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 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 generated.}

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HOPG interface. Monolayers obtained from oleic acid and Zimic results in terms of order. However, the defect-free engineering of surface-supported supramolecular assemblies on unconfined HOPG remains a major challenge for the whole field. Given the high commercial availability of alkylating reagents in the C_1−C_2 range, a large body of work has been carried out using alkyl chain-functionalized compounds. To the best of our knowledge, however, the attention dedicated to their unsaturated analogues featuring internal double bonds has been very limited. Deng et al. compared the assemblies of E-oleic acid and Z-oleylamine at the 1-phenyloctane (1-PO)/HOPG interface. Monolayers obtained from E-oleic acid at the 1-PO/HOPG interface were characterized by a high stability, while those deriving from the amine with Z-configuration were poorly stable. This comparative study was consistent in terms of chain length (oleyl = C_14) and double bond position (between carbon atoms 9 and 10), but the two structures investigated differed in double bond configurations (E vs Z) and end-group functionalities (carboxylic vs amino). The hypothesis that various parameters could play a role in the overall stability of the on-surface assemblies could not be ruled out. More recently, Shokri et al. suggested that the introduction of a Z-configured double bond in the side chains of bis(urea) molecules leads to the formation of long-range ordered polymers on graphite. However, the study was conducted with one chain length only (C_14), and the influence of the internal double bond was visible only after storage of the modified surface for 1 year. Although both studies independently posed the question of the influence of internal double bonds on on-surface self-assembly processes, no further investigations followed in this direction.

Intrigued by the chance to unravel the possible influence of internal double bonds on surface-supported supramolecular assemblies, we envisioned a system based on long carbon chains featuring internal double bonds symmetrically bound at the periphery of naphthalenediimides (NDIs). NDIs are electron poor and have a pronounced tendency to be deposited at the liquid/HOPG interface due to a highly favorable enthalpy of interaction. Symmetrical NDIs functionalized with fully hydrogenated, linear alkyl chains (C_n-NDI-C_n design) with a number of carbon atoms (n) in the 3−18 range were previously investigated at the 1-tetradecane/HOPG interface. Particularly relevant for the present work, alkyl chains with a number of carbon atoms equal to or greater than 13 units consistently afforded lamellar arrangements in which both the long carbon chains and aromatic cores lie flat on the surface, as visualized with scanning tunneling microscopy (STM). The morphology of the obtained monolayers was explained (lamellar), but the larger long-range-ordered areas obtained represented only a limited part of the surface (50 nm × 50 nm). In order to exploit the potential of supramolecular assemblies on surfaces, ordered areas larger than 100 nm × 100 nm (at least) are highly desirable. Relying on the consistency of the C_n-NDI-C_n design with n > 13 (lamellar arrangement), we hypothesized that extending the carbon chain length in the C_n-NDI-C_n design would be beneficial for expanding the order extent. Moreover, to answer the key question about the role of the internal double bonds, we envisioned a C_n-NDI-C_n system that features internal unsaturations in the carbon chain. Reducing these double bonds by catalytic hydrogenation should offer the possibility to compare compounds that belong to a very consistent molecular platform (long-chain NDIs) but that differ by a subtle structural modification (formally two hydrogen molecules).

We present the synthesis and on-surface investigation of uC_{28}-NDI and uC_{33}-NDI (unsaturated NDIs) and compare them to their hydrogenated counterparts C_{28}-NDI and C_{33}-NDI (saturated NDIs). The fully extended chemical structures are shown in Chart 1. The studied NDIs feature either 28 or 33 carbon atoms in the linear chain (C_{28} and C_{33}, 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 uC_{28}-NH_2 and uC_{33}-NH_2, also shown in Chart 1. We discover that the self-assembled monolayers obtained at the 1-PO/HOPG interface from the unsaturated 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 counterintuitive 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 uC_{28}-NH_2 and uC_{33}-NH_2 (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
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 \( \text{uC28} \), and C11 and C12 in \( \text{uC33} \)) 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 \( \text{uC28-NH2} \) and \( \text{uC33-NH2} \), respectively, after an initial screening of the reaction conditions. A related approach for obtaining discrete oligoethylenes (\( C_n \leq 400 \)) 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 methyamine 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 \( \text{uC28-NDI-uC28} \) and \( \text{uC33-NDI-uC33} \) 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 \( \text{C28-NDI-C28} \) and \( \text{C33-NDI-C33} \) 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 \( \text{C28-NDI-C28} \) and \( \text{C33-NDI-C33} \) 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 alky 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 alky chains are straight and parallel to each other and modulate the distance between the NDI cores (Figure 1a,c). The arrangement of the individual alky chains was determined from high-resolution STM images. We could identify two different...
The lengths of the unit cell vectors are labeled $a$ and $b$, and the internal angle is specified by $\gamma$ (see also Figure 5a,b).

