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Compact hydrogen-bonded self-assembly of Ni(II)-Salen derivative investigated using scanning tunneling microscopy

Marta Viciano-Chumillas,[†] Jérémy Hieulle,[‡] Talal Mallah,[*,†] and Fabien Silly[*,‡]

Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris Sud 11, 91405 Orsay, France, and CEA, IRAMIS, SPCSI, Hybrid Magnetic Nanoarchitectures, F-91191 Gif sur Yvette, France

E-mail: talal.mallah@u-psud.fr,Fax:+33(0)169154754;Tel:+33(0)169154749;
fabien.silly@cea.fr,tel:+33(0)169088019,fax:+33(0)169088446

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[*] To whom correspondence should be addressed

[†] Université Paris Sud 11

[‡] CEA

Abstract

The self-assembly of Ni(II)-salen derived complex bearing benzoate groups is investigated using scanning tunneling microscopy (STM). STM reveals that the molecules form a close-packed two-dimensional nanoarchitecture composed of hydrogen-bonded one-dimensional chains on graphite. The two-dimensional network results from the minimization of electrical dipolar interactions between salen chains and the complementarity of organic chain shape that allow the formation of a compact structure.

Engineering sophisticated metallo-organic nanostructures on surfaces is the focus of recent research interest.[1? ? ? ? ? ? ? ? ? ? ? ? ?] Controlling molecular self-assembly offers unique directions for the fabrication of two-dimensional (2D) supramolecular nanoarchitectures. The resulting structures can be tailored at the nanometer scale by exploiting molecule-substrate or intermolecular interactions.[2? ?] Molecular shape, size, structure and the nature of the substituent are key parameters driving the organisation of self-assembled nanoarchitectures. Researchers have focused on the synthesis of novel molecules to develop new concepts and new nanostructured organic thin films. The motivations range from fundamental science aiming at the understanding of the factors that govern the self-assembly,[3? ?] and the investigation of molecular characteristics, to more applied issues where the control of the organization over large areas may be exploited in the design of devices for photovoltaics[4] and molecular spintronics.[5]

Metal-salen based complexes (see 1a) are among the most fascinating metallo-organic systems because their chemical versatility and flexibility.[6] Their almost flat structure is particularly adapted to enhance molecule/substrate interactions. A variety of metal ions (dia- and paramagnetic) can be introduced in the coordination pocket leaving the overall molecular structure unperturbed, and numerous substituents can be placed on the phenol rings and the diamine bridge allowing the control of their self-assembly on surfaces. To date, hydrophobic interactions[7? ?] or weak dipolar interactions[8?] have been exploited for this purpose. Hydrogen-bonds (H-bonds) are well known to be at the origin of relatively large intermolecular interactions with predictable architectures due to their strength and directionality.[9] Such interaction can be exploited in the organization of metal-salen based complexes by placing carboxylic groups in the *para*- position of the phenol rings. The presence of such groups should lead to the formation of H-bonded one-dimensional (1D) chains on the surface, while the 2D organization is obviously less predictable. The carboxylic group can be directly linked to the phenol or can be spaced using benzyl rings thus tuning the length of the complex and the resulting chains, and orienting their 2D assembly.

In this report, we investigate the self-assembly of a Ni(II)-salen complex where R’ is *tert*-butyl and R is benzoic acid (1b). Scanning tunneling microscopy images show that the molecules self-

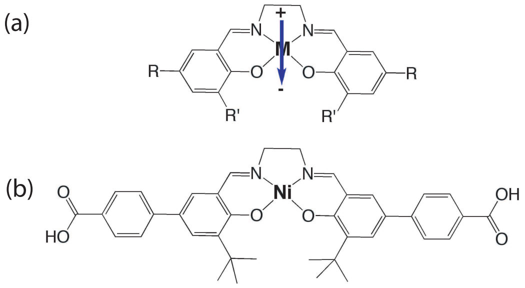

Figure 1: (a) Scheme of salen skeleton. Negative and positive molecular poles are indicated by (-) and (+), respectively. The arrow reflects the resulting molecular dipole. (b) Scheme of [Ni(H_2L)] complex.

assemble into a close-packed structure at the solid/liquid interface. This structure is composed of molecular rows stabilized by double H-bonds. The compact row packing appears to be governed by favorable row-shape complementarity and molecular dipolar interactions.

