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Dynamics and thermal stability of surface-confined metal–organic chains

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ABSTRACT

Understanding the dynamics and thermal stability of metallosupramolecular chains on surfaces is of relevance for the development of molecular connectors in nanoelectronics or other fields. Here we present a combined study using temperature-controlled STM and Monte Carlo simulations to explore the behavior of metal–organic porphyrin chains on Cu(111) based on two-fold pyridyl–Cu–pyridyl coordination motifs. We monitor their behavior in the 180–360 K range, revealing three thermal regimes: i) flexibility up to 240 K, ii) diffusion of chain fragments and partial dissociation into a fluid phase for T > 240 K, and iii) full dissolution with temperatures exceeding ~320 K. The experimentally estimated reaction enthalpy of the metal–organic bonding is ~0.6 eV. Monte Carlo simulations reproduce qualitatively our STM observations and reveal the preference for linear and extended supramolecular chains with reduced substrate temperatures.

1. Introduction

The design of molecular nanoarchitectures on surfaces is a rapidly advancing field, stimulated both by basic scientific interest and prospects for potential applications, including molecular electronics, spintronics, optoelectronics, sensors, catalysis, and molecular magnetism [1–11]. Particularly relevant are one-dimensional (1-dim) nanostructures, such as coordination chains that bear potential as molecular connectors between nanoscale objects [12]. Via the synthesis of appropriate molecular building blocks and the development of assembly procedures relying on the right balance between molecule–molecule and molecule–substrate interactions, various 1-dim systems have been realized on well-defined supports, including metals, highly-oriented pyrolitic graphite, semiconductors or insulators [9]. To this end, manifold assembly protocols were demonstrated, exploiting intermolecular association via non-covalent schemes such as dipole–dipole interactions [13,14], hydrogen bonding [13–17], π-stacking [18–21], coordination bonds [22–24], and indirect surface-mediated interactions [25,26], or via covalent coupling reactions [27–32]. However, the flexibility and thermal stability of the molecular wires, that might be decisive for potential applications, have been hardly addressed, though it is critical to explore functional limitations and improve thermal robustness.

Here we report a combined scanning tunneling microscopy (STM) and canonical Monte Carlo (MC) study probing the surface dynamics and thermal stability of metal–organic chains on Cu(111). To this end, we deposit a ditopic porphyrin derivative (PBP) equipped with pyridin-4-ylethynyl (≡CPyr) moieties expressing pyridyl–Cu–pyridyl coordination motifs with copper adatoms (cf. Fig. 1a) [24]. The programmed geometry and functionality of the molecular module, its conformational flexibility and the interaction with the substrate results in flexible metal–organic chains, stabilized by two-fold linear pyridyl–Cu coordination whereby the Cu centers are provided by the substrate [33]. We monitor the behavior of these 1-dim polymeric assemblies by variable-temperature STM from 180 to 360 K. Initially a high degree of flexibility appears at low temperature (180–240 K), followed by diffusion of entire chain fragments and partial dissociation into a fluid phase for T > 240 K, which is eventually almost fully dissolved at 320 K. An analysis of the chemical equilibrium between the fluid phase and metal–organic chains at specific temperatures yields a reaction enthalpy of the metal–organic bonding of ~0.6 eV. Monte Carlo simulations reproduce experimental results and reveal the preference for linear and extended supramolecular chains upon reduction of substrate temperature.

2. Experimental methods and materials

The experiments were performed using two independent custom-designed ultrahigh vacuum systems that hosted an Aarhus 150 STM (VT-STM, see www.specs.com) and a low-temperature STM (LT-STM, see www.lt-stm.com), respectively. The base pressure was below 2×10^{-10} mbar in the low temperature-STM system and below 5×10^{-10} mbar in the variable temperature-STM system. The Cu(111)

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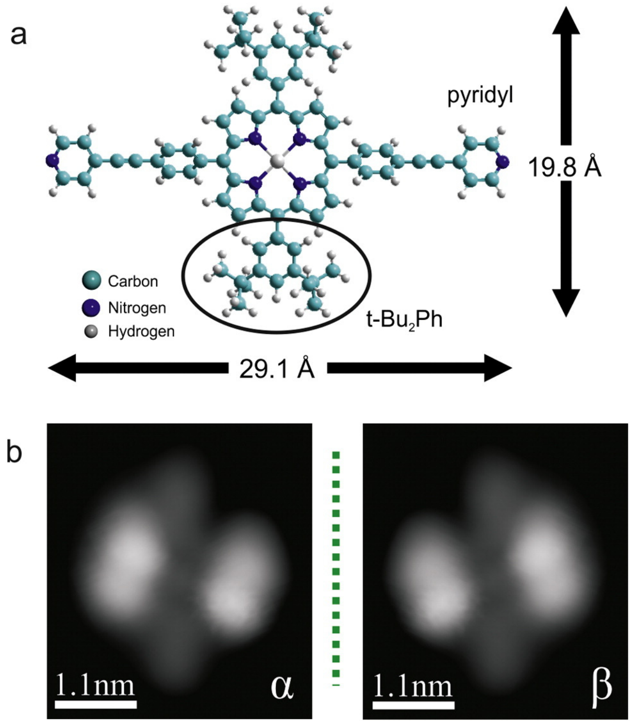

Fig. 1. Atomistic model of the isolated porphyrin derivate PBP and high resolution STM images of a single molecular species upon adsorption on Cu(111). a) Atomistic model of PBP after AM+ simulations in HyperChem package. b) High resolution STM images of the adsorption conformers of PBP, named α and β, respectively and measured at 6 K. The green dotted line displays the mirror plane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

substrate was prepared by standard cycles of Ar + sputtering (800 eV) and subsequent annealing to 723 K for 10 min. Next, molecules were deposited by organic molecular beam epitaxy (OMBE) from a quartz crucible held at 680 K after prolonged degassing, while the sample was kept at room temperature. The pressure during evaporation never exceeded 1×10^{-9} mbar. The molecular flow was about 0.14 ML/min, as derived from the STM measurements. The cooling rate for the low-temperature experiments was approximately 1 K/s in the temperature interval 300–100 K. All STM images were taken in constant-current mode with electrochemically etched tungsten tips and the V_{bias} was applied to the sample.

