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On-surface formation of two-dimensional polymer *via* direct C–H activation of metal phthalocyanine†

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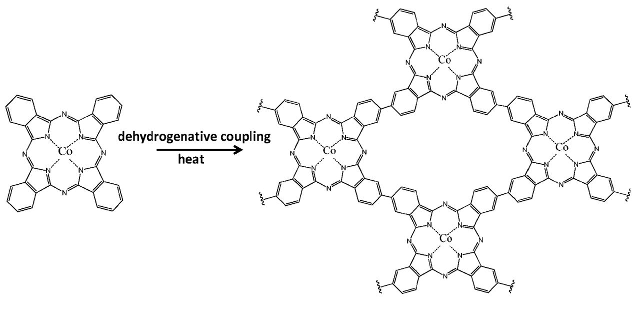
From high-resolution UHV-STM imaging and DFT calculations we successfully obtained a 2D polymer structure formed through direct C–H activation followed by an aryl–aryl coupling of a metal-phthalocyanine (CoPc) on Ag(110).

Two-dimensional (2D) polymers, which are covalently interlinked molecular sheets, have received considerable attention in recent years because of their unique and appealing properties.[1,2] Besides graphene and graphene-like 2D materials, as probably the most simple 2D polymers,[3] vast efforts have been devoted to the synthesis of covalently interlinked 2D polymers from molecular precursors *via* a bottom-up fabrication in the surface science community.[4–7] To date, the key idea has been to modify the aromatic molecular precursors by different functional groups, thus enabling specific chemical reactions, and to subsequently trigger these reactions, thus resulting in the formation of covalent interlinkages at predetermined sites. Several chemical reactions, such as polyester condensation,[8] the homo-coupling of terminal alkyne,[9] the cyclotrimerization of arylalkyne,[10,11] the metal-catalyzed polycyclization of tetracyanobenzene,[12] and the most-investigated dehalogenation reaction[13–15] have been employed to form 2D polymers on surfaces. However, remaining unwanted by-products on the surfaces[4,13] and the troublesome chemical syntheses on the molecular precursors have to be taken care of, which sometimes are presented as the limitation in the use of such strategies. In most recent studies, it has been demonstrated that the direct C–H activation of aromatic groups and the subsequent homocoupling of porphines[16] and quaterphenyl molecules[17] could be successfully achieved on surfaces, which implies a promising way for constructing conjugated nanostructures with little disturbance from remaining by-products and less chemical synthetic concerns. Thus, it is particularly interesting to explore the feasibility of constructing on-surface 2D polymers through the direct C–H activation of aromatic molecules.

Herein, first, we decided to choose an aromatic π-conjugated molecule with 4-fold symmetry to construct a conjugated 2D polymer. Since it seems hard to obtain a two-dimensional network from porphyrins,[16] in this work, we chose another typical molecule: a metal-phthalocyanine (CoPc, chemical structure shown in Scheme 1), which also belongs to the family of highly stable π-conjugated macrocyclic compounds that have been widely investigated in a broad range of applications, such as molecular electronics, gas sensing, light-harvesting and organic light-emitting diodes.[18,19] The CoPc molecule has four peripheral phenyl rings, which can be expected to undergo C–H activation and form 2D polymer structures on surfaces. From the interplay of high-resolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations, we show that the 2D polymer structures could indeed be formed by the CoPc molecule on Ag(110) through direct C–H activation. The formed 2D polymers were demonstrated to be quite robust against both thermal treatments and nano-scale mechanical 'forces'. These novel findings have extended the method of the on-surface formation of 2D polymers, and demonstrated that direct C–H activation is a feasible and more generalized way to build surface nanostructures. Moreover, the robust 2D polymer structure of such a kind of functional molecules could potentially enrich their applications in both scientific and technological research.

All the STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature



Scheme 1 Chemical structure of the CoPc molecule and schematic illustration of the formed 2D polymer structure.

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"Aarhus-type" STM,[20,21] a molecular evaporator and standard facilities for sample preparation. After the system was thoroughly degassed, the CoPc molecules (purchased from Tokyo Chemical Industry Co., Ltd) were deposited by thermal sublimation at ~570 K onto the substrates. The STM measurements were performed in a typical temperature range of 100–150 K, and scanning conditions: I_t = 0.5–1.0 nA, V_t = −1500 to −2500 mV. All the calculations were performed in the framework of DFT by using the Vienna Ab Initio Simulation Package (VASP).[22,23] The projector augmented wave method was used to describe the interaction between the ions and electrons.[24,25] Also, the Perdew–Burke–Ernzerhof generalized gradient approximation exchange–correlation functional was employed,[26] and van der Waals (vdW) interactions were included using the dispersion corrected DFT-D2 method of Grimme.[27] The simulated STM image was obtained using the Tersoff–Hamann method.[28] The atomic structures were relaxed until the forces on all the unconstrained atoms were ≤ 0.03 eV Å^{-1}.

