STM Analysis of a Chiral Helical One-dimensional Nickel(II) Coordination Polymer

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Z. Naturforsch. **2008**, *63b,* 1443 – 1446;
received October 2, 2008

C_2-symmetric nickel(II) salen complexes [NiL] **1** were deposited on a highly oriented pyrolytic graphite (HOPG) surface from their acetone solutions. They aggregate easily to single, segregated, homochiral polymeric chains of (*M*)-1D-^1_n[NiL] (**2**) on the substrate as also found in single crystals. In STM topography, the single helical 1D structures **2** found on the surface were in excellent agreement with the dimension of aligned dimeric aggregates of **1** obtained from X-ray crystallography. Weak intermolecular $Ni^{II}\cdots OMe$ coordinations (d_{MeO-Ni} = 0.35 nm) were found to be responsible for the formation of the chiral, helical and 1D assemblies on the substrate.

Key words: Coordination Polymer, Helical Structures, Scanning Tunneling Microscopy, Self-assembly, Chiral Nickel(II) Salen Complexes

Introduction

Coordination polymers are infinitely extended metal-ligand assemblies with bridging organic ligands. Such coordination polymers recently attracted much attention because of their topological design and potential applications in adsorption, catalysis, luminescence, magnetism *etc*. [1]. Thin films of coordination polymers, deposited [2] onto solid substrates or transferred by Langmuir-Blodgett techniques [3, 4], have been described with interests in vapour sensing [3] and conductivity [2]. Yet, a more detailed knowledge of the extended arrangements of such coordination polymers on surfaces is extremely scarce or subject to misinterpretation from instrumental artifacts [5]. In particular, reports on the synthesis and characterisation of isolated strands of one-dimensional (1D) coordination polymers on surfaces appear even more limited than those of 2D arrays [5c, 6]. Non-covalent supramolecular, hydrogen-bonded structures on surfaces, probed by scanning tunneling microscopy (STM), are already receiving more attention [7, 8], with two exemplifying recent studies involving a tetracarboxylic di-imide co-adsorbed with 1,3,5-triazine-2,4,6-triamine on Ag/Si(111) [9] and 4-[pyrid-4-yl-ethynyl]benzoic acid on Ag(111) [10]. It can be anticipated that high-resolution microscopy techniques, such as atomic force microscopy (AFM) and STM will be of increasing importance for an understanding of and new insights in the behaviour of coordination polymers [11 – 13]. Moreover, chirality is a topic extensively explored in chemistry and pharmacology, found in single molecules, supramolecular assemblies, and living organisms. Chiral molecules/assemblies adsorbed on surfaces are particularly interesting, due to their potential applications in biologically active chiral molecule recognition and separation, in preparation of biomaterials, as well as in the design of enantioselective catalysts [14]. In the course of our ongoing studies on 1D coordination polymers [15], we were interested to study the surface morphology after deposition of these chiral assemblies. For that purpose, we selected the enantiomerically pure 1D coordination polymer (*M*)-1D-^1_n[NiL] (**2**) (Fig. 1) [15a], built up by self-complementary L-tartaric acid-derived [15a, 16] monomers [NiL] (**1**), but readily depolymerise upon dissolution in organic solvents.

Results and Discussion

In this contribution, we describe a simple chiral surface preparation of isolated helical 1D strands of **2** on highly oriented pyrolytic graphite (HOPG) from an extremely dilute solution of nickel(II) salen complexes **1** and its analysis by STM [17, 18] under ambient conditions. The samples were conveniently prepared by depositing a droplet (5 μL) of the nickel(II) complex **1** solution onto the surface. After drying under open air, the samples were loaded into the mi-

