THE JOURNAL OF PHYSICAL CHEMISTRY Letters

pubs.acs.org/JPCL

Hydrogen-Bond-Mediated Biomolecular Trapping: Reversible Catch-and-Release Process of Common Biomolecules on a Glycine-Functionalized Si(111)7×7 Surface

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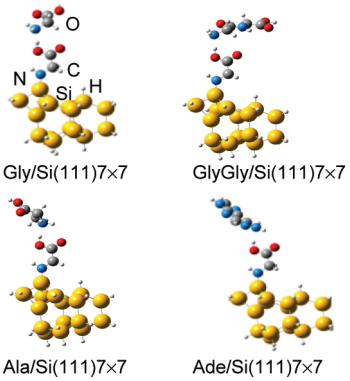
ABSTRACT Adsorption and desorption of several small prototypical biomolecules: glycine, glycylglycine, alanine, adenine, and thymine on a glycine-functionalized Si(111)7×7 surface have been investigated by X-ray photoelectron spectroscopy. Glycine has been found to adsorb on Si(111)7×7 through N−H dissociation, which makes the unreacted carboxyl group of the interfacial glycine adlayer an effective means to capture these biomolecules (except for thymine) through [O−H···N] hydrogen bonding. Furthermore, the captured molecules can be released simply by annealing to 120 °C for 10 s. This hydrogen-bond-mediated catch-and-release mechanism is supported by the appearance and disappearance of the characteristic hydrogen-bond N 1s features at 401.4 eV and is found to be reversible. The glycine-functionalized Si(111) surface therefore provides a flexible platform for potential applications as selective molecular traps, chemical sensors, and biomolecular electronic components.

SECTION Surfaces, Interfaces, Catalysis



In the "bottom-up" approach of creating molecular nanostructures and devices, molecules are deposited and organized into various patterns either by interactions with specific sites on the substrate or by interactions with the molecules themselves (as in a self-assembly process). A well-ordered substrate surface, such as Si(111)7×7 or Si(100)2×1, has been shown to be sufficiently reactive to facilitate adsorption of organic molecules into ordered monolayers in registry with specific sites on the substrate through, for example, [2+2] cycloaddition,[1,2] insertion reaction,[3] and other covalent bonding mechanisms.[4] On the other hand, adsorbate−adsorbate interaction, especially through hydrogen bonding, may lead to a well-organized self-assembled monolayer on unreactive surfaces (e.g., Au, Ag).[5−10] Many well-ordered patterns observed with scanning tunneling microscopy (STM) have been interpreted in terms of H-bonding among neighboring molecular adsorbates. Owing to its selectivity and directionality, H-bonding could facilitate ordering of molecules with both H-bond donor and H-bond acceptor functional groups. In particular, the [O−H···O] H-bonding among the carboxyl groups has been reported to lead to honeycomb patterns of 1,3,5-benzenetricarboxylic acid on Ag(111),[5] pairing of cysteine on Au(110),[6] and domain-boundary rows of isonicotinic acid on Ag(111).[7] The [N−H···O] H-bonding results in hexamers of pyrrolidone on Au(111)[8] and trimers of uracil on Cu(111),[9] while the [O−H···N] H-bonding gives rise to twin chains of 4-[*trans*-2-(pyrid-4-yl-vinyl)]-benzoic acid on Ag(111)[10] and a hexagonal superstructure of isonicotinic acid on Ag(111).[7] Although the observations of well-ordered STM patterns and the corresponding density functional theory (DFT) calculations generally support the existence of these H-bonds, X-ray photoelectron spectroscopy (XPS) and vibrational spectroscopy could offer more bond-specific information through the relevant peak shifts. For example, the N 1s binding energy of a H-bond acceptor (N) in the [O−H···N] H-bond is found to increase by more than 1 eV due to charge transfer from the N atom for isonicotinic acid,[7,11] diethanolamine,[12] ethylenediamine,[13] benzylic amide macrocycle,[14] and glycine.[15] In vibrational spectroscopy, a large decrease in the stretching frequency of the H-bond donor as a result of H-bond formation[16] has been reported for the self-assembly of 3-mercapto-*N*-pentadecylpropionamide on gold[17] and for a photoswitch consisting of bisthienylethene-pyridine and carboxyl-tetrathiafluvalene.[18]

