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Molecular dynamics simulation of a DOPA/ST monolayer on the Au(111) surface†

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In order to study the influence of molecular structure on the formation of a monolayer, two molecules have been considered, namely N-stearoyldopamine (DOPA) and 4-stearyl-catechol (ST). The difference between these two molecules is the amide group in DOPA. By investigating these monolayers at different surface areas per molecule, the molecular configurations of a DOPA/ST monolayer on the Au(111) surface were obtained. We conclude that for both kinds of molecules, the π-interaction between the catechol group and the Au(111) surface is important. Compared to experimental results, the catechol groups are found either parallel or perpendicular to the Au(111) surface in MD simulation. The difference between DOPA and ST systems is that when there are fewer molecules on the Au(111) surface, in the DOPA system, the amount of catechol groups perpendicular with their hydroxyls orienting towards the surface is less than that of the ST system. Further analysis of catechol groups and amide groups indicates that various kinds of hydrogen bonds formed in the DOPA system have a profound influence on the structure and regularity of the monolayer.

Introduction

The adhesive capability of blue mussel’s foot proteins has aroused interest in studying the adsorption of catechol containing molecules (DOPA and ST).1–3 A number of studies have revealed that an unusual frequent appearance of 3,4-dihydroxy-L-phenylalanine in the protein is the main reason for the unmatched adhesive ability.4–6 The adhesion is mainly due to the catechol group and the amide group. In other studies, 3,4-dihydroxy-L-phenylalanine has shown enhanced adhesion to a wide range of substrates such as TiO2,7,8 SiO2,7 and gold.9 For different types of substrates different adhesion mechanisms have been proposed. For example, for TiO2 in a humid environment the catechol part is able to form a bidentate binuclear complex with the surface.7 While for the adhesion on gold, the main mechanism proposed is due to the π-electron system.9,10 Moreover, hydrogen-bonding between 3,4-dihydroxy-L-phenylalanine molecules is also of possible importance for the formation of a strongly adhering layer.9

The Langmuir–Blodgett monolayer has received considerable attention as a functional surface for various applications.11–13 In this simulation, N-stearoyldopamine (abbreviated as DOPA) was used to create a monolayer that is expected to be able to act as an adhesion promoter between a substrate and a bulk polymer. This system has been studied experimentally by transferring a Langmuir–Blodgett film14 onto a gold substrate. A 4-stearyl-catechol (abbreviated as ST), essentially the same molecule but without the amide group, was also included in that study, because, while the catechol groups are the same, the amide group in DOPA is expected to play an important role in the formation of the monolayer and the configuration of molecules on the surface.

In this paper we report the molecular configurations of monolayers of N-stearoyldopamine (DOPA) and 4-stearyl-catechol (ST) on the Au(111) surface by means of molecular dynamics. A more detailed molecular view on the structure of the DOPA/ST monolayer is obtained with molecular dynamics than by means of experiments.14 By analyzing the orientations of head and tail groups of DOPA and ST, a molecular configuration which has not been reported in the experiments is revealed. The different catechol group configurations between DOPA and ST monolayers are also observed. These differences are further discussed with particular hydrogen bonds in the DOPA system. These results may be helpful for the further synthesis of an organic monolayer on metal surfaces.

Models and simulation details

A number of simulation studies have been performed to investigate the adsorption of organic molecules on a gold surface.15–20
In the present study, we employed the GolP\textsuperscript{21,22} force field that is designed to accurately account for both the electrostatic and the van der Waals interactions between organic molecules and surface (bulk) gold atoms. A series of chemisorptions (including the $\pi$ bonding) between an atom in the organic molecule and the gold surface are also considered in GolP with specific L-J interaction parameters.\textsuperscript{22} To model the image charges in the gold induced by the charge distribution of the organic matter, this force field employs point charges rotating around gold atoms. Also virtual sites located at the interstitial positions among the surface gold atoms are introduced to provide extra centers for Lennard-Jones (L-J) interactions. The need for these virtual sites can be rationalized by the presence of high electron densities at these locations and these virtual sites are important to obtain the correct adsorption behaviour. A collection of studies has shown that the GolP force field is effective\textsuperscript{23,24} in describing the configuration and energy of molecules adsorbed on a gold surface. For the interactions between and within the organic molecules, the OPLS\textsuperscript{25–27} force field was employed, because the GolP force field is designed to accurately account for both the electrostatic and van der Waals interactions between organic molecules adsorbed on a gold surface.