Complex **1** of formula [Ni(H_2L)] (H_4L is diaminoethane-*N,N'*-bis(*tert*-butyl-5-(4'-benzoic acid)salicyliden is obtained by the reaction of hydrated nickel(II) acetate and the salen-derived ligand H_4L in a mixture of methanol and dimethylformamide (for synthesis and characterization see supporting information file). A solutions of complex **1** in 1-octanol (98%, Acros) was prepared. A droplet of this solution was then deposited on a freshly cleaved graphite substrate. STM imaging of the sample was performed at the liquid/solid interface using a Pico-SPM scanning tunnelling microscope (Molecular Imaging, Agilent Technology). Mechanically etched Pt/Ir wires were used to obtain constant current images at room temperature with a bias voltage applied to the sample. STM images were processed and analyzed using the application FabViewer.[10]

The large scale STM image (2a) shows that molecules of complex **1** self-assemble at the liquid/graphite interface into close-packed 2D networks. Molecules lay flat on the surface (2b). Two molecular orientations are observed (2c). They are related by a 180° rotation angle along the row axis. High resolution STM images of molecules reveal intramolecular features, 2c. Complex **1** is not a perfectly flat molecule because the presence of the *tert*-butyl and ethylenediamine groups. *tert*-butyl groups therefore appear as bright spots in the STM images. In comparison molecular ethylenediamine groups appear as weaker protrusions.

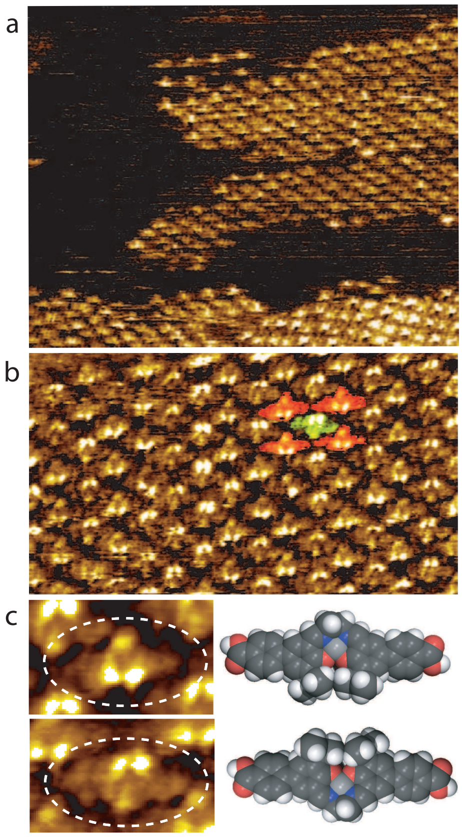

Figure 2: (a) Large scale STM image of **1** domains on graphite, 45×38 nm^2; $V_s = 0.8$ V, $I_t = 25$ pA. (b) High resolution STM image 20×11 nm^2; $V_s = 0.8$ V, $I_t = 35$ pA. Red and green colored molecules show the two orientations of the molecular building blocks in the organic layer. (c) Observed molecular orientation. Left: STM images of complex **1** (surrounded by white dotted ellipse). Right: Complex **1** model. Carbon atoms are dark gray, hydrogen atoms white, oxygen atoms are red, nitrogen atoms are blue and nickel atom is light gray, respectively.

The network unit cell, represented by red and green colored molecules in the STM image, 2b, is a parallelogram with ∼2.6 nm and ∼1.8 nm unit cell parameters and an angle of ∼83°. The assembly of complex **1** is composed of close-packed molecular rows stabilized by double H-bonds between molecular carboxylic groups. The row axis is indicated by blue arrows in 3a. Neighboring rows are shifted along their axis by half molecule length leading to the close-packed paving of the 2D space.

Molecules are colored in red and green in the STM image, 3a, according to their respective orientation, presented in 2c. The formation of rows in one direction (blue arrows in 3a,b) is attributed to the hydrogen bonds between the carboxylic groups of two different molecules. This is

