<table>
<thead>
<tr>
<th>Journal:</th>
<th><em>The Journal of Physical Chemistry</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID:</td>
<td>jp-2013-014493.R1</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>n/a</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>den Boer, Duncan; Massachusetts Institute of Technology, Chemistry Krikorian, Markrete; Massachusetts Institute of Technology, Chemistry Esser, Birgit; University of Bonn, Department of Chemistry Swager, Timothy; Mass. Inst. of Tech., Chemistry; Massachusetts Institute of Technology, Department of Chemistry 18-597</td>
</tr>
</tbody>
</table>
STM Study of Gold(I) Pyrazolates: Distinct Morphologies, Layer Evolution, and Cooperative Dynamics

Duncan den Boer, Markrete Krikorian, Birgit Esser, and Timothy M. Swager*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

E-mail: tswager@mit.edu

ABSTRACT

We describe the first study of trinuclear gold(I) pyrazolates on the molecular level by time-dependent Scanning Tunneling Microscopy (STM). On the graphite/1-octanoic acid interface dodecyl functionalized gold pyrazolates formed concentration-controlled morphologies. We found two types of monomeric packing and one dimeric type with two trinuclear gold pyrazolates next to each other on the surface. For an octadecyl functionalized derivative all studied concentrations resulted in a dimeric morphology. However, different concentrations led to different transient states during the layer evolution. At low concentrations, a transient monomeric state was present with the alkyl chains in a gauche-conformation that subsequently converted to a more optimized anti-conformation. At higher concentrations a less stable “line”
polymorph was observed. The confinement of the molecules to the surface led to cooperative
dynamics, in which two molecules in a dimer moved as if they were one particle. Furthermore, in
a higher level of cooperativity, the rotation of one dimer appears to induce rotations in coupled
neighboring dimers.

**Keywords:** molecular self-assembly, scanning probe microscopy, solid/liquid interface,
concentration, polymorphs, contrast

**Introduction**

The bottom-up creation of patterned surfaces by controlled self-assembly of molecules allows
molecular precision to be applied to emerging nanoscience and nanotechnology.\(^1\) For the
controlled construction of predictable and well-defined assemblies it is ideal to control the
specific adsorption of functional molecules at a surface,\(^3\) and understanding these assemblies on
the sub-molecular level will enable future designs. The necessary resolution for these studies is
provided by the Scanning Tunneling Microscope (STM), which can be operated under an
expanding range of conditions including the solid/liquid interface. A major advantage of a liquid
phase above the surface is that it acts as a reservoir of the functional molecules. This can allow
control of the morphology of a molecular monolayer by controlling the concentration of
functional molecules in the supernatant solution.\(^4\) Furthermore, the presence of the supernatant
solution assists in spontaneous dynamic processes such as diffusion and adsorption/desorption.

It is a continuing challenge to obtain a detailed understanding of the factors that control
complex and dynamic self-assembly processes.\(^10\) In this context, the study of spontaneous
dynamic processes at solid/liquid interfaces is of great interest, where molecules can be imaged
and the assembly is restricted by the reduced dimensionality. Examples of studies examining
spontaneous molecular level dynamics include Ostwald ripening,\textsuperscript{12–14} desorption/readsorption dynamics,\textsuperscript{15,16} conformational dynamics of single molecules,\textsuperscript{17} codeposition of solvent molecules,\textsuperscript{18,19} and transitioning from metastable to thermodynamically more favored polymorphs.\textsuperscript{20,21} In our studies we focused on the layer evolution and cooperative dynamics occurring in monolayers.

This study is focused on trinuclear gold(I) pyrazolates, \textbf{AuC12} and \textbf{AuC18} (Fig. 1). Trimeric gold complexes have been of interest since their discovery in 1970 by Vaughan.\textsuperscript{22} Their flat shape makes them very suitable for assembly on a flat surface and their electronic, optical, and chemical properties suggest utility as electronic materials and chemical sensors.\textsuperscript{23–27} Of special interest in the context of our work is the possible implementation of these molecules in chemical sensors. For example, carbon nanotube and graphene sensing devices generally require functional molecules adsorbed to their surface to improve sensitivity and selectivity.\textsuperscript{28–31} Therefore, our study of molecular layers of trinuclear gold(I) pyrazolates on a graphite surface is directed at gaining structural understanding to enable superior sensors.

