

On-Surface Dynamic Covalent Chemistry

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Abstract On-surface synthesis has become a very promising bottom-up approach to obtain a functional surface with designable chemical structures. Dynamic covalent chemistry is an interesting reaction strategy to form thermodynamically controlled products utilizing the reversible covalent bond as linkage, which can be formed, broken, and reformed during the reaction and therefore provide an incidence of error-checking and self-healing. In this chapter, we focused on the surface-assisted synthesis of molecular nanostructures using dynamic covalent linkers. By proper tuning the on-surface dynamic covalent reaction processes, highly ordered covalent bond connected nanostructures can be obtained on surfaces.

1 Introduction

One of the exciting prospects with the development of nanoscience and nanotechnology is to build up functional systems using molecules, which is not only a subject for fundamental surface science study, but also closely related to many emerging technologically important applications, such as catalysis, sensor, and organic electronics. The self-assembled molecular nanostructures on surface are driven by the molecule–substrate interaction and intermolecular interaction. The most important feature of the self-assembly is the highly ordered structure, which is generally thermodynamically favored. The key to achieve thermodynamic equilibrium is that the non-covalent interactions are generally weak and reversible. By tuning the weak but appreciable non-covalent interactions, a variety of supramolecular nanostructures on surfaces have been constructed. At the same time, the weak nature of the non-covalent interaction imposes great challenge to the molecular engineering of molecular nanostructures. For example, the self-assembly

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is generally very difficult to predict. Slight modification of molecular structures, even for homologue molecules with the very same functional groups, may result in the significant change of interaction modes and therefore the resulting architectures [1]. Moreover, molecular nanostructures fabricated by non-covalent interaction generally lack the necessary stability to be used in functional systems.

Recently, great attention has been paid to construct molecular nanostructures via covalent synthetic chemistry on surface [2]. The covalent bond is robust and suitable to be used to direct the topology of the resulted nanostructures. On one hand, the on-surface synthesis chemistry has unique features from the viewpoint of fundamental surface science. At a first glance, the chemical reactions taking place on the surface seem quite similar to the corresponding bulk reaction, since utilizing the same reaction precursors and reaction process. However, the introduction of surface provides an active element to modulate the reaction. Due to the surface-confinement effect, many reaction routes, which can take place in the three-dimensional space, probably cannot act [3]. In addition, the surface–molecule interaction may modulate the configuration and diffusion of precursors and intermediates on the surface and thereafter affect the reaction process. More obviously, the surface, especially the transition metal surface, may catalyze the reactions [4–8]. On the other hand, on-surface synthesis provides new venue to obtain molecular architectures. The covalent bond not only significantly improves the stability of the resulted nanostructures, but also may facilitate the charge transportation and thus brings great application prospects of the resulted nanostructures for electronic device application. Furthermore, the surface-assisted synthesized strategy could be a facile route to achieve novel nanostructures that cannot be constructed by other methods. For example, on-surface polymerization can overcome the solubility issue and has been applied to obtain highly regular polythiophene [9]. In addition, surface can be used as template and support to synthesize highly ordered 2D polymers, which is difficult to achieve from a solution-phase synthesis route [10].

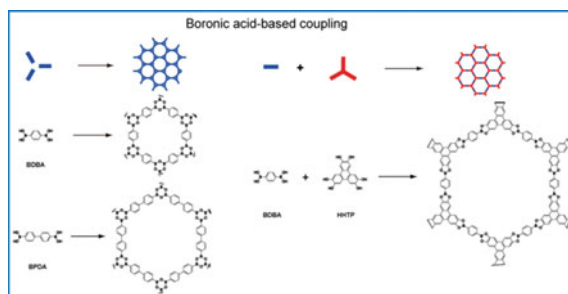
Recently, great progress has been made in the field of on-surface synthesis [11–14]. A variety of nanostructures, including one-dimensional lines, oligomers or polymers, macrocycles, and two-dimensional porous networks, have been successfully fabricated. The typical coupling reactions investigated in these studies include Glaser coupling, Ullmann coupling, Sonogashira coupling, boronic acid condensation, the reaction between boronic acid and diols, the schiff base coupling reaction, the polyester formation reaction, the polyimide formation reaction, and the polyimide formation reaction. Among them, we are particularly interested in applying dynamic covalent bonds as linkers during the construction of surface-assisted organic nanostructures. Compared to conventional covalent bond, the formation of the dynamic covalent bond is a thermodynamically controlled process. Dynamic covalent bond is reversible and can be reconstructed, and therefore, an error-checking and self-healing process can be realized during the reaction. By applying the dynamic covalent bonds, the most thermodynamically stable product can be obtained. Previously, dynamic covalent chemistry [15] has been widely explored to construct molecular nanostructures and to form responsive materials. When interfacing dynamic covalent bond with on-surface synthesis

strategy, the benign feature of reversibility has been demonstrated to be very important to facilitate the formation of highly ordered covalently linked molecular nanostructures.

In this chapter, we focus on the on-surface dynamic chemical reactions. The chapter is sectioned by coupling reaction types, such as boronic acid dehydration reaction, Schiff base coupling reaction, and others. Furthermore, each section is organized in term of the dimensionality of the targeted molecular nanostructures. Finally, a conclusion and outlook section conclude the chapter.

