Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

The Influence of Surface Proximity on Photoswitching Activity of Stilbene-Functionalized N-Heterocyclic Carbene Monolayers

Shahar Dery[+], Israel Alshanski[+], Evgeniy Mervinetsky[+], Daniel Feferman, Shlomo Yitzchaik, Mattan Hurevich*, and Elad Gross **

Institute of Chemistry and The Center for Nanoscience and Nanotechnology, The Hebrew University, Jerusalem 91904, Israel

Contents

1. Materials

All the solvents in this work were purchased from Bio-Lab and the chemical reagents from Sigma-Aldrich (Merck), unless stated otherwise.

2. Instrumentation

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed using an AXIS supra plus instrument (Kratos) with Al Kα (1486.6 eV) as the X-ray source. The binding energies were calibrated according to the core level (4f7/2) position of Au and Pt, located at 84.0 and 71.2 eV, respectively. XPS spectra analysis was performed with CasaXPS software.

Polarization modulation infrared reflection absorption spectroscopy

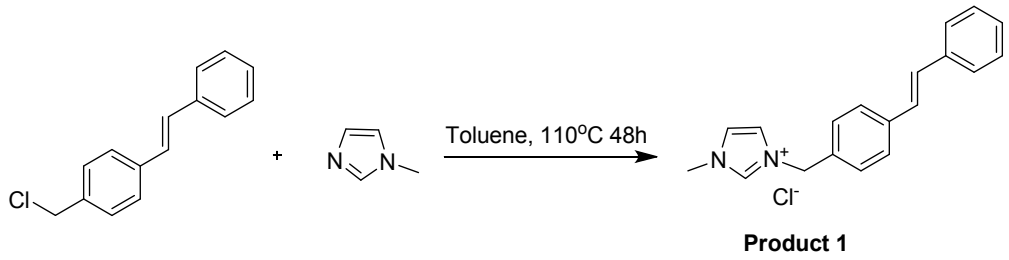
Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) measurements were conducted at room temperature under nitrogen atmosphere in a designated reflection absorption cell (Harrick Instruments, Inc.) with FTIR spectrometer (Vertex V70 with PMA-50, Bruker). Measurements were acquired with 1024 scans at a resolution of 4 cm^{-1} using mercury cadmium telluride (MCT) detector. In-situ PM-IRRAS measurements under UV irradiation were conducted by irradiation of the sample with UV LED (Prizmatix mic-LED; 365 nm; 1.0 mW/cm^2) for 20 min prior the IR measurement. FTIR measurements of thermal-isomerization were performed following 1 h of dark conditions.

Contact potential difference (CPD) measurements

Contact potential difference (CPD) measurements were conducted with Kelvin probe S (DeltaPhi Besocke, Jülich, Germany), with a vibrating reference gold electrode (work function = 5.1 eV) in a home-built Faraday cage under argon atmosphere. UV irradiation was carried out by using a UV LED (Prizmatix mic-LED; 365 nm; 1.0 mW/cm^2) coupled with optical fiber.

3. Synthesis

Synthetic procedure for preparation of Stilbene-NHC



Scheme S1: synthesis of product **1** conditions

200 mg (1 equiv.) of (E)-1-(chloromethyl)-4-styrylbenzene was dissolved in 5 mL of dry toluene. 110 µL (1.5 equiv.) of N-Methylimidazole were added to the solution and mixed for 48 hours at 110 °C. The product precipitated and the solvent was removed by decantation. The solid was rinsed twice with toluene, EtOAc and hexane and dried under vacuum. The reaction resulted a pure white solid with 84% yield and more than 99 % *trans* isomer which was analyzed by mass spectrometry and NMR spectrometry. ^{1}HNMR (DMSO, 500MHz): δ 9.25 (broad S, 1H), 7.82 (t, 1H), 7.73 (t, 1H), 7.65-7.68 (m, 2H), 7.60-7.63 (m, 2H), 7.42-7.45 (m, 2H), 7.36-7.42 (m, 2H), 7.25-7.32 (m, 3H), 5.43 (s, 2H), 3.87 (s, 3H). ^{13}CNMR (DMSO, 500MHz, analyses based on HSQC and HMBC)- 137.16, 129.79, 129.27, 129.22, 128.06, 127.43, 127.03, 124.5, 122.82, 52.05, 36.36. HRMS (ESI) calc d for C19H19N2+: 275.15 m/z found 275.19 and 585.28 C19H19N2+ corresponds to (M+) and (2M+ Cl^-) respectively