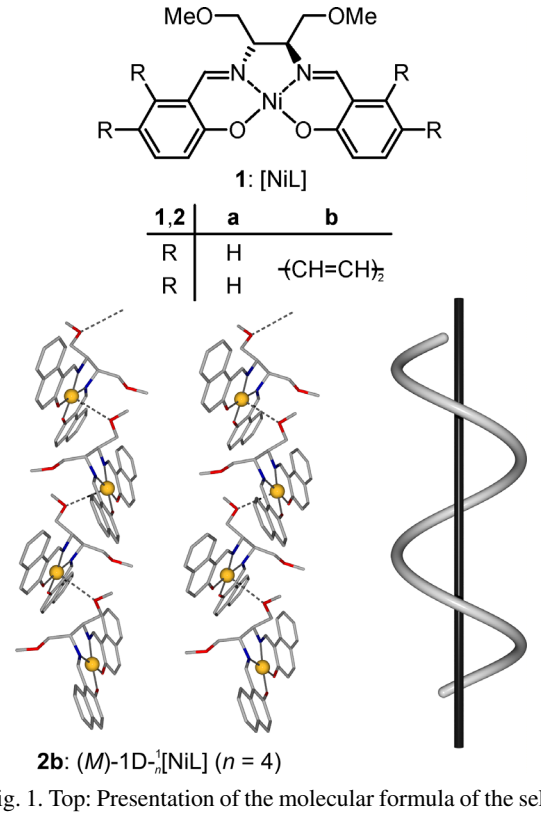

Fig. 1. Top: Presentation of the molecular formula of the self-complementary, enantiomerically pure nickel(II) salen complexes [NiL] (**1**). Bottom left: Stereo view (POVRAY presentation, colour code: Ni^{II} gold, O red, N blue, C grey, H atoms omitted for clarity; weak intermolecular $Ni^{II}\cdots OMe$ coordinations are indicated by dotted lines) of the enantiomerically pure helix (*M*)-1D-$^{1}_{n}$[NiL] (**2b**) in the solid state ($n = 4$). Bottom right: Schematic representation, highlighting the helical structure of the 1D coordination polymer (colour online).

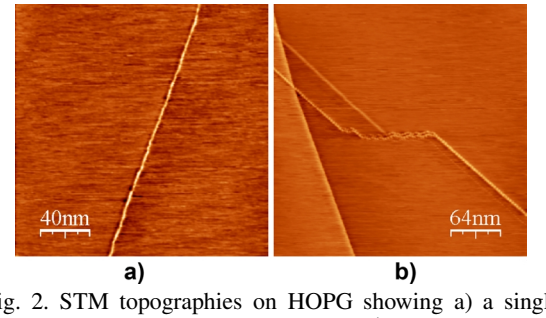

Fig. 2. STM topographies on HOPG showing a) a single strand of the nickel(II) polymer (*M*)-1D-$^{1}_{n}$[NiL] (**2b**) along a step edge on the surface; b) the aggregation of 1D-polymeric strands on the flat surface crossing a graphite step. Tip stabilisation parameters were 200 mV and 5 pA.

croscope. At lower concentrations only small domains of the HOPG surface were covered with the compounds. Fig. 2 shows large-scale STM topography images recorded in constant current mode. As seen from the STM image (Fig. 2a), the acetone solution of the nickel(II) salen complex **1b** forms polymeric single strand features upon solvent evaporation. As the bonding between the compound and the substrate is weak, the compound is preferably found next to graphite steps (Fig. 2a). Fig. 2b presents another low resolution STM image of the same complex demonstrating the aggregation to 1D polymers. Here polymer strands extend over the atomically flat terrace of the HOPG surface.