2 Boronic Acid Dehydration Reaction

The dynamic covalent chemistry involving boronic acid group has been well known. As shown in Scheme 1, self-condensation of three boronic acids with elimination of three water molecules can form the boroxine rings, whereas the condensation between boronic acid and catechol can lead to a boronate ester. Both reactions are highly reversible and can be applied to synthesize 2D and 3D materials. The first bulk covalent organic framework (COF) [16] material was synthesized by boronic acid dehydration reaction. The boronic acid-based coupling reactions have been applied to construct nanostructures on the surface. A series of boronic acid-based and boronate ester-based surface covalent organic frameworks (SCOFs) have been obtained as shown in Scheme 1. 1,4-benzenediboronic acid (BDBA) was utilized as building blocks to construct surface covalent organic frameworks on Ag(111) surface in ultrahigh vacuum (UHV) as shown in Fig. 1a [17]. Hexagonal network with pore size about 1.5 ± 0.1 nm was formed by BDBA on Ag(111) surface. SCOF-2, a hexagonal network with pore size about 2.9 nm as displayed in Fig. 1b, was synthesized by the co-condensation of BDBA and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP). During the synthesis process of SCOF-2, in order to avoid the self-condensation of the BDBA, a small amount of HHTP was untimely dropped on the Ag(111) surface.



Scheme 1 Molecular structures of diboronic acid and catechol building blocks. BDBA (1,4-benzenediboronic acid). HHTP (2,3,6,7,10,11-hexahydroxytriphenylene). BPDA (biphenyl-diboronic)

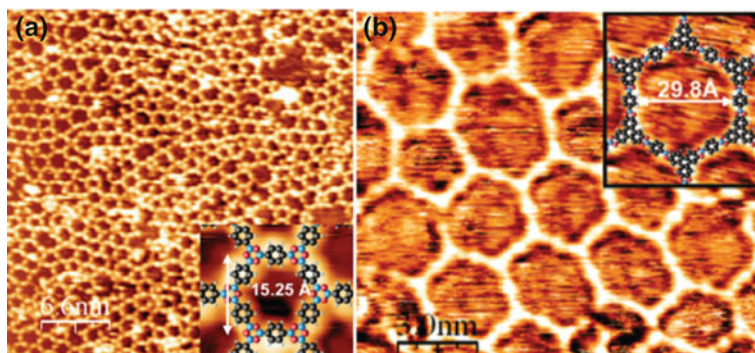


Fig. 1 **a** Self-condensation of BDBA. **b** Co-condensation of BDBA and HHTP. The corresponding structural models and the lattice parameters as indicated in the *Insets*. Copyright 2008 American Chemical Society

Other than the regular hexagonal networks, many polygon structures such as pentagon, heptagon, and octagon were formed at the same time. In the formation of covalent bond, a small number of faults resulted in the irregular polygon distribution. Deformation of the perfect hexagon structure or an incomplete ring closure in the boroxine may lead to the different polygons. Unfortunately, annealing the network at high temperature has little effect to remove the bond faults.

Obviously, the orderliness of the covalent networks from boronic acid-based condensation reactions is not comparable to that of supramolecular assembly. Since then, great efforts have been made to improve the quality of the boronic acid-based covalent networks. Dienstmaier and coworkers synthesized ordered surface covalent organic framework based on the condensation of BDBA (Scheme 1) in two different methods [18]. In method 1, the precursors were prepolymerized in a solvothermal condition to form oligomers, which were then casted on HOPG. Hexagonal frameworks with small domains up to 40 nm, which is related to the reaction temperature, were obtained. In method 2, they deposited the BDBA solvent on HOPG and directly heated the precursor-containing surface. By applying method 2, hexagonal frameworks with larger domain size were formed compared with method 1. Such a procedure was applied to reticular synthesis of a series of porous networks with tunable pore size ranging from 1.0 to 3.2 nm by choosing precursors with the same two boronic acid functionalities and different skeleton lengths [19].

In order to improve the regularity and increase the typically domain size of the SCOFs, thermodynamic equilibrium control method has been utilized in the surface-assisted synthesis. Guan and coworkers synthesized three highly ordered boronic acid-based SCOFs with large scales on the HOPG [20]. Figure 2a, b displays the SCOF from BPDA as the reaction precursor. They introduced $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ powder into the sealed autoclaves, which can release water molecular during the heating process. The water molecular can shift the reaction direction and control the chemical equilibrium of the dehydration reaction of

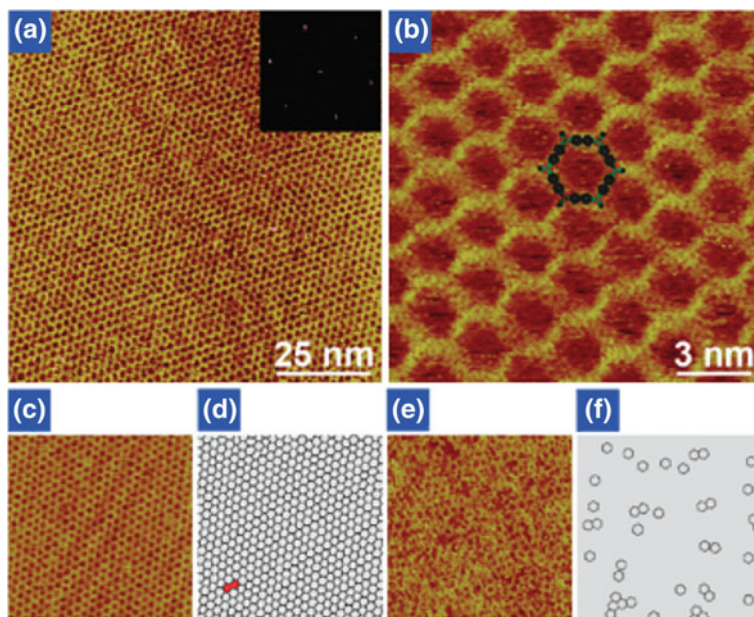


Fig. 2 **a** A STM image of SCOF on HOPG formed after dehydration of BPDA precursors at 150 °C. The *inset* depicts the corresponding FFT of the image. **b** A high-resolution STM image showing the hexagonal structure. Model of the hexagonal structures is overlaid and drawn to scale. **c** and **d** A STM image and the delineated image of SCOF obtained in the presence of H₂O. **e** and **f** A STM image and the delineated image of SCOF obtained without the presence of H₂O. Copyright Royal Society of Chemistry

