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Complex Structures Resulting from Carboxylic Acid Self-Assembly: Comparison of 2-Naphthoic Acid to Quinaldic Acid and 3-Quinoline Carboxylic Acid

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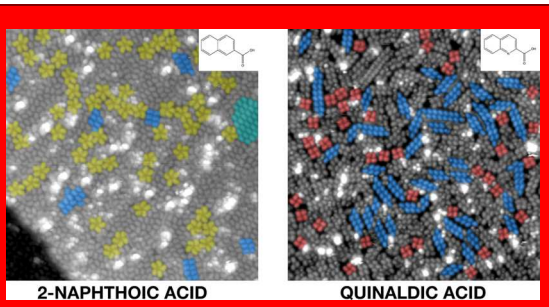
Scanning tunneling microscopy was used to study the self-assembly of three molecules on the Au(111) surface: 2-naphthoic acid, quinaldic acid, and 3-quinoline carboxylic acid. All three compounds consist of two fused six-membered rings functionalized at the same position with a carboxylic acid group. Despite their chemical similarity, widely different structures were observed to result from self-assembly after pulse deposition. 2-Naphthoic acid forms cyclically hydrogen-bonded pentamers, a metastable structure that transitions to rows of dimers upon gentle annealing. Quinaldic acid and 3-quinoline carboxylic acid form dimers, tetramers, and hexamers, but no pentamers. Differences in self-assembly between these three compounds are attributed to the ability of quinaldic acid and 3-quinoline carboxylic acid to form zwitterionic species.



INTRODUCTION

Molecular self-assembly is defined as the spontaneous process of bringing molecules together via noncovalent interactions to form highly organized structures without external direction. Micelle formation is a prototypical self-assembly process occurring in the natural world,[1] as is the formation of the DNA double helix through complementary base pairing.[2,3] Structures engineered by controlled self-assembly can be simple, such as atoms forming into local islands on metal surfaces[4,5] or thiolate monolayers on gold surfaces,[6,7] with increasing complexity including multilayer structures[8,9] and host−guest composites.[10,11] Additionally, self-assembly can be altered by the inclusion of various factors, including molecular functionalization,[12,13] charge separation,[14] and surface modification.[15] Self-assembly, along with the related fields of supramolecular chemistry and crystal engineering, has many practical applications including coatings,[16,17] nanoscale electronics,[18,19] and pharmaceuticals.[20,21]

In planning and designing self-assembled systems, carboxylic acid (COOH) groups are a common supramolecular synthon:[22] a functional group with a powerful and reliable effect on self-assembly with performance that can be counted on largely independent of the rest of the molecule to which it is attached. COOH groups generally form dimers with strong reciprocal hydrogen bonding, where the OH group is a hydrogen-bond donor and the C═O group an acceptor. COOH dimers are highly prevalent in the solid-state crystal structures of organic molecules.[23] Self-assembly based on COOH dimerization has been used to create linear structures on the nanoscale as well as a wide variety of branched networks.[24,25]

Recent work from our laboratory[26,27] has focused on the expansion of the COOH group beyond a simple synthon, showing that structures significantly more complex than dimers can arise when a molecule has additional hydrogen-bond donor or acceptor groups adjacent to COOH. This is the case even when the hydrogen-bonding activity of these groups is relatively weaker than average. For example, aromatic C−H groups are far weaker H-atom donors than COOH, but the presence of an aromatic C−H next to COOH acts to stabilize the formation of cyclic hydrogen-bonded pentamers in ferrocenecarboxylic acid.[28] We have observed similar effects in the formation of pentamers of indole carboxylic acids[29] and of hexamers of ferrocenedicarboxylic acid.[30]

In the current study, we take advantage of the sample preparation technique of pulse deposition in order to create surfaces on which molecules undergo nonequilibrium self-organization. The resultant structures are not a single thermodynamically favored structure but multiple kinetically trapped, metastable structures. In pulse deposition, small droplets of a low-concentration solution are introduced into vacuum. Rapid evaporation of the solvent results in a droplet that is increasingly smaller, cooler, and more concentrated. The dynamics at the solid-solution interface govern the subsequent self-assembly process, creating complex patterned surfaces that afford new insights into how intermolecular interactions guide the formation of structures in a molecule-by-molecule fashion.

