Constructing low-dimensional molecular networks on metal surfaces
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Chapter 1

Introduction

1.1 Motivation

Nanotechnology has been rapidly emerging as a cutting-edge discipline in science and technology aimed at controlling and optimizing matter on the atomic and molecular level to create artificial structures with potentially novel functions for a wide range of applications, e.g. information technology, medicine, electronics or materials science [1–5]. The key motivation for the rapid growth in nanoscience and nanotechnology is to find appropriate solutions for today’s technological, economic and societal challenges. The nano regime covers the range of 1 to 100 nm, coincident with the length scale of the basic unit of all natural materials and systems. At the nanoscale, the behaviour of materials exhibits not only significant changes in their properties with diminishing size, but also gives rise to totally new phenomena, such as quantum confinement or tunneling effects [6, 7]. Thus, by manipulating and tailoring matter at the length scale where unique properties can be initiated, nanotechnology offers a great possibility for the design and development of new classes of materials having better characteristics (e.g. faster, smaller, cheaper) for practical applications in all kinds of disciplines.

The birth of nanotechnology is often traced back to the talk “There’s plenty of room at the bottom”, given by physicist Richard P. Feynman at the meeting of the American Physical Society in 1959 [8]. In his talk, Feynman anticipated a possible revolution in human life if we could manipulate individual atoms and molecules to be used as the building blocks for the construction of nanoscale functional systems in a controlled way. He described such atomic scale fabrication as the bottom-up approach which is opposite to the top-down approach. A schematic illustration of these approaches is shown in Fig. 1.1. In general, the top-down approach is mainly based on lithography as well as cutting, grinding and etching techniques. For example,
lithography is usually used in the fabrication of integrated circuits where tiny transistors are designed, created and connected in complex circuits on a silicon wafer [9]. Although this technique is widely implemented in the manufacturing industry, there is a major disadvantage to this approach: the sizes of components are limited by either the wavelength of light used in lithography or the occurrence of leakage current induced by the tunneling effect. Furthermore, the high processing costs and multi-step operations are also major drawbacks of this approach [10]. In contrast, the bottom-up approach refers to processes where nanostructures can be constructed from nano- or subnano-scale objects (atoms or molecules) [11]. In this context, supramolecular chemistry dealing with non-covalent intermolecular interactions to build-up highly-ordered molecular networks by self-assembling of individual molecular building blocks is widely used for the construction of tailor-made functional nanostructures [12–15]. Moreover, the basic concept of supramolecular chemistry has also been employed to construct low-dimensional molecular networks upon adsorption of organic molecules on metal surfaces for broader applications [16, 17]. A schematic illustration of the on-surface self-assembly process is shown in Fig. 1.2. This method is currently regarded as a viable alternative to the traditional top-down techniques for the design and fabrication of future nanodevices for a wide range of potential applications [18, 19]. However, the main impetus for the development of the bottom-up approach came after the invention of the scanning tunneling microscopy by Gerd Binnig and Heinrich Rohrer in 1981, which for the first time allowed real space imaging of atomic structures.
To date, various sophisticated architectures of molecular networks stabilised by many types of non-covalent intermolecular forces such as hydrogen bonding, halogen bonding, van der Waals, metal-ligand coordination can be formed on metal surfaces through an appropriate choice of molecular building blocks and underlying substrates [20–25]. Although self-assembled molecular networks have a high degree of perfection via a self-correcting process due to the weak nature and the reversibility of the non-covalent bonds, it is realized that the formation of robust molecular networks are necessary to meet technical requirements for practical applications. In this respect, a controlled way to directly connect molecular building blocks adsorbed on metal surfaces by stronger interactions is essential to obtain improved thermal, mechanical and chemical stability and to facilitate efficient charge transport. A recent alternative is the creation of one- and two-dimensional (1D/2D) polymer networks by sublimation of appropriate monomers onto metal substrates and subsequent interlinking into covalently bonded molecular networks upon annealing [26–30]. A schematic illustration of the on-surface polymerization is shown in Fig. 1.3.

![Figure 1.2: Schematic representation of the supramolecular self-assembly process on metal surfaces. (Adapted from Ref. [16])](image)

Since their discovery over 30 years ago, conjugated polymers have been considered as a promising alternative to conventional silicon-based materials for a wide variety of applications, e.g. solar or photovoltaic cells which are expected to offer the potential for sustainable energy exploitation in the near future [31]. This is because these materials have desirable properties such as easy fabrication, cost-effectiveness, light-weight, large-area processability and tunable properties [32, 33]. Therefore, considerable research efforts have been directed towards the preparation of conjugated
polymers with improved characteristics. Nowadays, various conjugated polymers have been synthesized through traditional solution-based chemical routes [34]. Although these methods have led to the development of novel conjugated polymers, there are still several drawbacks. For example, chemical reactions in solutions require many synthetic steps in order to obtain the desired products. Moreover, purification processes are necessary to remove side products which may appear during the chemical reactions. In this regard, it is realized that one- or two-dimensional (1D/2D) conjugated polymers can be prepared in a “dry” process directly on metal surfaces. The main advantage of this protocol is that the absence of solvents allows a larger range of reaction temperatures in comparison to polymerization reactions in solution and thus, has attracted a great deal of attention over the last decade [35]. Currently, the construction of covalently linked polymer networks on metal surfaces can be achieved by various types of chemical reactions, including Ullmann coupling [36–38], cyclodehydrogenation [39], pyrimidine–pyrimidine coupling [40], Glaser-Hay coupling [41–43], Bergman cyclization [44] or protecting group chemistry-based coupling [45]. The summary of several reaction types for on-surface polymerization was reported by J. Björk et al. and shown in Fig. 1.4 [46].

