The Photoisomerization of Self-Assembled Monolayers of Azobiphenyls: Simulations Highlight the Role of Packing and Defects.

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SUPPORTING INFORMATION

Computational details.
The MM force field used in our calculations was the OPLS/AA [1] as implemented in TINKER [2]. In particular, the following functional form was used:

\[
E_{MM} = \sum_{\text{bond}}^{K_r} (R - R_0)^2 + \sum_{\text{angles}}^{K_\alpha} (\alpha - \alpha_0)^2 + \sum_{\text{improp. tors.}}^{K_\delta} (\delta - \delta_0)^2 + \sum_{\text{dihed. n=1}}^{4} \frac{C_n}{2} [1 + \cos(n\delta)]
+ \sum_{i<j}^{\text{atoms}} \frac{q_i q_j}{R_{ij}^2} + \sum_{i<j}^{\text{atoms}} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{R_{ij}} \right)^6 \right]
\]

where the first line describe the bonding interactions, and the second line the non bonding terms.

With respect to the OPLS/AA force field, some parameter were modified or added, mainly following the work of Pipolo et al [3] for the ABPT molecule and that of Vlugt et al [4] for the interaction with the gold atoms: these parameters are shown in Table S1 and S2. The Au atoms were frozen during the dynamics simulations: the Au-Au interactions were therefore not considered.

The MD simulations for the full MM systems where performed with the TINKER program package [2], using periodic boundary conditions. For all the four systems considered (all-trans, all-cis, one-trans and one-cis, see the main text) the dynamics were run for a total time of 10 ns at 300 K, with an integration time step of 1 fs. The first part of the MD, showing a drift in the total energy, was eliminated, keeping only the last 6, 3, 6, and 5 ns for all-trans, all-cis, one-trans and one-cis, respectively.

The QM/MM calculations were performed with our development version of the MOPAC2002 program [6], connected to TINKER for the treatment of the MM part. The QM moiety (see Figure 1) was described by the FOMO-CI method, using a semiempirical AM1 Hamiltonian reparameterized for azobenzene [7], which has proven to reproduce very accurately experimental and high-level ab initio data for that chromophore. No further reparameterization was attempted in the present case also because the absorption spectra of trans and cis ABPT are very similar to those of azobenzene [8, 9].

The electrostatic embedding was adopted and the QM-MM link was described using the “connection atom” approach of Antes and Thiel [10, 11]. In the QM/MM dynamics the periodic boundary conditions were not used; for this reason, the motion of selected carbon atoms belonging to the ABPT molecules located on the borders of the slab was restrained by applying a 3D harmonic potential. The QM/MM ground state equilibrations were performed at 300 K with the Bussi Parrinello thermostat.
Table S1: MM force field: parameters for bonded interactions. Presented are the parameters added/modified with respect to the standard OPLS/AA force field, as implemented in TINKER [2]. CB labels the “bridge” carbon atoms connecting the two phenyl rings. $R_0$ in Å, $K_r$ in kcal mol$^{-1}$ Å$^{-2}$, $\alpha_0$ in degrees, $K_\alpha$ in kcal mol$^{-1}$ rad$^{-2}$, $C_1$-$C_4$ in kcal mol$^{-1}$.

<table>
<thead>
<tr>
<th>Bond Stretching</th>
<th>$R_0$</th>
<th>$K_r$</th>
<th>Source</th>
</tr>
</thead>
</table>
| N N             | 1.2459  | 1385.1   | from ref. [3]|}
| C N             | 1.4124  | 567.94   | from ref. [3]|}

<table>
<thead>
<tr>
<th>Angle Bending</th>
<th>$\alpha_0$</th>
<th>$K_\alpha$</th>
<th>Source</th>
</tr>
</thead>
</table>
| C CB CB C       | 117.271     | 103.24     | from ref. [3]|}
| C C N N         | 119.127     | 87.204     | from ref. [3]|}
| C C S S         | 120.0       | 70.0       |              |

<table>
<thead>
<tr>
<th>Dihedral</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
<th>Source</th>
</tr>
</thead>
</table>
| C CB CB C       | 0.100     | -0.956    | 0.0167    | 0.394     | from ref. [3]|}
| C C N N C       | 0         | -40.0     | 0         | 0         |              |}

Table S2: MM force field: parameters for nonbonded interactions. Presented are the parameters added/modified with respect to the standard OPLS/AA force field, as implemented in TINKER [2]. CB labels the “bridge” carbon atoms connecting the two phenyl rings. CS and CN label the carbon atoms directly linked to S and N, respectively. $\sigma$ in Å, $\epsilon$ in kcal/mol, charges in a.u.