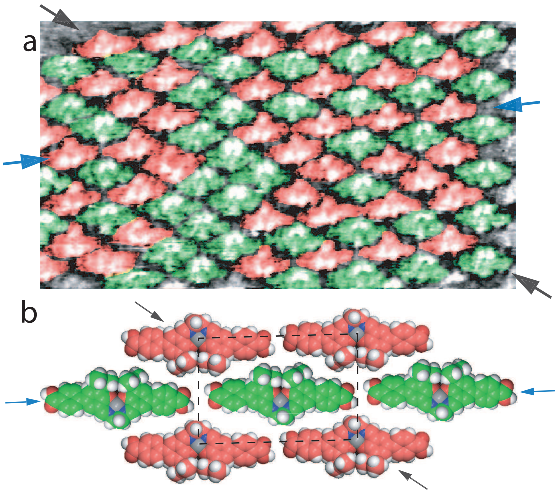

Figure 3: (a) STM image of the self-assembled complex **1** nanoarchitecture, 20×11 nm^2; V_s = 0.8 V, I_t = 35 pA. Molecules are colored in red or green false color according to their orientation, respectively. The blue arrows indicate the direction of a row where complex **1** are held by H-bonds. The black arrows indicate interactions between the different rows.)

expected since carboxylic acids are known to form dimers in the vapor phase.[11? ?] Within a row, molecules of **1** have preferentially the same orientation (blue arrows in 3). STM images reveal that the nanoarchitecture of complex **1** consists in a succession of rows with alternating orientation leading to a quasi ordered 2D organisation where a molecule with a given orientation is surrounded by four neighbors of the opposite orientation (3b). The analysis of the STM image suggests that the inter row interactions are governed by van der Waals (vdw) forces (along the black arrow direction in 3).

The adequate molecular row interpenetration appears to be at the origin of the excellent close-packing of the organic nanoarchitetcture. Defects in molecular orientation do not affect the compactness of the structure. These observations lead to the conclusions that (i) intra-row H-bonds and inter-row vdw forces together with the molecules shape are responsible of the stability and the compactness of the 2D network and (ii) the H-bonds and vdw interactions cannot account for the ordered pattern where neighbor molecules have opposite orientation. Metal-salen complex molecules have a two-fold symmetry axis along the direction bisecting the OMO and the NMN angles and have a dipolar moment along this direction,[8] as represented in 1a. The closest-neighbor molecules are the four molecules of the adjacent rows. Molecular dipolar interactions are minimized for the arrangement shown in 3b since closest-neighbor molecules have opposite orientation. This implies that molecules belonging to the same row have their dipolar moment oriented in the same direction. It results that the dipolar moments of adjacent row should preferentially be antiparallel. This is confirmed by the fact that from 90 molecules in 3a, 46 have their electric dipolar moment in one direction and 44 in the other direction thus leading to a zero net moment, despite the few molecular orientation "errors" observed.

In summary STM images reveal that complex **1** self-assembles into a close-packed structure at the solid-liquid interface on graphite. Interplay between directional H-bonds and dipolar interactions is at the origin of the formation of this 2D nanoarchitecture. Metal-salen derived complexes offer a rich ground play for tuning the self-assembly of functional molecules for developping novel structures for nanotechnology. Changing the length of the molecule by adding or removing benzyl groups in *para* position of the phenols is expecting to influence molecular dipolar interactions and therefore there self-assembly.

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Supporting Information Available

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Table of Contents (TOC) Image

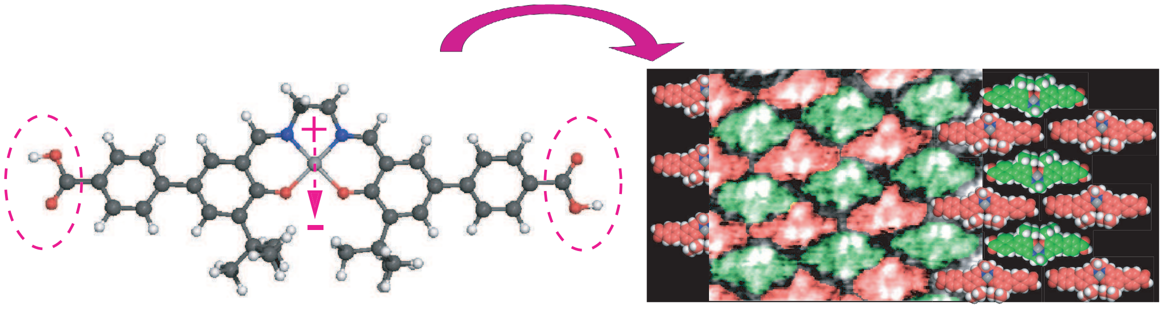

Figure 4: **Table of content:** The interplay between hydrogen bonding and dipolar interactions leads to the compact two-dimensional self-assembly of a Ni(II)-salen derivative complex on graphite.

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