The Au(111) surface containing surface virtual sites was built as a slab of 115.35 $\times$ 99.90 $\times$ 11.77 Å. A periodic boundary condition was prescribed to approximate an infinitely extended surface. All the gold atoms were fixed during the simulation. For the Au(111) surface of the present size, only marginally small differences exist between a reconstructed structure and an ideal surface.\textsuperscript{28,29} Thus, surface reconstruction of Au(111) was not accounted. The initial orientation of the organic molecules on top of the surface was taken to be perpendicular to the surface (see ESI,\textsuperscript{†} Fig. S1 for details). The height of the simulation box was taken to be 10 Å to ensure that there was sufficient vacuum space above the adsorbed layer. The surface area per molecule was controlled by changing the total number of molecules. For DOPA and ST, values of the surface area per molecule applied were approximately 25 Å\textsuperscript{2} per molecule (DOPA25 and ST25), 30 Å\textsuperscript{2} per molecule (DOPA30 and ST30), 34 Å\textsuperscript{2} per molecule (DOPA34 and ST34), and 40 Å\textsuperscript{2} per molecule (DOPA40 and ST40) respectively. These surface areas are characteristic values obtained from adsorption isotherms used for characterizing Langmuir–Blodgett films.\textsuperscript{14}

Molecular dynamics simulations were carried out using the Nosé–Hoover thermostat.\textsuperscript{30–32} The Verlet integrator\textsuperscript{33,34} was employed with a time step of 1 fs and a temperature of 300 K. The electrostatic contributions were calculated with the Particle Mesh Ewald approach (PME)\textsuperscript{35} using a 1.2 Å grid. For the L-J interactions a cut-off at 11 Å was used with a smooth switching-off starting at 10 Å. For each system energy minimization has been performed first. Then an equilibration NVT run was performed for 1 ns. Finally a NVT production run of 100 ps was carried out to generate the data used for the analysis. All the molecular dynamics have been performed with Gromacs 4.5.3.\textsuperscript{36–40} Visual Molecular Dynamics (VMD) was used for the visualization of the molecular configurations.\textsuperscript{41}

In order to characterize the configuration of the organic molecules adsorbed on the gold, several quantities have been selected to describe the geometry of the molecules.\textsuperscript{42–44} Fig. 1 shows the properties that have been monitored. The orientation of the aromatic rings is described by the angle $\theta$. To characterize the orientation and degree of stretching of the aliphatic tails, the vector $R_e$ that connects the carbon atoms labelled from 1 to 18 is employed. The persistence length $l_p$\textsuperscript{45,46} can be computed from
\begin{equation}
\langle R_e^2 \rangle = 2 l_p L_0 \left( 1 - \frac{l_p}{L_0} \right) \left[ 1 - \exp \left( -L_0/l_p \right) \right] \tag{1}
\end{equation}
where $\langle R_e^2 \rangle$ represents the average square of the end-to-end distance between the $C_1$ and $C_{18}$ atoms of the alkyl tails in the system. $L_0$ is the contour length from atom $C_1$ to $C_{18}$. By inverting this relation, $l_p$ is computed from a measured $(R_e^2)$ value and a known $L_0$ value. This persistence length is used to describe the apparent rigidity of alkyl tails for different surface areas per molecule, which probably increases due to packing effects with neighbor molecules. To distinguish stretched tails from less stretched ones we use the somewhat arbitrary criterion $r = |R_e|/L_0 > 0.8$ to define a stretched state. Such a criterion is needed because the angle $\phi_e$ describing the orientation of the tails with respect to the surface is most unambiguously defined for stretched chains.

