

## Dianhydride-Amine Hydrogen Bonded Perylene Tetracarboxylic Dianhydride and Tetraaminobenzene Rows

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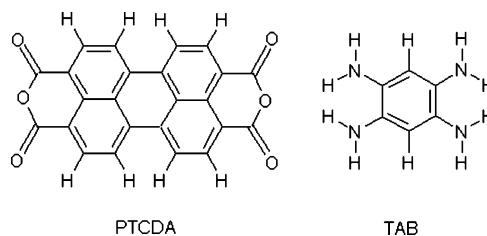
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We have investigated the coadsorption of perylene tetracarboxylic dianhydride (PTCDA) and tetraaminobenzene (TAB) on the Ag/Si(111)- $\sqrt{3} \times \sqrt{3}$  R30° surface using scanning tunneling microscopy. At room temperature, PTCDA islands with square and herringbone ordering are formed which, on exposure to TAB, are converted into an intermixed phase in which PTCDA and TAB form alternating rows. From our images, we determine the relative placement of TAB and PTCDA molecules and conclude that the row structure is stabilized by hydrogen bonding between dianhydride and diamine groups. We confirm that this hydrogen bonding junction is stable using ab initio calculations and show that the proposed geometry is consistent with calculated intermolecular dimensions.

Under suitable conditions, the sequential deposition of two different molecular species onto a surface can lead to the formation of intermixed phases with unusual and highly interesting order.<sup>1–8</sup> Although in many cases the codeposition of two adsorbed species leads to the formation of segregated islands consisting of a single molecular component, it has now been demonstrated that, through an appropriate choice of molecules, intermixed, or alloy, phases are also possible. One of the principal factors determining whether intermixing or segregation occurs is the relative strength of the relevant intermolecular interactions. Intermixed phases would be expected if the heteromolecular interaction between dissimilar molecules is stronger than the homomolecular interaction between pairs of identical molecules.

One way of controlling the relative strengths of these interactions is to incorporate functional groups within the molecules which promote noncovalent interactions, such as hydrogen bonding,<sup>9–14</sup> metal coordination,<sup>15,16</sup> or dipolar coupling.<sup>17</sup> Intermixed bimolecular arrays stabilized by noncovalent interactions with geometries corresponding to open networks, regular rows, and more complex arrangements have been reported by several groups. The resulting structures can have a large lattice constant and may be used as molecular templates controlling the adsorption of further adsorbed species.<sup>1</sup> These observations indicate that intermixed molecular phases have considerable potential for the formation of complex functional surfaces.

In this paper, we describe the formation of a new intermixed molecular phase which is formed when perylene tetracarboxylic acid (PTCDA) is coadsorbed with tetraaminobenzene (TAB) on the Ag/Si(111)- $\sqrt{3} \times \sqrt{3}$  R30° surface. The molecular structures of PTCDA and TAB are shown in Figure 1. The



**Figure 1.** Molecular structure of PTCDA and TAB.

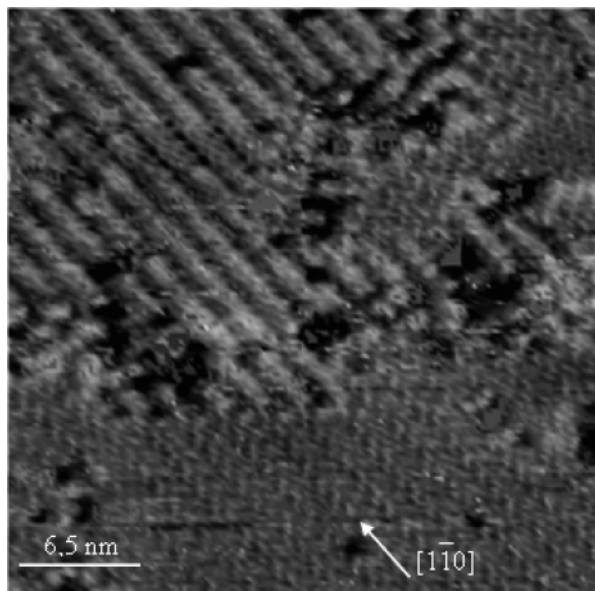
structure is formed under ultrahigh vacuum (UHV) conditions and is stabilized by hydrogen bonding between the dianhydride groups of PTCDA and the amine groups of TAB. A stable hydrogen bond between molecules incorporating these end-groups has not previously been reported in studies of solution phase or solid state chemistry, and we use ab initio numerical calculations to confirm the stability of this junction.