As shown in Fig. 1a, after deposition of CoPc on the Ag(110) substrate held at room temperature, island structures are formed. The single CoPc molecules within the island could be well resolved, while the molecules at the periphery of the islands have higher mobility and exhibit fuzzy shapes. The high-resolution STM image of single CoPc depicted in Fig. 1b clearly shows that the molecule is imaged as four lobes which originate from the phenyl rings, and one bright protrusion in the centre resulting from the cobalt atom.[29] The theoretical calculation of single CoPc on Ag(110) was also performed to obtain further insights. The DFT-optimized adsorption geometry and the corresponding STM simulation of CoPc on Ag(110) are shown in Fig. 1c and d, respectively. In comparing the high-resolution STM image and the simulated one, a good agreement on the single molecular morphology is achieved.

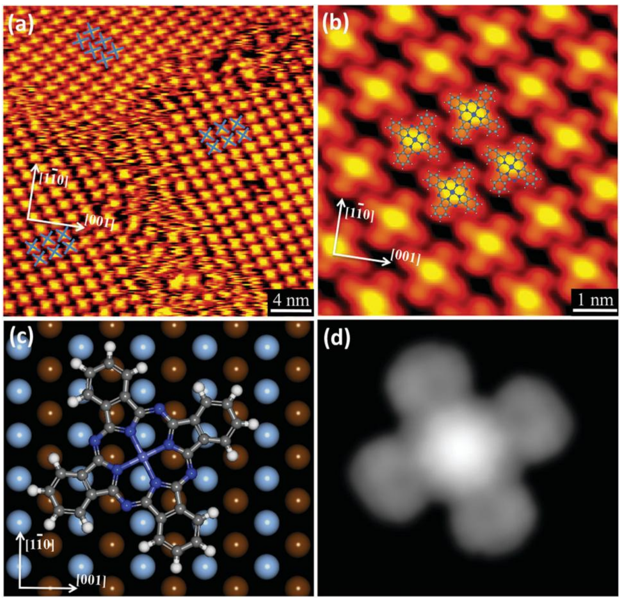

Fig. 1 (a) Large-scale and (b) close-up STM images of the self-assembled CoPc structure on Ag(110). The cross shapes in (a) and the molecular models in (b) are superimposed on the STM features of single CoPc molecules to indicate the molecular adsorption orientations and arrangements. (c) DFT-optimized adsorption geometry of CoPc on Ag(110) and (d) the corresponding STM image simulation.

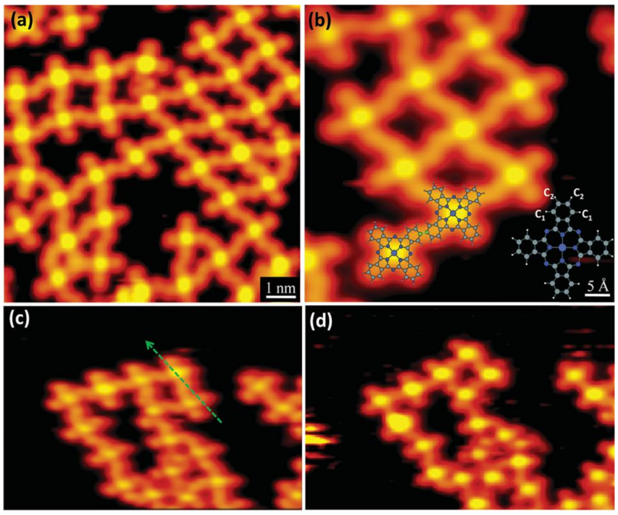

Fig. 2 (a) STM image of the 2D polymer structure formed by annealing the CoPc covered surface at ~680 K. (b) Close-up STM image of the 2D polymer structure shows that the intermolecular covalent linkages specifically occur at the C_2 sites of each of the phenyl rings of CoPc (*cf.* molecular model shown in the inset). The overlaid DFT-optimized CoPc dimer structure illustrates the molecular interconnection at the C_2 sites of the peripheral phenyl rings and the newly formed C–C bond is highlighted in green. STM images (c) and (d) demonstrate the robustness of the 2D polymer structure by lateral STM manipulation. The green arrow in (c) indicates the direction of the STM manipulation applied. Manipulation parameters: V_t = 5 mV, I_t = 4.1 nA.

To trigger the C–H activation and the subsequent aryl–aryl coupling of CoPc molecules, we annealed the CoPc covered surface up to about 680 K, and consequently we successfully obtained a 2D polymer structure of CoPc, as shown in Fig. 2. The CoPc unit could be well distinguished within the network structure (see Fig. 2), and its STM appearance is characteristically the same as that in the self-assembled structure (see Fig. 1b). A closer inspection of the network structure (see Fig. 2b) indicates that the majority of the CoPc molecules are jointed together in a uniform staggered fashion, *i.e.* the aryl–aryl coupling specifically occurs at the C_2 site of the CoPc molecule (*cf.* the molecular model in Fig. 2b). Just as the previously reported aryl–aryl coupling of a quaterphenyl molecule,[17] the electronic density of states at the intermolecular junctions of CoPc is rather smooth and seamless, which implies the covalent characteristic of molecular interlinkages. The equivalently scaled DFT-optimized CoPc dimer structure is superimposed on the STM image in Fig. 2b, which further verifies the aryl–aryl coupling of CoPc at the specific C_2 sites. Here, we think that the selective aryl–aryl coupling at the C_2 sites is mainly because of the smaller steric hindrance of the C_2–C_2 bonding than that of the C_1–C_1 or C_1–C_2 bonding. Note that the C–H activations of the alkyl groups were also demonstrated on surfaces.[30,31]