The gold(I) pyrazolates \textbf{AuC12} and \textbf{AuC18} contain long alkyl chains that promote organized assemblies of molecular layers on a graphite surface.\textsuperscript{32} It was expected that the molecular cores indicated by the red triangle in Fig. 1 would play a role in the assembly process as a result of $\pi$-$\pi$ and metal-$\pi$ interactions with the underlying graphite surface. We also anticipated a possible favorable matching with the graphite lattice (illustrated in Fig. 1c).
Results and Discussion

The gold(I) pyrazolates **AuC12** and **AuC18** were synthesized from the corresponding pyrazoles through reaction with \([\text{Au(SMe}_2\text{Cl]}}\) as shown in Scheme 1. **3** and **5** are accessible in two steps from acetyl acetone (**1**). Self-assembled monolayers of these gold complexes were studied by STM at the graphite/1-octanoic acid interface. A 5–10 µl droplet of a solution of the compound was applied to a freshly cleaved surface, and during the STM topography measurements the tip was immersed in the droplet. Different results were obtained for **AuC12** and **AuC18**, as will be described below.
Scheme 1. Synthesis of the trinuclear gold complexes $\text{AuC}_{12}$ and $\text{AuC}_{18}$.
AuC12: Concentration Dependent Morphologies

The self-assembly behavior of AuC12 was studied at different concentrations and generates distinct morphologies on the surface. These morphologies correspond to stable phases, with layers being monitored for at least four hours and often for more than 15 hours. The layers typically formed within minutes after the application of the droplet, and the corresponding concentration dependent morphology was observed immediately (Fig. 2a). This does not preclude a transient morphology, but simply means that any intermediate morphology was not stable long enough to be observed on the STM time scale, which is several minutes to obtain a topography measurement.

AuC12 at Low Concentrations

For concentrations of \(1 \times 10^{-6}\) M and lower a morphology was found wherein the molecules of AuC12 packed in a monomeric fashion and the functional centers of the molecules (depicted by the red triangles in Figs. 1 and 2) within each domain were oriented in the same direction, as shown in Fig. 2b. The unit cell of this packing arrangement was found to be \(a = 3.2 \pm 0.2 \text{ nm, } b = 3.4 \pm 0.2 \text{ nm, and } \gamma = 59 \pm 5^\circ\). The monolayer is dynamic with molecules switching direction and, in the process, joining a neighboring domain. Fig. 2b shows an example wherein several molecules switch direction between two sequential scan lines. The switching in this example may be induced by the tip, although mild scanning conditions were used (\(V_{\text{bias}} = -950 \text{ mV and } I_{\text{set}} = 10 \text{ pA}\)) to minimize these effects. A correlation average filtering procedure (see S.I.) constructed from a high resolution STM topography image shows the pyrazolate groups surrounding the center part containing the gold atoms and the alkyl groups on the surface (Fig. 2b, bottom panel). DFT calculations on this type of trinuclear gold complex show that the molecular electrostatic potentials are centered on the gold atoms and in the center of the
molecular core and are directed above and below the plane of the molecule.\textsuperscript{33,34} This explains the bright feature observed at the center of the molecule. When counting the alkyl groups there appear to be twelve in a unit cell, which is double the expected number for a single molecule of \textbf{AuC12} (see Fig. S1). This observation is explained by assuming a co-deposition of 1-octanoic acid solvent molecules. Co-deposition of solvent molecules has previously been observed by STM.\textsuperscript{18,19,35} This model is supported by the bright features in the measurement highlighted by the red circle in the center image of Fig. 2b. It has previously been shown that acid groups can produce bright features in STM topography measurements.\textsuperscript{36,37} Also in line with this interpretation is the area of the unit cell, which is $9.3 \pm 1.6 \text{ nm}^2$. The area of one molecule of \textbf{AuC12} adsorbed to a graphite surface is estimated to be $4.7 \text{ nm}^2$,\textsuperscript{38} which leaves $4.6 \pm 1.6 \text{ nm}^2$ for the six co-adsorbed octanoic acid molecules. The area of one octanoic acid molecule would be roughly $0.5 \text{ nm}^2$, which indicates that there is indeed sufficient space on the surface for co-adsorption and that this can therefore explain the “additional” observed alkyl chains. A molecular model is constructed including co-adsorbed octanoic acid molecules (depicted in blue), and is depicted in the bottom panel in Fig. 2b. It cannot be unambiguously determined which alkyl groups belong to \textbf{AuC12} and which to co-adsorbed solvent molecules, and therefore the proposed molecular model acts as a suggestion in this regard.
Figure 2: Concentration controlled polymorphs of AuCl₂. a) Overview of the final states. b) Polymorph with the monomers in the same direction. Top: STM topography, the unit cell is drawn: $a = 3.2 \pm 0.2$ nm, $b = 3.4 \pm 0.2$ nm, $\gamma = 59 \pm 5^\circ$. The red and yellow ovals indicate two separate domains with different directions of the functional centers. Inset: magnification, showing molecules changing direction between two scan lines. Center: correlation average. The red and yellow triangles indicate the molecular center and the gold atoms. The red circle indicates a bright feature that could correspond to the COOH group of a co-deposited 1-octanoic acid molecule. Bottom: proposed corresponding molecular model, the unit cell is drawn. Co-adsorbed 1-octanoic acid molecules are indicated in blue. c) Polymorph with the monomers in alternate directions. Top: STM topography, overview. Center: correlation average.
average, the unit cell is drawn: a = 2.6 ± 0.1 nm, b = 5.3 ± 0.2 nm, γ = 66 ± 10°. Inset: different correlation average with contrast optimized to observe alternate directions of centers. Bottom: proposed corresponding molecular model, the unit cell is drawn. One molecule is indicated in red. d) Dimeric polymorph. Top: STM topography, overview. The red circle indicates a single molecule, yellow ovals indicate dimers. Center: high resolution STM topography, the unit cell is drawn: a = 3.2 ± 0.1 nm, b = 3.9 ± 0.1 nm, γ = 65 ± 7°. Bottom: proposed corresponding molecular model, the unit cell is drawn. One molecule is indicated in red.