The Ag/Si(111)- $\sqrt{3} \times \sqrt{3}$  R30° surface is prepared by transferring a 3 mm  $\times$  7 mm piece of a p-type Si(111) wafer into a UHV system with base pressure of  $1 \times 10^{-10}$  torr. The Si is outgassed by annealing overnight prior to a flash anneal to 1200 °C for 60 s to form the Si(111)- $7 \times 7$  reconstructed surface. Ag is then sublimed onto the Si surface with the sample held at 500 °C. As a result the  $7 \times 7$  reconstruction is converted to a Ag/Si(111)- $\sqrt{3} \times \sqrt{3}$  R30° termination.<sup>18–20</sup> The choice of substrate is motivated by our previous studies which have shown that organic molecules may diffuse on this surface readily at room temperature and form ordered arrangements which are controlled by intermolecular, rather than molecule–substrate interactions. PTCDA (Aldrich) and TAB (This was prepared via conversion of TAB·4HCl (Aldrich) to the free base through treatment with aqueous NaOH solution and extraction into a CH<sub>2</sub>Cl<sub>2</sub> phase. Removal of the CH<sub>2</sub>Cl<sub>2</sub> solvent gives TAB without the need for further purification.) were loaded into Knudsen cells and deposited by sublimation. For TAB, the vapor pressure even at room temperature is sufficient to transfer

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**Figure 2.** STM image showing the herringbone reconstruction (lower part) of PTCDA together with the intermixed row phase of PTCDA and TAB (upper left) on the Ag/Si(111)- $\sqrt{3}\times\sqrt{3}$  R30° surface.

molecules to the surface without additional heating of the source material. Images of the resulting surface were acquired using a scanning tunneling microscope (STM) operating in constant current mode. The STM was housed in the UHV system and operated at room temperature. For the STM tips, we used electrochemically etched W wire. The tips were cleaned in the UHV using electron beam heating prior to use.

The deposition of sub-monolayers of PTCDA on the Ag/Si(111)- $\sqrt{3}\times\sqrt{3}$  R30° surface leads to the formation of three phases with square, herringbone, and hexagonal packing as described in our previous work.<sup>21</sup> Following a short (typically a few minutes) exposure of the surface to TAB, the PTCDA islands are found to coexist with a new phase in which extended parallel rows with alternating apparent brightness are formed. As we show below, this corresponds to an intermixed PTCDA/TAB phase. An image showing the herringbone reconstruction together with the new intermixed row phase is shown in Figure 2. By comparing these images with our previous work on the pure PTCDA herringbone phase,<sup>21</sup> we may readily identify the row direction and spacing within the new phase. The rows are parallel to the  $[1\bar{1}0]$  direction (see Figure 2) and have a spacing corresponding to  $3a$  where  $a = 6.65$  Å is the lattice constant of the Ag/Si(111)- $\sqrt{3}\times\sqrt{3}$  R30° surface.

