SUPPORTING INFORMATION

Spontaneous switching and fine structure of donor–acceptor Stenhouse adducts on Au(111)

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1. General Information

All chemicals were purchased as reagent grade from commercial suppliers (Merck, TCI) and used without further purification. The activated barbituric acid derivative was synthesized following the literature procedure.[1] The solvents used (Merck, ChemPur, PoCh) were of analytical grade quality. Methylene chloride (DCM) was dried over CaH_2 and distilled under an argon atmosphere. Toluene was pre-dried over molecular sieves type 3A, then further dried by heating with sodium and benzophenone, and subsequently distilled under an argon atmosphere. Deuterated solvents were purchased from Armar Chemicals or Eurisotop. Deionized water (18.3 MΩ·cm) was obtained from a Milli-Q station. Experiments were conducted at room temperature unless otherwise specified. The progress of organic reactions was monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F254 (0.2 mm) on alumina plates. The products were purified by column chromatography (CC) using Merck silica gel 60 (230-400 mesh ASTM). NMR spectra were recorded on a Bruker 400 MHz instrument and analyzed using MestReNova software. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, and coupling constants (J) in hertz (Hz). Quartz cuvettes were purchased from Hellma Analytics. Absorbance spectra were recorded using an Evolution220 spectrophotometer from Thermo Scientific and analyzed using Origin software. Photoswitching was achieved using a custom-made device. High-resolution ESI mass spectra were recorded on a SYNAPT spectrometer

2. Synthesis of thio-DASA
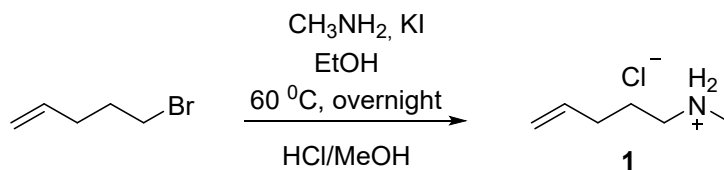
Synthesis of N-methylpent-4-en-1-aminium chloride (1): 5-Bromopentene (24.00 g, 154.00 mmol) was dissolved in the mixture of 33% solution of methylamine (300 mL in ethanol) and ethanol (150 mL). A small amount of KI was added (1.28 g, 7.71 mmol). The mixture was heated to 60 °C overnight and then cooled to 0 °C, acidified with 12 N HCl (pH < 2, 280 mL) and concentrated under vacuum. The residue was dissolved in 100 mL of water and the solution was evaporated. The procedure was repeated twice to remove traces of ethanol. The residue was dissolved in 120 mL of water and extracted with 220 mL of Et$_2$O. The aqueous solution was basified to pH > 12 with NaOH and extracted with Et$_2$O three times. The combined organic phases were dried over MgSO$_4$ and the mixture was carefully concentrated at 18 °C on a rotary evaporator. When a small amount of Et$_2$O was left, 240 mL of 1.25 M solution of HCl in MeOH was added and evaporated to dryness. The obtained gel was dissolved in a small amount of MeOH and precipitated with Et$_2$O. The residue was washed four times by Et$_2$O to afford the final product as a white solid **1** (18.00 g, 88 %).

^{1}H NMR (400 MHz, methanol-d_4): δ 5.83 (m, 1H), 5.12-5.01 (m, 2H), 2.99 (t, J = 7.9 Hz, 2H), 2.69 (s, 3H), 2.16 (q, J = 6.6 Hz, 2H), 1.8 (m, 2H). ^{13}C NMR (100 MHz, methanol-d_4): δ 136.48, 115.11, 48.49, 32.24, 30.06, 24.94.
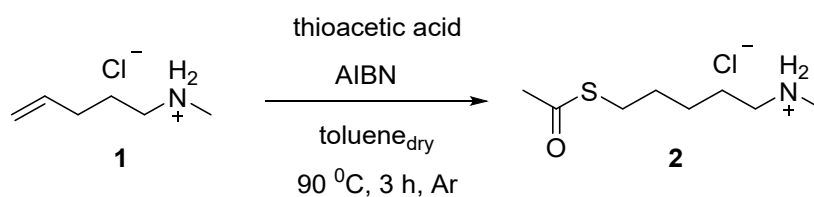
Synthesis of 5-(acetylthio)-N-methylpentan-1-aminium chloride (2): **1** (9.00 g, 66.35 mmol), AIBN (8.21 g, 50.00 mmol), thioacetic acid (21.03 g, 276.22 mmol), and 300 mL of dried toluene were added to a 500 mL round-bottomed flask under an argon atmosphere and heated at 90 °C for 3 hours. After 3 hours, the solvent was evaporated and the obtained slurry