To date, H-bonding has mostly been employed to produce two-dimensional molecular nanostructures, and the use of H-bonding to develop nanostructures beyond the monolayer is uncommon. For three-dimensional growth involving a second or additional adlayer on top of the first adlayer, H-bonding can offer important advantages particularly in building a structurally flexible system. Unlike the weak, long-range, van der Waals interaction, a H-bond is selective and sufficiently strong to enable a molecule in the first adlayer to "catch" and assemble an incoming molecule into the second adlayer in a controllable fashion. On the other hand, unlike the strong covalent bond, the H-bond is sufficiently weak, making it easy to break and

Received Date: September 21, 2010
Accepted Date: November 9, 2010
Published on Web Date: November 15, 2010

DOI: 10.1021/jz101315m | *J. Phys. Chem. Lett.* **2010**, *1*, 3385–3390

therefore enabling the first adlayer to "release" the captured molecules in the second adlayer by a simple stimulus such as mild heating. In effect, the adsorbates in the first adlayer serve as linker molecules that bind strongly to the substrate through covalent bonding at one end while "trapping" selective molecules (with compatible H-bonding groups) to form the second adlayer by H-bonding. By choosing appropriate molecules as the linkers for the first adlayer, the surface can be further functionalized in a reversible fashion with appropriate H-bond-compatible molecules.

We have recently found that deposition of glycine molecules on a Si(111)7×7 surface in ultrahigh vacuum leads to N−H dissociative adsorption of glycine and the formation of a deprotonated glycine adlayer through N−Si covalent bonding at the interface. We also observed that the formation of a second molecular glycine adlayer onto the interfacial (first) adlayer proceeds primarily by [O−H···N] H-bonding between the carboxyl group of the first-adlayer molecule and the amino group of a second-adlayer molecule.[15] An appropriately deposited glycine adlayer on Si(111)7×7 can therefore serve as a linker platform with its "dangling" carboxyl group available for trapping other molecules via H-bonding. In the present study, we demonstrate that such a platform can provide an effective "catch-and-release" mechanism for trapping a number of small biomolecules, including not just amino acids and peptides [glycine (Gly), alanine (Ala), and glycylglycine (GlyGly), but also DNA base groups [adenine (Ade)] but not thymine (Thy)]. Except for Thy, the respective N 1s XPS spectra collected after deposition and postannealing of these biomolecules on the Gly/Si(111)7×7 surface clearly support that the present "catch and release" mechanism is mediated by interlayer H-bonding.

Figure 1 shows the N 1s XPS spectra of Gly, GlyGly, Ala, Ade, and Thy on the Gly/Si(111)7×7 surface. We have also obtained XPS spectra of the C 1s and O 1s regions, and they offer supporting evidence for the adstructure evolution discussed below. For the Gly/Si(111)7×7 surface obtained by exposing 15 s of Gly to the 7×7 surface, the prominent N 1s peak at 399.1 eV can be attributed to N−Si species resulting from N−H dissociative adsorption of Gly on Si(111)7×7 (Figure 1a).[15] We have also shown in our recent work that the intensity of this peak is saturated at this exposure, indicating the formation of the first Gly adlayer at the interface. Appropriately, we have therefore chosen a 15 s exposure of Gly on Si(111)7×7 as the functionalized platform for subsequent experiments. Further Gly exposure to 120 s results in a new peak at 401.4 eV, which corresponds to [O−H···N] H-bonding between the carboxyl group of Gly in the interfacial (first) adlayer and the amino group of newly deposited Gly in the second and subsequent adlayers.[15] Apparently, the interfacial Gly molecules (in the first adlayer) "catch" the incoming Gly molecules by H-bonding. Because the intensity of the N 1s peak at 401.4 eV can be as large as 1.5 times that of the peak at 399.1 eV,[15] the observed H-bonding appears to occur beyond the adlayer H-bonded to the interfacial adlayer. After annealing at 120 °C for 10 s, the H-bond feature at 401.4 eV is almost completely removed, indicating that nearly all the Gly molecules attached through [O−H···N] H-bonding have desorbed. The interfacial Gly molecules therefore "release" the H-bonded Gly in the second adlayer after only a mild anneal