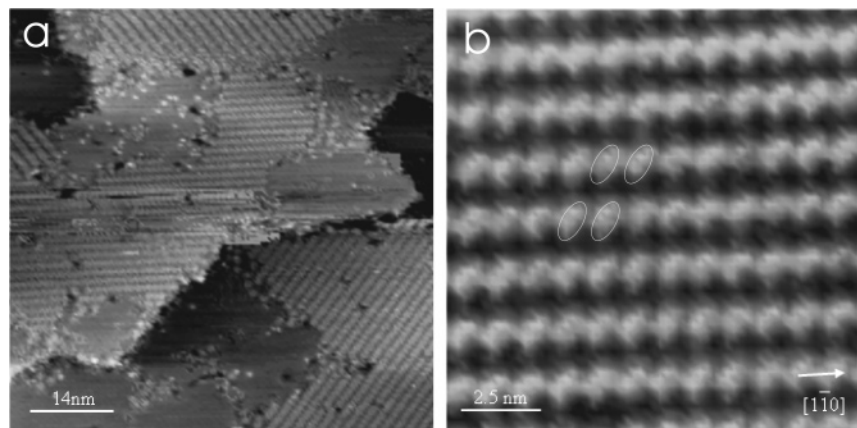
Exposure of the surface to TAB for extended periods (overnight) results in a complete conversion of the pure PTCDA islands into the intermixed row phase. Figure 3a shows an image of the surface under these conditions. As shown in Figure 3a, we observe islands with rows running along the three  $\{1\bar{1}0\}$  directions as expected for a surface with hexagonal symmetry. Higher magnification images (Figure 3b) reveal some intramolecular contrast in the bright rows. Specifically, we find rows of tilted quasirectangular features which we associate with PTCDA molecules. The spacing of these features parallel to the rows is  $\sqrt{3}a$ , 11.5 Å.

On the basis of the measured spacings, we propose a structural model for adsorption as shown in Figure 4. The placement of the PTCDA molecules is determined directly from our images and corresponds to a row of tilted molecules running in the  $[1\bar{1}0]$  direction. Similarly, the spacing of the PTCDA rows,  $3a$ , is determined directly from our images. The spacing of the bright rows is too large for this arrangement to be a close packed arrangement of PTCDA, and we attribute the low contrast rows to TAB molecules which bridge the gap between the anhydride groups of PTCDA molecules. This structure is stabilized through the formation of hydrogen bonds. The low contrast appearance of TAB is due to the larger highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO–LUMO) gap for this smaller molecule which gives rise to an apparent transparency in the images. According to our model, the separation of the center of the TAB and PTCDA molecules is  $\sqrt{3}a = 11.5$  Å. The proposed structure represents a  $(3\times 6)$  reconstruction with respect to the Si(111) surface.

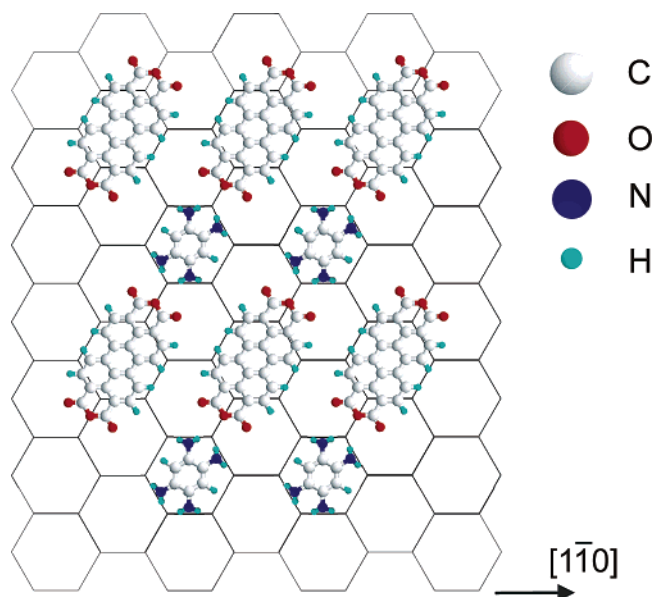
In our proposed model, the oxygen atoms of the anhydride groups are in close proximity to the hydrogen atoms of the amine groups of TAB, and we argue that the resulting hydrogen bonding stabilizes the row structure. This hydrogen bonding junction has not previously been reported, possibly because in the solution phase amines are known to react readily with anhydride groups.<sup>22</sup> We have therefore used ab initio density functional calculations to verify that the proposed anhydride–amine interaction leads to an energetically favorable intermolecular bond.