was washed four times with Et$_2$O. The crude precipitate was recrystallized from EtOAc and washed several times with EtOAc to give a pure product as a white solid **2** (5.76 g, 41%).

^{1}H NMR (400 MHz, methanol-d_4): δ 2.98 (t, J = 8.2 Hz, 2H), 2.89 (t, J = 7.2 Hz, 2H), 2.69 (s, 3H), 2.30 (s, 3H), 1.75-1.58 (m, 4H), 1.46 (m, 2H). ^{13}C NMR (100 MHz, methanol-d_4): δ 196.06, 48.80, 32.19, 29.13, 28.85, 27.96, 25.20, 25.03.
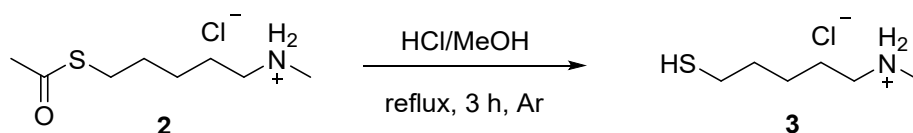
Synthesis of 5-mercapto-N-methylpentan-1-aminium chloride (3): **2** (5.60 g, 25.97 mmol) and 230 mL of 1.25 M HCl solution (259.70 mmol) in methanol were added to a 500 mL round-bottomed flask under an argon atmosphere and refluxed for 3 hours. Then the solvent was evaporated and the residue was washed with n-pentane three times. The product was obtained as a white solid **3** (4.65 g, 99%) after 1 day of drying in vacuum (slurry transformed to solid).

^{1}H NMR (400 MHz, methanol-d_4): δ 2.98 (t, J = 7.8 Hz, 2H), 2.69 (s, 3H), 2.53 (t, J = 7.1 Hz, 2H), 1.73-1.61 (m, 4H), 1.50 (m, 2H). ^{13}C NMR (100 MHz, methanol-d_4): δ 48.89, 33.04, 32.19, 25.23, 24.67, 23.19.
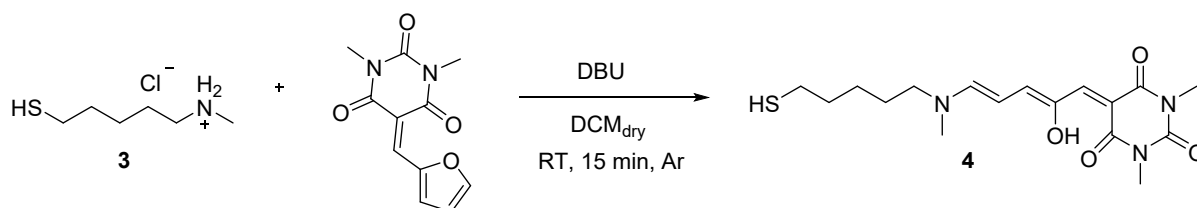
Synthesis of 5-((2Z,4E)-2-hydroxy-5-((5-mercaptopentyl)(methyl)amino)penta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4): To a solution of **3** (0.40 g, 2.36 mmol) in dry DCM (6 mL) was added activated barbituric acid derivative (0.72 g, 3.08 mmol) and DBU (560 μL, 3.75 mmol) under argon atmosphere at RT. The reaction mixture instantly turned deep purple. The mixture was stirred for 15 min in the absence of light. After that, contents were immediately transferred onto column chromatography on silica

(chloroform). The product was isolated by gradient elution starting with pure chloroform and ending with 1% v/v MeOH in chloroform and concentrated under vacuum. The obtained solid was dissolved in a small amount of chloroform and filtered through cotton in Pasteur pipette to remove the trace amount of silica gel. Finally, the product was precipitated by adding the ice-cold n-pentane and dried. The product was obtained as a dark purple solid **4 (thio-DASA)** (28.00 mg, 7%).