**AuC12 at Medium Concentrations**

For concentrations between 5 × 10⁻⁶ M and 4 × 10⁻⁵ M, the molecules of AuC12 adopt a different packing. The unit cell of this packing contains two AuC12 molecules pointing in different directions (see the inset of the center panel in Fig. 2c) and has dimensions a = 2.6 ± 0.1 nm, b = 5.3 ± 0.2 nm, and g = 66 ± 10° (Fig. 2c). The area per molecule is 6.3 ± 1.0 nm², a value smaller than that found in the packing at lower concentrations. A molecular model, constructed from the STM measurements, is depicted in the bottom panel of Fig. 2c. It shows a monomeric packing with the cores of the two AuC12 molecules in the unit cell pointing in opposite directions. Per molecule of AuC12 there is room for approximately three co-adsorbed 1-octanoic acid molecules.

**AuC12 at High Concentrations**

A dimeric packing of AuC12 was observed when the concentrations are between 4 × 10⁻⁵ M and 1 × 10⁻³ M (Fig. 2d). In this morphology the molecules displayed an ordered structure, in which molecular dimers appeared, as are indicated by the yellow ovals in the topmost panel of Fig. 2d. The unit cell for this packing was found to be a = 3.2 ± 0.1 nm, b = 3.9 ± 0.1 nm, and γ = 65 ± 7° and contains two molecules of AuC12. This structure is not due to a “double tip” artifact, as confirmed by the observance of a single molecule of AuC12 next to a hole in the layer (indicated by the red circle in the topmost panel of Fig. 2d). A correlation average of a high resolution topography measurement reveals the orientation of the molecular cores that are highlighted by the gold atoms and also the alkyl chains on the surface (center panel of Fig. 2d).
In this case the center of the molecular core does not show up as one bright spot, but there are individual spots that relate to the gold atoms in the molecular core. This difference is probably due to the specific tip geometry (as with different tips the dimeric morphology also had a single bright spot in the center of the molecular core). The STM topography measurements suggest a molecular model (bottom panel of Fig. 2d). An individual molecule of AuC12 in this dimer packing has an area of 5.7 ± 0.6 nm², lower than the values for the other two observed packings. This indicates that this morphology has the highest molecular density on the surface, nicely correlating with the higher density of molecules in the supernatant solution.

It is interesting to note that at an AuC12 concentration of 4 × 10⁻⁵ M in 1-octanoic acid, the dimeric morphology coexists with the monomer morphology, in which the centers point in alternate directions. This reproducible state was also found to be stable, with a constant relative abundance as long as 16.5 hours after the start of the experiment. The large error bars in Fig. 2a are the result of larger domain sizes than the scan size of the STM topography measurement, i.e. > 200 nm, and therefore within an STM scan only one of the two packings was observed.