Table S1. N1s and C1s to metal4f XPS peaks area ratio for stilbene-NHC/Au and stilbene-NHC/Pt

	Stilbene-NHC/Au	Stilbene-NHC/Pt
N1s/Metal4f	1.96E-3	1.95E-3
C1s/Metal4f	2.36E-2	3.55E-2

Supplementary Figures

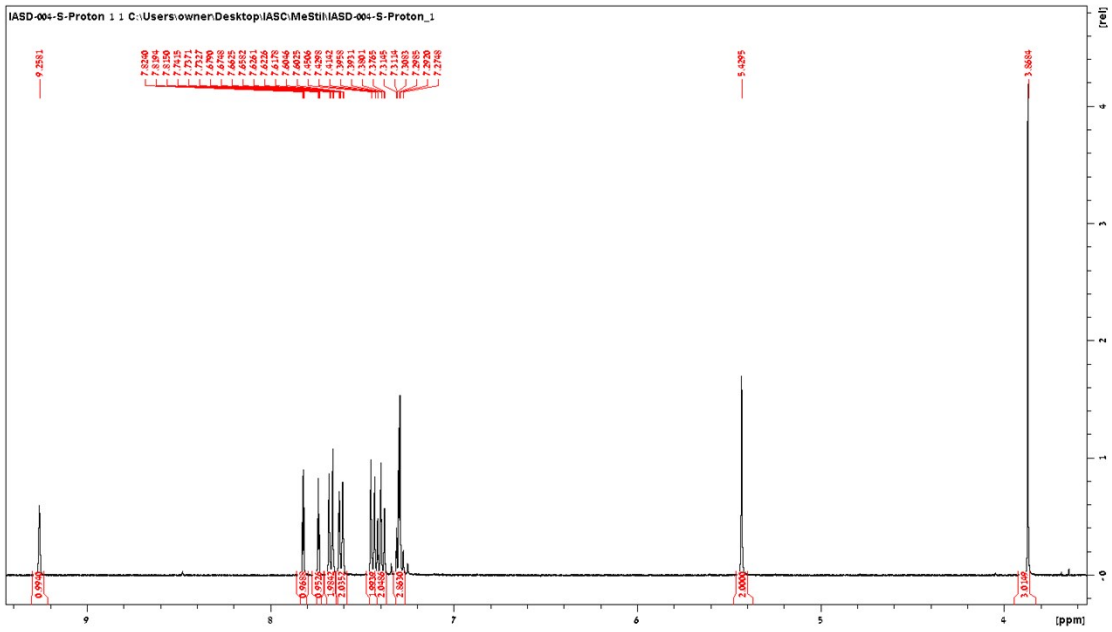


Figure S1: Proton NMR of product **1**