Such a covalently interlinked 2D polymer structure of CoPc demonstrates quite robust characteristic, as shown in Fig. 2c and d where we tried to apply a lateral STM manipulation on the structure. Surprisingly, only when we applied a relatively

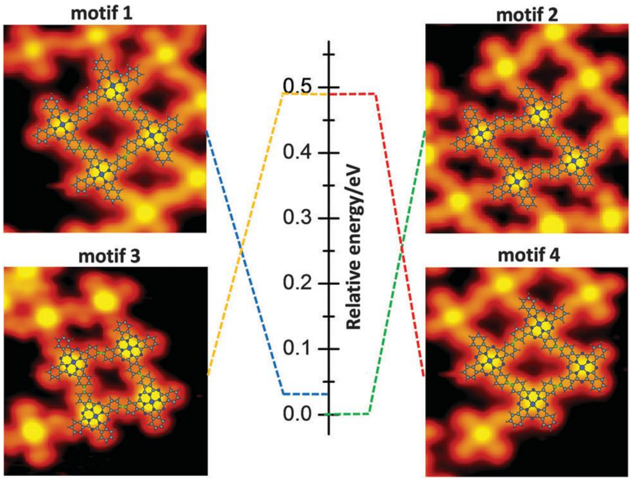

Fig. 3 STM images and corresponding gas-phase DFT-calculated models of the four basic structural motifs interlinked by four CoPc monomers. The relative energies of the four structural motifs are also shown.

large mechanical 'force', *i.e.* by increasing the tunneling current up to ∼4.1 nA while reducing the tunneling voltage down to ∼5 mV (*i.e.* reducing the resistance in the STM tunneling junction to ∼0.001 GΩ),[32,33] could the 2D polymer structure locally move away a bit while still remaining intact. Thermodynamically, this 2D polymer structure should not be damaged at temperatures as high as 750 K. In addition, the C–H activation barriers for phthalocyanine and porphine on Ag(110) have been calculated and are shown in Fig. S2, ESI.†

Meanwhile, we also realized, due to the fact that each CoPc molecule has eight equivalent C_2 sites, that the formed 2D network structures are actually not well ordered. A thorough and detailed analysis of the STM results revealed that there were basically four kinds of structural motifs within the network structures, as shown in Fig. 3. The corresponding calculated structural models of the four structural motifs indicate their different binding modes. It could be identified that the CoPc molecules within both motif 1 and motif 2 have the same orientations, respectively, and their arrangements are more regular than those of motif 3 and motif 4. The structural motifs 3 and 4 are enantiomers, *i.e.* they could be interconverted by flipping along the surface plane. Note that the enantiomers of motifs 1 and 2 are also found on the surface. The DFT calculations of these four structural motifs were also performed in the gas phase, and the optimized structural models are superimposed on the corresponding STM images with an equivalent scale, as shown in Fig. 3, where good agreements were achieved. Moreover, motifs 1 and 2 had similar stabilities and they were more stable than motifs 3 and 4 by about 0.47 eV, which probably results from the structural deformations in motifs 3 and 4. A statistical analysis of the occurrence of the four motifs was also performed and showed that the energetically less favorable motifs 3 and 4 had a lower probability of occurrence (see Fig. S3, ESI†).

Experiments were also performed on other single crystal substrates, including Au(111), Cu(100) and Cu(110), to explore the influence of the substrate in the formation of such 2D network structures (see Fig. S4, ESI†). On Au(111), the C–H activation occurred at ∼680 K, similar to that on Ag(110), while no well-defined nanostructures were observed. On Cu(100) and Cu(110), the C–H activation occurred at ∼530 K and ∼500 K, respectively, which are similar to our previously reported direct C–H activation of quaterphenyl molecule on Cu(110).[17] Still, structures with less regularity are found on these two surfaces. We believe that the on-surface mobility and reactivity of the CoPc molecule resulting from molecule–substrate interactions should be the key factor to determine the formed nanostructures, similar to the case of the formation of on-surface 2D polymers through dehalogenation.[34] It is noteworthy that no organometallic intermediates were observed.[35] While, the influences of possible organometallic complexes on the formation of the final structures could not be completely ruled out in the whole process, which still warrant further calculations.

In conclusion, from high-resolution UHV-STM imaging and DFT calculations, we demonstrated that a 2D conjugated polymer structure could be formed through direct C–H activation followed by an aryl–aryl coupling of a metal-phthalocyanine (CoPc) molecule on Ag(110). In this process, molecule–substrate interactions also play an important role in determining the formation of such on-surface 2D polymer structures. Here, further theoretical and experimental studies are warranted into the origin and generalities of the formation of 2D or even 3D polymer structures on different substrates through such pristine metal-phthalocyanine precursors for future applications.

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