The results presented so far have apparently changed upon extending the chain length. These features were less evident in the case of uC28-NDI-uc28 (Figure 2a), while they appeared more separated and resolved in the case of uC33-NDI-uc33 (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 uC33-NDI-uc33 than for uC28-NDI-uc28. Such behavior is attributed to the structural differences between the two molecules and corroborates the more remote position of the double bond with respect to the NDI core in uC33-NDI-uc33 (between C11 and C12) compared to uC28-NDI-uc28 (between C6 and C7).

The saturated carbon chains are expected to assume zigzag conformations on HOPG in a very similar fashion to alkyl chains and hence cover distances comparable to their saturated counterparts (C28 and C33). 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.\(^{44}\) 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 $^{13}$C NMR analysis of uC28NH$_2$ and uC33NH$_2$ 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, Lohn, et al. with on-surface bisimine formation.\(^{47}\) 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

<table>
<thead>
<tr>
<th>compound</th>
<th>$a$ [nm]</th>
<th>$b$ [nm]</th>
<th>$\gamma$ [deg]</th>
<th>lamellar phase</th>
<th>domain size average [nm$^2$]</th>
<th>domain size median [nm$^2$]</th>
<th>disordered areas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{28}$-NDI-C$</em>{28}$</td>
<td>4.45 ± 0.24</td>
<td>0.88 ± 0.08</td>
<td>85.21 ± 3.39</td>
<td>A and B</td>
<td>949</td>
<td>373</td>
<td>26 ± 5</td>
</tr>
<tr>
<td>uC$<em>{28}$-NDI-uC$</em>{28}$</td>
<td>4.53 ± 0.08</td>
<td>0.86 ± 0.10</td>
<td>87.33 ± 1.78</td>
<td>A</td>
<td>6764</td>
<td>2923</td>
<td>--</td>
</tr>
<tr>
<td>C$<em>{33}$-NDI-C$</em>{33}$</td>
<td>5.29 ± 0.49</td>
<td>0.99 ± 0.10</td>
<td>84.10 ± 5.28</td>
<td>A and B</td>
<td>1268</td>
<td>540</td>
<td>24 ± 8</td>
</tr>
<tr>
<td>uC$<em>{33}$-NDI-uC$</em>{33}$</td>
<td>5.27 ± 0.08</td>
<td>0.94 ± 0.06</td>
<td>84.93 ± 1.80</td>
<td>A</td>
<td>8026</td>
<td>3684</td>
<td>--</td>
</tr>
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</table>

The lengths of the unit cell vectors are labeled $a$ and $b$, and the internal angle is specified by $\gamma$. The measured values are $4.45 ± 0.24$ nm, $b = 0.88 ± 0.08$ nm, and $\gamma = 85.21 ± 3.39^\circ$ for C$_{28}$-NDI-C$_{28}$, and $a = 5.29 ± 0.49$ nm, $b = 0.99 ± 0.10$ nm, and $\gamma = 84.10 ± 5.28^\circ$ 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 NDI cores flat on 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$_{28}$-NDI-uc$_{28}$ (Figure 2a), while they appeared more separated and resolved in the case of uC$_{33}$-NDI-uc$_{33}$ (Figure 2b). Such behavior is attributed to the structural differences between the two molecules and corroborates the more remote position of the double bond with respect to the NDI core in uC$_{33}$-NDI-uc$_{33}$ (between C11 and C12) compared to uC$_{28}$-NDI-uc$_{28}$ (between C6 and C7).

The double bond is in line with previous reports on C$_{n}$-NDIs. The measured value are $4.45 ± 0.08$ nm, and $\gamma = 84.10 ± 0.08$ for C$_{33}$-NDI-C$_{33}$.

Such behavior is attributed to the structural differences between the two molecules and corroborates the more remote position of the double bond with respect to the NDI core in uC$_{33}$-NDI-uc$_{33}$ (between C11 and C12) compared to uC$_{28}$-NDI-uc$_{28}$ (between C6 and C7)."
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).

![Large-scale STM images (300 nm x 300 nm) of different NDIs at the 1-PO/HOPG interface: (a) C28-NDI-C28 (V_tip = 1 V, I_set = 100 pA), (b) uC28-NDI-uC28 (V_tip = 1 V, I_set = 80 pA), (c) C33-NDI-C33 (V_tip = 1 V, I_set = 100 pA), and (d) uC33-NDI-uC33 (V_tip = 1 V, I_set = 100 pA).](image1)

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, only 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) revealed that the interaction energy between neighboring chains becomes more favorable upon introducing the internal double bonds (Figure S41 and Table S1). Encouraged by these results, we focused on both C28-NDI-C28 and uC28-NDI-uC28 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. 47 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 $a = 44.8$ Å, $b = 8.5$ Å, and $\gamma = 90^\circ$ for C28-NDI-C28 and $a = 44.5$ Å, $b = 8.5$ Å, and $\gamma = 90^\circ$ 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 a 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 for C28-NDI-C28 appears more diffuse.
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.

Synthetic details, characterization of the new isolated compounds, in situ STM imaging at the liquid/solid interface, and computational details (PDF)

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Notes
The authors declare no competing financial interest.

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■ REFERENCES