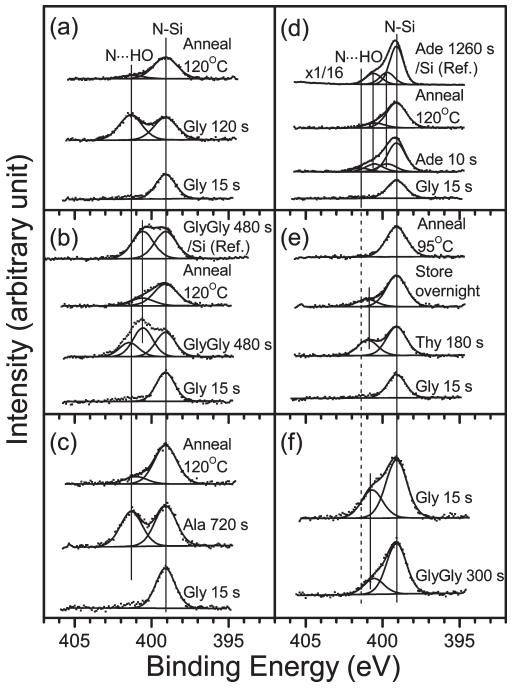


Figure 1. N 1s spectra of Si(111)7×7 functionalized by a 15-s exposure of glycine (Gly) before (lowest trace) and after exposure to (a) 120 s of Gly, (b) 480 s of glycylglycine (GlyGly), (c) 720 s of alanine (Ala), (d) 10 s of adenine (Ade), and (e) 180 s of thymine (Thy), and upon annealing at (a-d) 120 °C and (e) 95 °C for 10 s. N 1s spectra for bare Si(111)7 × 7 after exposure to (b) 480 s of GlyGly and (d) 1260 s of Ade are marked as reference (ref.). These spectra are compared with (f) the N 1s spectra of Si(111)7×7 functionalized by a 300-s exposure of GlyGly before and after 15 s of Gly exposure.

at 120 °C. To test whether the Gly/Si(111) surface can be reused after the first "catch-and-release" cycle, we have repeated the Gly exposure (e.g., 45 s) to the postannealed Gly/Si(111) surface and observed the reappearance of the H-bond feature at 401.4 eV, with little degradation of the functionalized platform. It is, however, crucial to make a judicious choice of the annealing temperature (i.e., the magnitude of current used in the direct current heating) that is sufficiently high to totally remove the H-bonded adlayers yet low enough to leave the interfacial adlayer intact (without dissociation). In this way, the functionalized platform can in principle be reused many times with the "reversible" catch-and-release process.

In order to test the generality of this catch-and-release approach, we repeat the deposition and desorption experiments on the Gly/Si(111)7×7 surface with different biomolecules. Figure 1b shows the N 1s spectrum of a 480 s exposure of GlyGly on the Gly/Si(111)7×7 surface. Evidently, in addition to the N−Si feature at 399.1 eV for Gly/Si(111)7×7, two new features at 401.4 and 400.6 eV are observed, and they can be attributed, respectively, to an [O−H···N] H-bonded adstructure as observed for the Gly case and to the amino or amide N not involved in bonding to the Gly/Si(111)7×7 surface. It should be noted that both the amino and amide [or C(O)NH] N atoms exhibit a similar N 1s binding energy at 400.6 eV.[19] Although it is not possible to identify from the N 1s spectrum alone which N atom in the GlyGly molecule is involved in the H-bonding, the amino N seems more likely, because the amino N is more basic

DOI: 10.1021/jz101315m | J. Phys. Chem. Lett. 2010, 1, 3385–3390

than the amide N, and the lone-pair electrons of the amino N are more geometrically accessible than those of the amide N. The intensities of these three N 1s features provide information on the extent to which the GlyGly adlayer attaches to the Gly interfacial adlayer by H-bonding. If all the deposited GlyGly molecules are H-bonded to the Gly molecules, the intensities of these three features should be equal to one another. However, the feature at 401.4 eV is found to be only about half as intense as the feature at 399.1 eV, which suggests that only half of the interfacial Gly molecules form the [O−H···N] H-bond with the GlyGly molecules. On the other hand, the feature at 400.6 eV appears slightly more intense than the interfacial N−Si feature, suggesting other GlyGly bonding arrangement with Gly that does not involve the [O−H···N] bonding. The ratio of GlyGly involved in the [O−H···N] H-bonding to those in the other bonding arrangement is about 2:1. For comparison, we show in Figure 1b the N 1s spectrum of a 480 s exposure of GlyGly directly onto a bare Si(111)7×7 substrate (i.e., without the 15 s exposure of Gly), in which no H-bonding feature (at 401.4 eV) is observed. GlyGly has been found to adsorb on the 7 × 7 surface in a bidentate configuration involving N−H dissociation of amino group and O−H dissociation of the carboxyl group or N−H dissociation of the amide group.[19] This demonstrates that it is the Gly molecules in the interfacial adlayer that "catch" the incoming GlyGly molecules with H-bonding. Furthermore, annealing the GlyGly adlayers at 120 °C for 10 s also totally removes the feature at 401.4 eV, without affecting the N−Si bonding in the interfacial Gly adlayer, which suggests that the GlyGly molecules attached by H-bonding to the Gly adlayer are released after the anneal. The residual intensity at 400.6 eV after the mild annealing indicates that a small number of the GlyGly molecules remain attached to the Gly adlayer, which suggests that this other bonding mode is stronger than the H-bonding.

