Surface-Confined Crystalline Two-Dimensional Covalent Organic Frameworks *via* on-Surface Schiff-Base Coupling
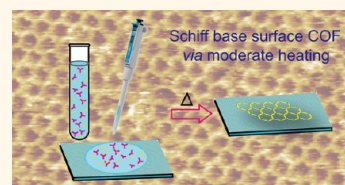
Lirong Xu,[†,‡] Xin Zhou,[†,§] Yanxia Yu,[†,‡] Wei Quan Tian,[†,§,*] Jun Ma,[†] and Shengbin Lei[†,‡,*]

[†]State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, 150080, People's Republic of China, [‡]Key Laboratory of Microsystems and Microstructures Manufacturing, Ministry of Education, Harbin Institute of Technology, Harbin, 150080, People's Republic of China, and [§]Institute of Theoretical and Simulational Chemistry, Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, 150080, People's Republic of China

ABSTRACT We performed a co-condensation reaction between aromatic aldehyde and aromatic diamine monomers on a highly oriented pyrolytic graphite surface either at a solid/liquid interface at room temperature or in low vacuum with moderate heating. With this simple and moderate methodology, we have obtained surface-confined 2D covalent organic frameworks (COFs) with few defects and almost entire surface coverage. The single crystalline domain can extend to more than 1 μm^2. By varying the backbone length of aromatic diamines the pore size of 2D surface COFs is tunable from ~1.7 to 3.5 nm. In addition, the nature of the surface COF can be modified by introducing functional groups into the aromatic amine precursor, which has been demonstrated by introducing methyl groups to the backbone of the diamine. Formation of small portions of bilayers was observed by both scanning tunneling microscopy (STM) and AFM, which clearly reveals an eclipsed stacking manner.

KEYWORDS: Schiff base · covalent organic framework · co-condensation · surface-confined reaction · STM

In the past decade, the self-assembling of molecules into well-ordered arrangements, especially so-called "nanoporous networks", has received much attention.[1,2] The research activities have revealed a number of previously unexplored aspects of monolayer formation such as control of the concentration and surface coverage, self-recognition and self-selection, and the effect of solvents.[3−6] These two-dimensional nanoporous materials have a broad range of potential applications, for instance, hosting and immobilizing a large variety of guest species so that the orientation of guest species can be determined and manipulated, thus offering a new concept for data storage.[7−9] These nanopores can also be chiral, which paves the way for future enantioselective adsorption/separation.[10−12] These nanopores have also been prospected to be used as reaction vessels, for instance, for the template synthesis of inorganic and organic nanoparticles.[13−15] However, such well-ordered crystalline supramolecular nanoporous networks are all sustained by noncovalent interactions such as van der Waals interactions, hydrogen bonds, dipole−dipole interactions, and, at most, metal−ligand coordination,[1,2,14] and thus their stability is restricted. Replacing the noncovalent connection between building blocks with covalent bond seems to be a straightforward solution, which should provide more robust connection and stability.[16,17] Inspired by the successful synthesis of covalent organic frameworks (COFs), on-surface synthesis of an extended surface-supported COF on a single crystalline surface has gained much attention recently.[18,19] Up to now, the formation of surface COFs based on Ulmann radical coupling and self-condensation of boronic acids has been thoroughly investigated.[20−23] Both experimental and theoretical studies have been carried out to improve the surface COF quality and understand the growth mechanism.[24−26] Hierarchical and sequential linking have been investigated in the search for more complex and more ordered surface COFs.[23,27] Other kinds of reactions,

including polyester condensation,[28] polyimide formation,[29] polyamide formation,[30] and polymerization between iron and 1,2,4,5-tetracyanobenzene (TCNB)[31] have also been explored. More and more surface-confined reactions are being discovered, and it may also be possible to use them for the preparation of surface COFs.[32,33] Most of the studies were carried out on single metal substrates under ultrahigh-vacuum (UHV) conditions. It is difficult to avoid unfavorable irreversible cross-linking, which leads to formation of disordered 2D and 3D nanostructures; thus in UHV conditions successful preparation of surface COFs was conducted under kinetically controlled conditions at low surface coverage in order to limit the supply of building blocks. Limited by the irreversible covalent bond formation most of the so-prepared surface COFs suffer from low surface coverage and a lack of long-range order. To date, the realization of long-range ordered high-quality surface COFs is still the key challenge of this area.[17,23]