Higher concentrations of AuC12 are not included in Fig. 2a as in that case the solution formed a gel. To apply a droplet to the surface involved heating, and therefore the exact concentration during the STM measurements was undetermined. Fig. S3 shows a short-lived “line” packing that was observed as a transient state in this concentration regime. The final state under these conditions was the dimeric packing.

AuC18: Layer Evolution and Transient Morphologies

Molecular layers of AuC18 on the graphite/1-octanoic acid interface display significant differences from those of AuC12. Although different AuC12 concentrations gave different morphologies on the surface, for AuC18 all concentrations in the studied range of 1 × 10⁻⁶–1 ×
$10^3$ M resulted in a dimeric packing within two hours after the start of the experiment (Fig. 3a).

In contrast to AuC12, we observed concentration dependent transient morphologies during the layer evolution.
Figure 3: Layer evolution of AuC18. a) Overview of the final states. b) Low concentrations: monomeric packing to dimeric packing. First panel: STM topography of patches of monomeric packing on the surface. Second panel: monomeric packing with non-straight alkyl chains 30–45 minutes after the start of the experiment. Red and yellow arrows point at identically ordered alkyl chains. Third panel: monomeric packing with straight alkyl chains 1 h after the start of the experiment. The unit cell is drawn: \( a = 4.2 \pm 0.1 \text{ nm}, b = 6.7 \pm 0.1 \text{ nm}, \gamma = 52 \pm 5^\circ \). Fourth panel: proposed corresponding molecular model, the unit cell is drawn. One molecule is indicated in red. c) Medium
concentration: dimeric packing. Top: STM topography, overview. Angle $\alpha$ denotes the angle between the two domains. The red circle indicates a single molecule, yellow ovals indicate dimers. Center: high resolution STM topography image, the unit cell is drawn: $a = 4.0 \pm 0.1$ nm, $b = 4.3 \pm 0.2$ nm, $\gamma = 63 \pm 7^\circ$. The yellow dashed line follows a main symmetry axis of the underlying graphite, the solid yellow line runs perpendicular to this and is a reference axis for the propagation axis, denoted by the red line. $\Phi$ is the angle between the reference axis and the propagation axis. The circles represent non-covered parts of the surface. Bottom: proposed corresponding molecular model, the unit cell is drawn. One molecule is indicated in red. d) “Line” polymorph coexisting with dimeric polymorph. Top: STM topography, overview. Center: Correlation average, the unit cell is drawn: $a = 3.2 \pm 0.2$ nm, $b = 8.9 \pm 0.2$ nm, $\gamma = 76 \pm 10^\circ$. Bottom: proposed corresponding molecular model, the unit cell is drawn. One molecule is indicated in red.

**AuC18 at Medium Concentrations**

Intermediate concentrations ($5 \times 10^{-5}$ M) of AuC18 in 1-octanoic acid did not display transient morphologies, and a dimeric morphology was formed within minutes after the application of the droplet. This dimeric morphology has a unit cell of $a = 4.0 \pm 0.1$ nm, $b = 4.3 \pm 0.2$ nm, and $\gamma = 63 \pm 7^\circ$ (Fig. 3c). Accordingly, every molecule of AuC18 covers an area of $7.7 \pm 1.0$ nm$^2$, and it is confirmed that this is not due to a “double tip” artifact, as single features were also observed next to holes or domain boundaries in the layer (indicated by the red circle in the top panel of Fig. 3c). The high resolution STM topography image in the center panel of Fig. 3c clearly shows the location of the molecular core with the individual gold atoms and the alkyl chains. Based on the STM topography measurements a molecular model is constructed, as shown in the bottom panel of Fig. 3c. The circles indicate small areas of the surface that are bare in the model, which can be observed in the STM topography measurements.

**Chirality of AuC18 Dimeric Packing**

The adsorption to a surface often leads to chiral motifs in a monolayer, even in achiral molecules. The dimeric packing of AuC18 is chiral, and molecular models of the two enantiomeric domains together with the corresponding STM measurements of the observed enantiomers are presented in Fig. 4. The difference between these two isomers that is the most
convenient to observe in the STM measurements is the direction of the alkyl tails indicated by the red circles.

