57 revealed that the interaction energy between neighboring chains becomes more favorable upon introducing the internal double bonds in the lamellar A organization. In the calculated molecular arrangements, the NDI cores lay flat and next to each other while the carbon...
chains interdigitate, in line with the experimental observations (Figure 5a for C28-NDI-C28 and Figure 5b for uC28-NDI-uC28). The distance between the hydrogen atoms of the aromatic C−H and the oxygen atoms of the neighboring imide moieties amounts to 2.5 Å for both C28-NDI-C28 and uC28-NDI-uC28, in line with the literature. This allows for unconventional hydrogen bonding interactions between adjacent NDI cores, which stabilize the molecular arrangement. Unconventional hydrogen bonding may additionally occur between the oxygen atoms of the imide moieties and the terminal methyl groups of the interdigitating chains from the adjacent row of NDIs, for both C28-NDI-C28 and uC28-NDI-uC28. The H−O distance varies in the 2.6−3 Å range in this case. The calculated unit cell values are \(a = 44.8\,\text{Å}, \quad b = 8.5\,\text{Å}, \quad \text{and} \quad \gamma = 90^\circ\) for C28-NDI-C28, and \(a = 44.5\,\text{Å}, \quad b = 8.5\,\text{Å}, \quad \text{and} \quad \gamma = 90^\circ\) for uC28-NDI-uC28, nicely matching with the experimental values (Table 1). This further confirmed the accuracy of the computational study. Finally, we compared the adsorption energies for both C28-NDI-C28 and uC28-NDI-uC28 in the lamellar phase A arrangement on graphene. Assemblies of C28-NDI-C28 adsorbed on graphene were 0.166 eV (3.83 kcal/mol) per molecule energetically more favorable than those of uC28-NDI-uC28. However, the experimental observation of improved long-range order with uC28-NDI-uC28 compared to C28-NDI-C28 and the stronger van der Waals interchain interactions between unsaturated C6 carbon chains (Figure S41 and Table S1) clearly point to more favorable intermolecular interactions in the case of uC28-NDI-uC28.

Considering that the unconventional hydrogen bonding occurring in the calculated lamellar phases of C28-NDI-C28 and uC28-NDI-uC28 should be very similar, if not identical, from the energetic point of view, we can only ascribe such “more favorable intermolecular interactions” to van der Waals forces.

We simulated an STM image for an individual molecule at a bias voltage of −1 V from the calculated lamellar phases of both C28-NDI-C28 and uC28-NDI-uC28. The individual molecules, as well as the corresponding simulated STM images at bias −1 V for C28-NDI-C28 and uC28-NDI-uC28, are shown in Figure 5c,d. Both C28-NDI-C28 and uC28-NDI-uC28 showed some level of distortion from a linear geometry of the carbon chains (Figure 5c,d, top part). Interestingly, the two E-configured double bonds (encircled by an orange ellipse in Figure 5d) were rotated by almost 90° with respect to the imaginary line that connects the nitrogen atoms of the NDI core in uC28-NDI-uC28 (Figure 5d, top part). As expected, the simulated STM images of C28-NDI-C28 and uC28-NDI-uC28 are almost identical with respect to the aromatic cores (Figure 5c,d, top parts). The main difference concerns the long carbon chains, with the clear presence of the internal double bonds in uC28-NDI-uC28 (Figure 5d). The two internal double bonds appear as bright spots, suggesting the presence of two localized areas of higher electronic densities along the carbon chains (Figure 5d). In stark contrast, the distribution of the electronic density along the carbon chains in C28-NDI-C28 is more uniform (Figure 5c,d, top parts).
density along the carbon chains of C28-NDI-C28 is more homogeneous and points to a discrete series of single bonds (Figure 5c). Consistently with the on-graphene optimized structure of uC28-NDI-uC28, the internal double bonds are rotated by almost 90°, also in the simulated STM image (Figure 5d). This peculiar feature may account for a different visualization of the internal double bond by STM. Such hypothesis seems to be consistent with the experimental STM images reported in Figure 2, in which one of the two double bonds appears more visible than the other one for both uC28-NDI-uC28 and uC33-NDI-uC33. This difference is more evident in the case of uC33-NDI-uC33 and it is probably due to an increased distance for the internal double bonds from the NDI core, which ultimately facilitates the imaging. Hence, the gratifying agreement between the calculations on uC28-NDI-uC28 and the experimental STM images on both uC28-NDI-uC28 and uC33-NDI-uC33 allowed us to generalize the conclusions to both unsaturated molecular systems.