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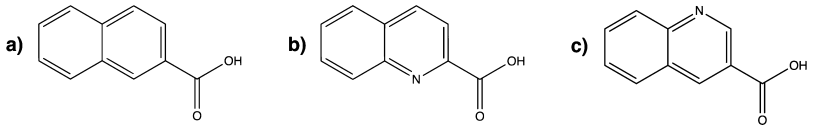

Figure 1. Chemical structures of (a) 2-naphthoic acid, (b) quinaldic acid, and (c) 3-quinoline carboxylic acid.

METHODS

Scanning Tunneling Microscopy (STM). Au(111)/mica samples were purchased from Keysight Technologies and prepared in high vacuum (10^{-5} to 10^{-8} Torr) through three cycles of argon sputtering (0.55 kV, 15 min) and annealing at ~400 °C for 15 min. After the samples were cooled, they were transferred to a high-vacuum load lock for pulse deposition. Solutions (17 mM) of 2-naphthoic acid and quinaldic acid, Figure 1a,b, respectively, were prepared in methanol and toluene. Solutions (17 mM) of 3-quinoline carboxylic acid, Figure 1c, were prepared in methanol. All solutions were prepared in air. All solutes were purchased from Sigma-Aldrich, and all solvents were purchased from Fisher Scientific. Solutions were injected into a pulsed solenoid valve (Parker Instruments, Series 9, IOTA ONE Driver, 0.5 mm diameter nozzle) and deposited onto clean Au(111)/mica. The samples were then transferred into an Omicron scanning tunneling microscope (LT-UHV, base pressure 5×10^{-10} Torr), where they were cooled to 77 K prior to imaging.

Density Functional Theory (DFT). All multimolecular energy optimizations were performed with the Q-Chem 5.0 software package. Structures of molecular clusters were optimized with the Perdew, Burke, and Ernzerhof exchange–correlation functional,[31] chosen for its broad applicability to organic systems. The 6-311++G(d,p) basis set was used in conjunction with Grimme's D3 dispersion correction.[32] Ring structures were generated such that pseudo-C_n (where n is the number of molecules) symmetry was approximated. All structures were started in a planar geometry. All structures were subjected to the Boys and Bernardi counterpoise correction to account for basis set superposition error.[33]

RESULTS AND DISCUSSION

Initial deposition of 2-naphthoic acid in methanol on Au(111) produced two primary structures, with pentamers being the majority species, as shown in Figure 2. The calculated structure of the pentamer is similar to previously observed systems such as ferrocenecarboxylic acid and indole carboxylic acids, where cyclic hydrogen bonding is stabilized by the presence of weaker hydrogen bonds, formed from C–H groups adjacent to COOH. In the past, this C–H stabilization of a hydrogen-bonded ring structure has only been observed from beta H-atom donors on five-membered rings; in contrast, here C–H stabilization is observed on a six-membered ring.

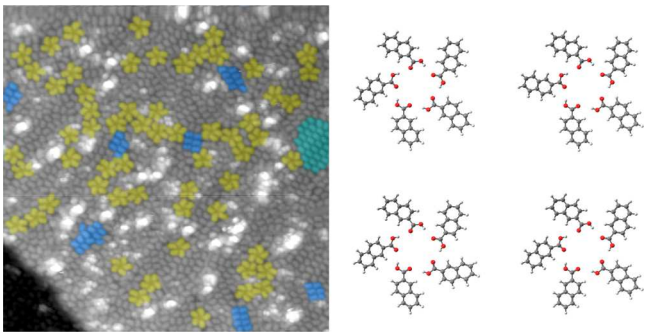

Figure 2. Left: STM image of 2-naphthoic acid adsorbed on Au(111), 350 × 350 Å. Representative pentamers, ordered dimer structures, and close-packed molecules are highlighted in yellow, blue, and cyan, respectively. Right: four distinguishable pentamer arrangements of 2-naphthoic acid.