In fact, all of the observed molecular packings should be chiral, as all molecular layers with an oblique unit cell share this property.\textsuperscript{40} However, an in-depth study of the chirality of all the morphologies is beyond the scope of this paper, and we have limited ourselves to the dimeric packing of AuC\textsubscript{18} as an example.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Chirality of the dimeric packing of AuC\textsubscript{18}. Left and right show the two enantiomers observed for the dimeric packing of AuC\textsubscript{18}. The red circles indicate the alkyl chains that assist in the identification of the isomer. Insets: the corresponding proposed molecular models.}
\end{figure}

AuC\textsubscript{18} at High Concentrations

At “high” concentrations ($8 \times 10^{-5} - 1 \times 10^{-3}$ M), the dimeric morphology coexisted with a “line” morphology at the start of the experiment, as depicted in Fig. 3d. Yet higher concentrations of the solution led to the formation of a gel state, similar to what was found for AuC\textsubscript{12}, and this concentration range was not studied. The unit cell for the “line” polymorph of AuC\textsubscript{18} was found to be: $a = 3.2 \pm 0.2$ nm, $b = 8.9 \pm 0.2$ nm, and $\gamma = 76 \pm 10^\circ$ and contains four molecules of AuC\textsubscript{18}. This morphology is less stable and therefore is hard to visualize by STM with high resolution. A model based on a correlation average is depicted in the bottom panel of
Fig. 3d. As the alkyl chains could so far not be visualized in detail, the model is constructed from the locations and directions of the molecular cores that are visible in the STM image combined with the determined values of the unit cell. The area per molecule for this polymorph corresponds to $6.9 \pm 0.9 \text{ nm}^2$. This area is lower than for the dimeric morphology, which could also be observed when the two polymorphs were present within one image. The higher molecular density on the surface for the “line” polymorph compared to that of the dimeric polymorph suggests that the “line” morphology will be favored at higher concentrations of the supernatant solution. However, within two hours this morphology had typically been replaced by the dimeric packing over the entire surface (both in scanned areas and remote areas that were previously unscanned). Hence the dimeric packing is thermodynamically more stable.

**AuC18 at Low Concentrations**

An interesting transition in the evolution of the layer formation occurs at “low” concentrations ($1 \times 10^{-6}$–$3 \times 10^{-5} \text{ M}$). In this range, the layer growth typically started as patches of a monomeric packing (top panel Fig. 3b and Fig. S4) that grew over time. Intriguingly, in our research a monomeric packing was observed that had many gauche segments of alkyl chains with initial layer formation (within the first half hour, second panel of Fig. 3b). Generally, STM images show alkyl chains in anti-conformations on the graphite surfaces, with optimal interactions with the underlying graphite lattice. In the observed transient morphology the alkyl chains appear less ordered. Even though at first glance there appears to be less order, the kinked alkyl chains are not randomly oriented on the surface. This is highlighted by the red arrows and the yellow arrows, both pointing at two alkyl chains in the same conformation. After approximately 15 minutes the alkyl chains assume an anti-conformation. The values for the unit cell remained unchanged, $a = 4.2 \pm 0.1 \text{ nm}$, $b = 6.7 \pm 0.1 \text{ nm}$, $\gamma = 52 \pm 5^\circ$, and contains two AuC18 molecules. A molecular
model for this packing is proposed in the fourth panel of Fig. 3b. It is likely that there are molecules of 1-octanoic acid co-adsorbed, as the experimentally determined area per molecule of \textbf{AuC18} in this packing is 11.1 ± 1.2 nm$^2$, while an estimated value for the area of one molecule of \textbf{AuC18} is only 6.6 nm$^2$\textsuperscript{38}. The observation of the transient kinked alkane polymorph suggests that even with non-optimized interactions between the alkyl chains of \textbf{AuC18} with the underlying graphite, the molecule is still somewhat immobile. It is therefore proposed that the molecular cores interact strongly with the underlying graphite. This could be explained by π-π and Au-π interactions on the graphite surface (illustrated in Fig. 1c). The solid/liquid interface dynamic processes present allow desorption and readesorption of the alkyl chains\textsuperscript{15,17} for the transition to a more optimized anti-conformation. Such a conformation optimizes both the interactions with the underlying graphite as well as with the neighboring alkyl chains.

The layer evolution at “low” concentrations involves a coexistence of the monomeric packing with the dimeric packing (an example is given in Fig. 5d), subsequently leading exclusively to the dimeric packing (typically 1.5 hours after the observation of the first patches of monomeric packing). This dimeric packing was also present in regions of the surface that were previously unscanned, indicating that this transition was not caused by the scanning or the presence of the STM tip.

The monomeric packing at “low” concentration range has a unit cell containing two molecules, similar to the monomeric morphology of \textbf{AuC12} with the functional centers pointing in alternate directions.