### Results and discussion

#### A. Single molecule adsorption

The situation of a single molecule adsorbed onto the gold surface has been considered (Fig. 2). Both DOPA and ST take a parallel orientation with respect to the surface. The linear structure of the alkyl tails is consistent with previous studies.\textsuperscript{47} Moreover, a relatively parallel orientation of catechol to the gold surface attributed to $\pi$ binding is also consistent with previous results.\textsuperscript{9,21} The binding energies between organic molecules and the gold surface are computed following the procedure of the GolP force field, in which Lennard-Jones

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\[ \text{Fig. 1 Quantities for characterizing molecular configuration on the gold surface.} \]

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\[ \text{Paper PCCP} \]

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\[ \text{Phys. Chem. Chem. Phys.} \]
contribution and electrostatic contribution are considered separately.22 The computed binding energy for DOPA is $-237.5$ kJ mol$^{-1}$ and $-224.7$ kJ mol$^{-1}$ for ST. Because of the lack of experimental results, it is hard to compare these energies with experimental observations. Upon comparison with the results of other organic molecules,21,47,48 we note that these binding energies are of the expected magnitude.

B. An overview of the monolayer structure

The density distributions for DOPA and ST simulation results as a function of distance from the gold surface are shown in Fig. 3. These density profiles are of the same magnitude compared to the experimental results (33 ± 8 Å for DOPA and 30 ± 8 Å for ST).14 All the density curves show a high peak at a distance around 4 Å from the gold surface, while at a distance of 3 Å the corresponding density is almost zero. This indicates that a high number of organic molecules are adsorbed with non-bonding interactions to the surface. Second, from 40 Å$^2$ per molecule to 25 Å$^2$ per molecule, the corresponding densities in the range from a distance of 15 Å to 30 Å (Fig. 3, x axis) gradually increase. These increases might be due to the change of orientation of the alkyl tails and the change of the average size corresponds approximately to the contour length of the molecules. It should be noted that even for DOPA25 and ST25, these values of density are not consistent with a nicely oriented monolayer with the catechols at the surface and the alkyl tails oriented perpendicularly to the surface. In such a monolayer, one would expect a density of about 750 kg m$^{-3}$ in the alkyl region (using 25 Å$^2$ per molecule). As a result, we expect that for all the conditions, the monolayers are not arranged in nicely ordered orientations (also see Fig. S2, ESI†). Analyses of alkyl tails and the head groups (including the amide group and the catechol group) for both DOPA and ST are displayed to reveal the detailed configuration in the following parts.

C. Orientations of alkyl tails

Statistics of contour lengths for ST and DOPA are displayed in Fig. 4. For both of the molecules, it is obvious that when the surface area per molecule is relatively small (such as 30 Å$^2$ per molecule and 25 Å$^2$ per molecule), most of the contour lengths of alkyl tails are in the range of 20–22 Å. When the surface area per molecule is relatively large (40 Å$^2$ per molecule and 34 Å$^2$ per molecule), most of the contour lengths of tails are within the range of 18–20 Å and 16–18 Å. The results indicate that the monolayer on the gold surface is more likely to be made up of stretched molecules when the surface area per molecule is small.
This can be attributed to the molecule packing with its neighboring molecules. The only exception is that we observe more molecules in the range of 20–22 Å for ST30 than for ST25.

The results of a quantitative analysis of the alkyl tails of DOPA and ST molecules are listed in Table 1. The data for a single non-adsorbed DOPA/ST molecule are also displayed for comparison. Compared to single DOPA/ST results, the relatively small block-averaging values for DOPA and ST on the gold surface indicate that the calculated \( R_i \) is representative. The average end-to-end distances \( R_i \) show the expected increase with decreasing surface area per molecule for both DOPA and ST. This increase in stretching tails is clearly characterized by the increase in the persistence length \( l_p \). There is a considerable increase in \( l_p \) (and correspondingly the percentage of \( r > 0.8 \)) from DOPA40 to DOPA25. However, for DOPA40 (ST40) and DOPA34 (ST34), the increase of \( l_p \) is not obvious. It may be the reason that the contribution of van der Waals interactions between molecules are not large enough during the change of surface area per molecule from 40 Å² per molecule to 34 Å² per molecule. Until the surface area per molecule decreased to 30 Å² per molecule, the van der Waals interaction between two molecules becomes important. Consequently, the alkyl tails are intended to be stretched and relatively perpendicular to the Au(111) surface (see the observation of \( R_i \), \( l_p \), and \( r \) for DOPA30/ST30 and DOPA25/ST25 in Table 1, Fig. 4 and 5, and Fig. S3, ESI†).