The product exists in two stable conformations due to restricted rotation around a carbon-nitrogen bond.[2] Conformer ratio: 2.6.

^{1}H NMR (400 MHz, methylene chloride-d_2)

Conformer 1 (major): δ 12.49 (s, 1H), 7.32 (d, J = 12.4 Hz, 1H), 7.11 (s, 1H), 6.81 (d, J = 12.4 Hz, 1H), 6.03 (t, J = 12.1 Hz, 1H), 3.44 (t, J = 7.1 Hz, 2H), 3.29 (s, 3H), 3.27 (s, 3H), 3.13 (s, 3H), 2.55 (q, J = 7.3 Hz, 2H), 1.67 (m, 4H), 1.42 (m, 2H).

Conformer 2 (minor): δ 12.49 (s, 1H), 7.27 (d, J = 12.2 Hz, 1H), 7.09 (s, 1H), 6.81 (d, J = 12.4 Hz, 1H), 6.07 (t, J = 12.1 Hz, 1H), 3.44 (t, J = 7.1 Hz, 2H), 3.29 (s, 3H), 3.27 (s, 3H), 3.26 (s, 3H), 2.55 (q, J = 7.3 Hz, 2H), 1.67 (m, 4H), 1.42 (m, 2H).

^{13}C NMR (100 MHz, methylene chloride-d_2)

Conformer 1 (major): 165.12, 162.94, 157.75, 151.74, 150.40, 146.43, 138.77, 102.45, 98.25, 59.43, 36.49, 33.34, 28.04, 27.93, 27.80, 24.90, 24.19.

Conformer 2 (minor): δ. 165.12, 162.94, 158.37, 151.74, 150.87, 146.43, 138.23, 102.52, 98.25, 51.14, 44.54, 33.46, 28.04, 27.93, 27.80, 25.93, 25.39.

HRMS (ESI) m/z: calc. for $C_{17}H_{26}N_3O_4S$: 368.1644 [M+H]$^+$; found: 368.1646.