An Ala molecule has its C_α atom bonded to a methyl group, replacing one of the two methylene H atoms (in a Gly molecule). Although the methyl group is generally nonreactive, it plays an important role in molecular assembly through the steric effect. Figure 1c shows that, like Gly and GlyGly, the appearance of the N 1s feature at 401.4 eV upon 720-s exposure of Ala and its removal upon postannealing at 120 °C for 10 s on the Gly/Si(111)7×7 surface clearly support the [O−H···N] H-bond mediated catch-and-release mechanism. We note that higher exposures of Ala to the platform have not led to a greater N 1s intensity of the H-bond feature than the N−Si species, in contrast to that found for the Gly exposures to the platform. This suggests that the presence of the methyl group reduces the probability of forming the [O−H···N] H-bond between Ala and Gly molecules likely due to the steric effect.

In order to test the efficacy of this catch-and-release approach to trapping ring-like biomolecules, we repeat the above experiments for two common DNA base group molecules: Ade and Thy. An Ade molecule has a double-ring structure with three pyridinic, one pyrrollic and one amino N atoms, of which only the pyrrollic N atom is not expected to act as a H-bond acceptor to form a H-bond (with the carboxyl group of Gly serving as the H-bond donor). This is because of delocalization of the lone-pair electrons of the pyrrollic N in the aromatic ring. For amino N, the formation of the [O−H···N] H-bond with the Gly/Si(111)7×7 surface has been demonstrated above for chain-like biomolecules. For the pyridinic N, the formation of the [O−H···N] H-bond has also been reported on the basis of large N 1s binding energy shifts to the higher binding energy side.[7,11−14] Figure 1d compares the N 1s spectrum of a 10 s exposure of Ade to Gly/Si(111)7×7 with that of a thick Ade film (1260-s exposure) on pristine Si(111)7×7. The reference N 1s spectrum of the thick Ade film on the 7×7 surface exhibits three components at 399.1, 399.7, and 400.6 eV with an intensity ratio of 3:1:1, which can be assigned to the pyridinic, amino, and pyrrollic N atoms, respectively. The N 1s binding energy of the pyrrollic N is higher than that of the amino N due to the contribution of the lone-pair electrons of the pyrrollic N to the aromatic ring.[20] Both the pyridinic N and the N−Si species for the Gly/Si(111)7×7 interface essentially exhibit the same binding energy. For the N 1s spectrum of the 10 s exposure of Ade to the Gly/Si(111)7×7 surface, an additional weak component at 401.4 eV, attributable to an [O−H···N] H-bonded species, is evident (in addition to the three components found in the reference spectrum). Interestingly, the intensity of this H-bond feature is estimated to be ∼20% of that of the N−Si species in the Gly/Si(111)7×7 surface, which suggests that only one in five interfacial Gly molecules is involved in trapping an Ade molecule, possibly due to the relatively large size of an Ade molecule and the availabilities of additional bonding configurations to Ade adsorption. The nature of the observed bonding features for Ade on Si(111)7×7 will be discussed in more detail elsewhere.[21] Annealing the Ade adlayers on Gly/Si(111)7×7 at 120 °C for 10 s also removes the H-bonded N 1s feature at 401.4 eV, confirming the similar release mechanism found for the chain-like molecules.