The angle \( z_i \) indicating the tilt of the alkyl tails with respect to the gold surface is also analyzed (Table 1). This analysis only considers the stretched molecules obeying the criterion of \( r > 0.8 \). As expected, when the surface area per molecule is smaller, more molecules are oriented perpendicular to the surface (also shown in Fig. S3, ESI†). The distribution of the orientations is similar for both DOPA and ST.

### D. Structure of catechol parts

Catechols are important functional groups for the DOPA and ST adsorbed onto an inorganic surface.\(^{10,12}\) Therefore, the configuration of the catechol groups has been studied. According to the statistics of distances between the aromatic rings and the gold surface (Fig. S4, ESI†), most of the catechol groups are located within a distance of 10 Å from the gold surface, which means most of the catechol groups interact with the gold surface. This is the reason why we will mainly focus on the catechol groups in this range in the following analysis.

As indicated in Fig. 1, a catechol group is considered to be in a layer when the geometric center of its aromatic ring is positioned in that layer. When analyzing catechol groups on the gold surface, the catechol groups are discriminated in different layers by the interactions between a catechol group and the gold surface. Since no center-of-rings are present at distances closer than 3 Å to the surface, the first layer is taken to be 3–4 Å (Table 2). In this first layer most of the aromatic rings are directly interacting with the gold surface. The second layer is 4–10 Å, in which molecules have van der Waals and Coulomb interactions with the surface but are also influenced to a large extent by the other molecules. In the remaining space (>10 Å), in which fewer catechols are found, the rings do not interact directly with the surface. The absolute number and percentage of catechols in each layer are listed in Table 2. It can be seen that most of the catechol groups are in the 3–10 Å region. ST30 shows the smallest percentage of catechol groups in the region of the >10 Å layer while ST25 shows a considerable increase of catechol groups in the same layer. It is also important to note that comparing ST25 to ST30, the increased number of catechol groups in the >10 Å layer is approximately equal to the increased number of ST molecules in the system (from 391 to 460). This result indicates that for ST molecules, an optimum surface area per molecule adsorbed onto the gold surface is probably around 30 Å². When the surface area gets smaller, some molecules have to stay in the upper layer (>10 Å) of the surface. For DOPA25 and DOPA30, the percentage of the catechol group in this region (>10 Å) remains constant. Moreover, a relatively uniform order is obtained when the surface area per molecule gets smaller (from 30 Å² per molecule to 25 Å² per molecule). This may be attributed to the existence of amide groups.

The dihedral angles between the aromatic rings and the gold substrate in each layer are analyzed in Fig. 6. The preferred
The orientation for catechol groups in the 3–4 Å layer is nearly parallel to the surface. The rings with centers in the 4–10 Å and in the >10 Å layers show no preference for a parallel orientation. The interaction between the gold atoms and the aromatic rings of the catechol groups in the 3–4 Å layer is attributed to the strong π bonding.50–52 There are somewhat more parallel rings for ST than for DOPA. The graph of ST25 shows a considerable decrease of the percentage of parallel catechol groups compared to ST30. This is consistent with the previous analysis (Table 2). For DOPA molecules, when the surface area per molecule gets smaller (30 Å² per molecule and 25 Å² per molecule), a considerable increase of perpendicular catechol groups in the 4–10 Å layer is observed. Snapshots of the catechol groups in the 3–4 Å and the 4–10 Å layers for DOPA25 are given in Fig. 7. Combining the distribution graph in Fig. 6, the results show that with the gradual saturation of catechols in the 3–4 Å layer, a number of catechol groups locate inside the 4–10 Å layer in a relatively vertical position to the gold surface. Thus, we observed the increase of vertical catechol groups from 40 Å² per molecule to 25 Å² per molecule for DOPA and from 40 Å² per molecule to 30 Å² per molecule for ST (Fig. 6). For ST25, the 3–4 Å layer and the 4–10 Å layer get saturated and catechol groups in the >10 Å layer take random orientation. On the other hand, the gold surface is not saturated yet from 40 Å² per molecule to 34 Å² per molecule (DOPA and ST). Thus, the percentage of catechol groups in the 3–4 Å layer remains constant and the increase of the absolute number is observed (Table 2 and Fig. 6).

