

# STM observation of 12-hydroxyoctadecanoic acid and its 4,4'-bipyridinium salt self-assembled on a graphite surface†

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Received (in Cambridge, UK) 15th February 1999, Accepted 17th May 1999

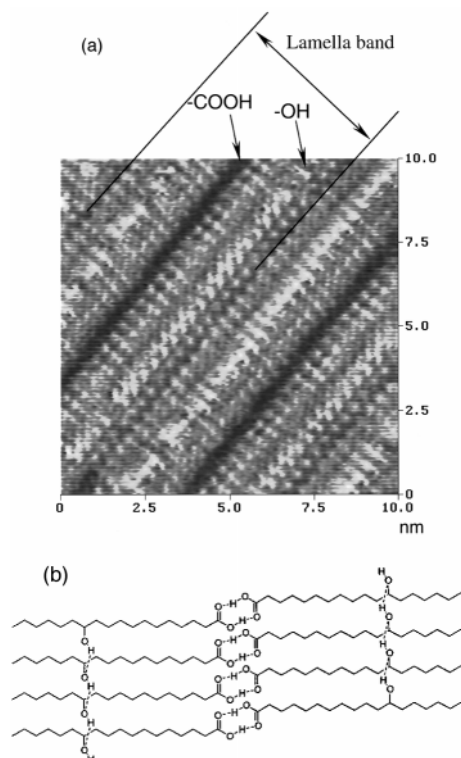
Self-assembled monolayers of the gelling agent, 12-hydroxyoctadecanoic acid and its 4,4'-bipyridinium salt have been observed on the solution graphite interface using scanning tunnelling microscopy (STM) and the molecular patterns are discussed with respect to the intermolecular hydrogen bond network.

Some types of amphiphiles act as gelling agents for organic solvents.<sup>1</sup> Among them, 12-hydroxyoctadecanoic acid (12-HOA) has attracted extensive attention from fundamental as well as practical points of view.<sup>2–4</sup> A wide range of solvents can be gelled by 12-HOA and hence this reagent has been applied to the recovery of spilled oil or disposal of used kitchen oil.<sup>1</sup> It has been pointed out that non-covalent weak interactions are responsible in controlling the self-assembling mode and the stabilization of aggregates.<sup>1,4,5</sup> The presence of the hydroxyl group in 12-HOA seems particularly important to the gelling ability of 12-HOA since stearic acid does not show this

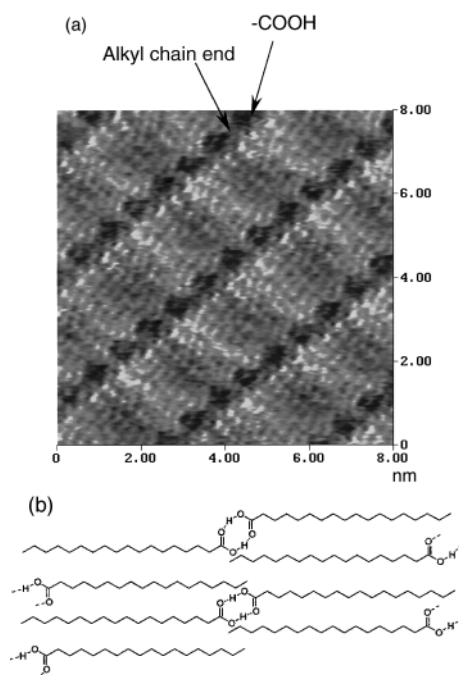
property. A structural model of a 12-HOA aggregate has been proposed by Terech *et al.* on the basis of neutron and X-ray scattering investigations.<sup>6</sup> An infinite network of hydrogen bonds between hydroxy groups has been suggested to stabilize the plate-like building unit, which is interconnected leading to construction of a three-dimensional fibrous polymer.<sup>6</sup>

Scanning tunnelling microscopy (STM) has provided molecular images of self-assembled molecules at atomic resolution.<sup>7,8</sup> Monolayers of self-assembled amphiphiles including fatty acids have been directly observed at solution–solid interfaces by STM and the morphologies of the two dimensional crystals discussed and interpreted in terms of intra- and inter-molecular hydrogen bonds.<sup>9–12</sup> We have attempted to observe directly the molecular patterns of the monolayers formed with 12-HOA and stearic acid as well as their 4,4'-bipyridinium salts, to clarify the molecular interaction, especially the role of the hydrogen bond network on the molecular assembly and gel formation ability.

A warm solution (*ca.* 0.5 wt%) of racemic 12-HOA (Aldrich Co.) in octylbenzene was applied on the surface of freshly cleaved highly oriented pyrolytic graphite (HOPG). Upon cooling to room temperature (23–26 °C), the solution became a gel. We have successfully observed the STM image of a self-assembled monolayer of 12-HOA on the HOPG surface under an organic gel layer.<sup>13</sup> Fig. 1(a) and 2(a) show the STM images of 12-HOA and stearic acid over a scan area of 10 × 10 nm along with their possible geometries [Fig. 1(b) and 2(b)]. Edges



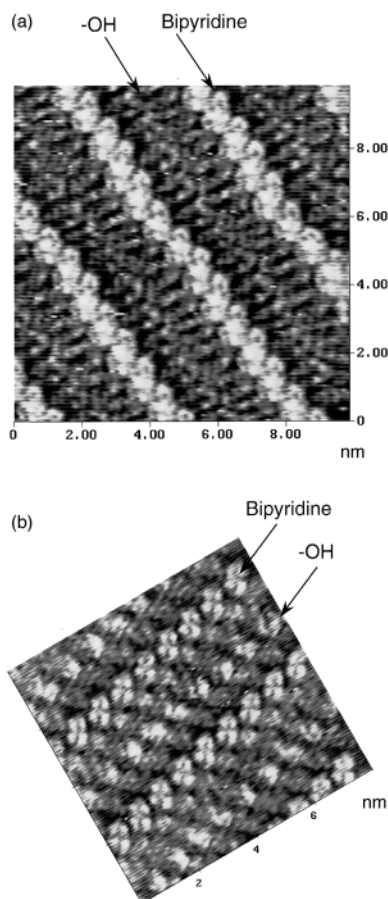
**Fig. 1** (a) The STM image (10 × 10 nm) of a 12-HOA monolayer self-assembled on an HOPG surface. The image was obtained in constant current mode with a tungsten tip. Bias voltage and tunneling current were −1.47 V (tip negative) and 266 pA, respectively. (b) A possible geometry of the molecular alignment.