Though there still remains a lot of experimental and theoretical work to do in order to understand the mechanism governing on-surface polymerization, it is generally agreed that the reversibility of the reaction plays an important role in determining the quality, *i.e.*, the ordering and continuity of the surface COF. Recently, Wan and Lackinger have reported the successful synthesis of long-range -ordered surface COFs based on condensation of boronic acids in either a closed or open vessel.[21,34] Both their experiments revealed that for obtaining high structural quality surface COFs it is important to carry out the reaction under slightly reversible reaction conditions, *i.e.*, in the presence of water. Single crystalline domains more than 200 nm × 200 nm in size have been observed. However, unfortunately the boroxine linker connecting this kind of surface COF can slowly decompose in ambient environment due to the reversible ring-opening reaction, thus limiting its further use as a nanotemplate or nanoreactor.[35]

As another alternative, Schiff-base coupling on solid surfaces is especially interesting. It is stable in ambient conditions and even in aqueous solution in a wide range of pH.[36−38] The lone pair electrons of nitrogen make the Schiff-base group a good ligand for coordination; thus Schiff-base surface COFs can be potentially used in the field of chemical sensing and catalysis. Linderoth *et al.* first proved the possibility of on-surface covalent interlinking of an aromatic aldehyde and aliphatic amine on a Au(111) surface in UHV conditions. Then they tried the condensation between a trialdehyde and a diamine, which resulted in a 2D branched polymer.[37] Using a soft solution methodology Kunitake *et al.* successfully fabricated extended 2D frameworks *via* a surface-mediated Schiff-base reaction between an aromatic amine and aldehyde monomers from an aqueous solution under delicate pH control.[38]

In our present work, we pursue a simple and moderate method to synthesize diverse 2D extended

Scheme 1. Molecular structure of monomers: 1, benzene-1,3,5-tricarbaldehyde; 2, *p*-phenylenediamine; 3, benzidine; 4, *o*-tolidine; 5, 4,4″-diamino-*p*-terphenyl.

aromatic isoreticular Schiff-base surface COFs on a highly oriented pyrolytic graphite (HOPG) surface with almost complete surface coverage, which were characterized by STM and AFM under ambient conditions. The good crystallinity (single domain larger than 1 square micrometer) represents the highest quality of surface COF ever reported up to now.

Triangular aromatic aldehyde and linear aromatic diamines were used as precursors (Scheme 1). The synthesis of surface COFs in our study was carried out by either mixing the linker **1** with diamine in octanoic acid and allowing them to polymerize at the octanoic acid/HOPG interface at room temperature or mixing them in dimethylsulfoxide (DMSO) and polymerized on a surface with moderate heating. This straightforward and simple preparation method allowed us to synthesize a series of regular and extended surface COFs based on the co-condensation of **1** with aromatic diamines of different length. Long-range ordered Schiff-base surface COFs with few defects and almost entire surface coverage were obtained. The corresponding isoreticular pore sizes were from ∼1.7 to 3.5 nm. Our STM and AFM characterization of the so-prepared surface COFs revealed perfect single crystalline domains more than 1000 nm × 1000 nm in size, which is even better than the crystallinity of 2D supramolecular assemblies based on noncovalent interactions. This paves the way for the application of surface COFs as nanotemplates and nanoelectronics, both requiring high crystallinity. We have also demonstrated the functionalization of surface COFs by introducing methyl groups to the backbone of diamine. This allows the fine-tuning of pore size and chemical environment, which is important for applications as nanotemplates, nanoreactors, and chemical sensors. Though the so-prepared surface COFs are dominantly monolayer, the formation of a bilayer was also detected in some areas, and the high-resolution STM images unambiguously confirmed that the bilayers are stacked in an eclipsed manner.[39]