![Figure 1.3](image)

**Figure 1.3:** Schematic illustration on the formation of 1D/2D covalently linked molecular networks on metal surfaces. (Adapted from Ref. [29])

Over recent years, graphene, a flat monolayer of sp²-bonded carbon atoms arranged into a two dimensional honeycomb lattice has emerged as a fascinating material for a wealth of promising applications [47]. Although graphene possesses
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extremely high carrier mobility, it suffers from the lack of a band gap and a low efficient optical absorption in the wide range of visible spectra, which hampers its potential for practical applications in electronic and optoelectronic devices [48]. However, for narrow stripes of graphene, so-called graphene nanoribbons, a band gap has been predicted. In this context, researchers have recently developed an efficient approach for an atomically precise fabrication of graphene nanoribbons via thermally induced Ullmann coupling of halogenated molecular precursors on metal surfaces [49, 50]. Using the same protocol, Fuchs et al. recently reported that the precise alignment of graphene nanoribbons into an armchair orientation can be obtained by using the vicinal Au (788) surface as a template [51]. These armchair graphene nanoribbons clearly exhibit a sizable electronic band gap due to the narrow width of the ribbons. Very recently, Crommie et al. demonstrated the possibility to vary the width of graphene nanoribbons with the aim of tuning their band gap via covalent coupling reactions of two different molecular building blocks [52]. Thus, the on-surface polymerization apparently exhibits potential for creating a novel class of nanostructures with atomically controlled features which cannot be obtained through conventional top-down approaches.

![Figure 1.4: Summary of reaction types used for on-surface synthesis: (a) halogen-based covalent assembly, (b) cyclohydrogenation, (c) pyrimidine–pyrimidine coupling, (d) Glaser-Hay, (e) Bergman cyclization, (f) protecting group chemistry-based coupling. (Taken from Ref. [46])](image-url)
1.2 Thesis outline

In light of the observations mentioned above, the present thesis is motivated by the vital role of the bottom-up approach in nanotechnology for the construction of low-dimensional molecular networks. Thus, there are two main topics addressed in this thesis. The first topic deals with the fabrication of 2D supramolecular networks on metal surfaces. Various types of non-covalent interactions were employed to build-up highly-ordered self-assembled molecular networks. The interplay between molecule-substrate and molecule-molecule interactions as well as the influence of functional end groups on the resulting intermolecular interactions was carefully investigated. The second topic is associated with the construction of covalently linked polymer networks on metal surfaces using two different strategies: Ullmann coupling reactions and protecting group chemistry. In addition, the catalytic role of the underlying substrate and the effect of the number and position of halogen substituents in on-surface Ullmann reactions were also considered. The present thesis is organized as follows:

Chapter 2 briefly reviews the up-to-date fundamental understandings of molecules at metal surfaces. The focus is placed on the influence of key parameters on the molecular self-assembly and on-surface polymerization processes with the aim of obtaining high quality molecular networks in a controlled way.

Chapter 3 gives a short outline on the basic principles of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED), which were the key techniques to obtain the experimental results presented in this thesis.

Chapter 4 discusses the effect of interplay between molecule-molecule and molecule-substrate interactions for the formation of 2D supramolecular networks of metal-free naphthalocyanine on Au(111) studied by a combination of STM, XPS and LEED. The results show that although the molecular network is mainly driven by dominating intermolecular interactions, the role of the Au(111) substrate in the structural formation cannot be neglected.

Chapter 5 focuses on the construction of 2D supramolecular networks of Br-functionalized pyrene derivatives on Au(111) by halogen bonding. This study
demonstrates the possibility to steer the resulting intermolecular interactions and thus, final the molecular structures by tuning the number and positions of bromine substituents in the chosen pyrene derivatives.

**Chapter 6** reports the heat-induced formation of molecular coordination networks of porphyrin derivatives on Au(111) stabilized by an unusual threefold cyano-gold coordination motif. Moreover, we could demonstrate that the dimensionality of the molecular networks can be tuned between 1D to 2D using either a *cis-* or a *trans-*porphyrin derivative.

**Chapter 7** presents the on-surface polymerization of Br-functionalized pyrene derivatives based on Ullmann coupling reactions on Cu(111) and Au(111) surfaces. The effect of the underlying substrates in the structural formation of the polymer networks was studied.

**Chapter 8** deals with the formation of covalently linked polymer networks of biphenyl derivatives on Ag(111) using concepts of protecting group chemistry. Due to the flexibility in choosing protecting groups and molecular cores, our results may offer a promising protocol for the development of future novel polymer structures.
References

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