<table>
<thead>
<tr>
<th>Lennard Jones</th>
<th>Site</th>
<th>$\sigma$</th>
<th>$\epsilon$</th>
<th>Source</th>
</tr>
</thead>
</table>
| S               | 4.45 | 0.25     |             | from ref. [4]|}
| CS              | 3.50 | 0.066    |             |              |

<table>
<thead>
<tr>
<th>Pair</th>
<th>Site</th>
<th>$\sigma$</th>
<th>$\epsilon$</th>
<th>Source</th>
</tr>
</thead>
</table>
| S Au            | 2.400| 8.4650   |             | from ref. [4]|}
| CS Au           | 3.365| 0.1373   |             |              |
| CAu             | 3.173| 0.0640   |             | from ref. [5]|}
| HAu             | 2.746| 0.0414   |             | from ref. [5]|}
| NAu             | 3.225| 0.1630   |             |              |

<table>
<thead>
<tr>
<th>Electrostatic</th>
<th>Atom</th>
<th>Charge</th>
<th>Source</th>
</tr>
</thead>
</table>
| N               | 0.25 | from ref. [3]|}
| CN              | 0.25 | from ref. [3]|}
| CB              | 0.0  | from ref. [3]|}
| CS              | 0.18 |             |              |
| S               | -0.18|         |              |

[12], starting from geometries sampled from the MD simulations referred above and using a time step of 0.1 fs. The same integration time step of 0.1 fs was also employed in the QM/MM surface hopping nonadiabatic dynamics simulations (both for the nuclear and for the electronic degrees of freedom). The quantum decoherence was approximately taken into account using our energy based correction (EDC), with $C = 1.0$ hartree [13].
Figure S1: Snapshot of the unit cell of the all-trans SAM, side view. The Au atoms are shown as dots, the S atoms are larger yellow circles. The 12 rows of ABPT molecules are clearly distinguishable.

Figure S2: Snapshot of the unit cell of the all-cis SAM. The Au atoms of the upper layer are shown as small dots, the S atoms as larger yellow circles. Left panel: side view. Right panel: top view. In the latter case, the lower phenyl rings are in blue, the azobenzene moieties in green and the upper phenyl rings in purple.
Figure S3: Distributions of the tilt angle $\theta$ for the rows of the all-trans SAM. The distributions are built as histograms taking account all molecules in each row and all time steps of the MD simulation starting from $t = 4$ ns. The numbering of the rows is the same as in Fig. 2.
Figure S4: Distributions of the tilt orientation angle $\phi$ for the rows of the all-trans SAM. The distributions are built as histograms taking account all molecules in each row and all time steps of the MD simulation starting from $t = 4$ ns. The numbering of the rows is the same as in Fig. 2.
Figure S5: Electronic energy difference (eV) between $S_1$ and $S_0$ versus CNNC dihedral (degrees) at hopping points. Excited ABPT molecule in row 6. Positive values of the energy difference for $S_1 \rightarrow S_0$ hops and negative values for backward $S_0 \rightarrow S_1$ hops. Green: reactive (i.e. isomerizing) trajectories. Red: trajectories not giving rise to isomerization.

Figure S6: Electronic energy difference (eV) between $S_1$ and $S_0$ versus CNNC dihedral (degrees) at hopping points. Excited ABPT molecule in row 3, 4 or 5. Positive values of the energy difference for $S_1 \rightarrow S_0$ hops and negative values for backward $S_0 \rightarrow S_1$ hops.
References