3. Characterization of thio-DASA
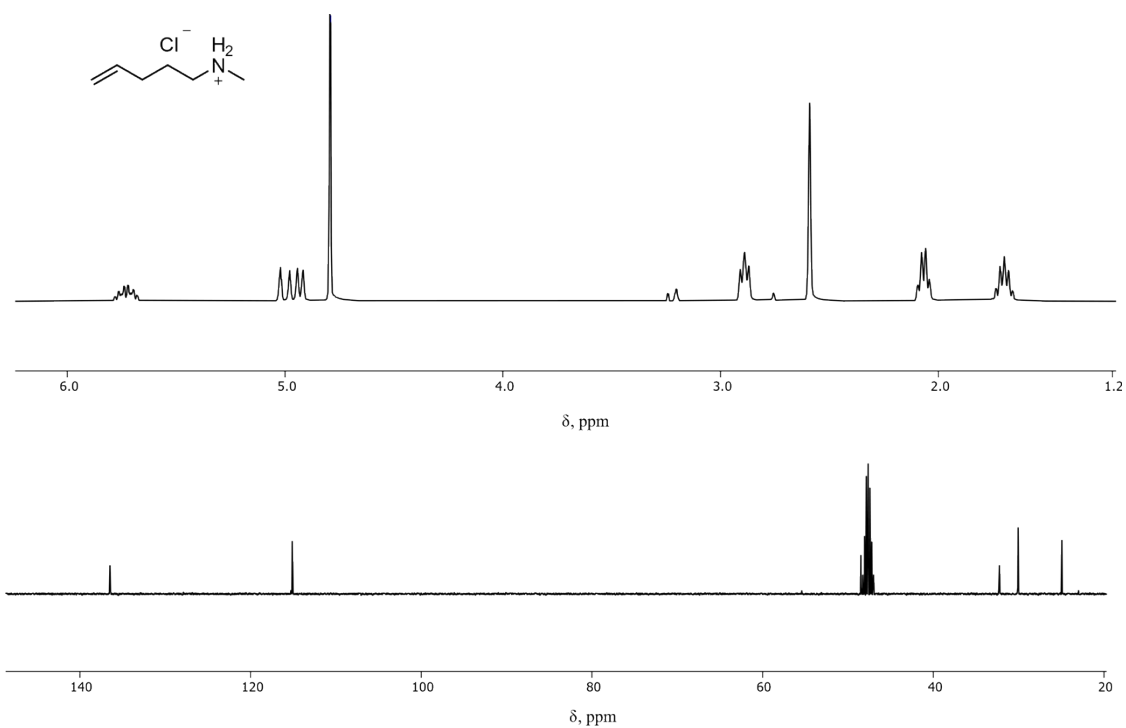

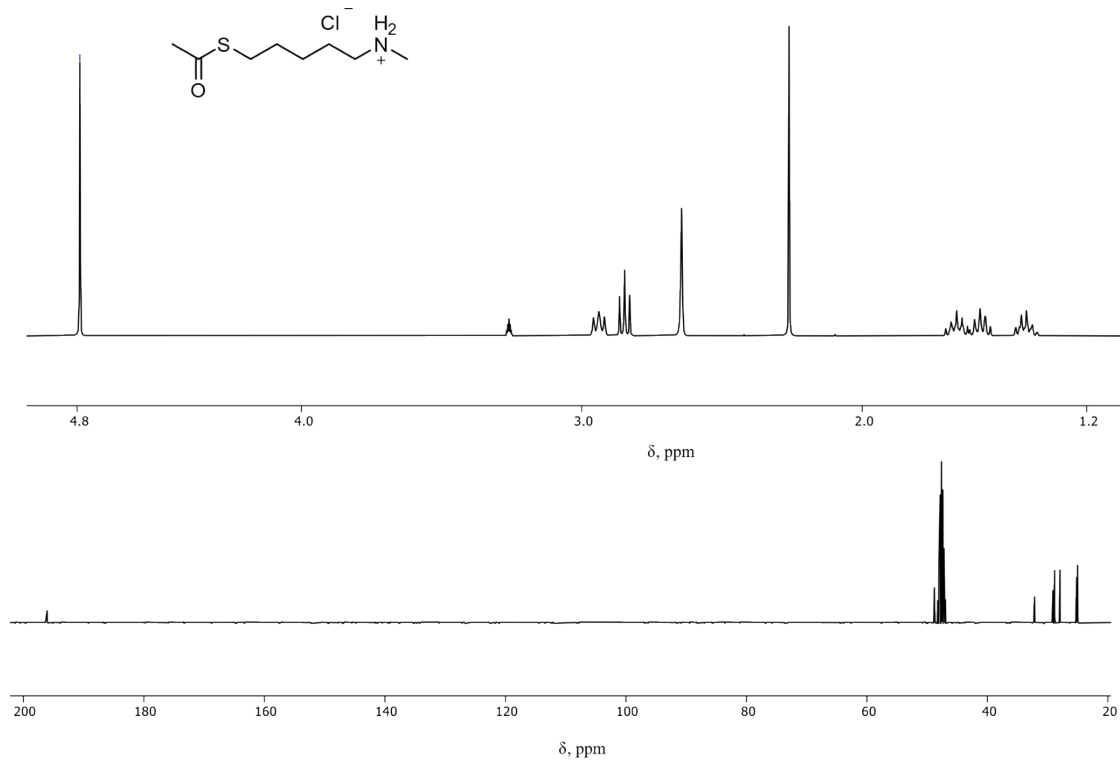Fig. S1 ^{1}H and ^{13}C NMR spectra of **1** in methanol-d_4, 298 K.