Although features corresponding to pentamers are prevalent on the surface, they lack uniformity. Previous studies have seen pentamers in C_5-symmetric orientations exclusively, as the C–H groups in the beta position relative to COOH were chemically inequivalent.[26,34] 2-Naphthoic acid deviates from this trend because of the availability of two chemically equivalent C–H groups in the beta position relative to COOH. Because of this chemical equivalence, each molecule in the superstructure has two available conformations, resulting in a total of 32 permutations of pentamers, with four being distinguishable and shown in Figure 2.

Clustering behavior was also studied for two related molecules, quinaldic acid and 3-quinoline carboxylic acid. Like 2-naphthoic acid, each of these molecules consists of fused six-membered rings, with the same position of the carboxylic acid group. They differ by the substitution of one of 2-naphthoic acid's C–H groups for a nitrogen atom. For quinaldic acid, this nitrogen is adjacent to the carboxylic acid; for 3-quinoline carboxylic acid, it is separated by another carbon. Both molecules could in principle arrange identically to 2-naphthoic acid's pentamer configuration. For 3-quinoline carboxylic acid in particular, the nitrogen is remote from the COOH and C–H groups involved in hydrogen bonding.

Figure 3 shows that neither molecule formed pentamers after pulse deposition. Instead, quinaldic acid formed C_4-symmetric tetramers and two forms of dimers, while 3-quinoline carboxylic acid produced a disordered surface with only a few hexamers and dimers. We attribute this disparity in observed self-assembled structures to the formation of zwitterionic species for the nitrogen-containing molecules. To form a zwitterion, an intramolecular proton transfer occurs from COOH to the ring nitrogen—for the purposes of

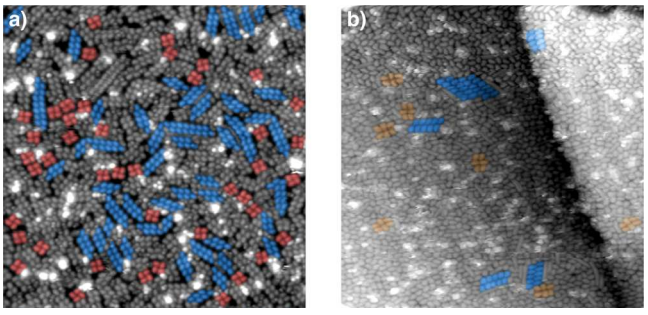

Figure 3. STM images of (a) quinaldic acid, 400 × 400 Å and (b) 3-quinoline carboxylic acid, 350 × 350 Å on Au(111). Representative dimers, tetramers, and hexamers are highlighted in blue, red, and orange, respectively.

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intermolecular interactions, NH^+ becomes the hydrogen-bond donor instead of COOH. While typically a zwitterion would be stabilized by a polar solvent, charge−charge interactions between closely packed molecules could also play a stabilizing role. This is what occurs in the solid-state structure of quinaldic acid, which is composed of a 50/50 ratio of carboxylic to zwitterionic species.[35] While the solid-state structure is three-dimensional, many of the strong pairwise interactions are between coplanar molecules. A similar stabilization may occur in self-assembly of these molecules into monolayers, where there is the additional presence of the metal surface to stabilize the charges. Additionally, while 2-naphthoic acid would not be expected to interact with the surface, it is possible that quinaldic acid and 3-quinoline carboxylic acid could have some degree of molecule−surface interaction, which could play a significant role in the formation of the observed self-assembled structures.

Calculations obtained using DFT of per-molecule binding energies for a range of cluster sizes in the gas phase are shown in Figure 4. These calculations predict similar stability for 2-naphthoic acid dimers and pentamers, in line with what is observed in STM images. In contrast, while quinaldic acid and 3-quinoline carboxylic acid follow similar trends for energy versus hydrogen-bonded cluster size, pentamers are not observed for these molecules.