boronic acid. Therefore, this strategy significantly promoted the degree of the reversible dehydration reaction, and the miss-linked defects have more chances to be remedied. As shown in Fig. 2c, d, the coverage of the ordered hexagonal SCOF can achieve 98 % and the size of ordered domain can reach more than 200 nm when using H₂O as equilibrium control agent. In contrast, without the present of water, only about 7 % hexagonal ring was found on the HOPG as shown in Fig. 2e, f, according to the statistical analysis. Similarly, by applying water as chemical equipment agent, a series of boronic acid dehydration-based 2D COFs with different pore sizes and large domain sizes were synthesized on the surface. Such an equilibrium control method can be understood by Le Chatelier's principle. The boroxine reaction is a dynamic covalent reaction with H₂O as by-product. Adding water to the closed system can change the Gibbs energy of the reaction and shift the reaction backward to favor the correction of defects and promote the self-healing abilities. Finally, the highly ordered surface nanostructures with thermodynamically more favored hexagonal structures were obtained.

A covalent organic framework based on a two-step strategy though the sequential boronic acid dehydration reaction and Ullmann reaction has been prepared by Faury et al. [21]. They utilized p-bromo-benzene boronic acid, a

bifunctional molecule, and had the potential to take place boronic acid dehydration reaction and Ullmann reaction, as building block. When annealing the molecules under UHV conditions on Au(111) surface, the boronic acid dehydration reaction firstly took place and resulted in boroxine rings-linked trimers. With increasing temperature, the Ullmann reaction was activated and a final porous network could be formed. This sequential synthesis strategy gives us new inspiration in the surface-assisted synthesis of complex structures.

3 Schiff Base Reaction

Imines, or C=N, is an important functional unit and has multiple applications in organic synthesis, such as for the preparation of metal complex and shape-persistent macrocycles [22, 23]. The generation of imine bond from aldehyde and amine groups is reversible and is a dynamic covalent bond. The Schiff base reaction unusually takes place under mild reaction conditions and has attracted great interests for on-surface synthesis. Many surface nanostructures with different topologies, such as the molecules, the oligomers, and the COFs, have been successfully constructed.

3.1 Surface Schiff Base Reactions

Weigelt et al. utilized octylamine and aromatic dialdehyde as building blocks and directly got a covalent interlinked product through surface-assisted synthesis. Experiments were carried out on Au(111) under UHV conditions. The ex situ STM and near-edge X-ray absorption fine structure spectroscopy experiments certified that the diimine can be directly obtained by on-surface synthesis [24].

Exchange reaction is an important feature of dynamic covalent chemistry. For example, the primary amine can react with imine group to result in transimination. Such process has been extensively explored in solution phase to form so-called dynamic covalent library. Ciesielski and coworkers investigated surface-mediated transamination process and compared with solution processes. The reactions were carried out between a long aliphatic-equipped dialdehyde (A) and three α,ω -diamines (B₂, B₆, B₁₂) with different lengths of aliphatic chains at the liquid–solid surface [25]. Firstly, the formation of monolayer diimines A₂B₂, A₂B₆, and A₂B₁₂ was achieved by the reaction of A with B₂, B₆, and B₁₂, respectively, and observed by in situ STM. When B₆ solution was added to the preexisting A₂B₂ structure, A₂B₆ layer was obtained. Then, the addition of B₁₂ solution led to the formation of A₂B₁₂ monolayer. However, the reverse experiment from A₂B₁₂ to A₂B₆ can only be realized by the presence of large excess of B₆ at the solid–liquid interface and over a period of time. More interestingly, the A₂B₂ cannot be formed even further adding the concentration of B₂ solution. The control experiments carried out in solution phase indicate that the transamination reaction can take place smoothly and

the mixture of the A_2B_2 , A_2B_6 , and A_2B_{12} can be obtained independently to the transformation sequence. The results confirmed that the molecule–surface interaction is the critical selective force that drives the on-surface reactions, which is different from the solution reaction.

3.2 Schiff Base Reaction Induced Self-assembly

Generally, self-assembly process is driven by weak interactions, such as van der Waals forces and hydrogen bonds. In most cases, building blocks were firstly synthesized in solution by normal organic routes and then loaded on the surface for surface self-assembly process. However, by dynamic covalent chemistry, the formation process of building blocks and the reaction process of building blocks can take place on the surface at the same time. When surface reactions are combined with self-assembly process, the surface nanostructures can be tuned and novel nanoarchitectures can be obtained.

Li and coworkers demonstrated the Schiff base reaction induced transformation of surface assembly. 1,3,5-tri(4-formylphenyl)benzene, which carries three aldehyde groups, is observed to form lamellar structures on HOPG by self-assembly [26]. When another building block 5-aminoisophthalic acid was added, the nanostructure changed from lamella to honeycomb network. The structure transition resulted from the reaction of the two building blocks. The Schiff base reaction occurring at the liquid–solid interface between aldehyde and amine led to a carboxyl group-containing triangular imine oligomers. By the hydrogen bonds of the carboxyl terminus, the triangular imine oligomers self-assembled and the hexagonal nanostructure were formed. Furthermore, the on-surface Schiff-base reaction can be utilized to construct chiral nanostructures [27].