In a Thy molecule, two N atoms contribute their lone-pair electrons to the aromatic π-electron system, and they, unlike those in Gly, GlyGly, Ala, and Ade, cannot form an [O−H···N] H-bond with an interfacial Gly molecule. This is verified by the absence of the H-bond feature at 401.4 eV in the N 1s spectrum for a 180-s exposure of Thy on the Gly/Si(111)7×7 surface, shown in Figure 1e. In addition to the N−Si feature at 399.1 eV, a new feature at 401.0 eV is also observed and found to correspond to that for a thick Thy film on bare Si(111)7×7 (400.9 eV, not shown) and on a Au foil (401.2 eV).[22] This N 1s feature is therefore assigned to the N atoms in Thy that are not directly involved in bonding to Gly/Si(111)7×7, which indicates the absence of [O−H···N] H-bonding. It is of interest to note that the intensity of this N 1s feature at 401.0 eV decreases by 75% over the 30-m measurement period of the XPS experiment (not shown). As illustrated in the N 1s spectrum for the sample with a 180-s exposure after storing in ultrahigh vacuum for an extended period (15 h) (Figure 1e), desorption of Thy could proceed even without X-ray irradiation until only a small amount of molecules (that are likely attached directly to the Gly adlayer) remains. The easy desorption of Thy with and without X-ray irradiation suggests the lack of strong bonding among Thy themselves and with the Gly/Si(111)7×7 surface. This N 1s feature at 401.0 eV can be completely removed by mild annealing at a lower temperature of 95 °C for 10 s, confirming that the interactions between the Thy molecules adsorbed on Gly/Si(111)7×7 are weaker than the [O−H···N] H-bonding.

Finally, we examine whether a platform obtained by exposing 300 s of GlyGly to Si(111)7×7 could produce a similar

DOI: 10.1021/jz101315m | J. Phys. Chem. Lett. 2010, 1, 3385–3390

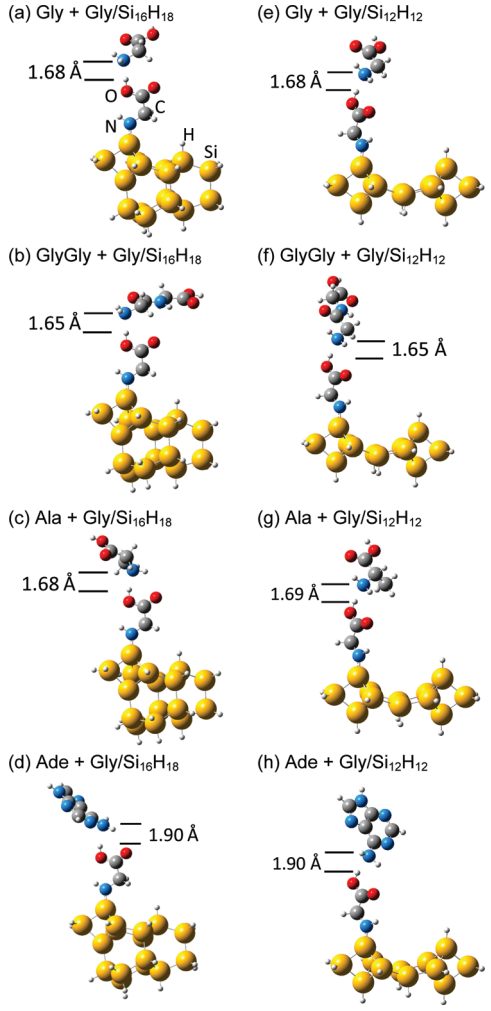


Figure 2. Equilibrium structures of (a,e) Gly, (b,f) GlyGly, (c,g) Ala, and (d,h) Ade H-bonded to Gly adsorbed on $Si_{16}H_{18}$ (left column) and $Si_{12}H_{12}$ (right column) model surfaces, all obtained by DFT/B3LYP Gaussian 03 calculations using a 6-31G++dp basis set.

trapping capability as the Gly/Si(111)7×7 surface. As shown in our recent work, GlyGly molecules in the interfacial (first) adlayer could bond to Si through amino and amide N atoms in a bidentate configuration, leaving the carboxyl end group free for further interaction with incoming molecules.[19] Figure 1f compares the N 1s spectra of GlyGly/Si(111)7×7 before and after a 15-s exposure of Gly. Evidently, no new feature attributable to the [O−H···N] H-bonding has been found near 401.4 eV after the Gly exposure, which suggests that the carboxyl groups of GlyGly in the interfacial adlayer are not suitable for forming H-bonding with the amino group of Gly. This is likely due to steric hindrance and/or unfavorable bonding orientation or to the availability of another more preferable bonding route such as [N−H···O] H-bonding.[19]