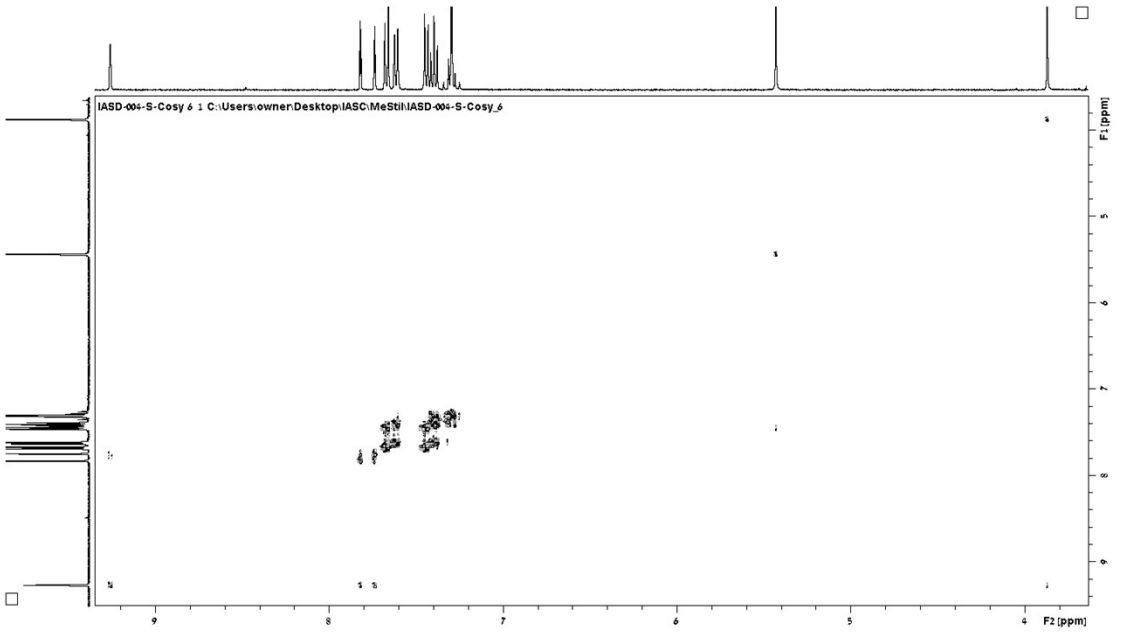


Figure S2: COSY NMR of product **1**

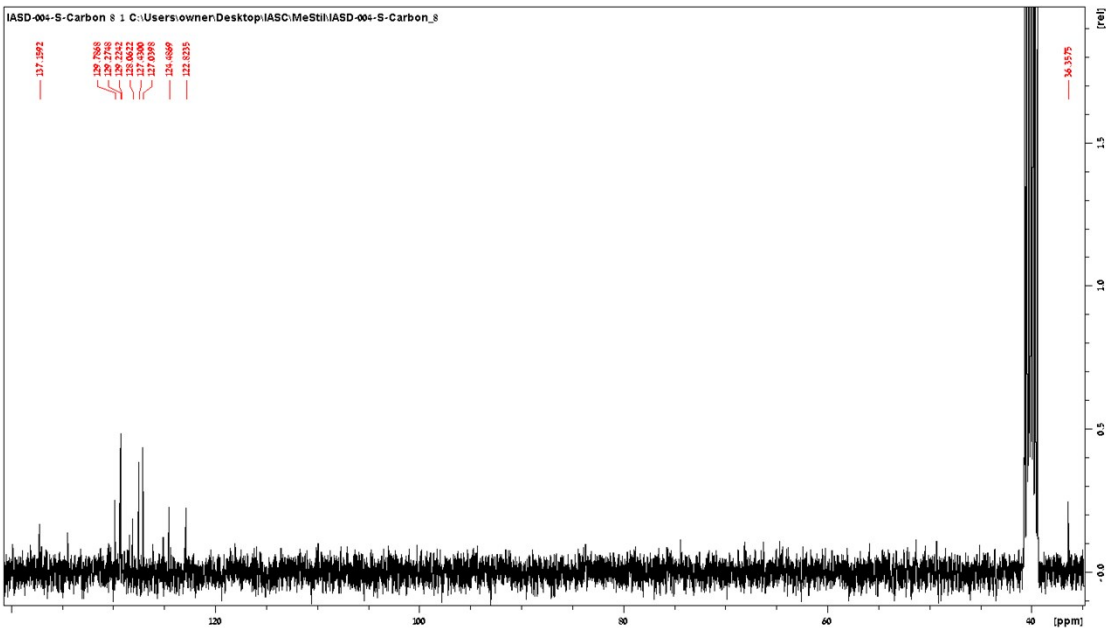


Figure S3: Carbon NMR of product **1**

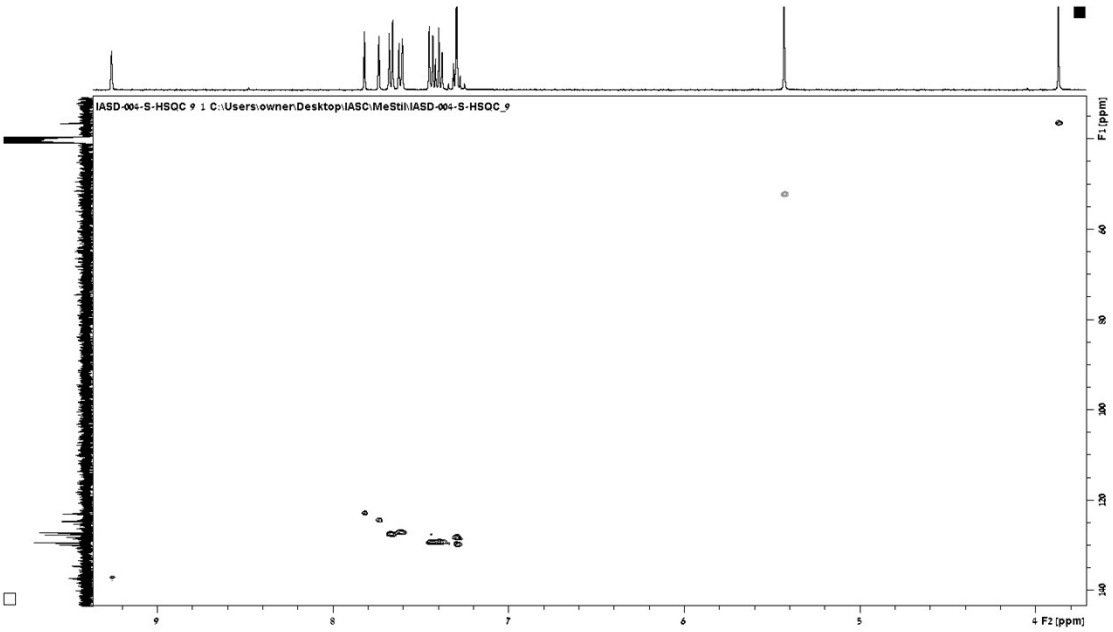


Figure S4: HSQC NMR spectrum of product **1**

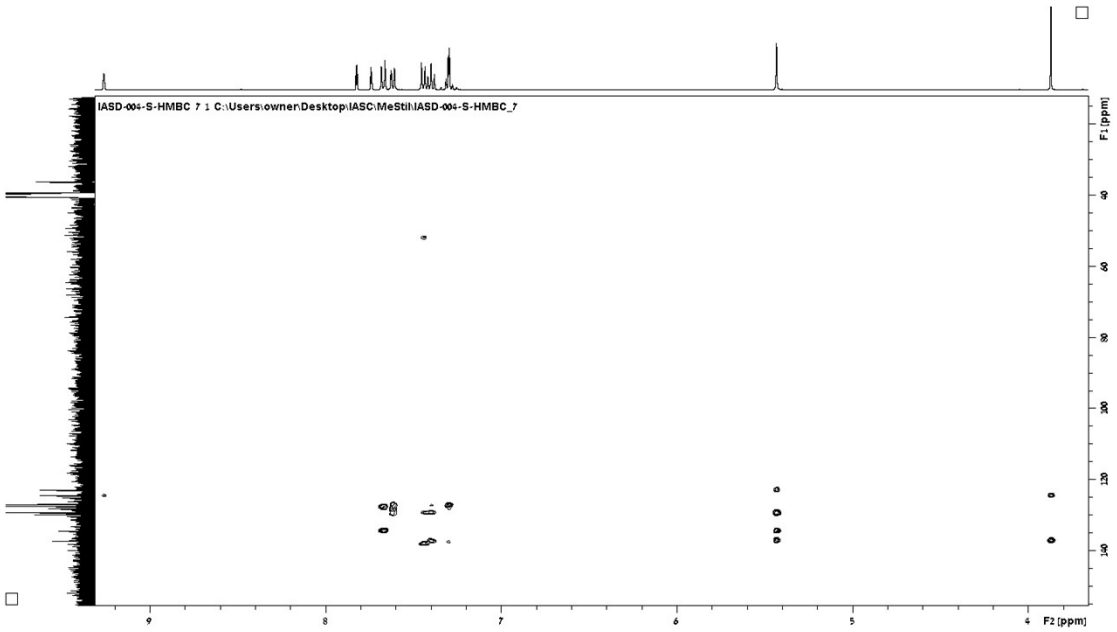