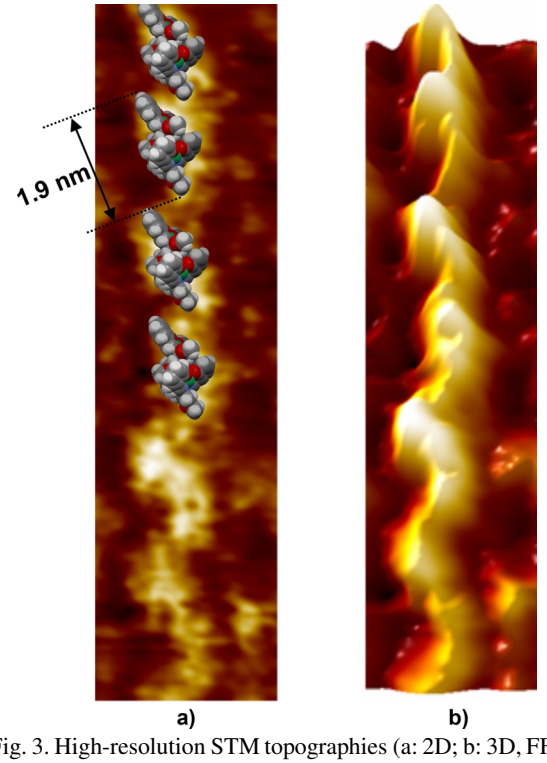

Fig. 3. High-resolution STM topographies (a: 2D; b: 3D, FFT filtered) of the nickel(II) salen coordination polymer (*M*)-1D-$^{1}_{n}$[NiL] [**2a**], caused by weak intermolecular $Ni^{II}\cdots OMe$ coordinations of monomers **1a**, highlighting the helical structure. In the scan area (3.5×12 nm^2), six dimeric aggregates of **1a** are found. In Fig 3a, four dimers of **1a** are superimposed on the picture as CPK representations in order to highlight the proposed helicate deposition. Colour code: Ni^{II} green, O red, N blue, C grey, H white. Tunneling conditions were 200 mV and 10 pA (colour online).

In Fig. 3, a constant-current STM topographic image of a single polymer strand, obtained at a positive sample bias of 200 mV and 10 pA tunneling current, is presented. The high-resolution image represents a helical [19] strand of **2a** with a diameter of approxi-

mately 1.3 nm, which is conforming to the monomeric diameter of 1.2 nm obtained from crystallographic data of **1a**. In addition, the length of the helical 3D reliefs in Fig. 3 is best reflected by an assumption of dimeric aggregates of **1a**, which is proven by the superposition of the picture with true to scale CPK representations of such dimers of **1a** obtained from the X-ray structure data. Most interestingly, the observation of these dimers evidences the existence of weak intermolecular coordinations of the methoxy donor in the ligand backbone to the nickel(II) centres of a neighbouring chiral monomer of **1a**, as in the crystal. Therefore, these interactions ($d_{MeO-Ni} = 0.35$ nm) are responsible for the formation of 1D-polymeric helical structures **2a** on the HOPG surface. In contrast, introduction of alkyl substituents on the aromatic moiety prevents the formation of analogous polymers, as already observed in the solid state [15a]. This result suggests also that weak interactions (van der Waals forces, π-π interactions) between the substrate and the sterically unhindered aromatic groups of absorbed **2a** are responsible for sufficient grip on the HOPG surface. Because of the numerous reports [5] of artefacts caused by solvent-substrate interactions and HOPG cleaving, extensive studies were performed to determine the effects of the solvent on imaging. Strand **2a** shown in Fig. 3 was only observed, when salen complexes **1a** were present on freshly cleaved HOPG.

Experimental Section

STM instrumentation

All measurements were carried out using a home built STM head equipped with a commercially available low current control system (RHK Technology) under ambient conditions. Before adding the solution onto the substrate surface, we ensured that the tunneling tip had a sufficiently high resolution by observing the atomic lattice of the HOPG surface. Different settings for the tunneling current and the bias voltage were used, ranging form 5 to 50 pA and $\pm$50 to $\pm$200 mV, respectively. The concentration of the solutions of **1** was 10^{-9} M. All images were recorded in constant current mode. Different tips and samples were used to check for reproducibility and to ensure that no image artefacts were introduced by the tips or samples. Flattening of the images was carried out to compensate for tilting of the substrate and scan line distortions, and a Gaussian filtered transform was employed to remove scanning noise in the STM images. The scan frequency was varied between 2 to 5 Hz. Resolution was 256×256 points for topography measurements. We used Pt-Ir (90/10) tips mechanically cut from wires with a diameter of 0.25 mm.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft SPP 1137 "Molecular Magnetism" (SA 276/26-1–3), SA 276/27-1–2, SA 276/29-1, and SFB 583. The generous allocation of premises by Prof. Dr. K. Meyer at the Lehrstuhl für Anorganische und Allgemeine Chemie (Universität Erlangen-Nürnberg) is gratefully acknowledged.

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