Experimental and Theoretical Analysis of Hydrogen Bonding in Two-Dimensional Chiral \(4',4'''-(1,4\text{-Phenylene})\text{bis}(2,2':6',2''\text{-terpyridine})\) Self-Assembled Nanoarchitecture

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ABSTRACT: The two-dimensional self-assembly of \(4',4'''-(1,4\text{-phenylene})\text{bis}(2,2':6',2''\text{-terpyridine})\) molecules is experimentally and theoretically investigated. Scanning tunneling microscopy (STM) shows that this molecular building block forms a compact chiral supramolecular network on graphite at the 1-octanol/graphite interface. The molecules adopt a side-by-side arrangement inside the organic domains. In contrast, the molecules are arranged perpendicularly at the domain boundary. Detailed theoretical analysis based on the density functional theory (DFT) shows that these arrangements are stabilized by double and single hydrogen bonds between pyridine groups. Only the molecular peripheral pyridine groups are involved in the hydrogen bonds stabilizing the long-range ordered molecular nanoarchitectures.

INTRODUCTION

Engineering novel organic nanoarchitectures through bottom-up strategy and molecular self-assembly is attracting increasing interest over the past decade. Predicting and controlling self-assembly is a prerequisite to fabricate well-defined nanoarchitectures with specific local electronic properties. Hydrogen bonding is an appealing intermolecular interaction to govern molecular self-assembly due to the high selectivity and high directionality of this bond. Hydrogen bonds (C–H···O) or (O–H···O) hydrogen bonds, respectively. The pyridine group is an interesting alternative to these substituents because of its flexibility. This group is not only expected to drive molecular self-assembly through the formation of double hydrogen bonds (C–H···N) between neighboring molecules, but the N atom can be located in different position of the benzene ring. The flexibility of this group opens new opportunities to engineer new architectures. Specific pyridine-based molecular building blocks have been recently synthesized for application in the fields of supramolecular chemistry and materials science. Hydrogen-bonded two-dimensional nanoarchitectures have been engineered using pyridine-based molecular building blocks. The conformation of terpyridine compounds can change in organic nanoarchitectures according to Wang et al. Peryperrhedral pyridine groups can adopt a trans or cis conformation to confer stability to the molecular self-assembly. However, the strength of molecular bonds has not yet been assessed in terpyridine-compound self-assembly.

In this paper, we investigate the self-assembly of \(4',4'''-(1,4\text{-phenylene})\text{bis}(2,2':6',2''\text{-terpyridine})\) molecules at the 1-octanol/graphite interface. Scanning tunneling microscopy (STM) reveals that the molecules self-assemble into a two-dimensional close-packed chiral nanoarchitecture. Molecules are arranged side-by-side inside the molecular domain whereas molecular are arranged perpendicularly at the domain boundary. Density functional theory (DFT) modeling reveals that this structures is stabilized by double and single hydrogen bonds between pyridine groups.

EXPERIMENTAL AND THEORETICAL METHODS

Solutions of \(4',4'''-(1,4\text{-phenylene})\text{bis}(2,2':6',2''\text{-terpyridine})\) in 1-octanol (99%, Acros) were prepared. A droplet of this solution was then deposited on a graphite substrate. STM imaging of the samples was performed at the liquid/solid interface using a Pico-SPM (Molecular Imaging, Agilent Technology) scanning tunneling microscope. Cut Pt/Ir tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample. STM images were processed and analyzed using the application FabViewer. To model the molecular arrangement of the calculations 4',4'''-(1,4-phenylene)bis(2,2':6',2''-terpyridine) molecules simulations were performed using the ab initio SIESTA package. SIESTA is based on the localized numerical orbital basis set, periodic boundary conditions, and the first-principles scalar-relativistic norm-conserving Troullier-Martins pseudopotential factorized in the Kleinman–Bylander form. We

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used Perdew, Becke, and Ernzerhof (PBE)\textsuperscript{41} generalized
gradient approximation for the exchange and correlation,
which was found previously to be adequate in representing
hydrogen bonding between DNA base molecules.\textsuperscript{42} In each
calculation, atomic relaxation was performed until forces on
atoms were less than 0.01 eV/Å in the cases of dimers and 0.03
eV/Å in the cases of monolayers. The effect of the vdW forces
in the assembly of molecules on the surface has been
considered thanks to the vdW-DF \textit{ab initio} method.\textsuperscript{43–45} The
energetics of each gas-phase monolayer, calculated using
SIESTA, is characterized by its stabilization energy, which is
composed of two components: the interaction and deformation
energies. If the former characterizes the strength of
intermolecular interaction (it is negative), the latter shows
the energy penalty due to inevitable deformation of molecules
in the final structure (and is positive). The calculated energies
include the basis set superposition error (BSSE) correction\textsuperscript{46}
due to the localized basis set used. To analyze bonding in the
relaxed structures, the electron density difference (between the
total density and that of all individual molecules in the
geometry of the combined system) was found to be especially
useful because the hydrogen bonding is known to be well
characterized by the “kebab” structure associated with
alternating regions of excess and depletion of the electron
density along the donor–hydrogen–acceptor line of atoms.\textsuperscript{42}