CONCLUSIONS

We presented the synthesis and self-assembly at the 1-PO/HOPG interface of C28-NDI-C28, C33-NDI-C33, uC28-NDI-uC28, and uC33-NDI-uC33. The molecular structures only differ by the presence/absence of precisely positioned internal double bonds in their molecular skeletons. These compounds self-assembled into lamellar arrangements characterized by parallel aromatic cores that lay flat on the surface, and aliphatic chains that modulate the distance between such cores. The longer the chain, the larger the distance, implying that the entire molecular system lays flat on the surface. The packing of the long carbon chains results into two different arrangements: one in which the tails are interdigitated (lamellar phase A), and a second one where the long tails arrange diagonally, without interdigitation (lamellar phase B). We find the presence/absence of the simple double bonds to be the critical parameter for the selection of the chain arrangements. The fully saturated compounds present a combination of both self-assembly motifs, whereas the unsaturated molecules are capable of selecting the fully interdigitated arrangement. Such difference is magnified and reflected on the long-range order of the generated monolayers, with the unsaturated compounds forming much larger domains (in some cases larger than 15 000 nm²). This contrasts starkly with the locally ordered, yet globally disordered, monolayers of the saturated compounds.

The experimental results were also corroborated by computational studies, which suggest stronger van der Waals interactions between unsaturated carbon chains as a possible explanation. Showing the paramount role played by internal double bonds in the self-assembly of long carbon chain derivatives on surfaces, our results point to the use of “simple” internal double bonds as a critical structural parameter for obtaining long-range order in surface-supported supramolecular processes. We envision the application of our findings toward post-functionalization of non-covalently functionalized surfaces and highly dynamic and smart functional substrates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c00765.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Elemans, J. A. A. W.; Lei, S.; De Feyter, S. Molecular and Supramolecular Networks on Surfaces: From Two-Dimensional Crystal Engineering to Reactivity. Angew. Chem., Int. Ed. 2009, 48, 7298–7332.

(2) Woodruff, D. P. Modern Techniques of Surface Science, 3rd ed.; Cambridge University Press, 2016.
(3) Van Hove, M. A. From Surface Science to Nanotechnology. Catal. Today 2006, 113, 133−140.

(4) Förch, R.; Schönherr, H.; Jenkins, A. T. A. Surface Design: Applications in Bioscience and Nanotechnology; Wiley-VCH, 2009.

(5) Casalini, S.; Bortolotti, C. A.; Leonardi, F.; Biscarrini, F. Self-Assembled Monolayers in Organic Electronics. Chem. Soc. Rev. 2017, 46, 40−71.

(6) Bartels, T. Tailoring Molecular Layers at Metal Surfaces. Nat. Chem. 2010, 2, 87−95.

(7) Barth, J. V.; Costantini, G.; Kern, K. Engineering Atomic and Molecular Nanostructures at Surfaces. Nature 2005, 437, 671−679.

(8) Lu, W.; Lieber, C. M. Nanoelectronics from the Bottom Up. Nat. Mater. 2007, 6, 841−850.

(9) Phillipson, R.; Lockhart De La Rosa, C. J.; Teyssandier, J.; Walke, P.; Waghray, D.; Fujita, Y.; Adsoeajoj, J.; Mali, K. S.; Asselberghs, I.; Huyghenbaert, C.; et al. Tunable Doping of Graphene by Using Physisorbed Self-Assembled Networks. Nanoscale 2016, 8, 20017−20026.