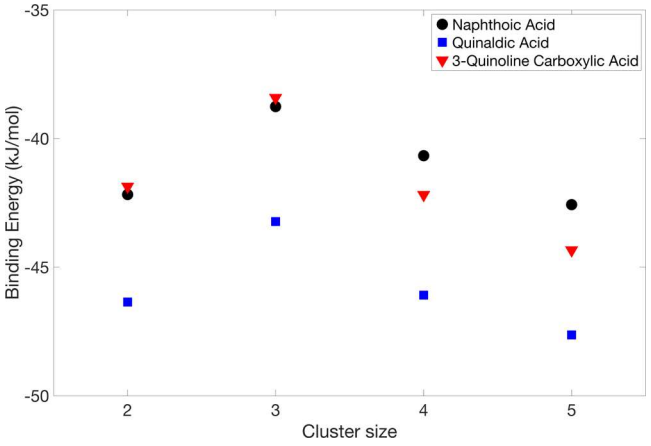

Figure 4. Predicted per-molecule binding energies of cyclic clusters of 2-naphthoic acid (black), quinaldic acid (blue), and 3-quinoline carboxylic acid (red) for clusters of size $n = 2-5$. Cyclic clusters above $n = 5$ were not observed.

There is additional evidence that the tetramers observed for quinaldic acid are not hydrogen-bonded via a cyclic arrangement of COOH groups: the observed features are significantly more compact than would be predicted from such a tetramer. Figure 5a shows a DFT-calculated structure of a tetramer of quinaldic acid overlaid on top of a composite image of an STM image of the same. The fit is noticeably poor, with a considerable portion of the modeled structure occupying space outside the composite tetramer. In contrast, Figure 5b shows the proposed structure of a zwitterionic tetramer of quinaldic acid overlaid on the same composite image. This structure was not generated via DFT, as it would not meet the convergence criteria set for the remaining calculated structures. Instead, the N−H···O bond distance was matched to that of the solid-state structure observed in Figure 7, while simultaneously trying to minimize the repulsive interactions of the negatively charged oxygen.

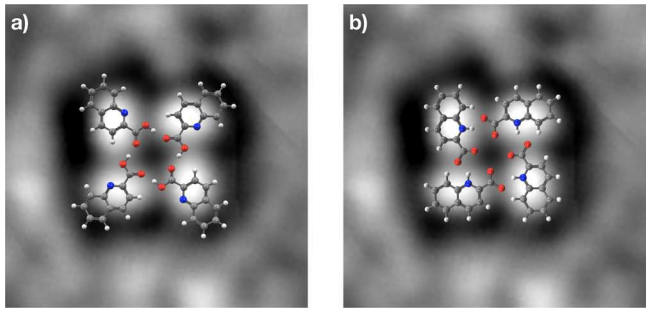

Figure 5. (a) Tetramer of quinaldic acid in the carboxylic acid isomer, predicted from DFT, overlaid on a 27 × 27 Å STM composite image of quinaldic acid's tetramers. (b) Model of a tetramer of quinaldic acid in the zwitterionic isomer, with the N−H···O bond distance matched to solid-state observations.[35]

Some of the structures that self-assemble after pulse deposition are metastable, as is shown by a thermal annealing experiment. After 1 day in ultrahigh vacuum at room temperature, the surface features evolve into considerably different supramolecular structures, which are shown in Figure 6. Most notably, pentamers of 2-naphthoic acid are not observed in annealed samples but rather are characterized mainly by an ordered dimer phase previously only observed as a minority species in the as-prepared sample. Annealed quinaldic acid structures show a new, complex structure with a six-molecule repeating unit. Of particular note in this structure is the presence of "T"-type interactions between the molecules. These interactions resemble the interactions of the zwitterionic form in the solid state, as seen in Figure 7.

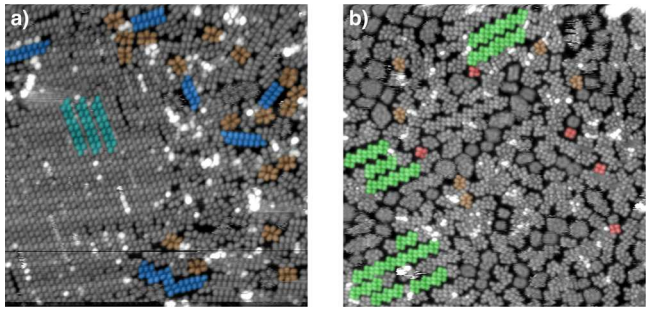

Figure 6. STM images of (a) 2-naphthoic acid, 400 × 400 Å and (b) quinaldic acid, 500 × 500 Å. Samples were thermally annealed at 25 °C. Dimers have been highlighted in blue, close-packed interactions in cyan, hexamers in orange, tetramers in red, and an ordered, six-molecule species in green.

