

Self-Assembly of Alkyl Substituted Schiff Base and Its Cu(II) Complex Observed on Solution–Graphite Interface by Scanning Tunneling Microscopy

Pu Qian,[#] Hiroshi Nanjo, Norio Sanada, Toshiro Yokoyama, and Toshishige M. Suzuki*
Tohoku National Industrial Research Institute, 4-2-1 Nigatake, Miyagino-ku, Sendai, 983-8551

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Self-assembled monolayer of Schiff base ligand, *N*-octadecylsalicylaldehyde (**C₁₈Sal**) has been observed by scanning tunneling microscope on the solution–graphite interface and the molecular geometry has been assigned. The molecular pattern of the Schiff base immediately changed upon addition of Cu(II) associated with *in situ* complexation and formation of a new molecular framework.

Monolayers of long alkyl chain compounds physisorbed on a flat substrate have been directly observed with scanning tunneling microscope (STM) at atomic resolution.¹ They form characteristic molecular patterns, which have been interpreted in terms of intermolecular and molecule–substrate interactions.² STM technique has been applied as one of the excellent approaches to obtain topological information of liquid crystals.³ Liquid crystals having metal binding sites have attracted recent attention since they can form a wide variety of molecular alignments by the choices of metal ions and coordination geometry.⁴ Therefore particular interests may be drawn to the direct observation of morphology variation upon metal complex formation. However such change of molecular pattern associated with metal complex formation has rarely been examined by STM. For the discussion and interpretation of molecular patterns, relative location of functional groups should be identified from the obtained STM images. Conjugated π -electron system and transition metal ion may play the role of “marker” in a molecular image since area of higher electronic conductance appears as remarkably bright spot.⁵ In the present paper we attempted to observe directly the molecular alignment of the Schiff base containing a long alkyl chain and aromatic moiety on solution–graphite interface. The transformation of molecular pattern upon complex formation with Cu(II) ion was followed and the possible geometry of the resulted complex has been assigned.

The Schiff base ligand, *N*-octadecylsalicylaldehyde (**C₁₈Sal**) was synthesized by the condensation reaction of 1-aminooctadecane and 2-hydroxybenzaldehyde in ethanol. Bright yellow crystals of **C₁₈Sal** deposited on standing at room temperature were isolated and recrystallized from ethanol. Found: C, 80.59; H, 11.78; N, 3.67%. Calcd for C₂₅H₄₃NO: C, 80.36; H, 11.60; N, 3.74%. The Cu(II) complex, [Cu(**C₁₈Sal**)₂] was prepared by mixing **C₁₈Sal** with copper(II) acetate in 2 : 1 molar ratio in methanol. Greenish yellow crystals were isolated. Found: C, 74.01; H, 10.69; N, 3.44; Cu, 7.54%. Calcd for C₄₀H₈₄N₂O₂Cu: C, 74.24; H, 10.39; N, 3.46; Cu, 7.80%. 1-Phenyl octane for preparation of monolayers was purchased from Aldrich Chem. Co. and used as received. Highly oriented pyrolytic graphite (HOPG) substrates were purchased from TOYO Corporation and cleaved prior to use. Samples of STM measurements were prepared by applying a drop of near saturated solution of the ligand **C₁₈Sal** or the metal complex in 1-phenyl octane onto the surface

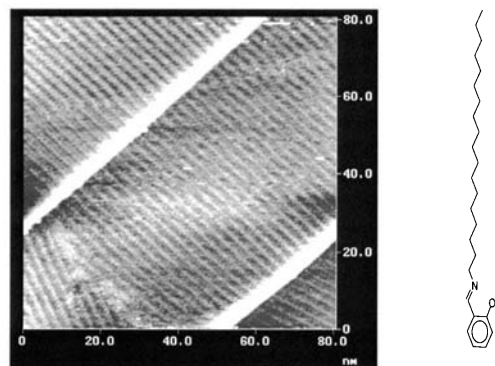


Figure 1. The STM image of monolayer (80 × 80 nm) of **C₁₈Sal** self-assembled on a graphite surface. The image was obtained in constant current mode with a tungsten tip. (Z-range: 0.5 nm, bias voltage: 1.50 V, tip positive, tunneling current: 229 pA).

of freshly cleaved HOPG. The STM images were obtained in constant current mode using a NanoScope IIIa STM (Digital Instruments). The tunneling tip was a Pt/Ir tip purchased from Digital Instruments or a tungsten tip, which was sharpened by electrochemical etching prior to use. All of the observation were carried out at 20 ± 1 °C.

Like many other compounds having long alkyl chain, **C₁₈Sal** formed two-dimensional crystals on the solution–graphite interface. Figure 1 shows the STM image of the monolayer in a scan area of 80 × 80 nm in which self-assembled molecular array was clearly observed as stripes. The domain boundaries of adjacent 2D crystals are observed associated with the step–terrace structure of graphite. A high-resolution image of the monolayer is given in Figure 2 over scan area of 10 × 10 nm, where clear contrast of the molecular image is observed. The brighter region and the darker region can be attributed to the conjugated π -electron systems and the methylene groups of alkyl chains, respectively.⁵ Thus, Schiff base moiety acts as a “marker” group to determine the relative location of molecules. Interdigitated molecular arrangement as illustrated in Figure 2b can rationalize the obtained image in which the Schiff base moieties alternately point in opposite direction. The molecular long axis of **C₁₈Sal** appears to be inclined with an angle of ca. 60° vs the orientation of the band.