Figure S5: HMBC NMR spectrum of product **1**

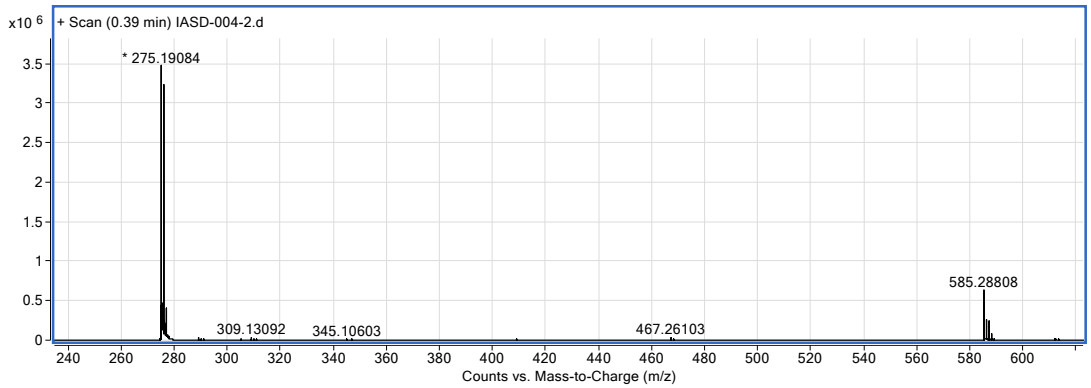


Figure S6: HRMS of product **1**. 275.15 m/z corresponds with M+ and 585.28 m/z corresponds with 2M+ Cl^-

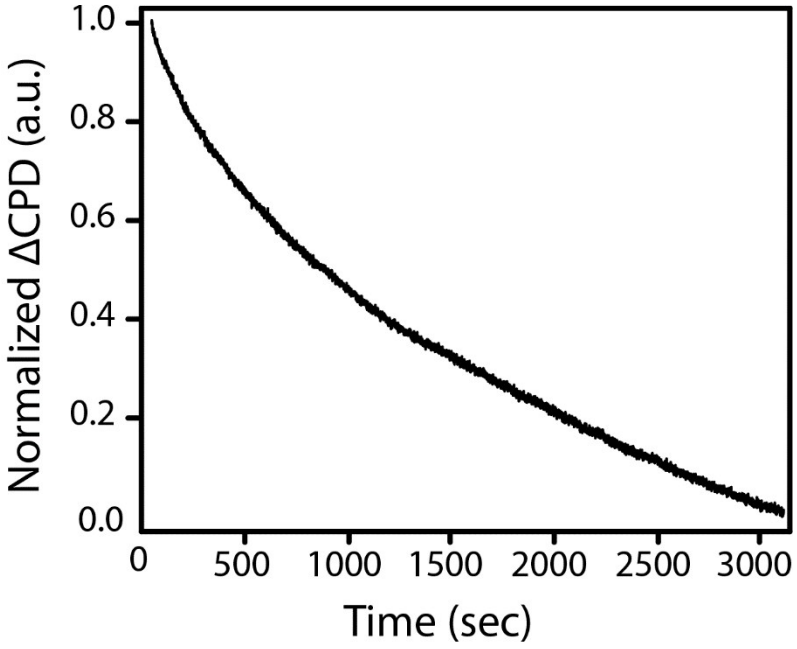


Figure S7. ΔCPD decay curve of thermal relaxation of Stilbene-NHC/Au

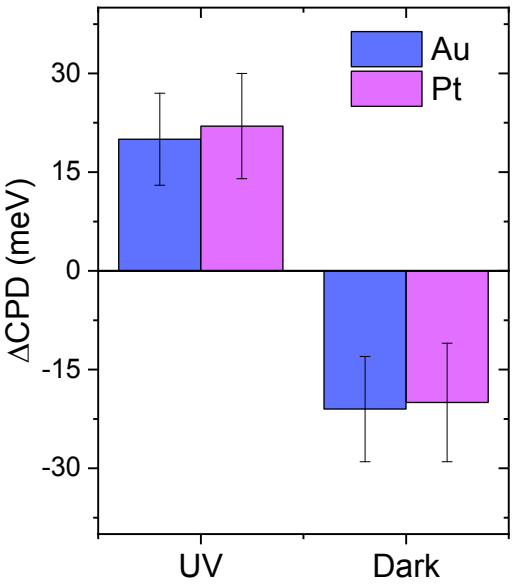


Figure S8. ΔCPD under UV irradiation and relaxation cycles of dimethyl-NHC monolayer on Au and Pt surfaces. Error bars represent the SD values measured based on three different UV/Dark cycles with three samples.