RESULTS AND DISCUSSION

The general reaction scheme of benzene-1,3,5-tricarbaldehyde and aromatic diamide precursors is illustrated in Figure 1. Through elimination of one
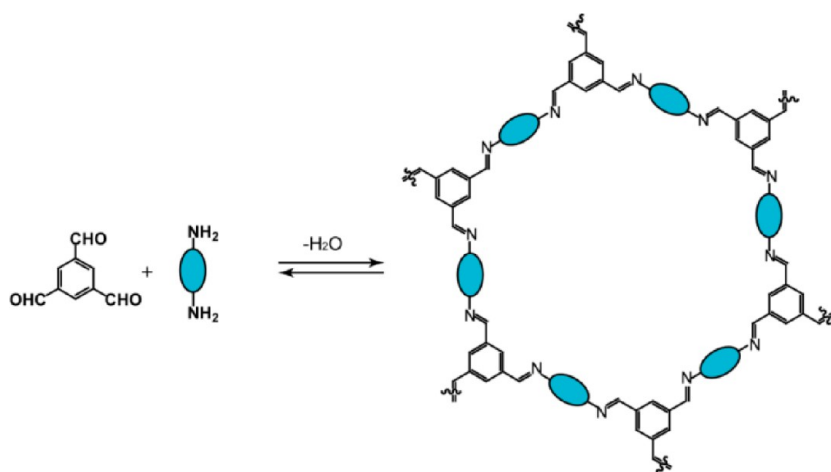
Figure 1. Reaction scheme of benzene-1,3,5-tricarbaldehyde and different aromatic diamines into hexagonal surface COFs. The organic backbones of aromatic diamines are symbolically represented by ellipses.
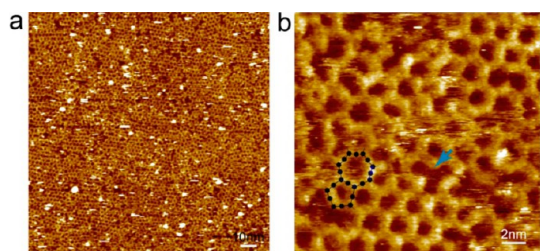

Figure 2. (a) Large-scale STM image of surface COF_{1+2}' at the octanoic acid/HOPG interface. (b) High-resolution STM image of surface COF_{1+2}'; a pentagonal neighboring with heptagonal pore is highlighted by an overlaid schematic model, and a typical polygon resulting from incomplete condensation is indicated by a blue arrow. The tunneling conditions were $I = 0.05$ nA, $V = 0.50$ V.

water molecule, $-CHO$ and $-NH_2$ undergo a co-condensation reaction and form a Schiff-base framework.[38] If tricarbaldehyde **1** fully reacted on the HOPG surface with diamine **2**, **3**, **4**, and **5** (Scheme 1), they can form extended honeycomb networks with hexagonal pores, resulting in a surface-confined covalent organic framework with tunable pore size. The vertex of the hexagon is occupied by a phenyl group of **1**, and the side of the hexagon is composed of the organic backbone of the aromatic amine monomer.

Synthesis of Surface COF_{1+2}' at the Liquid/HOPG Interface. Schiff-base coupling of **1** and **2** was previously reported by Wang *et al.* in the solution synthesis of bulk COF-LZU1.[39] For the on-surface coupling, the simplest preparation procedure in our study was the *in situ* synthesis at the solid—liquid interface at room temperature. Extended adlayers of π-conjugated surface COF_{1+2}' were observed by STM several minutes after deposition (Figure 2a). The reaction takes place quite fast on the surface, and the resulting surface COF covers the entire surface. High-resolution STM images illustrate that the surface COF is composed of well-ordered honeycomb domains tens of nanometers in size. Though most of the domains follow almost the

same orientation, small derivations also exist, which can be reflected from the scattered FFT pattern of the image (Figure S1). This implies that the interaction of the surface COF with the graphite substrate is weak. Most of the pores are hexagons, highlighting the completeness of the reaction (Figure 2b). Large polygons resulting from the incomplete reaction can also be observed as the one highlighted with a blue arrow in Figure 2b. It is very interesting that a typical defect, one heptagon neighboring with a pentagon, was frequently observed in the 2D surface COF, which is similar to the Stone—Wales defect structure of graphene.[40] This kind of defect was also observed in other covalently bonded 2D honeycomb networks,[20,41] however, never in the noncovalent ones. The lattice parameters of this surface COF were measured to be $a = b = 2.1 \pm 0.1$ nm, $\alpha = 60 \pm 2°$. The hexagonal pore size was 1.7 ± 0.1 nm, which is in good agreement with that expected from the chemical structure and DFT simulation (see Supporting Information), confirming the covalent bond formation.