E. Difference between ST and DOPA configurations

The configurations of catechol groups in the 4–10 Å layer for DOPA and ST are clearly illustrated in Fig. 8. Fig. 8a shows that in the case of ST34, the hydroxyl groups are mainly at the gold surface. However, for DOPA34 (Fig. 8b), fewer hydroxyl groups are at the gold surface. With the decrease of surface area per molecule, some of the catechol groups in DOPA30 orient with their hydroxyls pointing towards the gold surface. Thus, for ST30 (Fig. 8c) and DOPA30 (Fig. 8d), the two configurations become similar. For ST25 (Fig. 8e) and DOPA25 (Fig. 8f), almost the same configurations of hydroxyl groups in the 4–10 Å layer are obtained.

<table>
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<tr>
<th>Name</th>
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<th>ST34</th>
<th>ST30</th>
<th>ST25</th>
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<th>DOPA34</th>
<th>DOPA30</th>
<th>DOPA25</th>
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<td>98</td>
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<tr>
<td>(15.6%)</td>
<td>(17.8%)</td>
<td>(9.7%)</td>
<td>(24.3%)</td>
<td>(23.9%)</td>
<td>(27.1%)</td>
<td>(22.8%)</td>
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<td>126</td>
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<td>(46.6%)</td>
<td>(42.8%)</td>
<td>(40.2%)</td>
<td>(30.2%)</td>
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<td>(32.1%)</td>
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<td>460</td>
<td>287</td>
<td>336</td>
<td>391</td>
<td>460</td>
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<td>79.8</td>
<td>73.3</td>
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<td>85.6</td>
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<td>(66.6%)</td>
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<td>(50.6%)</td>
<td>(48.9%)</td>
<td>(48.9%)</td>
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<td>-OH from catechols in 4–10 Å</td>
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<td>231.9</td>
<td>60.8</td>
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* Total number of hydroxyls is two times the number of molecules. * d is calculated as the distance between the O atom in hydroxyl and the gold surface.

Fig. 6 Distributions of dihedral angles (°) of catechol groups for both DOPA and ST. The three different layers are discriminated via different kinds of interactions between molecules and the gold surface, namely 3–4 Å, 4–10 Å and >10 Å.

Fig. 7 Snapshot for DOPA25 catechol groups configurations in the 3–4 Å layer (left) and 4–10 Å layer (right).
According to previous discussion, the difference between ST and DOPA monolayers can be summarized. For the ST system, when the surface area per molecule gets smaller (from 40 Å² per molecule to 30 Å² per molecule), the gold surface is gradually occupied by catechol groups and gets saturated at 30 Å² per molecule. After that, when the surface area per molecule decreases to 25 Å² per molecule, the additional ST molecules are mainly positioned relatively far from the gold surface (>10 Å layer, Table 2). For the DOPA system, when the surface area per molecule gets smaller (from 40 Å² per molecule to 25 Å² per molecule), DOPA molecules are gradually tightly packed with their catechol groups positioned vertically on top of the gold surface. The amide groups are also gradually aggregated in the upper layer of the gold surface (Fig. S5, ESI†). Therefore, a more ordered monolayer is expected for DOPA when the surface area per molecule is relatively small.

F. Analysis of the hydrogen bond network

Hydrogen bonds in the system can greatly affect the molecular structure and properties, such as stability of molecules and viscosity of polymers. In addition, the intermolecular hydrogen bond can also affect the excited state reactions and spectroscopy. Thus, analyzing hydrogen bonds may be effective for understanding the adsorption mechanism.

In the present system, the different configuration between DOPA and ST monolayers is probably because of the presence of the amide groups located near the aromatic ring in DOPA introducing extra intermolecular hydrogen bonds. In order to analyze the hydrogen bonds formed from different groups, three types of hydrogen bonds have been considered. The number of each kind of hydrogen bonds is listed in Table 3 for both ST and DOPA molecules (although the overall number of type 3 is somewhat larger for ST) as a consequence of the tight packing.

For ST25, with the increased number of total molecules compared to ST30, only a slight increase of hydrogen bonds has been observed. This result indicates that in ST25, a number of catechol groups do not form hydrogen bonds. This also indicates that the interaction between ST molecules is relatively weak. Combining the analysis of catechol groups and the configuration of alkyl tails, the conclusion that the most favorable surface area per molecule for ST adsorbed onto the gold surface is around 30 Å² has been proved. Some of the ST molecules are positioned with the catechol groups far from the gold surface (>10 Å, Table 2) at 25 Å² per molecule. Due to the relatively weak interaction between ST molecules, these molecules may be easily removed from the surface. This also explains the “isolated islands” AFM image for ST in the experiments.

