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COMMUNICATION

The impact of grafted surface defects on the on-surface Schiff-base chemistry at the solid-liquid interface.

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We investigate the effect of covalently modified graphitic surfaces on the formation of single-layer covalent organic frameworks (sCOFs) at the solid-liquid interface. The impact of different densities of grafted aryl species was tested on the on-surface synthesis of three distinct imine-based 2D sCOFs. The grafted aryl species that act as defects provide steric barriers to the progress of the Schiff-base reaction, and can be locally removed to start the 2D polymer healing process. This unique strategy provides a general approach to study *in situ* this dynamic covalent on-surface chemistry.

Single-layer covalent organic frameworks (sCOFs) have attracted great attention due to the appealing properties anticipated for graphene-like 2D polymers.¹ Much effort has been focused on reaching high-quality, large-scale sCOFs; and impressive results have been achieved in the last years.²⁻⁴ However, controlling the topology, size, shape and dispersity of the material is still difficult.⁵ In order to tackle this challenge, a better understanding of the on-surface reaction is needed.

Most reports focus on creating sCOFs in a controlled ultra-high vacuum (UHV) environment, mainly *via* di-radical coupling after metal-catalyzed homolytic carbon-halogen cleavage.⁶

However, C-C bond formation is highly irreversible, as are most covalent reactions. Under these non-reversible conditions, the as-prepared two-dimensional (2D) sCOFs suffer from small domain sizes and non-uniform frameworks.⁷ Dynamic Covalent Chemistry (DCC)⁸ offers an alternative for this synthetic irreversibility, and is typically active for certain reactions at the solid-liquid interface or under atmospheric control. Under these conditions, molecular building-blocks form robust, yet reversible, bonds under thermodynamic equilibrium.⁹ Among DCC reactions, the condensation between an aldehyde and an amine to create an imine bond is particularly interesting because it takes place under mild conditions, and is affected by a number of factors (*e.g.* temperature, concentration, pH, humidity) that can, in turn, serve to regulate the reaction.¹⁰

In a previous study, we were able to optimize concentration and molar ratio of imine-based sCOFs' precursors, affording full surface coverage of a nearly defect-free 2D polymer.¹¹ Nonetheless, new approaches are required to bring insight into the factors that affect 2D polymer growth in view of directing the propagation of this on-surface polymerization towards a product with well-defined 2D polymer size and shape.

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Electronic Supplementary Information (ESI) available: details of STM measurements and covalent modification of HOPG using cyclic voltammetry, on-surface synthesis of imine-based sCOFs on bare HOPG and on modified HOPG surfaces, and details of scratching experiments. See DOI: 10.1039/x0xx00000x

Fig. 1 Scheme of the general strategy followed in this work towards greater control on sCOF on-surface synthesis. (a) Covalent attachment of 3,5-bis-*tert*-butylbenzenediazonium (TBD) species to the HOPG surface; followed by on-surface Schiff-base 2D-sCOF formation at the solid-liquid interface; along with chemical structure of the molecular precursors. (b) STM nanoshaving process that locally removes covalently bound TBD species, with *in situ* on-surface imine polymerization reaction.

Here, we present such strategy. Highly oriented pyrolytic graphite (HOPG) surfaces have been covalently modified by grafting different densities of 3,5-bis-*tert*-butylbenzenediazonium (TBD) species under electrochemical control.^{12–15} This protocol, which can be finely tuned as a function of the concentration of TBD, provides a set of modified supports available to template the 2D Schiff-base condensation of benzene-1,3,5-tricarbaldehyde (BTA) with *p*-phenylenediamine (PDA), 4,4''-diamino-*p*-terphenyl (DATP) or 9,10-bis(*p*-aminophenylethynyl)anthracene (AABA), respectively (Fig. 1a). The grafted aryl species act as surface defects and affect the DCC reaction, providing a simple strategy to investigate the aspects dictating this dimensionally controlled polymerization and reach fundamental understanding of on-surface reactivity.¹⁶ Furthermore, using nanolithography, grafted molecules were locally removed leading to dynamic sCOFs confined in nanocorrals of defined size and shape (Fig. 1b).