\section*{RESULTS AND DISCUSSION}

The chemical structure of the \(4',4''\textsuperscript{′},(1,4	extsuperscript{-phenylene})\textsuperscript{bis-}
(2,2':6',2''-terpyridine)\) molecule is presented in Figure 1.
This 2-fold symmetry molecule is a H-shaped molecule. Its
skeleton consists of a central benzene ring connected to two
peripheral terpyridine groups.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{4',4''\textsuperscript{′},(1,4-Phenylene)bis(2,2':6',2''-terpyridine) molecule
\((C_{36}H_{24}N_{6})\). Carbon atoms are gray, hydrogen atoms are white, and
nitrogen atoms are blue, respectively.}
\end{figure}

Figure 2a, the large scale STM image, reveals that \(4',4''\textsuperscript{′},(1,4-	extsuperscript{-phenylene})\textsuperscript{bis-}
(2,2':6',2''-terpyridine)\) molecules self-assemble
into large close-packed nanoarchitectures at the 1-octanol/
graphite interface. The molecules are entirely covering the
graphite surface. This molecular arrangement is chiral and is
stable during STM imaging. The two enantiomeric structures
are visible in the high resolution STM images presented in
Figure 2b,c. Intramolecular features corresponding to the
integrated density of states of the molecule appear distinctly in
the high resolution STM images, Figure 2b,c. The molecules
forming the chiral network unit cells have been colored in
yellow, red, blue, and green as a guide for the eyes. Neighboring
molecules are arranged parallel to each other. The model of this
self-assembled nanoarchitecture is presented in Figure 4a. The

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{(a) Large scale STM image of \(4',4''\textsuperscript{′},(1,4	extsuperscript{-phenylene})\textsuperscript{bis-}
(2,2':6',2''-terpyridine)\) chiral nanoarchitecture on graphite, \(30 \times 26\)
nm\(^2\), \(V_{t} = 0.5\) V, \(I_{t} = 180\) pA. The two enantiomeric domains
are presented in the high-resolution STM images: (b) \(9 \times 8\) nm\(^2\), \(V_{t} = 0.5\)
V, \(I_{t} = 180\) pA; (c) \(9 \times 7\) nm\(^2\), \(V_{t} = 0.5\) V, \(I_{t} = 180\) pA. Molecules
comprising the unit cell are in red, green, blue, and yellow in (b) and
(c).

An STM image of the domain boundary is presented in
Figure 3. The molecules at the edge of the domains have been
colored in red and green, as a guide for the eyes. The molecules
of neighboring domains are aligned (red, green molecules). The
two domains are separated by a molecular row (molecules
colored in yellow and blue). The molecules of this row are
parallel to each other, but they are rotated by 80° with respect
to the molecules of the domains. The molecules of the side-by-
side arrangement are epitaxially oriented on the graphite
surface. The perpendicular molecules are in contrast aligned in

\section{CONCLUSION}

The assembly of \(4',4''\textsuperscript{′},(1,4	extsuperscript{-phenylene})\textsuperscript{bis-}
(2,2':6',2''-terpyridine)\) molecules on graphite is
consistent with a kebab structural model. The self-
assembly process occurs in a 1-octanol/graphite interface
solution and is driven by hydrogen bonding and van der Waals
forces. The STM images reveal the formation of large close-packed
nanoarchitectures with a chiral network structure. The
self-assembly process is reversible, and the nanoarchitectures
are stable during STM imaging. The structural integrity of the
nanoarchitectures is maintained even in the presence of
solvent molecules. The results of this study provide insights
into the self-assembly of \(4',4''\textsuperscript{′},(1,4	extsuperscript{-phenylene})\textsuperscript{bis-}
(2,2':6',2''-terpyridine)\) molecules on graphite and
have implications for the design and fabrication of
nanoarchitectures for various applications.
the molecules were adopting a planar configuration in these calculations.

In our calculations, the whole molecular structure is modeled and the possibility that molecular structure can adopt different configurations is also taken into account. For the parallel and perpendicular networks, two unit cells were considered. The unit cells are composed of two and four molecules, respectively. The two geometries reveal a similar stabilization energy and energy per molecule for the two nanoarchitectures (Table 2).