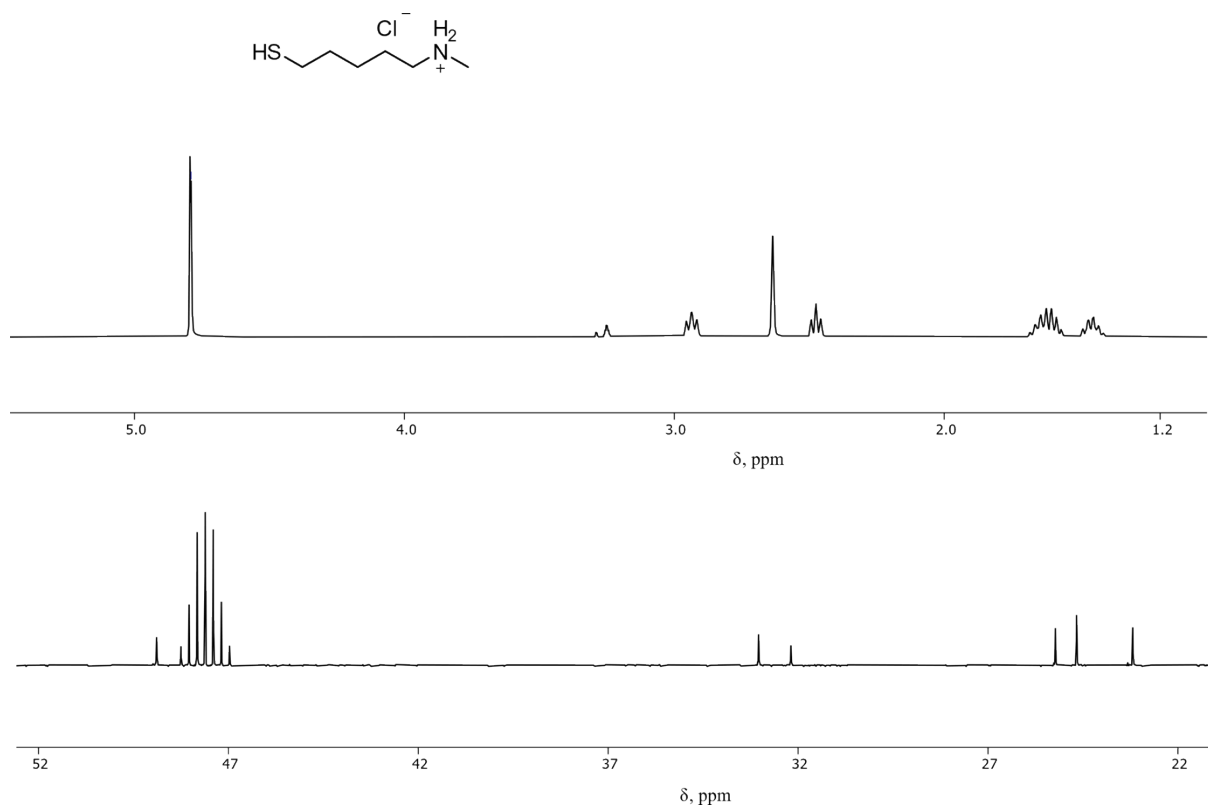Fig. S2 ^{1}H and ^{13}C NMR spectra of **2** in methanol-d_4, 298 K.