**Fig. 2** (a) The STM images (8 × 8 nm) of a stearic acid monolayer self-assembled on an HOPG surface. The image was obtained in constant current mode with a tungsten tip. Bias voltage and tunneling current were −1.58 V (tip negative) and 682 pA, respectively. (b) A possible geometry of the molecular alignment.

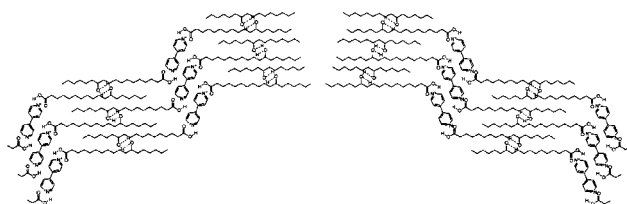
† Colour versions of the STM images in Fig. 1–3 can be electronically accessed (<http://www.rsc.org/suppdata/cc/1999/1197>).

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**Fig. 3** The STM images of a self-assembled monolayer of 12-HOA-bpy. These two molecular orientations are mirror images. The images were obtained in constant current mode with a tungsten tip. (a) The scan area is  $10 \times 10$  nm; bias voltage and tunneling current were 1.18 V (tip positive) and 216 pA, respectively. (b) The scan area is  $8 \times 8$  nm; bias voltage and tunneling current were 1.41 V (tip positive) and 459 pA, respectively.

of multi-layers were not observed in any STM images indicating that the observed images are those of monolayers. Like stearic acid, 12-HOA molecules orient parallel to each other and thick dark areas are observed. The molecular axis orients perpendicularly to the dark stripes forming a centrosymmetric molecular pattern. An interdigitated geometry, in which the head groups alternately point in opposite directions has been suggested for the molecular alignment of stearic acid<sup>9</sup> and other saturated fatty acids<sup>9</sup> (Fig. 2). Thus the dark moiety has been assigned to carboxyl head groups.<sup>9</sup> The distance between the dark regions for stearic acid corresponds to its molecular length (*ca.* 2.5 nm) whereas that for 12-HOA is roughly double the molecular length of 12-HOA assuming that the alkyl chain is fully expanded. Therefore, the 12-HOA molecules are likely to associate in a head to head manner at carboxylic acid groups located in adjacent rows. Two brighter bands observed between thick black stripes can be attributed to the hydroxy groups on the C12 positions. The zigzag shaped dark area at the center of the image corresponds to the lamella boundary between the alkyl



**Fig. 4** Schematic representation of a possible molecular alignment for a 12-HOA-bpy monolayer.

chain termini. The possible molecular alignment is depicted in Fig. 1(b) where intermolecular hydrogen bonds effectively link 12-HOA molecules to form a macromolecular sheet. This molecular pattern, involving an infinite hydrogen bond network, coincides with the plate-like structure in the internal building block of 12-HOA aggregates proposed by Terech *et al.*<sup>6</sup>

In order to confirm our interpretation to the observed images, we have attempted to insert 4,4'-bipyridine (bpy) as a marker between carboxyl groups. A conjugated  $\pi$ -electron system such as bpy might be prominent in a molecular image since areas of higher electronic conductance tend to give brighter images. A mixture of 12-HOA and bpy (2:1) in octylbenzene solution formed a monolayer on HOPG, the molecular image of which is shown in Fig. 3. Remarkably bright regions corresponding to bpy moieties are now observed while the thick dark stripes disappeared. A similar phenomenon is observed in the monolayer image of bpy and stearic acid. Therefore the thick dark band in Fig. 1(a) can consistently be assigned to the region where hydrogen bonded carboxyl head groups are located. Bipyridine molecules sandwiched with 12-HOA appear to be inclined with respect to the alkyl chain at an angle of *ca.* 30°. The distance between the bpy centers is *ca.* 3.6–3.7 nm, which is much longer than that estimated from the molecular lengths of 12-HOA (2.5 nm) and bpy. When the alkyl chains in adjacent rows are associated at the hydroxyl groups as shown in Fig. 4, the observed bpy separations can be rationalized. Interestingly, enantiomeric molecular patterns are found in this system [Fig. 3(a) and 3(b)]. One plausible interpretation is that the racemate 12-HOA-bpy monolayer spontaneously segregates into different domains due to homochiral association at hydroxy groups.<sup>12,14</sup> Fig. 4 shows the proposed molecular arrangement of a 12-HOA-bpy monolayer in which hydroxy groups in vicinal rows are associated to form a polymeric hydrogen bond network. The infinite network of hydrogen bonds might play an important role for building up of the supramolecular assembly of aggregates. It is of note that the bpy salt of 12-HOA also shows gelling ability towards various solvents.

This research was performed as a part of Regional Consortium R&D program conducted by The New Energy and Industrial Technology Development Organization.

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Communication 9/01218D