Calculations were performed using the SIESTA package.<sup>23,24</sup> The code implements density functional theory (DFT) within the linear combination of atomic orbitals (LCAO) approximation. The Perdew–Burke–Erzerhof generalized gradient approximation was implemented.<sup>25</sup>

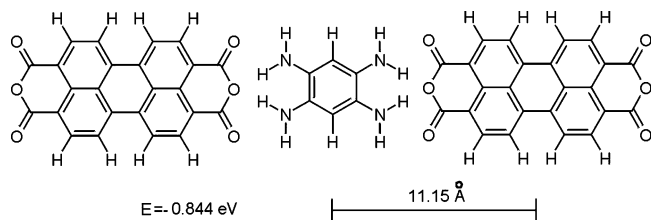
Core electrons were represented by core-corrected pseudopotentials constructed according to the method described by Troullier and Martins,<sup>26</sup> while double- $\zeta$  basis sets with polariza-



**Figure 3.** (a) Large area STM image showing domains of the intermixed row phase of PTCDA and TAB following overnight deposition of TAB. (b) Higher magnification image showing intramolecular contrast within the rows.



**Figure 4.** Schematic diagram of the proposed PTCDA–TAB network on the Ag/Si(111)- $\sqrt{3}\times\sqrt{3}$  R30° surface.



**Figure 5.** Diagram showing the calculated separation of PTCDA–TAB–PTCDA molecules.

tion functions were used to describe the valence electrons. The radius within which the atomic orbitals are strictly localized is defined in the SIESTA code by the energy shift, which in our calculations was set to 0.1 mRy.

Geometry optimization was performed using the conjugate gradient method. The geometry was considered to have converged when the forces on the atoms differed by less than 0.1 eV Å<sup>-1</sup>. A default convergence tolerance of 10<sup>-4</sup> eV was employed for the self-consistent field cycle at each stage of the optimization. The basis set superposition error is known to introduce errors in calculations employing localized basis sets. Counterpoise corrections as described by Boys and Bernardi<sup>27</sup> have therefore been used in this work to reduce the numerical error in the calculation of the interaction energies. We note that calculations of hydrogen bonding using a similar approach have recently been reported.<sup>28,29</sup>

Calculations were performed using a single TAB molecule interacting with two PTCDA molecules in an arrangement which mimics the proposed hydrogen bonding system (Figure 5). A stabilization energy due to intermolecular interactions of 0.84 eV was obtained, which equates to an energy of 0.42 eV for each individual PTCDA–TAB junction. The calculated spacing between the centers of PTCDA and TAB was 11.15 Å, in close agreement with the value determined from our STM images, 11.5 Å. Overall, these numerical results confirm that the diamine–anhydride interaction is stabilized by hydrogen bonding in agreement with our proposed model for the PTCDA–TAB mixed phase. We have also considered an alternative arrangement in which TAB is rotated by 90° as compared with Figure 5. This arrangement is also stabilized by H bonding

(stabilization energy 1.07 eV) but predicts a PTCDA–TAB spacing of 10.26 Å which is not consistent with the measured spacing.

The complete conversion of all PTCDA domains to the mixed row phase is of particular relevance to the formation of molecular templates.<sup>1</sup> We have previously shown that perylene tetracarboxylic diimide (PTCIDI) interacts with melamine to form a honeycomb network. However, it is not generally possible to convert all PTCIDI domains into the intermixed honeycomb. The reason for this is that the single component PTCIDI islands are stabilized by a double hydrogen bond between adjacent diimide groups.<sup>14,21</sup> Although the melamine–PTCIDI interaction is stronger, since it arises from a triple rather than a double hydrogen bond, the competition between the PTCIDI–melamine and PTCIDI–PTCIDI intermolecular interactions limits the incorporation of PTCIDI in the honeycomb network which in turn limits the maximum surface coverage of the PTCIDI–melamine network. The complete incorporation of PTCDA in the row phases may therefore be understood as a consequence of the much weaker PTCDA–PTCDA interaction and the absence of an effective competition between homomolecular and heteromolecular interactions. Accordingly, this result implies that the anhydride–diamine hydrogen bonding junction might be well-suited to the formation of honeycomb networks with high surface coverage if incorporated in molecules with suitable geometry.

In conclusion, we have shown that hydrogen bonding between diamine and anhydride groups can stabilize intermixed surface phases of organic molecules. This junction has not previously been observed in other branches of chemistry and the stability and geometry of the proposed structure have been verified using density functional calculations. The complete conversion of all surface adsorbed PTCDA into the intermixed row phase makes this junction a promising candidate for the formation of two-dimensional molecular templates.

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