(10) Slater, A. G.; Beton, P. H.; Champness, N. R. Two-Dimensional Supramolecular Chemistry on Surfaces. Chem. Sci. 2011, 2, 1440−1448.

(11) Tober, Y.; Tahara, K.; De Feyter, S. Award Accounts Adaptive Building Blocks Consisting of Rigid Triangular Core and Flexible Alkoy Chains for Self-Assembly at Liquid/Solid Interfaces-Conjugated Molecules for on-Surface Self-Assembly, and Functionalization of Graphitic Surfaces. Bull. Chem. Soc. Jpn. 2016, 89, 1277−1306.

(12) Ilan, B.; Florio, G. M.; Hybertsen, M. S.; Berne, B. J.; Flynn, G. W. Scanning Tunneling Microscopy Images of Alkane Derivatives on Graphite: Role of Electronic Effects. Nano Lett. 2008, 8, 3160−3165.

(13) Mali, K. S.; Adsoeajoj, J.; Ghijsens, E.; De Cat, I.; De Feyter, S. Exploring the Complexity of Supramolecular Interactions for Patterning at the Liquid-Solid Interface. Acc. Chem. Res. 2012, 45, 1309−1320.

(14) Yang, T.; Berber, S.; Liu, J.-F.; Miller, G. P.; Tománek, D. Self-Assembly of Long Chain Alkanes and Their Derivatives on Graphite. J. Phys. Chem. B 2008, 128, 124709.

(15) Giancarlo, L. C.; Fang, H.; Rubin, S. M.; Bront, A. A.; Flynn, G. W. Influence of the Substrate on Order and Image Contrast for Physisorbed, Self-Assembled Molecular Monolayers: STM Studies of Functionalized Hydrocarbons on Graphite and MoS 2. J. Phys. Chem. B 1998, 102, 10255−10263.

(16) Xie, Z.; Xie, Z.; Xu, X.; Tang, J.; Mao, B. W. Reconstruction-Dependent Self-Assembly of n-Alkanes on Au(111) Surfaces. J. Phys. Chem. B 2000, 104, 11719−11722.

(17) Chen, Q.; Yan, H. J.; Yan, C. J.; Pan, G. B.; Wan, L. J.; Wen, G. Y.; Zhang, D. Q. STM Investigation of the Dependence of Alkane and Alkoy (C18H38,C19H40) Derivatives Self-Assembly on Molecular Architecture of Salophen Complexes on Liquid-Graphite Interface. Eur. J. Inorg. Chem. 2007, 2007, 4028−4034.

(18) Dickerson, P. N.; Hibberd, A. M.; Oncel, N.; Bernasek, S. L. Hydrogen-Bonding versus van Der Waals Interactions in Self-Assembled Monolayers of Substituted Isophthalic Acids. Langmuir 2010, 26, 18155−18161.

(19) Barth, J. V.; Weckesser, J.; Cai, C.; Günter, P.; Bürgi, L.; Jeandupeux, O.; Kern, K. Building Supramolecular Nanostructures at Surfaces by Hydrogen Bonding. Angew. Chem., Int. Ed. 2000, 39, 1230−1234.

(20) Slater, A. G.; Perdigão, L. M. A.; Beton, P. H.; Champness, N. R. Surface-Based Supramolecular Chemistry Using Hydrogen Bonds. Acc. Chem. Res. 2014, 47, 3417−3427.

(21) Zhou, H.; Ang, H.; Yu, J.-H.; Nanci, A.; Rochefort, A.; Wuest, J. D. Frustrated 2D Molecular Crystallization. J. Am. Chem. Soc. 2007, 129, 13774−13775.

(22) Greissl, S.; Lackinger, M.; Edelwirth, M.; Hietschold, M.; Heckl, W. M. Self-Assembled Two-Dimensional Molecular Host-Guest Architectures From Trimesic Acid. Single Mol. 2002, 3, 25−31.