**Comparing \textbf{AuC12} and \textbf{AuC18} assembly**

Our STM measurements suggest some general difference in the assembly of \textbf{AuC18} and \textbf{AuC12}. The monomeric packing of \textbf{AuC18} having kinked alkanes is likely formed as a result of
longer alkyl groups that immobilized the compound even with non-optimized interactions with the underlying graphite. Also, for the study of the evolution of layer formation, longer alkyl chains slow down the self-assembly process, which enabled us to visualize transient states. The observation that the molecules of $\text{AuC}_{18}$ have a dimeric equilibrium packing in this concentration range suggests that this packing is thermodynamically more favorable. When comparing the packings for $\text{AuC}_{12}$ to the packings for $\text{AuC}_{18}$, we can see that due to the longer alkyl groups, a monomeric packing of $\text{AuC}_{18}$ leads to a larger porosity on the surface (i.e. there is more “uncovered” graphite area) than a monomeric packing of $\text{AuC}_{12}$. Also, the dimeric packing for $\text{AuC}_{18}$ leads to only a very small part of the surface being uncovered (indicated by circles in Fig. 3c) while for the dimeric packing of $\text{AuC}_{12}$ there are still uncovered parts present (as can be seen in the high resolution STM measurements depicted in Fig. 2c). The difference between the porosity of the different packings of $\text{AuC}_{18}$ is therefore larger than for the different packings of $\text{AuC}_{12}$, which would therefore lead to a driving force for the molecular layer to transform to the dimeric packing of $\text{AuC}_{18}$. 
Contrast Differences in STM Topography

An interesting aspect of the molecular layers is revealed by comparing the apparent heights of the trimeric gold complexes on the surface. Fig. 5a and S8 show a molecular layer of $\text{AuCl}_2$ in the monomeric morphology with the functional centers pointing in alternate directions. Fig. 5b shows a cross-section. As is apparent from the cross-section, the two molecules of $\text{AuCl}_2$ in the unit cell have different apparent heights, i.e. one of the two rows appears higher than the other by approximately 50%.

A similar effect is also observed when the apparent height of molecules of $\text{AuCl}_8$ in the monomeric packing is compared to the dimeric packing (Figs. 5c and d). The molecules in the monomeric packing appear about 50% higher. This cannot be explained by a change in the tip, as both cross-sections are done in the same scan lines with the same tip. This difference in contrast is clearly apparent in the inset of Fig. 5c. Two molecules (indicated by the red circle) appear to be a dimer. However, according to the contrast, only the right one is in the dimeric packing, while the left one has the same contrast as the surrounding molecules of $\text{AuCl}_8$ in the monomeric packing.
Figure 5: Contrast differences. a) Correlation average constructed from an STM topography of molecules of AuCl$_2$ in a monomeric packing with the centers in alternate directions b) Cross-section corresponding to the dashed line in (a). c) Molecular layer of molecules of AuCl$_8$ coexisting in a monomeric morphology and a dimeric morphology. Inset: magnification of (c). Red circle indicates an apparent dimer with different contrasts. d) Cross-sections with the dashed trace corresponding to the dashed line in (c), and the solid trace corresponding to the solid line in (c).

Crystal structures of non-alkylated trinuclear gold pyrazolates show that the molecule is planar,\textsuperscript{33} and we expect that this is also the case on the graphite surface in the different molecular packings and therefore that the observed contrast difference is not due to a difference in the height of the molecular core. It has previously been shown that a difference in registry with an underlying surface can lead to changes in contrast of molecules imaged by STM (and is generally accepted as the cause of the often observed moiré patterns in a molecular layer on top of graphite).\textsuperscript{36,41,42} In fact, some research groups use the difference in contrast as a way to quantify the mismatch of adsorbed molecules with the registry of the underlying graphite.\textsuperscript{43} We
therefore propose that this is the explanation for the observed contrast differences for \textbf{AuC12} and \textbf{AuC18}. We speculate that for the molecules with a higher apparent height, the electronic coupling with the underlying graphite is more favorable. An observation that seems to support this is that the molecules of \textbf{AuC12} in the monomeric morphology with the molecular cores pointing in alternate directions with lower apparent height also appear to be more mobile and hence, only weakly bound to the surface (see Fig. S2).