For obtaining highly ordered surface-confined COFs, the understanding of the growth mechanism is very important. The multiply misorientated domains in the surface COF_{1+2}' may indicate the growth at the solid/liquid interface happens simultaneously at different sites. One proof supporting this hypothesis is the observation of domain boundaries resulting from incomplete reaction due to space confinement, as shown in Figure 3b and c. As indicated by the white arrows at such boundaries, only two out of the three aldehyde groups reacted with the amines. Due to the limited space, the third aldehyde group was not approachable by amine monomers. This kind of domain boundary is possible only where the growth happens simultaneously at different sites and two or more growing domains meet together. The black and red arrows in Figure 3c indicate the other two defects, where one aldehyde and one amine building block was missing, respectively.
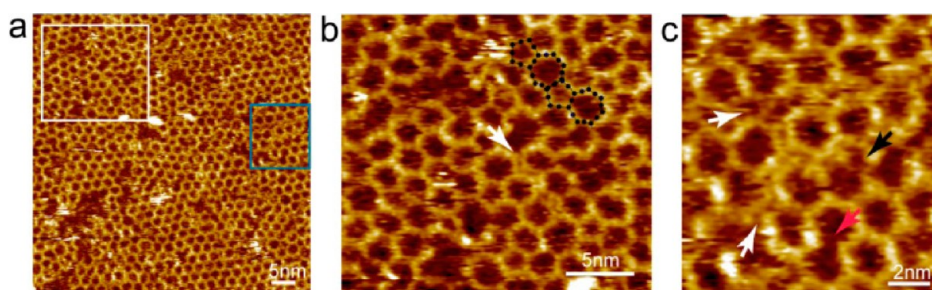
Figure 3. (a) STM image showing clearly the domain boundaries resulting from incomplete condensation. (b and c) Digital magnifications of the areas marked by the white and blue rectangles, respectively. The tunneling conditions were $I = 0.05$ nA, $V = 0.50$ V.

Though the surface COF$_{1+2}'$ can be synthesized by surface condensation at room temperature at the octanoic acid/HOPG interface, applying a similar approach for the condensation of **1** with **3**, **4**, and **5** failed. Only amorphous polymers were observed even after days of reaction at room temperature or heating to 40 °C (Figures S2 and S3). Thus we switched to an alternative approach where the monomers were dissolved in DMSO and then a mild thermal treatment was applied.

Synthesis of Surface COF$_{1+2}$, Surface COF$_{1+3}$, Surface COF$_{1+4}$, and Surface COF$_{1+5}$ at the Gas/Solid Interface. The realization of stable long-range ordered 2D surface COF material might be the utmost challenge for on-surface chemists.[17,23] Though the *in situ* synthesis of surface COF$_{1+2}'$ is successful, the regularity still needs to be improved. The co-condensation reaction at the gas/solid interface is carried out in a vacuum oven at 140 °C with a base pressure of <133 Pa. The higher temperature may increase the reversibility of the reaction and also the diffusion rate of the building blocks, and thus help to improve the regularity of the surface COF. The low vacuum facilitates the removal of solvent, unreacted monomers, and the byproduct, water, during the heating procedure (the co-condensation process), leaving a surface COF with entire surface coverage and avoiding multilayer formation. Our comparative experiment at ambient pressure confirmed the importance of vacuum conditions. In comparison with the surface COF prepared at ambient pressure, the one obtained under vacuum showed better crystallinity and uniformity (Figures S4–S7). Besides, unreacted monomers or oligomers within the pores (Figure S6) were largely reduced.

In order to obtain a variety of isoreticular 2D SCOFs, the backbone of the diamine can be elongated by adding phenyl groups one by one. This can result in a (S)COF with larger pores and periodicity while with the topology remaining unchanged. This principle has been successfully carried out for bulk boronic acid-derived COFs and on-surface condensation of diboronic acids.[42,43] This strategy can be used for the design of host systems for functional guest molecules with different sizes.[44]
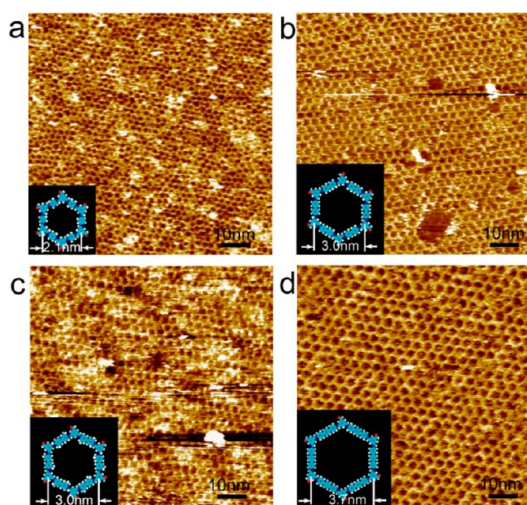

Figure 4. Large-scale STM image of surface COF$_{1+2}$ (a), surface COF$_{1+3}$ (b), surface COF$_{1+4}$ (c), and surface COF$_{1+5}$ (d). The inset shows the chemical structure of a hexagonal pore of every 2D surface COF, respectively. The tunneling conditions were $I = 0.05$ nA, $V = 0.50$ V.