Liu and coworkers constructed nanoporous networks by self-assembly of melamine-capped molecules through surface-assisted synthesis method [28]. When melamine (MA) reacted with twofold symmetrical terephthalaldehyde (TPA) as shown in Fig. 3a, a hexagonal porous network was obtained as shown in Fig. 3c. Two molecules MA reacted with one molecule TPA leading to the formation of candy-shaped imine oligomers. Then, the imine oligomers self-assembled through the hydrogen bonds existing at the unreacted MA units, and therefore, a porous network was formed. When MA reacted with threefold symmetrical 1,3,5-triformylbenzene (TFB) displayed in Fig. 3b, a hexagonal nanostructure with pore size about 1.3 nm was obtained as shown in Fig. 3d. Three molecules MA reacted with one molecule TFB leading to windmill-shaped imine oligomers. Then, the imine oligomers self-assembled through the hydrogen bonds existing at the unreacted MA units, and therefore, a porous network was formed. The on-surface Schiff base reaction taking place between melamine and aldehyde with different symmetries resulted in molecules terminated by MA. The hydrogen bonds formed between the unreacted amines of the MA play a significant role in the nanostructure

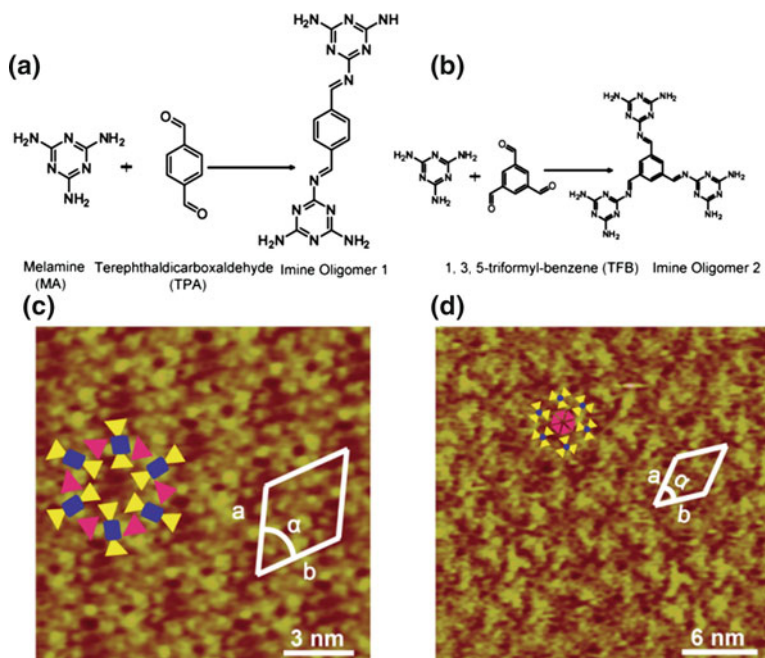


Fig. 3 **a** Chemical structures of imine oligomer 1. **b** Chemical structures of imine oligomer 2. **c** High-resolution STM image of imine oligomer 1. **d** High-resolution STM image of imine oligomer 2. Copyright Wiley-VCH

formation process. The combination of the surface coupling reaction and assembly processes provides a new perspective to the fabrication of surface nanostructures.

3.3 The Schiff Base Reaction-Based Covalent Organic Frameworks

Two-dimensional COFs, which have monolayer thick sheet and covalently bonded linkage, are expected to display unique properties resulting from the reduced dimensionality, planer structures. Many SCOFS have been fabricated on the surface by Schiff base coupling.

Tanoue and coworkers synthesized a series of 1D imine-linked polymers and 2D porous networks at the interface of Au(111) surface through thermodynamic control method by controlling the pH of the solution [29]. A pair of the building blocks 4,4'-diaminostilbene dihydrochloride (ASB) and terephthalaldehyde (TPA) was utilized as example. Mixing the ASB and TPA in water at room temperature results in an irreversible oligomer. However, when the pH was lower than the pK_a of the amine group of the ASB, the reaction shifted to the left direction

because of the protonation of the amine. By tuning pH of the solution, the chemical equilibrium of the Schiff base reaction can be controlled, and thus, more ordered domains of polymeric structures can be obtained.

Liu and coworkers constructed highly ordered SCOFs through Schiff base coupling [30]. Molecules with threefold symmetry and twofold symmetry were chosen as precursors for on-surface Schiff base reaction, as shown in Fig. 4a. A gas–solid interface method was exploited. As shown in Fig. 4b, the building block A was first deposited on HOPG by drop-casting, and the substrate was then placed in a sealed autoclave containing another building block B. During the heating progress, building block B can be vaporized and deposited on the HOPG, and therefore, the polymerization progress between building block A and B took place. During the reaction progress, the gas-phase dosing of the building block B determines the growth, and the disordered oligomers can be significantly reduced. As shown in Fig. 4c, d, the method can be applied to obtain highly ordered SCOFs with typical domain size larger than 200 nm. In contrast, heating the HOPG

