Supporting Online Material for

Creating Favorable Geometries for Directing Organic Photoreactions in Alkanethiolate Monolayers

Moonhee Kim, J. Nathan Hohman, Yang Cao, Kendall N. Houk,* Hong Ma, Alex K.-Y. Jen,* Paul S. Weiss*

*To whom correspondence should be addressed. E-mail: houk@chem.ucla.edu (K.N.H.); ajen@u.washington.edu (A.K.-Y.J.); psw@cnsi.ucla.edu (P.S.W.)

Published 11 March 2011, Science 331, 1312 (2011)
DOI: 10.1126/science.1200830

This PDF file includes:

Materials and Methods
SOM Text
Figs. S1 to S3
References
Materials and Methods

Materials

9-(4-mercaptophenylethynyl)anthracene (MPEA) and disulfide PEA were synthesized as described previously (1-3). Ultraviolet (UV)-visible spectra of MPEA (100 µM in ethanol) and disulfide PEA (100 µM in tetrahydrofuran) in solutions were collected by using a Evolution 600 UV-Vis spectrometer (Thermo scientific, West Palm Beach, FL). Disulfide PEA shows only a single absorbance at 280 nm (spectra not shown), in contrast to three peaks (383, 401, and 421 nm) of MPEA as shown in Fig. S1.

Calculation

Density functional theory calculations to determine the stable geometry and relative energies of MPEA in gas phase were performed with the Gaussian 03 program (4). Geometries for different dihedral angles of molecular conformations in the MPEA were optimized using the density functional theory with the B3LYP functional and the 6-31G(d) basis set (5).

SOM Text

Molecular Conformation Effect

9-(4-mercaptophenylethynyl)anthracene is composed of three π systems; an anthracene, an acetylene, and a thiophenol. The anthracene moiety and the mercaptophenyl ring are rotated about the ethynyl bond into the planar and orthogonal configurations between the planar (0º) and the orthogonal (90º) molecular conformations of MPEA.

Energy and conductivity vary as the anthracene and the mercaptophenyl rings rotate around the ethynyl bond. The relevant dihedral angle was scanned from 0º to 90º in steps of 10º and the geometry was optimized without further restrictions. Figure S2 shows the relative electronic energies and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The planar conformation has the lowest relative electronic energy and the smallest gap. The rotational barrier from the planar to the orthogonal conformation is 1.0 kcal/mol.

The calculated frontier molecular energy levels and corresponding orbital energies of MPEA in planar and orthogonal conformations are shown in Fig. S3. The energy gap between the HOMO and the LUMO for the planar MPEA (3.01 eV) is slightly smaller than for the orthogonal conformation (3.29 eV). The frontier molecular orbitals of the planar MPEA are fully delocalized along the entire molecule. In contrast, the frontier molecular orbitals of the orthogonal MPEA remain localized in either the anthracene (HOMO and LUMO) or the mercaptophenylethynyl backbone (HOMO–1 and LUMO+1).
Fig. S1. Ultraviolet-visible absorption spectra of 9-(4-mercaptophenylethynyl)anthracene (MPEA) in ethanol solution.
Fig. S2 The calculated electronic energy profile (A) and the energy gap (B) between the HOMO and the LUMO of MPEA as the function of relative ring orientations about the ethynyl bond.
Fig. S3 Frontier molecular orbitals and corresponding energy levels (HOMO–1, HOMO, LUMO, LUMO+1) of the planar (0º) and orthogonal (90º) conformations of MPEA. The gap energy between the HOMO and LUMO of the planar MPEA (3.01 eV) is smaller than that of the orthogonal MPEA (3.29 eV).
References

4. M. J. Frisch et al., *Gaussian 03, revision c.02* (Gaussian, Inc., Wallingford, CT, 2004).