Well-defined SCOFs with adjustable pore size and periodicity can be prepared with the same synthesis procedure with Schiff-base coupling of **1** with **2**, **3**, **4**, and **5**, respectively. Representative STM images of all frameworks are shown in Figure 4. After treatment at 140 °C in vacuum conditions, co-condensation of **1** and **2** yields a surface COF with almost complete surface coverage (Figure 4a). The structure is the same as surface COF$_{1+2}'$, which resulted from *in situ* Schiff-base coupling of **1** and **2** at the liquid/HOPG interface, while with fewer defects and misorientated domains. The diameter of the hexagonal pores was 1.7 ± 0.1 nm, which is in good agreement with the chemical structure model and confirms the covalent bond formation. Comparing Figure 4a with Figure 2a we can see that the surface COF$_{1+2}$ prepared with mild heating at 140 °C shows better quality. Bigger domains and fewer defects were observed. Domain boundaries as shown in Figure 3a were not revealed, indicating that the reaction was more complete and showed higher reversibility at elevated temperature. A comparative experiment carried out at 80 °C in vacuum conditions showed that domain boundaries resulting from

incomplete reaction still exist (Figure S8), which confirms that a higher temperature is necessary. Thus 140 °C was used for the preparation of all the remaining surface COFs.

Highly ordered 2D surface COF$_{1+3}$, surface COF$_{1+4}$, and surface COF$_{1+5}$ with adjustable pore size and periodicity can be obtained through similar thermal treatment of **1** with **3**, **4**, and **5**. Representative STM images are shown in Figure 4b−d. The long-range order and structural perfection of the framework can be seen from the images. The topography is dominated by hexagonal structure. The experimental lattice parameter of these *p*6 symmetric 2D surface COFs are $a = b = 3.0 \pm 0.1$, 3.0 ± 0.1, and 3.7 ± 0.1 nm and $\alpha = 60 \pm 2°$. The sizes of the hexagonal pores were 2.6 ± 0.1, 2.4 ± 0.1, and 3.5 ± 0.1 nm, respectively, which agree well with that expected from the chemical structure and confirms the covalent bond formation. The brighter areas are attributed to residual unreacted monomers filling the pores or oligomers overlaid on the surface COF. STM images of surface COF$_{1+3}$ and surface COF$_{1+5}$ show large uniform domains with regular hexagonal pores. The perfection in ordering might indicate that the thermal treatment provides better reaction reversibility.

For the synthesis of surface COFs on a HOPG surface, although a basically well-ordered monolayer is dominant, the formation of islands of bilayer structure was also observed. This is true for all the surface COFs in our current work. Figure 5 shows typical bilayers of surface COF$_{1+3}$ and surface COF$_{1+5}$. The second layer shows brighter contrast in comparison with the first layer. The section profile (Figure S10) indicates the height of the bilayer is nearly two times that of the monolayer, which confirms the formation of a bilayer. From the hexagonal lattice of the high-resolution STM image (Figure 5b and d), it can be concluded that the second layer sits exactly on top of the first layer with no observable shift. Thus with the aid of high spacial resolution of STM imaging we can unambiguously conclude that the bilayer surface COFs stack in an eclipsed manner.

Our STM characterizations provide direct evidence of high uniformity and crystallinity of the surface COFs prepared with the mild thermal treatment in vacuum conditions. The STM observations also indicate that the surface COFs are mainly monolayer. To further confirm the quality of the surface COFs in larger scale, we have performed AFM characterization, and the result is shown in Figure 6.