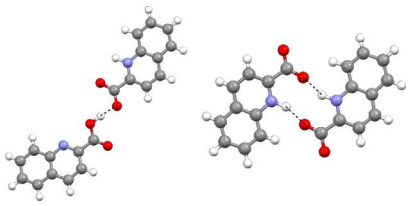

Figure 7. Pairwise interactions extracted directly from the solid-state structure of quinaldic acid.[35] The solid state consists of a 50/50 mixture of the carboxylic acid and zwitterionic forms.

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The effect of solvent on the pulse deposition process and consequent self-assembly was also examined. Toluene was used during the deposition of quinaldic acid and 2-naphthoic acid to see if zwitterion production would be suppressed in a nonpolar solvent. STM images of as-prepared samples after deposition are shown in Figure 8; quinaldic acid showed a strong preference for the six-molecule structures first observed after room-temperature annealing. Tetramers and dimer chains were still present; however, their prevalence was substantially reduced. 2-Naphthoic acid showed similar behavior, favoring the highly ordered domains of dimer interactions observed after room-temperature annealing over pentamers. The occasional pentamer and hexamer were observed at the grain boundaries between these regions.

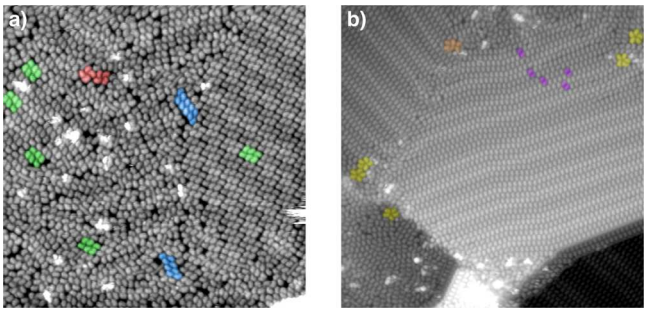

Figure 8. STM images of (a) quinaldic acid, 450 × 450 Å and (b) 2-naphthoic acid, 350 × 350 Å, pulse deposited in toluene on Au(111)/mica. Dimers have been highlighted in blue, tetramers in red, pentamers in yellow, hexamer in orange, ordered six-molecule species in green, and close packing in purple.

The finding that zwitterions are present in self-assembled structures even after pulse deposition from toluene is a surprising one. The first possibility is that proton transfer occurs as a result of adsorption, with the highly polarizable metal surface playing the role of a polar solvent in stabilizing molecular charges. The second possibility is that these charges are stabilized by intermolecular interactions; the proton transfer would then occur either upon self-assembly or beforehand in the concentrated, rapidly evaporating droplet produced by the pulse deposition process. We also cannot discount the possibility that zwitterion formation was impacted by the presence of trace amounts of water within the toluene. Whichever the case may be, local environment plays a key role in the formation of surface species whenever separation of charge is a possibility for the system.

CONCLUSIONS

Self-assembly of 2-naphthoic acid after pulse deposition on Au(111) produces cyclically hydrogen-bonded pentamers, a structure that has not previously been observed for six-membered rings. Pentamers are a metastable species that relaxes to a dimer-row structure over time at elevated temperature. Quinaldic acid and 3-quinoline carboxylic acid would, by their structural similarity to 2-naphthoic acid, also be expected to form pentamers. Instead, they produce a variety of other structures which are attributable to the ability of these molecules to form zwitterions. Suppressing the formation of zwitterions in solution through the use of nonpolar toluene as a solvent does not reduce the importance of zwitterions in the self-assembled structures that are produced. The comparison between 2-naphthoic acid, quinaldic acid, and 3-quinoline carboxylic acid shows that even subtle changes in molecular structures have significant impact on molecular assembly. This work also helps to clarify the cases where electronic structure calculations are not useful for predicting the arrangement of self-assembled monolayers. The ongoing work aims to generalize these results to a broader range of molecular systems. Comparison studies on different substrates will also help clarify the interplay between molecule−molecule and molecule−surface interactions that drive structure formation in self-assembly.

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Notes

The authors declare no competing financial interest.

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