The sCOF system formed by BTA and the shorter di-amino linker PDA was first investigated on a low-density (6000–14000 molecules μm^{-2}) grafted HOPG substrate. The modified surface was prepared according to previous literature using a 0.1 mM TBD aqueous solution.^{15, 17} Then, 5 μL of a mixed octanoic acid solution of BTA and PDA was applied on top of the functionalized substrate at room temperature (see Supporting Information for further experimental details). Remarkably, a very high surface coverage sCOF (88%) is achieved for this system immediately after deposition (Fig. 2a). For the small pore PDA-based sCOF, it is more difficult to discern where in the network the grafted species are located. Even so, the observed grafts are either included in the network, or represent a domain boundary, as they inhibit any

network formation when they agglomerate (see blue areas in Fig. 2). When included in the network, they can be either located inside the pores of the COFs, not causing any disruption to the framework; or in the edges, inducing some network defects (typically missing linkers or 7- and 5-membered rings, as depicted in the magnifications of Fig. 2). Let's note that such effects are commonly observed for imine-based sCOF systems, also on unmodified substrates.^{4, 11, 18–20} In comparison to sCOFs grown on bare HOPG, an increased number of network mismatches could be accounted for (S3 in the S.I.). When drop-casting the reactive mixture onto a very densely grafted HOPG surface (60000–90000 pins μm^{-2}), the BTA-PDA-based sCOF could surprisingly accommodate to this modified substrate, despite the extremely low surface area available for COF adsorption, and cover 86% of the surface (Fig. 2b). The sCOF_{BTA-DATP} system was also investigated on variable density grafted surfaces yielding extended 2D polymer networks (98% coverage both for low- and high-density grafting) with very few defects (Fig. 2c,d). On the other hand, the AABA-based system proved to be more affected by the grafted species on the surface than the previous systems. Still, the adaptability of the Schiff-base chemistry is able to overcome the steric hindrance raised by the modified substrate, and cover 82% of the HOPG surface on low-density grafted HOPG (Fig. 2e). However, on the highly-grafted substrate, sCOF_{BTA-AABA} could not be formed, and only disordered oligomers could be imaged by STM (Fig. 2f).

These experiments show the great extent to which the studied dynamic covalent sCOF systems are capable of adapting. This on-surface reaction is able to surmount the important steric hindrance produced by an increasing amount of grafted TBD molecules on the substrate. The obtained

results on low-density grafted surfaces indicate that sCOFs displaying large pores adapt better to imperfect surfaces. Actually, very large and nearly perfect networks of sCOF_{BTA-DATP} could be obtained (see Fig. S3 in the SI). Note that despite the fact that DATP is a shorter monomer than AABA, and should in principle provide a smaller pore, the latter contains a bulky anthracene moiety that partially fills the sCOF cavity. When considering highly defective substrates, the two systems that succeed at reacting on the surface are: (1) once again the system which produces the larger pores (*i.e.* sCOF_{BTA-DATP}), and can therefore easily accommodate bulky grafted molecules; but also (2) the one formed by the smallest molecular precursors (*i.e.* sCOF_{BTA-PDA}) that are thus able to fit in reduced areas. On the other hand, the AABA building-block with higher relative surface area cannot complete the reaction with BTA on the high-density modified surface. Despite the adaptability of the DCC systems, the increase of grafted pins on the surface resulted in more defective sCOF products of smaller size, broader size spread, and lower coverage.

Next, we studied how the network would respond to the local removal of grafted molecules by means of STM based lithography, *i.e.* nanoshaving.^{16, 21–23} Efficient removal of the grafted molecules is achieved by operating the STM under high current and low bias conditions (typically 0.2 nA and -0.001 V), which bring the STM tip in close proximity to the surface. The process parameters are accurately controlled by the Keysight PicoLITH 2.1 software package. Importantly, nanoshaving is performed *in situ*, meaning that the grafted molecules are removed inside a liquid containing the respective COF precursors (Fig. 1b). In the systems grown on low-density grafted surfaces, some structural changes could be observed after locally freeing the network of grafted surface defects, but the sCOF remains formed (see Fig. S4a in the SI). In contrast, when applying nanoshaving conditions to the sCOFs grown on

high-density grafted HOPG surfaces (PDA and DATP based), not only the grafts were removed but the underlying 2D polymer was also destroyed. Interestingly, as the experiment was carried out at the solid-liquid interface, in the presence of the reactive precursors, we could observe how the sCOF was regenerating as we kept scanning the same area. A representative example of this phenomenon is depicted in Fig. 3. Additional STM data can be found in the SI (Fig. S4b and S4c).