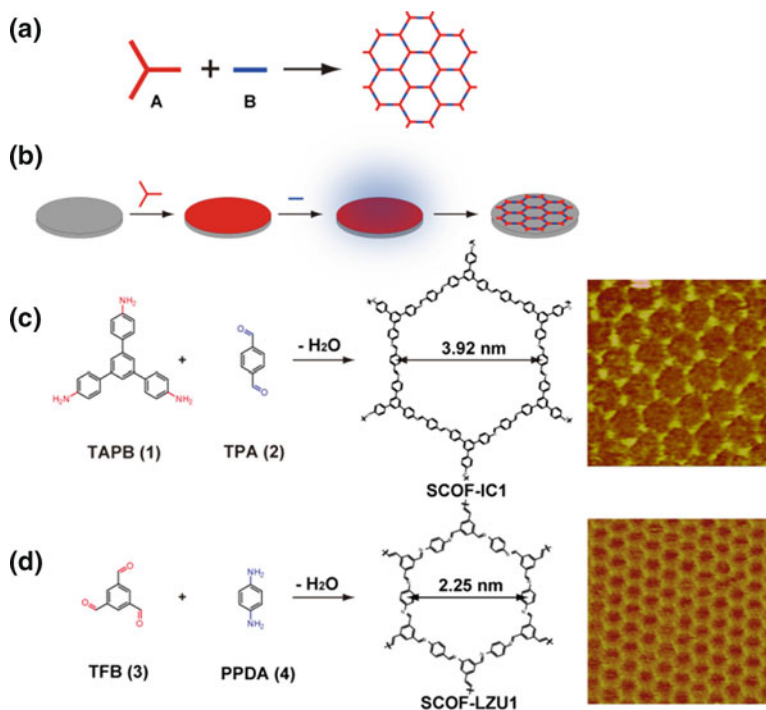


Fig. 4 Schematic diagram of SCOFs formation. **a** Condensation of two precursors A and B carrying different reactive partner groups results in the formation of SCOF. **b** Scheme diagram for solid–vapor interface reaction. **c**, **d** Condensation of trigonal precursors TAPB or TFB and linear precursors TPA or PPDA can form SCOF-IC1 or SCOF-LZU1, respectively. Copyright American Chemical Society

preloaded with the mixtures of precursors A and B in the same experimental conditions only gives SCOFs with small domains and lot of defects. The results confirm the importance of the growth process control for on-surface synthesis.

From the viewpoint of reticular design, the porous networks with the same dimension can be designed by isomeric routes via exchanging the reaction groups on precursors with different symmetry. It is interesting to carry out comparative study to understand the thermodynamics and kinetics of the isomeric routes. Liu and coworkers fabricated a range of isomeric SCOFs with larger pore size by schiff base coupling reaction and investigated their growth processes [31]. One pair of the

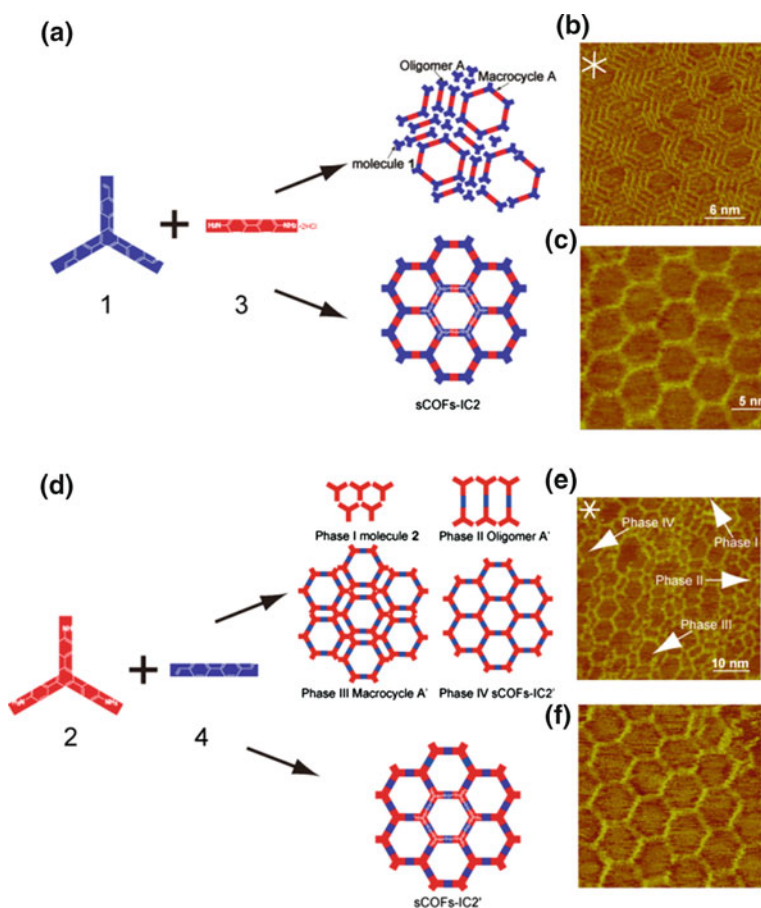


Fig. 5 a Molecular structures of monomers **1**, **3** and their reaction products. b High-resolution STM images of reaction product of **1** + **3** at lower temperature. *White lines* indicate graphite symmetry axes. c High-resolution STM image of SCOF₁₊₃ at higher temperature. d Molecular structures of monomers **2**, **4** and their reaction products. e High-resolution STM images of reaction product of **2** + **4** at lower temperature. *White lines* indicate graphite symmetry axes. f High-resolution STM image of SCOF₂₊₄ at higher temperature. Copyright Wiley VCH

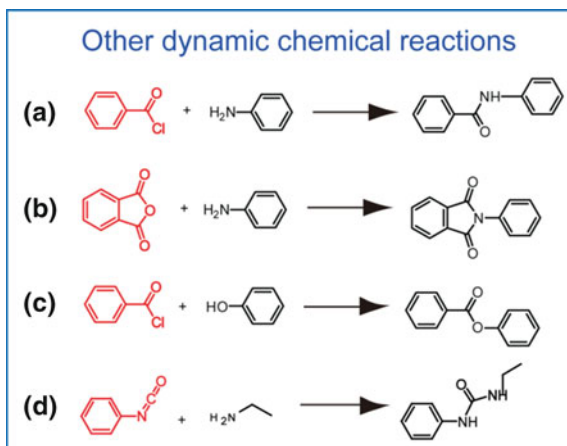
building blocks was a threefold symmetrical aromatic aldehyde **1** and a two-fold symmetrical aromatic amine **3** as shown in Fig. 5a. At a lower reaction temperature, a mixed assembly structure composed of unreacted monomer **3**, partially coupled linear oligomer, and ring structure. Interestingly, the mixed assembly shares the similar assembly motif to the close-packing assembly of pure molecule **1** on HOPG at room temperature. When reacted at a high temperature, SCOFs₁₊₃ can be obtained as displayed in Fig. 5c. In the isomeric synthetic route, the terminal reactive groups were exchanged in two aromatic skeletons, as shown in Fig. 5d. At a low reaction temperature, mixed assembly structures of molecule **2**, the oligomer A' and macrocycle A', and SCOFs₂₊₄ were got as shown in Fig. 5e. Again, the assembly motif is determined by the intermolecular interactions between the terminal amine groups. At a high temperature, large scales of SCOFs₂₊₄ can be obtained. This experimental phenomena demonstrated that there exists a competition between the self-assembly and surface reaction. By changing the reaction temperature, the surface mobility of the building blocks and the molecular–surface interaction is changing, which leads to the evolutions of the nanostructure from blended assemblies structures to SCOFs.