Fig. S3 ^{1}H and ^{13}C NMR spectra of **3** in methanol-d_4, 298 K.
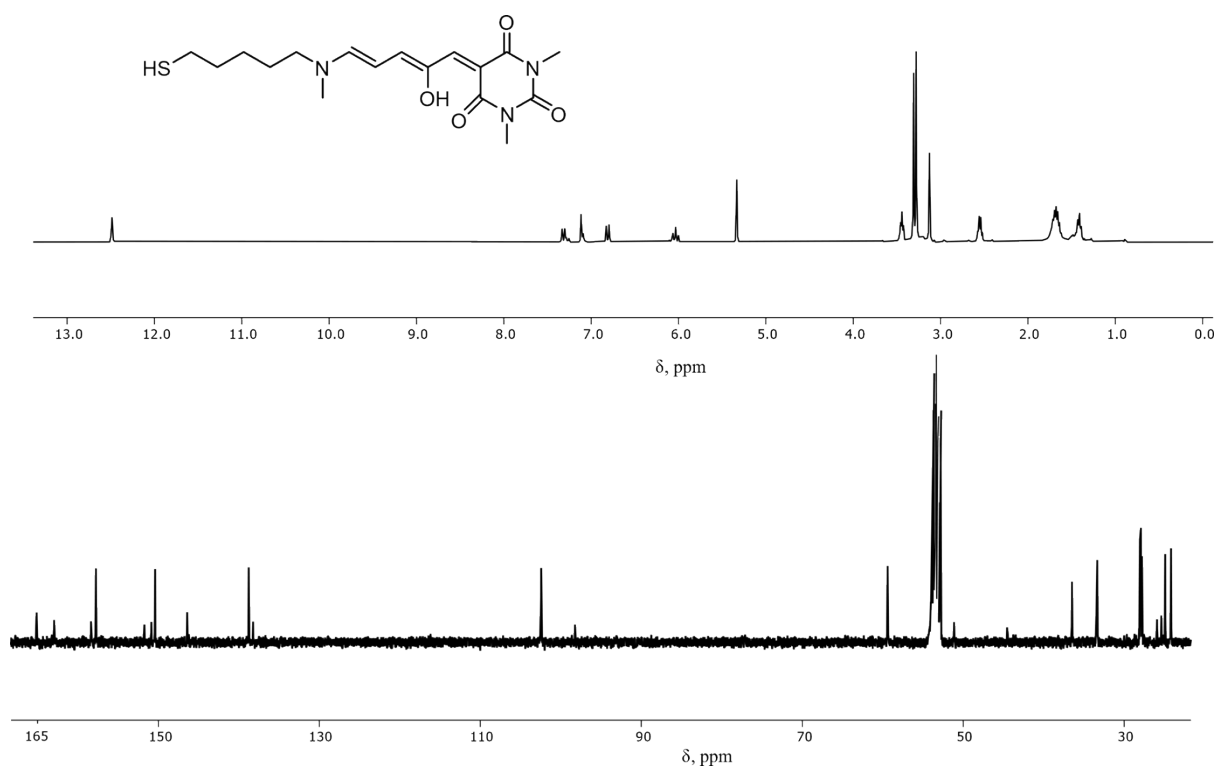

Fig. S4 ^{1}H and ^{13}C NMR spectra of DASA in methylene chloride-d_2, 298 K.