(23) Van Esch, J.; De Feyter, S.; Kellogg, R. M.; De Schryver, F.; Feringa, B. L. Self-Assembly of Bisurea Compounds in Organic Solvents and on Solid Substrates. Chem. - Eur. J. 1997, 3, 1238−1243.

(24) De Feyter, S.; Grim, P. C. M.; Van Esch, J.; Kellogg, R. M.; Feringa, B. L.; De Schryver, F. C. Nontrivial Differentiation between Two Identical Functionalities within the Same Molecule Studied by STM. J. Phys. Chem. B 1998, 102, 8981−8987.

(25) Giesquiere, A.; Abdel-Mottaleb, M. M. S.; De Feyter, S.; De Schryver, F. C.; Schoonbeek, F.; van Esch, J.; Kellogg, R. M.; Feringa, B. L.; Calderone, A.; Lazzaroni, R.; Bredas, J. L. Molecular Architecture of Bis-Urea Substituted Thiophene Derivatives at the Liquid/Solid Interface Studied by Scanning Tunneling Microscopy. Langmuir 2000, 16, 10385−10391.

(26) Llanes-Pallas, A.; Matena, M.; Jung, T.; Prato, M.; Stöhr, M.; Bonifazi, D. Tri-modal Engineering of Linear Supramolecular Miniatures on Ag(111) Surfaces Controlled by Complementary Triple Hydrogen Bonds. Angew. Chem., Int. Ed. 2008, 47, 7726−7730.

(27) Vijayaraghavan, S.; Ecija, D.; Auwärter, W.; Joshi, S.; Seufert, K.; Drach, M.; Nieckarz, D.; Szabelski, P.; Aursichio, C.; Bonifazi, D.; et al. Supramolecular Assembly of Interfacial Nanoporous Networks with Simultaneous Expression of Metal-Organic and Organic-Bonding Motifs. Chem. - Eur. J. 2013, 19, 14143−14150.

(28) De Ruijter, G.; Lahav, M.; Van Der Boom, M. E. Pyridine Coordination Chemistry for Molecular Assemblies on Surfaces. Acc. Chem. Res. 2014, 47, 3407−3416.

(29) Stepnow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X.; Cai, C.; Barth, J. V.; Kern, K. Steering Molecular Organization and Host−Guest Interactions Using Two-Dimensional Nanoporous Coordination Systems. Nat. Mater. 2004, 3, 229−233.

(30) Matena, M.; Björk, J.; Wahl, M.; Lee, T.-L.; Zegenhagen, J.; Gade, L. H.; Jung, T. A.; Persson, M.; Stöhr, M. On-Surface Synthesis of a Two-Dimensional Porous Coordination Network: Unraveling Adsorbate Interactions. Phys. Rev. B: Condens. Matter Mater. Phys. 2014, 90, 125408.

(31) Gutzler, R.; Fu, C.; Dadvand, A.; Hua, Y.; MacLeod, J. M.; Rosei, F.; Perepichka, D. F. Halogen Bonds in 2D Supramolecular Self-Assembly of Organic Semiconductors. Nanoscale 2012, 4, 5965.

(32) Yoon, J. K.; Son, W.; Chung, K.-H.; Kim, H.; Han, S.; Kahng, S.-J.; Visualizing Halogen Bonds in Planar Supramolecular Systems. J. Phys. Chem. C 2011, 115, 2297−2301.

(33) Zhang, J. L.; Zhong, S.; Zhong, J. Q.; Niu, T. C.; Hu, W. P.; Wee, A. T. S.; Chen, W. Rational Design of Two-Dimensional Molecular Donor−Acceptor Nanostructure Arrays. Nanoscale 2015, 7, 4306−4324.

(34) Wang, Q. H.; Hersam, M. C. Room-Temperature Molecular-Resolution Characterization of Self-Assembled Organic Monolayers on Epitaxial Graphene. Nat. Chem. 2009, 1, 206−211.