The canonical MC simulations used the same procedure with the conventional Metropolis sampling that was described in detail in our previous works [34,35]. The simulations were performed on a 200 by 200 lattice site with periodic boundary conditions using 1000 molecules and 1000 metal atoms, for energy unit $\varepsilon = -1$. The effect of temperature, T, on the morphology of the adsorbed overlayer was monitored during the cooling procedure in which the simulated system was slowly cooled down from $T = 0.5$ to $T = 0.01$ within 500 equal decrements, each comprising 2×10^7 MC steps where one MC step is a single attempt to move an adsorbed atom or molecule. The units of energy and temperature in the proposed general model can be chosen in an arbitrary self-consistent way.

3. Results

The porphyrin derivative PBP is an extended ditopic linear linker, presenting a tetrapyrrolic core with a Zn center substituted at *para* positions with two phen-1,4-diylethynylpyridyl (PhC ≡ CPyr) and two 3,5-di-tert-butyl (t-Bu$_2$Ph) moieties at the 5,15 and 10,20 meso-positions, respectively. As we reported recently, upon adsorption on Cu(111) the molecular species displays a great degree of flexibility in three ways [24]: i) rotation of the meso-substituents around the macrocycle-phenyl axis within the limits of steric repulsion and balanced by the interaction with the substrate; ii) distortion of the macrocycle core, giving rise to the characteristic "saddle-shape"; and iii) flexibility of the PhC ≡ CPyr legs. High-resolution STM studies at low temperature identify two conformational isomers (cf. Fig. 1b,c), whereby the tert-butyl groups are visualized as bright protrusions and the functional PhC ≡ CPyr moieties as elongated dim rods.

The preparation conditions during deposition ensure an appreciable density of highly mobile Cu step edges and adatoms to coordinate to the pyridyl endgroups. Fig. 2a shows an STM overview image of a submonolayer deposition of PBP during which the substrate was held at 350 K. Upon cooling down, the adatoms and molecular species engage in a two-fold pyridyl–Cu–pyridyl coordination (cf. Fig. 2b,c), resulting in the formation of flexible chains, characterized by racemic chain fragments aligned with the dense-packed directions of the substrate, chain portions forming an angle of ±15° with respect to those directions, and pyridyl–Cu–pyridyl angles varying from 90° to 180° that give rise to the characteristic sinuosity as described previously [24].

Importantly, the metal–organic bond was reported to be robust under perturbative STM tip-induced manipulation [24]. Such behavior indicates a robust and adaptive bonding [36] with potential functionalities as versatile metallosupramolecular connectors. Moreover, we observe that the coordination chains start to move spontaneously upon increasing the substrate temperature. Fig. 3a shows consecutive STM images at 180 K, where molecular arrangements are clearly identified. Although the pattern is overall stable at the timescale of the experiment, notable changes are detected, predominantly associated with movements of the molecular wires' flexible tails. At 210 K these thermal displacements are augmented both in frequency and length proportion of the moving tail (cf. Fig. 3b).

With a further temperature increase to 240 K, the displacement of longer chain segments (cf. pink shaded areas in Fig. 4a), and the flexible movement of inner chain portions (cf. violet shaded areas in Fig. 4a) appear, while simultaneously the thermal threshold for the dissolution of metal–organic bonds is overcome (cf. blue contour and green areas in Fig. 4a), which results in diffusion of single molecules and migration of entire detached chain fragments. At 270 K minor proportions of the scanning areas appear fuzzy, i.e., not in detail resolvable by STM, which is associated with highly mobile individual species of a two-dimensional fluid phase. All chains present fragments dissolving and reassembling. However, the tails of the chains attached to step edges seem more stable, thus anticipating their potential for potential molecular connectors (cf. Fig. 4b). In fact, at 300 K the assembly mechanism of the chains becomes discernible. The fluid phase now covers about one third of the surface. The persisting chains preferentially start at step edges or impurities, and subsequently some of their inner/peripheral fragments undergo dissolution/reshaping processes, resulting in new connections between chains (cf. Fig. 4c). The higher stability of the anchoring point is manifested when the substrate temperature is increased to 320 K. The surface fluid is now the dominant phase coexisting with some metal–organic chains attached to step edges (cf. Fig. 4d). At $T = 360$ K the chain fraction is finally reduced to almost zero, whereby molecules can only be found at steps or dislocations, forming short segments involving two or three linkers.

Thus, by controlling the substrate temperature between 180 and 360 K, we could monitor the dynamic behavior and thermal stability of flexible 1-dim coordination polymers. In previous studies, the surface diffusion of molecules and supramolecules has been explored experimentally [11,37–46] and theoretically [46–49]. In our study we distinguish three thermal regimes. Under cryogenic conditions, the metal–organic chains remain stable and all molecular species are involved in the coordination. From 180 K to 210 K, the wires wiggle on the surface while keeping the connectivity of the chains. At temperatures exceeding 240 K the thermal energy suffices to break metal–organic coordination

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