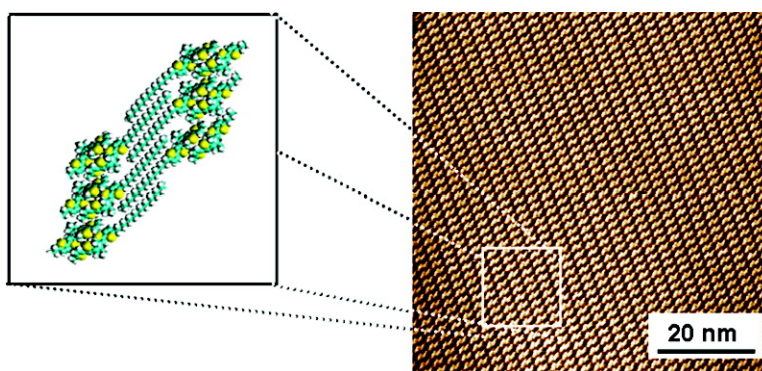


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## Locking of Helicity and Shape Complementarity in Diarylethene Dimers on Graphite

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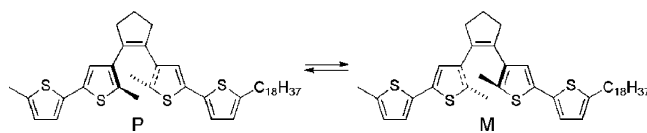
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Induction of helical chirality in achiral condensed phases is of high importance in various fields, including liquid crystalline technology.<sup>1</sup> It is, however, still not well understood how helical chirality is obtained, enhanced, modulated, or preserved in supramolecular systems.<sup>2</sup> Interfacial assemblies provide model systems to study these phenomena because of geometrical restrictions introduced by 2D confinement.<sup>3</sup> Scanning tunneling microscopy (STM) investigations of surface-induced chirality in organic monolayers of achiral compounds<sup>4</sup> have shown that, at interfaces, the formation of a chiral element arises either from molecule–substrate interactions imposing a twist between the lattice of the physisorbed molecules and the surface<sup>4a</sup> or from specific intermolecular interactions such as H-bonding<sup>4b</sup> or metal/ligand complexation<sup>4c</sup> which create supramolecular nanostructures.<sup>5</sup> Recently, helical shape recognition between enantiomers has also been evidenced for rigid molecules such as helicenes<sup>6</sup> or tetracenes.<sup>7</sup> In these cases, the physisorption of molecules with a rigid helicity, in vacuum and at low temperature, followed by shape recognition led to the formation of multimeric nanostructures.

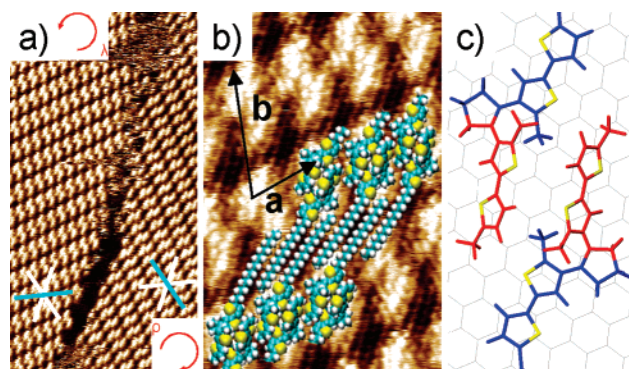
In this contribution, we show that helical chirality emerges from an achiral solution of a flexible diarylethene derivative because of atropisomerism on the surface.<sup>8</sup> Atropisomerism occurs because the rotational interconversion between two preferred conformers is sterically hindered on the surface. Moreover, we show that shape recognition occurs between atropoisomers having similar helicities and leads to the formation of homochiral dimers.

In solution, diarylethenes such as molecule **1** (Figure 1) are free to adopt a number of energetically similar conformations. In their preferred conformations, the two methyl groups grafted on the thiophene at the center of the conjugated unit are pointing in either the same direction (parallel orientation)<sup>9</sup> or in opposite directions (antiparallel orientation). In the latter case, the overall conformation of the molecule is helical, and depending on the sign of the helix, the conformers are described as P or M isomers.<sup>10</sup> However, in solution and at room temperature (rt), the interconversion between P and M helices is so fast that these forms cannot be distinguished. Under these conditions, a solution of diarylethene **1** in 1-phenyloctane is consequently achiral.<sup>8</sup>

After application of a drop of solution of **1** in 1-phenyloctane onto highly oriented pyrolytic graphite (HOPG), a well-ordered monolayer is formed over a few hundreds of nanometers. Figure 2a shows an STM image in which two different domains of the monolayer have a comparable orientation with respect to the scanning direction. In each of these domains, STM highlights the formation of (homochiral, *vide infra*) molecular dimers (see also Figure 2b). These domains are not equivalent because the sigmoidal-



**Figure 1.** Schematic representation of the interconversion occurring at room temperature between P and M conformers of diarylethene **1** in solution. The synthesis of **1** is described in the Supporting Information.