The molecular patterns of the Schiff base ligand immediately changed upon addition of copper(II) acetate dissolved in 1-phenyl octane and ethanol on the graphite due to *in situ* complex formation. The STM image observed in this way coincided with that obtained from the isolated complex i.e., [Cu(**C₁₈Sal**)₂]. The STM image of the complex was separately obtained by applying a drop of 1-phenyl octane solution of isolated [Cu(**C₁₈Sal**)₂] on graphite. Thus more stable molecular framework was formed by rapid complexation and self-assem-

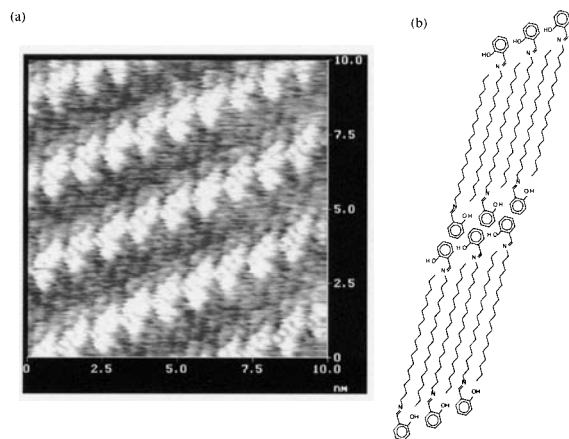


Figure 2. (a) High resolution STM image of monolayer (10×10 nm) of $C_{18}Sal$ (Z-range: 0.5 nm, bias voltage: 1.41 V, tip positive, tunneling current: 266 pA). (b) A schematic representation of possible molecular geometry.

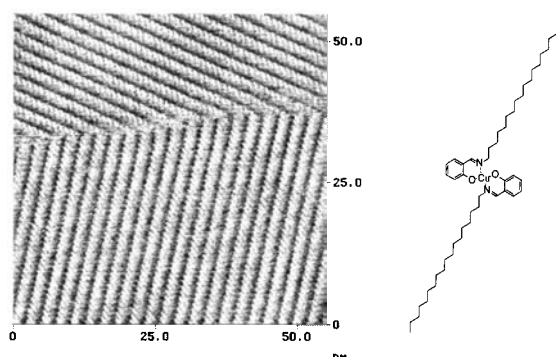


Figure 3. The wide range feature of $[Cu(C_{18}Sal)_2]$ monolayer (55×55 nm) observed by STM (Z-range: 0.5 nm, bias voltage: 1.44 V, tip positive, tunneling current: 128 pA).

bly, followed by rearrangement on the graphite surface upon addition of Cu(II) ion. Figure 3 shows the stripe shaped monolayer of Cu(II) complex over a scan area of 55×55 nm. Although the constituent molecule is achiral, two domains of mutually mirror images were clearly observed with the rotational angle of 110° . They can not be superimposed to each other by rotation and translation operations within the surface plane. Similar spontaneous segregation of enantio-morphous domains has been observed in self-assembled achiral molecules.⁶ Figure 4 shows the high-resolution image of the complex over scan area of 8×8 nm, where the brighter column corresponds to the ligand π -electron system and central metal ion. Each bright unit appears to consist of three spots, which can be attributed to two aromatic rings and central Cu(II) ion. The image is consistent with the square-planar *bis* geometry of the similar Cu(II)-Schiff base complexes.⁷ The length of alkyl chain agrees with that expected for a fully expanded conformation. From the relative location of alkyl chains, the molecular alignment can be assigned to interdigitated structure with two sets of ligands taking *trans* geometry around Cu(II) ion. The

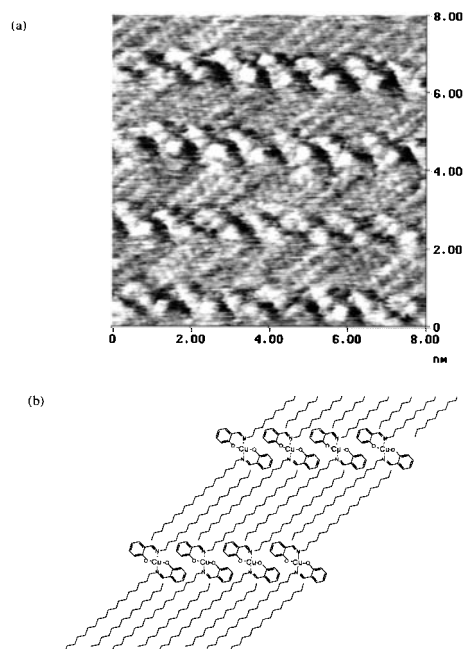


Figure 4. (a) The high resolution image of $[Cu(C_{18}Sal)_2]$ monolayer (8×8 nm) (Z-range: 0.5 nm, bias voltage: 1.24 V, tip positive, tunneling current: 123 pA). (b) Proposed molecular alignment of the $[Cu(C_{18}Sal)_2]$ on the graphite surface.

possible molecular alignment of the Cu(II) complex is schematically represented in Figure 4b, by which the STM images can be reproduced. We also confirmed that Pd(II) formed a similar self-assembled molecular pattern on graphite surface, in which the complex takes *trans-bis* configuration.

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References and Notes

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