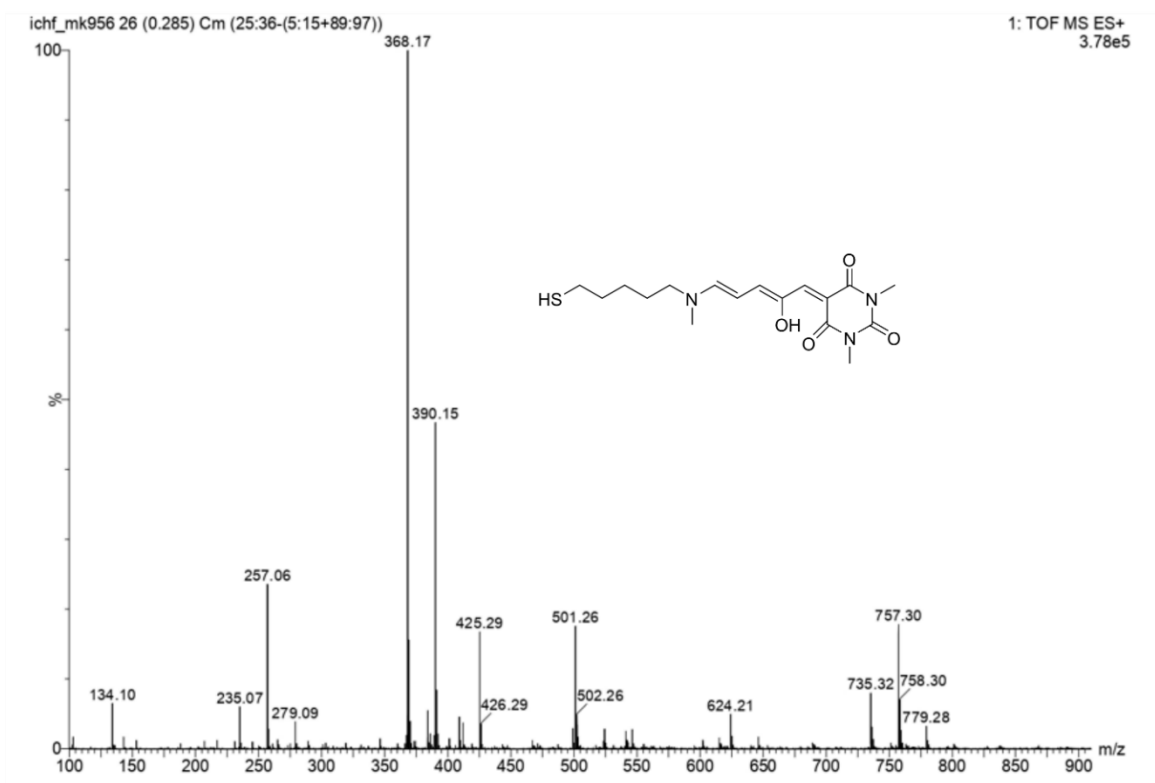| Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O	S
368.1646	368.1644	0.2	0.5	6.5	C17 H26 N3 O4 S	1060.9	n/a	n/a	17	26	3	4	1

Fig. S5 Mass spectrum of DASA under electrospray ionization in positive ion mode.
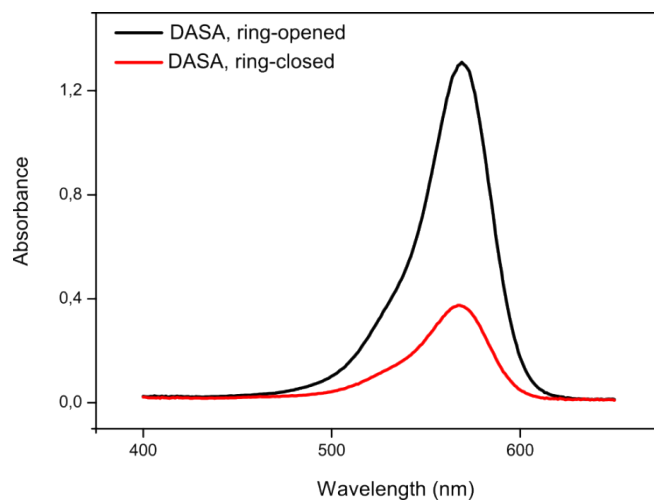
4. Isomerization experiments