In Figure 2, we summarize plausible H-bonding configurations as represented by calculated adsorption structures of Gly, GlyGly, Ala, and Ade H-bonded to Gly adsorbed on two different sites of a model Si(111)7×7 surface. Details of these calculations will be given elsewhere.[19] Briefly, the equilibrium structures were optimized by using the DFT method with the B3LYP hybrid functional[23−25] in the Gaussian 03 software.[26] In accordance with the dimer−adatom-stacking fault model of Takayanagi et al.,[27] we used a $Si_{16}H_{18}$ cluster[28] to represent the adatom−restatom sites at the faulted half of the Si(111)7×7 unit cell, with the adatom−restatom distance fixed at 4.57 Å.[29] We also employed a $Si_{12}H_{12}$ cluster[30] to represent the center adatom−adatom pair across the dimer wall, with the adatom−adatom distance constrained at 6.65 Å. Evidently, for the chain-like molecules, the bond length for the [O−H···N] H-bond is 1.65−1.69 Å, while that for Ade is 1.90 Å. These bond lengths are in good accord with the expected value of a H-bond (generally from 1.6 Å to 2.7 Å), and they appear to be essentially identical for the adstructures at the adatom−restatom site (Figure 2, left) and the dimer wall site (Figure 2, right).

We have employed a Gly adlayer adsorbed to the Si(111)-7×7 surface (through strong N−Si covalent bonding) to provide a functionalized platform for trapping biomolecules with appropriate N atoms to form [O−H···N] H-bonds with the free carboxyl groups of the deprotonated Gly molecules. This functionalized platform is found to be highly effective in capturing both chain-like (Gly, GlyGly, and Ala) and ring-like molecules (Ade). In a molecule such as Thy, where an appropriate H-bond acceptor is not available, no capture is observed. The capture efficiency appears to follow the decreasing order of Gly > Ala > GlyGly > Ade, which is most likely due to steric hindrance during the H-bond formation and the availability of N lone-pair electrons. The captured molecules can be easily released by breaking the H-bond with mild annealing at 120 °C for 10 s. This "catch and release" process is verified by the appearance and disappearance of the [O−H···N] H-bond feature at 401.4 eV. In contrast, a GlyGly-functionalized surface is unable to capture Gly molecules due to the absence of the [O−H···N] H-bonding. The Gly-functionalized Si(111)7×7 surface can therefore be used as a versatile biomolecular trap in biosensing, molecular recognition, and/or other molecular electronics applications.

The experiments were performed in an ultrahigh vacuum multichamber system (Omicron Nanotechnology, Inc.) with a base pressure lower than 5×10^{-11} mbar. The analysis chamber was equipped with an XPS spectrometer consisting of a SPHERA hemispherical electron analyzer with a seven-channeltron detector assembly and a monochromatized Al Kα source (1486.7 eV photon energy), and with a variable-temperature scanning probe microscope for atomic-resolution STM imaging. Single-side polished Si(111) chips (11 × 2 mm^2, 0.3 mm thick) with a resistivity of 5 mΩ cm (Virginia Semiconductors) were used as the substrates. Large terraces of 7×7 surface reconstruction were observed with STM after outgassing the Si substrate at 400 °C overnight followed by flash-annealing at 1200 °C several times by direct-current heating. A separate preparation chamber was used for deposition of the biomolecules. Powders of Gly (98.5% purity, Aldrich), GlyGly, Ala, Ade, and Thy (all 99% purity, Aldrich) were loaded into effusion cells (designed for low-temperature evaporation of organic materials, MBE-Komponenten) and outgassed thoroughly overnight. The evaporation temperatures used for the deposition of Gly, GlyGly, Ala, Ade, and Thy on the 7×7 substrate were 140, 175, 130, 133, and 108 °C, respectively. The molecular identity of these

DOI: 10.1021/jz101315m | J. Phys. Chem. Lett. 2010, 1, 3385–3390

biomolecules during deposition was confirmed by their cracking patterns obtained in situ by using a quadrupole mass spectrometer. By monitoring the saturation of the N 1s peak intensity for the N−Si feature, we first deposited a monolayer of Gly on a clean Si(111)7×7 substrate at room temperature (with a 15 s exposure).[15] We define a monolayer of Gly as the coverage that corresponds to saturation of the N 1s peak intensity for the N−Si feature. The resulting Gly/Si(111)7×7 surface was then used for subsequent deposition of Gly, GlyGly, Ala, Ade, or Thy, and the follow-up desorption experiments. Mild sample annealing was achieved by passing a direct current (∼1 A) through the sample for 10 s, with the approximate sample temperature monitored by using a nearby thermocouple. XPS measurement was made after each deposition and desorption experiments. The N 1s peak of the N−Si species for Gly/Si(111)7×7 was found to locate at 399.1 eV binding energy with the Si $2p_{3/2}$ peak at 99.3 eV, in excellent accord with the literature values.[15] The spectra were fitted with Gaussian−Lorentzian lineshapes and a linear background by using the CASA-XPS software.

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ACKNOWLEDGMENT This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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