**Cooperative Dynamics of AuC18 Dimers**

In addition to the layer evolution, other dynamic effects were also studied by time-dependent STM. Cooperative dynamic processes were observed during the monitoring of molecular layers of \textbf{AuC18} in the dimeric packing. Two molecules of an \textbf{AuC18} dimer were regularly observed to move in a cooperative fashion such that the dimer appeared to rotate on the surface as if it were a single particle. An example is given in Fig. 6a, wherein one dimer (indicated by the yellow circle in the magnification) is pointing vertically in the first STM topography measurement, and three minutes later the same dimer is pointing horizontally. It is not expected that the molecules of \textbf{AuC18} forming a dimer have an attractive interaction with each other. Lateral dimers do not exist in solution but form as a result of the underlying graphite surface. It is proposed that even though there is no specific attractive interaction expected between two members of a dimer, there still is a favorable geometric fit for two of the molecules to be in close proximity, which leads to a “gearing” or coupling of the rotational dynamics.
Figure 6: Cooperative dynamics: rotations of AuC18 dimers. a) Two subsequent STM topography measurements with a time interval of three minutes of a layer of AuC18 in the dimeric morphology. White arrows indicate the slow scan direction. Insets: Magnification of the area of interest. The rotation of a single dimer of AuC18 is indicated by the yellow circles. b) Subsequent STM topography measurements with a time interval of three minutes showing several subsequent rotations of dimers of AuC18. White arrows indicate the slow scan direction. In the first images the yellow ovals indicate two dimers that rotate at the same time. The red circles indicate a nearby dimer rotating as well. The yellow arrows point at a dimer that was rotated for several scan lines, then rotates back, after which the other dimers also return to their original orientation. c) STM topography image of AuC18 in the dimeric morphology, illustrating the disruption of the layer by a dimer in a different orientation (indicated by the yellow circle). d) Subsequent STM topography images with a time interval of three minutes, showing the change of orientation of a whole domain of dimers of AuC18. White arrows indicate the slow scan direction. The orientation of the domain is indicated by the dashed yellow lines. The yellow circle indicates an area with seemingly less immobilized dimers.

Beyond the cooperative movement of the two molecules in a dimer, a higher level of cooperativity was also observed. It appears that a dimer’s rotation can induce neighboring dimers to rotate as well as illustrated in Fig. 6b. In the first images the yellow ovals indicate two dimers rotating simultaneously (in the same time interval between being imaged by the STM). These rotations appear to induce a nearby dimer to rotate as indicated by the red circles. After several
minutes a dimer nearby is rotated for a short amount of time (imaged for a few scan lines, indicated by the yellow arrow), after which the dimer returns to its original orientation. This is then followed by the other rotated dimers to rotate again and return to their original orientation.

A more extreme example of such cooperative rotation can be seen in Fig. 6d. Here a whole domain of dimers of AuC18 changes its orientation three times in a row. The yellow circle indicates an area where after this final rotation the dimers of AuC18 have a “blurry” signature. This is possibly the result of dimers moving on a time scale too fast for STM visualization. This is not a tip artifact, since in the right part of the image (next to the yellow circle) this effect is not seen, even though these molecules are imaged by the same tip (as the fast scan direction is horizontal).

Such a cooperative effect of a whole domain is a surprising phenomenon. We think that several factors might be involved to facilitate such an effect.

1) In Fig. 6a the rotation starts at a domain boundary. At such boundaries, molecules are often less immobilized than in the center of a domain. Also in Fig. 6d, a domain boundary is nearby the domain that changes direction.

2) These rotations might be facilitated by the fact that the unit cell is not square. This asymmetry disrupts the surrounding dimers in the monolayer and introduces local strain. An STM topography image (Fig. 6c) shows a dimer of AuC18 molecules (yellow circle) that has a different orientation and disrupts the dimers surrounding it. The disruption in the layer makes it more favorable for a nearby dimer to also rotate.

3) The solid/liquid interface allows for dynamic processes such as desorption and readsoption of the alkyl chains.\textsuperscript{15,17} It is also important to realize that the molecules as a whole can stay adsorbed to the surface during the rotation.
4) In the observed contrast differences in Fig. 5, our hypothesis is that a bright contrast is related to a more favorable coupling to the underlying surface. The dimeric packing of \textit{AuC18} was less bright than the monomeric packing, which might suggest a less favorable coupling to the graphite and therefore might be less immobilized. This is consistent with the observation that such dimers can rotate on the surface.

5) It is possible that the rotations are influenced by the STM tip and are not completely spontaneous. However, varying the scanning parameters (\(V_{\text{bias}}\), \(I_{\text{set}}\), scan speed and scan angle) in an attempt to induce these dynamics has so far proven unsuccessful.