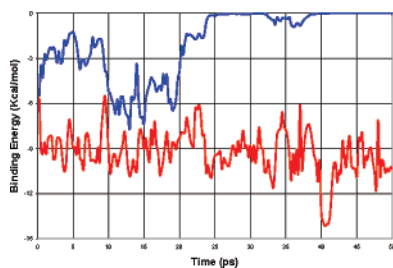


**Figure 2.** (a) Enantiomorphic domains ( $\lambda$  and  $\rho$ ) formed by diarylethene-based dimers. The orientations of the main crystallographic axes of graphite are schematically represented by white lines. The relevant reference axis for the respective domains is indicated in blue:  $52.5 \times 27.3 \text{ nm}^2$ , 24 pA,  $-322 \text{ mV}$ . (b) High-resolution image and proposed packing model obtained by force-field calculations:  $9.55 \times 6.30 \text{ nm}^2$ , 35 pA, 311 mV. (c) A dimer on HOPG. The blue parts of the molecules are those directly adsorbed on HOPG. The red ones correspond to the moieties which are not directly adsorbed.

shaped dimers which constitute them are mirror images. Besides the formation of locally chiral monolayers, it is remarkable that **1** forms chiral dimers on the surface. Surface-induced molecular dimers arranged in rows have already been observed on HOPG, on Au(111), and on MoS<sub>2</sub>.<sup>11</sup>

Within a dimer, the length of the bright contrast features ( $\sim 1.5 \text{ nm}$ ) corresponds to the length of an individual conjugated head ( $\sim 1.65 \text{ nm}$ ). Alkyl moieties are visible under the aspect of straight lines in the darker regions. The corresponding unit cell ( $a = 1.7 \pm 0.1 \text{ nm}$ ,  $b = 3.0 \pm 0.1 \text{ nm}$ ,  $\alpha = 61 \pm 3^\circ$ ) contains one dimer. The angle between the unit cell vector **a** and main symmetry axes of HOPG is  $+20 \pm 3^\circ$  ( $\rho$ ) or  $-20 \pm 3^\circ$  ( $\lambda$ ), depending on the chirality of the domain, indicating that the self-assembly is surface-mediated.

The size of the structures observed in high-resolution STM images (Figure 2b) rules out the possibility that the molecules physisorb in the parallel conformation because the overall length of **1** adsorbed in parallel orientation would be consistently smaller than observed.<sup>9,12</sup> Also, because of its folded geometry, the parallel



**Figure 3.** Molecular dynamics trajectory showing the molecule–molecule binding energy for two types of dimers (heterodimers PM and homodimers PP) on HOPG, at room temperature, extracted from the total energy of the system. Blue line: PM dimer. Red line: PP dimer. The curve shows that, after 20 ps, the heterodimer dissociates, whereas the homodimer remains stable.

**Table 1.** Average Molecule–Molecule Binding Energy and Standard Deviation for the Two Dimers on Graphite, Based on the MD Simulations Shown in Figure 3

dimer	binding energy (kcal/mol)	STD (kcal/mol)
PM	−1.85	2.21
PP	−9.27	1.45

conformer is unlikely to allow for stabilizing molecule–molecule or molecule–substrate interactions. Moreover, as all experiments are carried out in the dark, we exclude that **1** adsorbs in a photoisomerized form. We therefore assume that **1** exclusively physisorbs in its antiparallel conformation on HOPG.

Dimer formation, as observed experimentally, suggests that an energetically favorable interaction occurs between either prochiral (PM/MP) or chiral (PP and MM) pairs of adsorbed molecules. In order to understand the stereochemistry of these dimeric building blocks, molecular dynamics (MD) have been performed for PP and for PM dimers on the HOPG surface, at rt and in a dry situation, that is, without solvent molecules.<sup>13</sup> The calculations show a dissociation of the prochiral dimer on the surface, while the chiral dimer remains intact, due to favorable interactions between the molecules and the surface; for example, the alkyl chains can be fully adsorbed on graphite and among the molecules themselves. In order to evaluate the strength of the interactions between the molecules, the molecule–molecule binding energy for homodimers and heterodimers on HOPG (Figure 3) has been extracted from the total energy of the system (including the surface binding energy), over a MD trajectory of 50 ps. From these curves, it appears that on graphite the PP dimer is clearly more stable than its PM counterpart, which dissociates after 20 ps. High-temperature simulations at 400 K confirmed this trend. Table 1 summarizes these results by showing the average binding energy and the standard deviation for the two types of dimers. A detailed analysis of the components of the binding energies of the dimers shows that the main difference in their stability arises from weak van der Waals interactions acting between the two helices. Therefore, we propose that the difference of stability between the dimers is due to a better locking between the conjugated heads of the molecules in the PP (and MM) dimers rather than from a better adsorption of the alkyl chains on the surface of HOPG. This means that both the molecular locking, in terms of relative position of the helices (which determine the shape of the dimer), and the binding energy depend on the details of the molecular geometries. The fact that PP and MM dimers are the most stable dimers added to the fact that the two domains of Figure 2a are mirror images and form an angle which is not 60° with respect to each other suggest that these domains are formed by either PP or MM dimers.

These conclusions on stability of the prochiral or chiral dimers of **1** have been further confirmed by MD simulations including solvent molecules. For this, the solvent was introduced in the model by adding two layers of solvent molecules on the top of the surface and by using the dielectric constant of 1-phenyloctane. The results show that both dimers are stabilized by a few kcal/mol due to the presence of the solvent molecules. However, since the stabilization is comparable for both dimers, the PP dimer remains significantly more stable than the PM dimer. For the latter, the kinetics of the dissociation slows down, probably due to a cage effect of the solvent molecules. Finally, an additional indication about the structure of the dimer building block of the monolayer arises from the fact that with PM dimers it is not possible to build a monolayer matching the structure observed with STM. In contrast, the monolayer of PP dimers as modeled by force-field simulations is in good agreement with the experiment.

In conclusion, we have shown that chiral domains are formed at the liquid/solid interface by achiral diarylethenes because of surface-induced atropisomerism. On the surface of HOPG, these molecules with a locked helicity form dimers by shape complementarity. Molecular dynamics show that these dimers of diarylethenes are chiral dimers (PP and MM), rather than prochiral dimers (PM and MP). These results add to our understanding of how chirality can emerge in 2D systems.

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**Supporting Information Available:** Synthesis and characterization of **1**, schematic representation of its parallel conformation, and description of STM experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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