A condensation reaction between aromatic amine and aldehyde was performed by Xu and coworkers on HOPG at solid–liquid interface at room temperature or by moderate heating under the conditions of low vacuum [32]. Through this mild method, SCOFs have been constructed on HOPG. Xu and coworkers used a threefold symmetric 1,3,5-tricarbaldehyde and a series of diamines with different aromatic backbone lengths as building blocks and obtained a series of SCOFs with tunable pore size ranging from 1.7 to 3.5 nm. They also fabricated the COFs on single-layer graphene on copper foil by CVD and applied DFT simulations to investigate the electronic structures and the SCOF–graphene interaction [33].

4 Other Dynamic Chemical Reactions for On-Surface Synthesis

Apart boronic acid dehydration reaction and schiff base coupling, many chemical reactions have been applied in surface-assisted synthesis, as shown in Scheme 2. Based on the reaction displayed in Scheme 2a, a trifunctional acid chloride and a bifunctional amine have been utilized as precursors to fabricated nanostructures on Ag(111) surface in UHV conditions [34]. By changing the annealing conditions, a series of corresponding oligomers and disordered two-dimensional polyamide covalent networks with different pore sizes were obtained. Jensen and coworkers applied melamine and trimesoyl chloride as building blocks and carried out on-surface synthesis experiment on Au(111) surface under UHV conditions [35]. They found that new diamide structures formed between adjacent melamine domains at room temperature. With annealing temperature increase, larger oligoamides were formed and the melamine domains transformed into a close-packed arrangement resulting from the incorporation of melamines into the original phase. Based on the

Scheme 2 Other dynamic chemical reactions utilized in the surface-assisted synthesis



reaction shown in Scheme 2b, 3,4,9,10-perylenetetracarboxylic dianhydrides and 2,4,6-tris(4-aminophenyl)-1,3,5-triazine have been used as building block of on-surface synthesis on Au(111) surface under UHV conditions [36, 37]. When annealing at a low temperature, the authors could only get H-bonded structures increasing temperatures, and amic acid intermediates began to be formed. Further temperature increase resulted in surface polyimide networks. By applying 1,3,5-tris(4-hydroxyphenyl)benzene and benzene-1,3,5-tricarbonyl trichloride as building blocks, a novel COF based on polyester condensation as shown in Scheme 2c has been fabricated on Au(111) surface [38]. Variable-temperature STM and XPS were adopted for in situ characterization, which confirmed the growth of hexagonal porous networks with uniform pore size about 2 nm. By means of low-temperature STM, the construction of polyimide films resulting from the condensation between diamines and dianhydrides in the UHV conditions has been investigated on Au(111). Based on the chemical reaction shown in Scheme 2d, the condensation reaction of 1,4-diaminobutane(1,4-DAB) with 1,3- and 1,4-phenylene diisocyanate (PDI) on Au(111) in UHV has been investigated by Greenwood and coworkers [39]. They chose an aliphatic diamine as one of their building blocks, which introduced chirality into the final structures by functionalizing the sp^3 -hybridized methylene backbone. Urea oligomers formed at room temperature for each isocyanate isomer. When the temperature was increased, the length of the oligomer chains increased and finally extended ordered domains of oligomers were formed.

5 Conclusions and Outlook

Dynamic covalent bond not only has the robustness of conventional covalent bond but also can be reformed like the weak interaction in supramolecular chemistry. Through dynamic covalent chemical reaction, the growth process is more inclined to produce ordered structures due to the existence of correction and self-healing

process thanks to the natural reversibility of these formed bonds. Therefore, applying dynamic covalent chemistry in the surface-assisted synthesis is a promising bottom-up strategy to obtain regular nanostructures with covalent linker.

Compared to the solution-phase reaction, on-surface dynamic covalent chemistry has some unique features. When the reaction takes place on a surface, due to the surface confined effect, the mobility and movement of the building blocks is severely restricted. The precursors have different freedom on the surface compared to in the solution-phase reaction conditions. The involvement of adsorption, desorption, diffusion, and reaction steps in the whole process makes on-surface synthesis equally, if not more, complicated than the solution-phase reaction. Therefore, simply introducing the dynamic covalent chemistry into the on-surface synthesis is not a guarantee to achieve ordered nanostructures due to the characterization of the surface science. A lot of factors must be taken into consideration to regulate the reversibility of the dynamic covalent bond and the kinetics of the chemical reaction.

With great efforts in the past decade, a deep insight into the physical chemistry of on-surface synthesis has been gained and effective synthesis methods have been developed to make the final nanostructure more regular. Through surface-assisted synthesis based on dynamic covalent chemical bonds, we have achieved a series of macromoleculars, novel nanostructures, and two-dimensional covalent porous networks which combine stability and regularity. In particular, the chemical equilibrium control has been demonstrated in several different reaction systems and could be a universal strategy to tune the regularity. By surface-assisted synthesis, functionalized surfaces have been achieved, which can be and has the potential to be applied in making molecular devices, solar cells, molecular sieves, and gas absorption [40, 41]. In particular, two-dimensional organic frameworks, which have a structure similar to graphene, are the most challenging covalent structures to date from a synthesis perspective. By applying proper reaction control methods, highly ordered SCOF structures have been achieved. This gives a new perspective to design and fabricate complex nanostructures. Finally, we envision that the fundamental principle gained from the study of on-surface dynamic covalent chemistry can be beneficial to tailor more challenging non-reversible coupling reactions.