For DOPA, type 2 (amide–hydroxyl) hydrogen bonds are dominating when there is relatively sufficient space for each molecule (DOPA40 and DOPA34). This indicates that type 2 hydrogen bonds are energetically favored. For DOPA40 and DOPA34, the parallel rings in the 3–4 Å layer have amide groups that lie in plane with catechol groups (Fig. S5, ESI†). These amide groups mainly formed the type 2 hydrogen bonds. When the gold surface is not fully occupied (DOPA40 and DOPA34), amide groups and catechol groups form hydrogen bonds proportionally. However, when the surface area per molecule shrinks to 25 Å² per molecule, the number of type 2 hydrogen bonds decreases. This is because amide groups in DOPA25 are positioned relatively far from the gold surface. The DOPA30 is

![Fig. 8 Configurations of the catechol groups located in the 4–10 Å layer. (a) ST34; (b) DOPA34; (c) ST30; (d) DOPA30; (e) ST25; (f) DOPA25. The statistics of surface hydroxyl are displayed in Table 2. For DOPA40 and ST40, the configuration is similar to that of DOPA34 and ST34.](image-url)

### Table 3 Statistics of hydrogen bonds

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<th>Type</th>
<th>ST40</th>
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<th>ST30</th>
<th>ST25</th>
<th>DOPA40</th>
<th>DOPA34</th>
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<td>3</td>
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<td>201.8</td>
<td>344.1</td>
<td>428.4</td>
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<td>0.285</td>
<td>0.288</td>
<td>0.286</td>
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<td># of molecules</td>
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</tbody>
</table>

Hydrogen bonds follow the definition of Gromacs. Type 1: amide–amide hydrogen bonds; type 2: amide–hydroxyl hydrogen bonds; type 3: hydroxyl–hydroxyl hydrogen bond (see Fig. S6, ESI for further information). The results are calculated by averaging hydrogen bond numbers over all the slides. The average distance (row 4) is the donor–acceptor distance.
Concluding remarks

In this contribution, a more detailed view of the molecular configurations of a DOPA/ST monolayer on the Au(111) surface is obtained than experiment alone. The catechol groups with the hydroxyls oriented towards the gold surface are observed in the simulation as well as in the experiment. However, we also observe a number of catechol groups parallel to the gold surface. This configuration is not observed in the experiment but is reasonable according to the possible \( \pi \)-bonding interaction. Furthermore, the role of intermolecular hydrogen bonds is discussed. When comparing the results of DOPA and ST, the different configuration of catechol groups adsorbed on the Au(111) surface is because of strong hydrogen bonds between hydroxyl groups and amide groups in DOPA. On the other hand, configurations of DOPA monolayers at lower molecular densities (DOPA40 and DOPA34) are not well organized due to the hydrogen bond network. However, these hydrogen bonds may also keep the integrity of the DOPA monolayer. This may explain the different AFM graphs of DOPA and ST in the experiment.

More importantly, the simulation indicates that in a Langmuir–Blodgett transfer, configuration of molecules on the substrate is not solely dependent on area–pressure isotherms obtained from compressing the monolayer on the water surface. For ST molecules, although the monolayer can be compressed to a relatively small surface area per molecule (e.g. 25 Å\(^2\) per molecule), the optimum surface area for ST adsorbed onto the gold surface is calculated to be around 30 Å\(^2\) per molecule due to the saturation of catechol groups on the gold surface. For DOPA, with the existence of amide groups, a relatively ordered monolayer may be achieved at a smaller surface area per molecule (e.g. 25 Å\(^2\) per molecule) in simulation. The simulation result may prove that using a smaller surface area per molecule for DOPA (e.g. smaller than 30 Å\(^2\) per molecule) a monolayer of fine structure on the gold surface can also be obtained. One limitation of our simulation is that in the present study, only an ideal Au(111) surface is considered. While in experiment, the Au(111) surface may be a surface with steps and defects. According to other studies, possible Au–O sorption might happen at the defective site. Thus, further studies based on experiments and simulations are expected to investigate similar systems to validate the method and the results.

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Notes and references
