Supporting Information

Amine-Directed Hydrogen-Bonded Two-Dimensional Supramolecular Structures

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Experimental Section

Sample Preparation and set up:
A gold bead, presenting well-ordered Au(111) facets on which wide (>100 nm) terraces could be easily found, was used as the substrate. Before all experiments, the substrate, the Teflon cell and the O-ring (Viton) were cleaned by immersion in hot piranha solution (1:3 H₂O₂ (J. T. Baker, CMOS)/ H₂SO₄ (96%, J. T. Baker, CMOS) for 1h (Caution! The piranha solution is a very strong oxidizing reagent and can be dangerous. Protective equipment including gloves and glasses should be used at all times.) and then rinsed and heated up in ultra-pure deionized (DI) water obtained from a Thermoscientific Barnstead Easypure II purification system equipped with a UV lamp (water resistivity >18 MΩ.cm). A hydrogen flame was used to anneal the bead, followed by quenching in hydrogen-saturated ultrapure DI water. The Au bead was quickly transferred to the Teflon STM electrochemical cell and immersed under potential control in electrolyte solutions.

Materials:
1,3,5-triaminobenzene trihydrochloride (95%, SINova)
1,3,5-trimethylbenzene (99% extra pure, Acros organics)
1,3,5-benzenetricarboxylic acid (95%, Sigma –Aldrich)
H₂SO₄ (99.999%, Sigma –Aldrich)

Solutions:
1 mM 1,3,5-triaminobenzene trihydrochloride in 0.05 M H₂SO₄ (pH ~ 1).
1 mM 1,3,5-triaminobenzene trihydrochloride in H₂SO₄ (pH ~ 5.5).
1 mM 1,3,5-benzenetricarboxylic acid in 0.05 M H₂SO₄ (pH ~ 1).
1,3,5-trimethylbenzene as is.

For preparing self-assembled monolayer in acidic solution, molecular solution in 0.05 M H₂SO₄ (99.999%, Sigma Aldrich) was used as the electrolyte solution. For preparing self-assembly monolayer in near neutral solution, molecular solution in H₂SO₄ (pH ~ 5.5) was used as the electrolyte solution.
Formation of polymerized triaminobenzene

Poly-TAB is a network of TAB molecules formed by an average loss of 1.3 NH$_3$ per ring with few unreacted amino groups (Figure 1a). Formation of Poly-TAB occurs upon polymerization of triaminobenzenium cations in moderately acidic/neutral solution and at room temperature. Observation of large poly-TAB transparent sheets (Figure 1b) in our moderately acidic/neutral solution of TAB/H$_2$SO$_4$ (pH ~ 5.5) (Figure 1c, blue) confirms presence of triaminobenzenium cations. On the other hand, in acidic solution of TAB/H$_2$SO$_4$ (pH ~ 1), we did not observe formation of poly-TAB transparent sheets (Figure 1c, red).

Synthesis of poly-TAB occurs upon formation of covalent bonds between TAB molecules and needs the loss of an average of 1.3 NH$_3$ per ring. In order to make covalent bonds, NH$_3$ groups need to approach the amine group of the neighboring molecules in a proper orientation. In the solution phase, the freedom of rotating causes higher probability for the molecules to approach in the proper direction to the neighboring molecules to form the covalent bond. However, molecules adsorbed on the surface have fewer directions to move along and form bonds with neighboring molecules and due these restrictions they may not be able to become close enough to form covalent bonds. Thus, formation of poly-TAB due to loss of NH$_3$ groups does not happen directly on the surface upon adsorption of TAB molecules.

![Figure SI 1](image-url)
**Structural details of triaminobenzene network**

**Figure SI 2.** a) Molecular structure of TAB with the hydrogen-hydrogen distances determined using Chemdraw and calculated length of TAB molecule, b) six TAB molecules forming the hexagonal structure drawn based on a real 3-D molecular model.

**References:**

(2) Iwan, A.; Sek, D. *Progress in Polymer Science* 2011, 36, 1277.