THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

Low-Threshold Reversible Electron-Induced and Selective Photoinduced Switching of Azobenzene Derivatives under Ambient Conditions

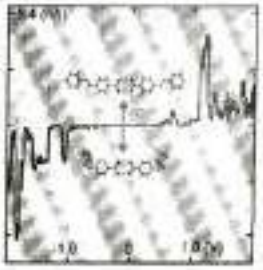
Khushboo Yadav,[†] Sayantan Mahapatra,[†,‡] Thomas Halbritter,[§,∥] Alexander Heckel,[§] and Thiruvancheril G. Gopakumar[*,†]

[†]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India

[§]Institute for Organic Chemistry and Chemical Biology, Goethe-University Frankfurt, Max-von-Laue-Str. 9, 60438 Frankfurt, Germany

Supporting Information

ABSTRACT: Mono-carboxyl-functionalized azobenzene and arylisopyrazole have been employed for electron-induced and photoinduced switching under ambient conditions. The microscopic structure and the switching behavior is understood using scanning tunneling microscopy. The carboxyl functional group in these molecules offers low threshold energy for the electron-induced reversible switching compared with nonfunctionalized azobenzene. The low threshold is understood using charged intermediate states during the switching. A selectivity has been observed for the photoinduced switching. Because of strong hydrogen bonding, only the five phenyl groups in the molecules change their configuration.



Molecules that possess interchangeable electronic states (associated with configurations of molecules) are possible switches for future molecular electronics. Azobenzene (AB) and its derivatives form a unique class of photoactive molecules and undergo reversible cis−trans isomerization upon illumination of light[1−3] and hence have the ability to convert light into molecular mechanical motion.[4] AB derivatives have also been demonstrated as smart adsorbents with photoregulated gates.[5,6] The associated electronic structure of these two states (cis and trans), particularly when adsorbed on surface, makes these type of molecules as molecular switches.[7,8] Several derivatives of AB have revealed molecular level switching on surfaces by light,[9−15] electric field,[17] and tunneling electrons.[8,16,17]

Under ultrahigh vacuum (UHV) and using low-temperature scanning tunneling microscopy (STM), switching (trans−cis isomerism) of several AB derivatives has been understood at the molecular level.[8,10,11,13−16] Certain efforts have also been made for switching of AB derivatives at the solid/liquid interface[18−22] and at the solid/air interface.[23,24] It would be interesting to achieve controllable switching of AB derivatives under ambient conditions from the point of view of its applicability at room temperature. For this, rigid adlayers of AB derivatives stabilized through strong intermolecular interactions may be of importance. Molecules with carboxyl functional groups are known for the formation of stable adlayers through dimer hydrogen bonding. In contrast with AB, the functionalization of AB with carboxyl group leads to well-defined growth of molecular islands on highly oriented pyrolytic graphite (HOPG) stabilized via carboxyl hydrogen bonding.[25]

In this Letter, we report the reversible electron- and light-induced switching of 4-(phenylazo) benzoic acid (PABA) and 4-((1,3,5-trimethyl-1H-pyrazol-4-yl)diazenyl) benzoic acid (PyABA) (cf. Figures 1a and 2a) on HOPG/air interface using STM. Compared with AB, PABA and PyABA show low threshold voltage for electron-induced switching. This is attributed to a stable charged electronic state of the molecules and is stabilized most likely due to the presence of the functional group. Whereas the photoinduced switching of PABA shows a periodicity along a molecular row of its adlayer, PyABA shows switching of all molecules. In addition, the strong intermolecular interaction (due to the carboxyl group) offers a selectivity in the part of the molecules, which is switching.

Figure 1b depicts the constant current STM topography of ultrathin film (prepared from solution by drop-casting) of trans-PABA molecules on an HOPG basal plane. A mesh-averaged image (according to Hercas et al.[26]) is shown in the inset of Figure 1b. Scaled trans-PABA molecules are superimposed on the averaged image in Figure 1c. The ground state of PABA at room temperature is the trans state and therefore

Received: September 18, 2018
Accepted: October 16, 2018
Published: October 16, 2018

DOI: 10.1021/acs.jpclett.8b02871
J. Phys. Chem. Lett. 2018, 9, 6326−6331