6) It is important to realize that the rotations in Fig. 6d appear to have occurred simultaneously, but that this is within the time resolution of three minutes. We expect there to be a sequence of events, similar to Fig. 6b.

\textbf{Conclusion}

Trinuclear gold complexes form organized assemblies on the surface of graphite. For their implementation in devices involving a molecular surface layer, it is important to understand the processes present during the molecular self-assembly. This is true not only for these molecules, but for other functional molecules as well, and our findings are therefore relevant in a more general sense.

We described herein studies of two trinuclear gold complexes, \textit{AuC12} and \textit{AuC18}, by Scanning Tunneling Microscopy at the solid/liquid interface. Molecules of \textit{AuC12} were found to form distinct morphologies (monomeric and dimeric) on the graphite surface, depending on the concentration of the solution. For \textit{AuC18} the results were different: in the studied concentration range all layers ended up in the same dimeric morphology. Using time-dependent STM studies it was possible to study the layer evolution on the molecular level, and different transient
morphologies were present at different concentrations. At lower concentrations a morphology was observed in the early assembly process that did not have the characteristic “straight alkyl chain” morphology that is typically observed in STM measurements, but instead the alkyl chains had a kinked gauche conformation. Still, there was order present in this morphology with a unit cell containing two molecules of \textbf{AuC18}. Over time these alkyl chains converted to an anti-conformation. It is proposed that the non-optimized kinked structure is a kinetic state and that the functional centers of the molecules have an interaction with the underlying graphite and play a role in the early stages of assembly.

Contrast differences between the different morphologies and also between molecules within one morphology were observed and proposed to be caused by a different registry of the molecules with the underlying graphite.

Finally, it was observed that molecules of \textbf{AuC18} in a dimeric morphology on the surface can move in a cooperative fashion in such a way that a dimer appears to rotate as if it were a single particle. In a higher level of cooperativity such rotations seem to induce nearby dimers to rotate as well, which can go as far as a whole domain of dimers of \textbf{AuC18} changing orientation. It is important to realize that in specific circumstances a small variation (the rotation of one dimer) can have an amplified effect. For the implementation of functional molecules in devices such insights in the self-assembly processes can give handles to control the final morphology of the layer.

\textbf{Acknowledgement}

This research was supported by the National Science Foundation (DMR-1005810), Air Force Office of Scientific Research (FA9550-10-1-0395) with the purchase of an AFM/STM system,
the Center for Excitonics and Energy Frontier Research Center funded by the Department of Energy, Office of Basic Energy Sciences (DF-SC0001088), a Marie Curie International Outgoing Fellowship within the 7th European Community Framework Programme for D.d.B (273837), and a postdoctoral fellowship by the German Academy of Sciences for B.E. (LPDS 2009-8).

Supporting Information Available

Experimental and synthetic procedures, scanning parameters for the figures, and additional STM measurements are included. This material is available free of charge via the Internet at http://pubs.acs.org/.
References


    Crossley, M. J.; Van Enckevort, W. J. P.; Hendriksen, B. L. M.; Elemans, J. A. A. W. et
    al. Little exchange at the liquid/solid interface: defect-mediated equilibration of

17) Xu, H.; Minoia, A.; Tomovic, Z.; Lazzaroni, R.; Meijer, E. W.; Schenning, A. P. H. J.;
    De Feyter, S. A Multivalent Hexapod: Conformational Dynamics of Six-Legged
    Molecules in Self-Assembled Monolayers at a Solid-Liquid Interface. ACS Nano 2009, 3,
    1016–1024.

18) De Feyter, S.; Gesquière, A.; Abdel-Mottaleb, M. M.; Grim, P. C. M.; De Schryver, F.
    C.; Meiners, C.; Sieffert, M.; Valiyaveettil, S.; Müllen, K. Scanning Tunneling
    Microscopy: A Unique Tool in the Study of Chirality, Dynamics, and Reactivity in

    Müllen, K.; Calderone, A.; Lazzaroni, R.; Brédas, J. L. Dynamics in Physisorbed
    Monolayers of 5-Alkoxy-isophthalic Acid Derivatives at the Liquid/Solid Interface

20) Elemans, J. A. A.W.; Lensen, M. C.; Gerritsen, J.W.; Van Kempen, H.; Speller, S.; Nolte,
    R. J. M.; Rowan, A. E. Scanning Probe Studies of Porphyrin Assemblies and Their
    2073.

    Sonoda, M.; De Schryver, F. C.; De Feyter, S.; Tobe, Y. Two-Dimensional Porous