These experiments show that the higher the grafting density, the more the nanolithography conditions affect the underlying covalent network. As we have seen, the grafted species often act as domain boundaries, and therefore, their presence can decrease the domain size of the sCOF. The overall substrate-molecule interactions of the fragmented polymer being weaker, (partial) desorption of the sCOF is observed after applying rough nanolithography conditions. As a matter of fact, by following this nanoshaving strategy one could engineer a 2D polymer of specific size, shape and orientation by precisely de-grafting a well-defined area.²⁴ As a proof of concept, it was essayed to nanoshave a specific area of the densely-grafted HOPG surface in the presence of BTA and AABA precursors, which are otherwise unable to form a sCOF due to steric hindrance (as shown in Fig. 2f). Interestingly, after de-grafting a precise area, the formation of sCOF_{BTA-AABA} 2D oligomer of corresponding size and shape started (see Fig. S5 in the SI). It shall be noted that when moving to fully-grafted surfaces, nanoshaving-induced competitive adsorption processes from unidentified strongly-adsorbing species (which prevent the full growth of the 2D sCOF) arose, despite extensive rinsing protocols.

In this work we have seen how it is possible to affect 2D polymers by precisely pre-modifying the supports for on-surface reaction. Nucleation, diffusion and growth are three separated and kinetically-dominated processes involved in 2D

Fig. 3 Successive STM images displaying (c-f) the regeneration sCOF_{BTA-DATP} on high-density grafted HOPG 168 min after the nanoshaving process (a,b). Imaging conditions: $I_{\text{set}} = 50 \text{ pA}$, $V_{\text{bias}} = -0.86 \text{ V}$. The underlying sCOF_{BTA-DATP} in (a, b) was destabilized after nanoshaving, causing the partial desorption of the 2D polymer (c). Then, a regular and good quality sCOF_{BTA-DATP} starts to reform progressively from the reactive dangling ends located at the borders of the nanoshaved area. This slowly regenerating sCOF_{BTA-DATP} covers most of the available surface area, is interconnected with the remaining sCOF_{BTA-DATP} and follows its same orientation.

crystallization. A low density of nuclei, high diffusion rate and a slow growth rate allow for error-checking reversible processes that can ultimately deliver large, ordered and stable 2D sCOFs. By isolating the mentioned steps, one can reach a better understanding of the polymerization process and aim at controlling the growth kinetics during the formation of covalent bonds. Introducing grafted surface defects raises steric barriers that necessarily impede surface diffusion of unreacted monomers or small oligomers. Nonetheless, almost fully covered surfaces are still obtained for sufficiently porous networks, even when the grafting density is very high. It can thus be concluded that the reactivity of the precursors is not diminished by the grafted surface defects. Rather, depending on the grafting density, product intermediates with variable stability were obtained, as exemplified by nanoshaving experiments. It was indeed seen how lower molecular weight sCOFs were preferably adsorbed on high density covalently-modified HOPG, which were vastly affected by the grafts' removal process. Overall, this approach provides the possibility to include a termination step to the polymerization, otherwise impossible, by saturating the surface with grafted molecules. In a living polymerization reaction such as this one, as long as precursors are provided to the active network, the molecular weight of the 2D polymer increases. Random grafting has been carried out in this particular study, but *via* patterned grafting the dispersity of the 2D polymer could be controlled to produce sCOF oligomers with a well pre-defined size. As a matter of fact, theoretical calculations indicate the possibility to fine-tune the bandgap of the 2D polymer by the crystallite size.²⁵

Conflicts of interest

There are no conflicts of interest to declare.

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