The perpendicular arrangement of molecular dimers is slightly more stable than the parallel configuration when two molecules are considered. In contrast, the perpendicular arrangement appears to be less stable when four molecules in the unit cell are considered (Table 2). The density of the perpendicular arrangement (0.47 mol/nm²) is slightly larger than the one of the parallel arrangement (0.44 mol/nm²). In fact, the perpendicular configuration of tetramers becomes less stable because it induces a distortion of molecular conformation in the unit cell. The molecular peripheral pyridine groups are rotating with respect to the molecular plane; i.e., the terpyridine groups are then not flat. This rotation weakens the hydrogen bond between neighboring molecules and increases the energy of the molecular arrangement.

The calculations reveal that the unit cell (containing one molecule) of the parallel arrangement is stabilized by two double H-bonds highlighted by dark blue circles in Figure 4c. In comparison, the monolayer based on the perpendicular tetramers (Figure 5c) contains two molecules per unit cell, which is stabilized by two double H-bond (dark blue circles) and two single H-bonds (light blue circles), Figure 5c. The gray circle highlights a charge rearrangement, which does not correspond to a H-bond. The unit cell of the parallel arrangement is therefore stabilized by a higher number of H-bonds per molecules than the unit cell of the perpendicular arrangement. However, calculations only reveal a small difference in energy between the two assemblies (Table 3), which indicates that the hydrogen bonds between neighboring molecules are stronger in the perpendicular tetramer than in the aligned tetramers when the monolayer is formed. The difference in strength between the two assemblies can be observed in the “kebab” plot in Figures 4 and S. In these plots, the alternating regions of depletion and excess of the density along the H-bonds characterize the strength of the bonding. The molecules are bonded to each other through two N···H−C bonds between their peripheral terpyridine groups in the parallel arrangement, Figure 4b. In contrast, the N atom of the molecular central terpyridine group is not involved in any H···H interaction.

### Table 2. Calculated Energies: Building Blocks and Calculated Energies of the 4′,4″′-(1,4-Phenylene)bis(2,2′:6′,2″-terpyridine) Nanoarchitecture

<table>
<thead>
<tr>
<th>Structure</th>
<th>Parallel</th>
<th>Perpendicular</th>
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</thead>
<tbody>
<tr>
<td>Dimer</td>
<td>Tetramer</td>
<td>Dimer</td>
</tr>
<tr>
<td>Molecular block</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy (eV) (PBE)</td>
<td>-0.35</td>
<td>-0.87</td>
</tr>
<tr>
<td>BSSE Energy (eV)</td>
<td>0.04</td>
<td>0.2</td>
</tr>
<tr>
<td>$E_{coh}$ (eV) per molecule</td>
<td>0.18</td>
<td>0.22</td>
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</tbody>
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In comparison, the central pyridine group is forming a H-bond with the periperical pyridine group of a neighboring molecule in the perpendicular arrangement, when only four molecules are considered, Figure 5b. It should be noticed that the electrostatic plot shows an incomplete “kebab” in the proximity of the nitrogen atom of each terpyridine groups, which underlines the weakness of this bond. The calculations presented in Figure 5c reveal that the central pyridine group is not involved in H-bonding when the tetramer periodic images are chosen to interact between each other to mimic the monomer periodic structure experimentally observed in Figure 3. The calculated gas-phase close-packed and perpendicular configurations are in good agreement with experimental observations, Table 1. The perpendicular configuration does, however, present some slight differences. These are probably induced by the molecular distortion, which leads to a noticeable nonplanar configuration. The presence of a surface is expected to reduce this effect and limit the variation of molecular

<table>
<thead>
<tr>
<th>structure</th>
<th>parallel</th>
<th>perpendicular</th>
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</thead>
<tbody>
<tr>
<td>energy (eV) (PBE)</td>
<td>-1.16</td>
<td>-1.06</td>
</tr>
<tr>
<td>BSSE energy (eV)</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td>$E_{\text{coh}}$ (eV)</td>
<td>-0.29</td>
<td>-0.27</td>
</tr>
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</table>
CONCLUSION

In this paper we investigated the two-dimensional self-assembly of 4,4′-(1,4-phenylene)bis(2,2′:6′,2″-terpyridine) on a graphite surface. Molecules adopt a side-by-side arrangement inside the monolayer but are arranged perpendicular to the domain boundary. Experimental observations and calculations reveal that the molecules form a close-packed structure stabilized by double and single hydrogen-bonds. Calculations show that the molecular configuration is less planar in the perpendicular molecular packing than in the molecular parallel packing. The flexibility of terpyridine groups open new opportunities to engineer new organic nanoarchitectures on surfaces.

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Notes
The authors declare no competing financial interest.

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REFERENCES