References

1. Zhang, X., Chen, T., Yan, H.-J., Wang, D., Fan, Q.-H., Wan, L.-J., Ghosh, K., Yang, H.-B., Stang, P.J.: Engineering of linear molecular nanostructures by a hydrogen-bond-mediated modular and flexible Host–Guest assembly. *ACS Nano* **4**(10), 5685–5692 (2010)
2. Gourdon, A.: On-surface covalent coupling in ultrahigh vacuum. *Angew. Chem. Int. Ed.* **47** (37), 6950–6953 (2008)
3. Lin, T., Shang, X.S., Liu, P.N., Lin, N.: Multicomponent assembly of supramolecular coordination polygons on a Au(111) surface. *J. Phys. Chem. C* **117**(44), 23027–23033 (2013)
4. Fan, Q., Wang, C., Han, Y., Zhu, J., Hieringer, W., Kuttner, J., Hilt, G., Gottfried, J.M.: Surface-assisted organic synthesis of hyperbenzene nanotrroughs. *Angew. Chem. Int. Ed.* **52** (17), 4668–4672 (2013)

- Liu, J., Ruffieux, P., Feng, X., Mullen, K., Fasel, R.: Cyclotrimerization of arylalkynes on Au (111). *Chem. Commun.* **50**(76), 11200–11203 (2014)
- Lewis, E.A., Murphy, C.J., Liriano, M.L., Sykes, E.C.H.: Atomic-scale insight into the formation, mobility and reaction of Ullmann coupling intermediates. *Chem. Commun.* **50**(8), 1006–1008 (2014)
- Eichhorn, J., Strunskus, T., Rastgoo-Lahrood, A., Samanta, D., Schmittel, M., Lackinger, M.: On-surface Ullmann polymerization via intermediate organometallic networks on Ag(111). *Chem. Commun.* **50**(57), 7680–7682 (2014)
- Fan, Q., Wang, C., Han, Y., Zhu, J., Kuttner, J., Hilt, G., Gottfried, J.M.: Surface-assisted formation, assembly, and dynamics of planar organometallic macrocycles and zigzag shaped polymer chains with C–Cu–C bonds. *ACS Nano* **8**(1), 709–718 (2013)
- Lipton-Duffin, J.A., Miwa, J.A., Kondratenko, M., Cicoira, F., Sumpter, B.G., Meunier, V., Peregichka, D.F., Rosei, F.: Step-by-step growth of epitaxially aligned polythiophene by surface-confined reaction. *Proc. Natl. Acad. Sci. USA* **107**(25), 11200–11204 (2010)
- Schlutter, F., Rossel, F., Kivala, M., Enkelmann, V., Gisselbrecht, J.P., Ruffieux, P., Fasel, R., Mullen, K.: Pi-conjugated heterotriangulene macrocycles by solution and surface-supported synthesis toward honeycomb networks. *J. Am. Chem. Soc.* **135**(11), 4550–4557 (2013)
- Mendez, J., Lopez, M.F., Martin-Gago, J.A.: On-surface synthesis of cyclic organic molecules. *Chem. Soc. Rev.* **40**(9), 4578–4590 (2011)
- Zhang, X., Zeng, Q., Wang, C.: On-surface single molecule synthesis chemistry, a promising bottom-up approach towards functional surfaces. *Nanoscale* **5**(18), 8269–8287 (2013)
- El Garah, M., MacLeod, J.M., Rosei, F.: Covalently bonded networks through surface-confined polymerization. *Surf. Sci.* **613**, 6–14 (2013)
- Liu, X.-H., Guan, C.-Z., Wang, D., Wan, L.-J.: Graphene-like single-layered covalent organic frameworks, synthesis strategies and application prospects. *Adv. Mater.* **26**(40), 6912–6920 (2014)
- Rowan, S.J., Cantrill, S.J., Cousins, G.R.L., Sanders, J.K.M., Stoddart, J.F.: Dynamic covalent chemistry. *Angew. Chem. Int. Ed.* **41**(6), 898–952 (2002)
- Côté, A.P., Benin, A.I., Ockwig, N.W., O’Keeffe, M., Matzger, A.J., Yaghi, O.M.: Porous, crystalline, covalent organic frameworks. *Science* **310**(5751), 1166–1170 (2005)
- Weigelt, S., Busse, C., Bombis, C., Knudsen, M.M., Gothelf, K.V., Strunskus, T., Wöll, C., Dahlbom, M., Hammer, B., Lægsgaard, E., Besenbacher, F., Linderoth, T.R.: Covalent interlinking of an aldehyde and an amine on a Au(111) surface in ultrahigh vacuum. *Angew. Chem.* **119**(48), 9387–9390 (2007)
- Dienstmaier, J.F., Gigler, A.M., Goetz, A.J., Knochel, P., Bein, T., Lyapin, A., Reichlmaier, S., Heckl, W.M., Lackinger, M.: Synthesis of well-ordered COF monolayers: surface growth of nanocrystalline precursors versus direct on-surface polycondensation. *ACS Nano* **5**(12), 9737–9745 (2011)
- Dienstmaier, J.F., Medina, D.D., Dogru, M., Knochel, P., Bein, T., Heckl, W.M., Lackinger, M.: Isoreticular two-dimensional covalent organic frameworks synthesized by on-surface condensation of diboronic acids. *ACS Nano* **6**(8), 7234–7242 (2012)
- Guan, C.-Z., Wang, D., Wan, L.-J.: Construction and repair of highly ordered 2D covalent networks by chemical equilibrium regulation. *Chem. Commun.* **48**(24), 2943–2945 (2012)
- Faury, T., Clair, S., Abel, M., Dumur, F., Gigmes, D., Porte, L.: Sequential linking to control growth of a surface covalent organic framework. *J. Phys. Chem. C* **116**(7), 4819–4823 (2012)
- Acharyya, K., Mukherjee, S., Mukherjee, P.S.: Molecular marriage through partner preferences in covalent cage formation and cage-to-cage transformation. *J. Am. Chem. Soc.* **135**(2), 554–557 (2013)
- Jin, Y., Zhu, Y., Zhang, W.: Development of organic porous materials through schiff-base chemistry. *Cryst. Eng. Comm.* **15**, 1484–1499 (2013)
- Weigelt, S., Busse, C., Bombis, C., Knudsen, M.M., Gothelf, K.V., Lægsgaard, E., Besenbacher, F., Linderoth, T.R.: Surface synthesis of 2D branched polymer nanostructures. *Angew. Chem. Int. Ed.* **47**(23), 4406–4410 (2008)