Figure 6a shows a height image of surface COF$_{1+5}$ scanned within a more than 10 μm area. On the terraces of HOPG the surface COF$_{1+5}$ shows very high uniformity with some conglobations 30−50 nm in diameter. These conglobations line up along step edges and are considered to be aggregates of polymers formed from a condensation reaction, most likely
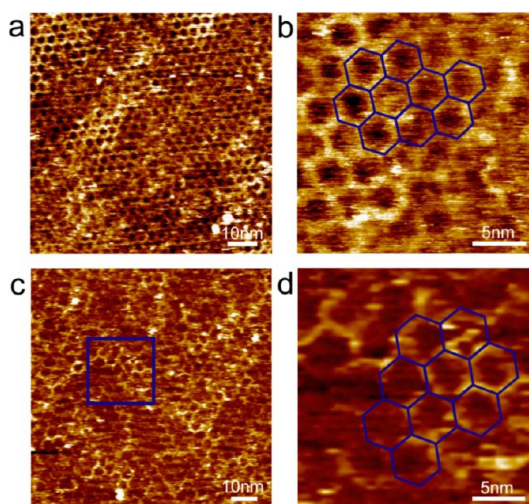

Figure 5. (a) Large-scale STM image of bilayer surface COF$_{1+3}$. (b) High-resolution STM image of bilayer surface COF$_{1+3}$. (c) Large-scale STM image of bilayer surface COF$_{1+5}$. (d) Digital magnification of the area marked by the blue rectangle. The second layer shows brighter contrast in comparison with the first layer, and the first and second layer exhibit eclipsed stacking, as indicated by the blue hexagons. The tunneling conditions were I = 0.1 nA, V = 0.5 V.
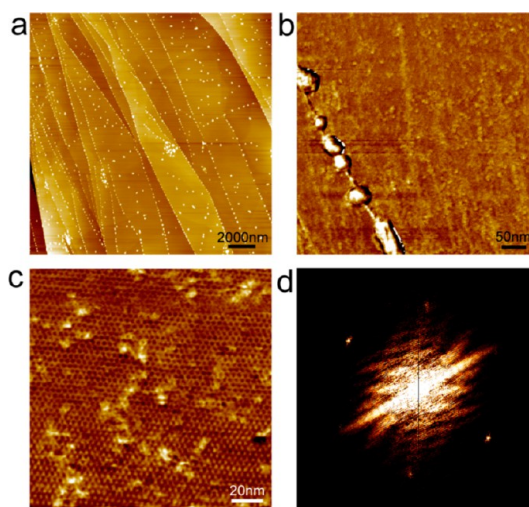

Figure 6. Height (a) and phase AFM images (b and c) of the surface COF$_{1+5}$ show excellent full surface coverage. (d) Corresponding FFT pattern of image (b). The nearly perfect long-range ordering could be seen from both the high-resolution phase image and the FFT pattern.

amorphous. A close-up observation on the flat terrace (Figure 6b) reveals that the surface is covered with uniform honeycomb networks with perfect crystallinity: the FFT (Figure 6d) of the phase image shows only one set of diffraction dots, which proves that the whole area is a single crystalline domain. AFM characterization revealed a single crystalline domain larger than 1 square micrometer, though we believe that actually the size is even bigger. One surprising point is that even the step edges of HOPG do not interrupt the continuity of the surface COF: the networks in the

lower left of Figure 6b show good continuity with the other parts. High-resolution AFM images also confirm the existence of the bilayer (Figure 6c), which appears as small protrutions with a height of ~0.5 nm. The phase image in Figure 6c also confirms the eclipsed stacking of the second layer.

DISCUSSION AND CONCLUSIONS

In the present work, we applied simple methodologies for the preparation of surface COFs with few defects and high uniformity at octanoic acid/HOPG or gas/HOPG interfaces. The on-surface coupling at the liquid/HOPG interface represents the simplest preparation procedure, which invloves only dissolving monomers **1** and **2** in octanoic acid and then drop-casting onto a HOPG surface at room temperature. An extended surface COF was obtained at the liquid/HOPG interface spontaneously.

On the other hand the on-surface condensation *via* mild heating under low vacuum exhibits wider adaptability to a variety of monomers. The higher reaction reversibility and diffusion rate at elevated temperature enable formation of surface COFs with high uniformity and crystallinity. Utilizing this approach, four well-ordered honeycomb Schiff-base surface COFs were prepared on a chemically inert HOPG surface. All of the surface COFs prepared show almost complete full surface coverage and high structural quality. STM and AFM characterizations confirmed that the so-prepared surface COFs are dominantly monolayer; only limited bilayer islands and oligomers were observed. Structural versatility of the surface COFs was realized by co-condensation of **1** with four different aromatic amides, respectively. By varying the size (or the groups) of the aromatic amides, a series of isoreticular Schiff-base surface COFs were prepared. The corresponding pore sizes were from ~1.7 to 3.5 nm. These 2D surface COFs with different pore sizes are good candidates to host different functional guest molecules.[45] They also have potential to be used as filters or nanoreactors. The geometrical and electronic structures of surface COF$_{1+2}$ and surface COF$_{1+3}$ were explored using the DFT method (see SI). The repeating periods estimated from the DFT optimized conformation agree well with that measured from STM images, which confirmed the covalent connection of the surface COFs.