25. Ciesielski, A., El Garah, M., Haar, S., Kovaricek, P., Lehn, J.M., Samori, P.: Dynamic covalent chemistry of bisimines at the solid/liquid interface monitored by scanning tunnelling microscopy. *Nat. Chem.* **6**(11), 1017–1023 (2014)
26. Li, Y., Wan, J., Deng, K., Han, X., Lei, S., Yang, Y., Zheng, Q., Zeng, Q., Wang, C.: Transformation of self-assembled structure by the addition of active reactant. *J. Phys. Chem. C* **115**(14), 6540–6544 (2011)
27. Hu, F.-Y., Zhang, X.-M., Wang, X.-C., Wang, S., Wang, H.-Q., Duan, W.-B., Zeng, Q.-D., Wang, C.: In Situ STM investigation of two-dimensional chiral assemblies through schiff-base condensation at a liquid/solid interface. *ACS Appl. Mater. Interfaces* **5**(5), 1583–1587 (2013)
28. Liu, X.-H., Wang, D., Wan, L.-J.: Surface tectonics of nanoporous networks of melamine-capped molecular building blocks formed through interface schiff-base reactions. *Chem. Asian J.* **8**(10), 2466–2470 (2013)
29. Tanoue, R., Higuchi, R., Enoki, N., Miyasato, Y., Uemura, S., Kimizuka, N., Stieg, A.Z., Gimzewski, J.K., Kunitake, M.: Thermodynamically controlled self-assembly of covalent nanoarchitectures in aqueous solution. *ACS Nano* **5**(5), 3923–3929 (2011)
30. Liu, X.-H., Guan, C.-Z., Ding, S.-Y., Wang, W., Yan, H.-J., Wang, D., Wan, L.-J.: On-surface synthesis of single-layered two-dimensional covalent organic frameworks via solid-vapor interface reactions. *J. Am. Chem. Soc.* **135**(28), 10470–10474 (2013)
31. Liu, X.-H., Mo, Y.-P., Yue, J.-Y., Zheng, Q.-N., Yan, H.-J., Wang, D., Wan, L.-J.: Isomeric routes to schiff-base single-layered covalent organic frameworks. *Small* **10**(23), 4934–4939 (2014)
32. Xu, L., Zhou, X., Yu, Y., Tian, W.Q., Ma, J., Lei, S.: Surface-confined crystalline two-dimensional covalent organic frameworks via on-surface schiff-base coupling. *ACS Nano* **7**(9), 8066–8073 (2013)
33. Xu, L., Zhou, X., Tian, W.Q., Gao, T., Zhang, Y.F., Lei, S., Liu, Z.F.: Surface-confined single-layer covalent organic framework on single-layer graphene grown on copper foil. *Angew. Chem. Int. Ed.* **53**(36), 9564–9568 (2014)
34. Schmitz, C.H., Ikononov, J., Sokolowski, M.: Two-dimensional polyamide networks with a broad pore size distribution on the Ag(111) surface. *J. Phys. Chem. C* **115**(15), 7270–7278 (2011)
35. Jensen, S., Greenwood, Früchtl H.A., Baddeley, C.J.: STM investigation on the formation of oligoamides on Au(111) by surface-confined reactions of melamine with trimesoyl chloride. *J. Phys. Chem. C* **115**(17), 8630–8636 (2011)
36. Treier, M., Fasel, R., Champness, N.R., Argent, S., Richardson, N.V.: Molecular imaging of polyimide formation. *Phys. Chem. Chem. Phys.* **11**(8), 1209–1214 (2009)
37. Treier, M., Richardson, N.V., Fasel, R.: Fabrication of surface-supported low-dimensional polyimide networks. *J. Am. Chem. Soc.* **130**(43), 14054–14055 (2008)
38. Marele, A.C., Mas-Balleste, R., Terracciano, L., Rodriguez-Fernandez, J., Berlanga, I., Alexandre, S.S., Otero, R., Gallego, J.M., Zamora, F., Gomez-Rodriguez, J.M.: Formation of a surface covalent organic framework based on polyester condensation. *Chem. Commun.* **48**(54), 6779–6781 (2012)
39. Greenwood, J., Früchtl, H.A., Baddeley, C.J.: Surface-confined reaction of aliphatic diamines with aromatic diisocyanates on Au(111) leads to ordered oligomer assemblies. *J. Phys. Chem. C* **117**(9), 4515–4520 (2013)
40. Wan, S., Guo, J., Kim, J., Ihee, H., Jiang, D.: A belt-shaped, blue luminescent, and semiconducting covalent organic framework. *Angew. Chem. Int. Ed.* **48**(18), 3207 (2009)
41. Baughman, R.H., Eckhardt, H., Kertesz, M.: Structure-property predictions for new planar forms of carbon: Layered phases containing sp^2 and sp atoms. *J. Chem. Phys.* **87**(11), 6687–6699 (1987)