The low vacuum helps the removal of unreacted monomers, solvent, and water molecules during the thermal treatment, which was confirmed by comparison with surface COFs obtained under ambient pressure. More residual monomers and oligomers were revealed on the samples prepared under ambient pressure, though long-range ordered surface COFs can also be obtained. The fact that long-range ordered surface COFs can be obtained under both ambient pressure and low vacuum indicates that temperature is more important than the existence of water to verify the reaction reversibility during the on-surface synthesis of these surface COFs.

It was interesting that in surface COF$_{1+2}$′ and surface COF$_{1+2}$ we had observed the 5+7 defects, which is an analogue of the typical Stone−Wales defect of graphene. These structures are only observed in the covalently connected surface-confined networks and in one way proved the structural similarity of the honeycomb surface COFs to that of graphene. In addition, we have demonstrated the possibility of functionalizing the Schiff-base surface COFs by introducing methyl groups to the backbone of amine monomers. In this way the pore size of a surface COF can be accurately adjusted (2.6 ± 0.1 nm for surface COF$_{1+3}$ *vs* 2.4 ± 0.1 nm for surface COF$_{1+4}$) without changing the repeating period. If replaced by other alkyl or hydroxyl groups, *etc.*, the size, polarity, and functionality of the surface COFs can be engineered. This opens the perspective of future experiments to introduce other active groups to modify the pore size, polarity, and reactivity of surface COFs for utilizing them as nanotemplates, nanoreactors, and catalysis.

Both STM and AFM characterizations have revealed the formation of a bilayer structure, though only in small areas. Molecularly resolved images unambiguously confirmed that for all four surface COFs the first and the second layer exhibited eclipsed stacking. Considering the conjugated chemical structure and coordination ability of Schiff bases, these highly ordered Schiff-base surface COFs can be good candidates for further applications in the field of nanoelectronic devices, nanoreactors, heterocatalysis, and chemical sensors.

MATERIALS AND METHODS

Benzene-1,3,5-tricarbaldehyde (**1**), *p*-phenylenediamine (**2**), benzidine (**3**), *o*-tolidine (**4**), 4,4″-diamino-*p*-terphenyl (**5**), octanoic acid, and dimethylsulfoxide were purchased from J&K and used without further purification. For sample preparation of a 2D surface COF at an octanoic acid/HOPG interface, **2** and **1** were dissolved in octanoic acid with a mass concentration of 0.1 mg/g, respectively. Then a small amount of mixing solution with a mol ratio of about 3:1 was directly applied to freshly cleaved HOPG at room temperature. For sample preparation of 2D surface COFs at the gas/HOPG interface, the monomers were

first dissolved in DMSO with a mass concentration of 1 mg/g, respectively. Then the aromatic amine and aromatic aldehyde were mixed in a mol ratio of about 3:1. Then the solutions were diluted 100 times. A ~5 μL amount of the mixing solution was drop-cast on the freshly cleaved surface of HOPG. The drop-cast samples were positioned in a preheated vacuum oven equipped with a rotary-vane vacuum pump at 140 °C for ~30 min with a pressure of <133 Pa. The low vacuum helps the evaporation of the solvent, water, and unreacted monomers during the thermal treatment. The samples were taken out of the oven and cooled to room temperature, then characterized by scanning

tunneling microscopy (STM). Co-condensation of **2** and **1** and of **5** and **1** was also performed under ambient pressure at 140 °C for ~30 min as control experiments. STM measurements were performed by using an Agilent 5100 scanning probe microscope with mechanically formed Pt/Ir (80/20) tips under ambient conditions. All images were taken in the constant current mode. The calibration of STM images was carried out by using an atomic resolution HOPG lattice. AFM measurements were performed by using an Agilent 5100 scanning probe microscope in the tapping mode. The chemical structure models were built with HyperChem software.

Conflict of Interest: The authors declare no competing financial interest.

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