Fig. S6 Absorption spectra of DASA (0.08 mM) in a 1:1 mixture of chloroform and toluene shown before (black) and after (red) LED irradiation at 570 nm for 1 min. The persistence of the open form of the photoswitch in the spectrum after the irradiation is attributed to rapid back-isomerization, resulting from the extended time (~33 s) required to record a full-range spectrum.
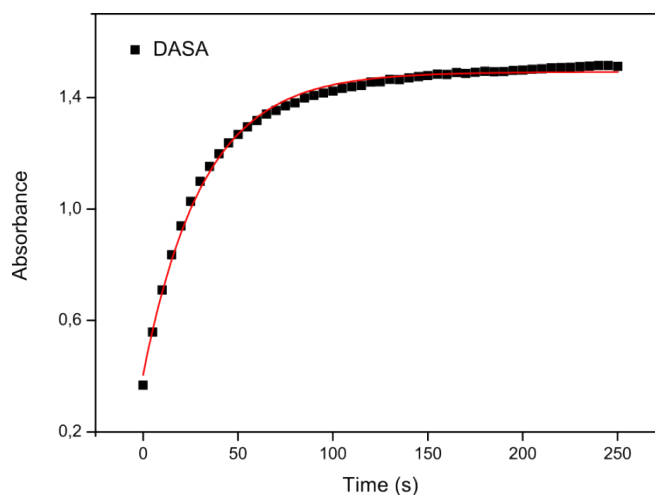

Fig. S7 Absorbance-time plot recorded at 569 nm for the solution of DASA in the chloroform-toluene mixture, illustrating the return of the photoswitch to the open form following the cessation of irradiation.

5. Scanning tunneling microscopy

Reconstructed Au(111) surface was prepared by vacuum deposition of Au film (~200 nm thickness) on a freshly cleaved mica surface followed by annealing in flame of propane-butane gas at 350-400 ^{0}C. STM images of prepared surface are taken in n-tetradecane (n-$C_{14}H_{30}$, 99% purity, Aldrich), reveal atomically flat terraces with the 23×√3 "herringbone" reconstruction.[3] The STM images with resolution of reconstruction are used to determine the crystallographic orientation of the sample with respect to the scan direction. The DASA molecules are dissolved in ethanol (C_2H_5OH) at room temperature. The droplet of prepared solution is applied onto Au(111) substrate immediately after annealing (within 2 minutes). In order to protect the surface from atmospheric influence the measurements are performed in n-tetradecane medium. The STM measurements were carried out in a thin layer of deposited solution using a Solver Pro M (NT-MDT). For STM tip we use mechanically cut Pt/Ir (80:20) wire. Typical imaging conditions are 100-800 mV in tunneling voltage and 100-500 pA in tunneling current. The error of measured distances is within 5% and was verified by comparison with STM image of atomic structure of highly oriented pyrolytic graphite. All STM images are recorded in the constant-current mode. No filtering procedures are used.

6. Quantum-chemical calculations

To gain a deeper insight into morphology of SAM, the quantum-chemical calculations are applied to both open and closed forms being in a neutral charge configuration in the gas phase. The geometry optimization and electronic structure calculations are carried out at the density functional theory (DFT) level with the hybrid B3LYP[4,5] functional and the split valence basis set 6-31G* using GAUSSIAN'03 program package. Analytic second derivative calculations, which yield the harmonic vibrational frequencies, are carried out at the relaxed geometries to ensure that each optimized conformation has no imaginary frequencies and thus corresponds to a global minimum on the potential energy hypersurface.

The calculations reveal that energetically favorable optimized ground state of open form corresponds to its planar linear conformation of the photochromic molecular backbone, which is realized by intramolecular OH---O hydrogen bond that leads to the elongation of the C=O bond to be involved. The optimized bent shape of the closed form is stabilized by intramolecular OH---N hydrogen bonding and characterized by half the shorter height of the backbone: estimated height of ~1.8nm for the open form and ~1.4nm for the closed form. The

open form demonstrates a calculated dipole moment of 9.52D that is oriented along the long (vertical) molecular axis, while the corresponding value for closed form is about 12.15D having direction almost along the short molecular axis (parallel to the substrate) and being perpendicular to the long one, can play a significant role in electrostatic lateral improvement of the SAM structure. The difference in STM contrast between the both forms can be associated with inelastic tunneling due to resonance in the frontier HOMO and LUMO level (Table S1) as well as to the specificity of local dipoles distributed in the functional groups causing a non-zero projection along the STM electric field. So, the bright spots in STM images were defined by the estimated size of the photochromic heads and the shapes of frontier molecular wave functions.
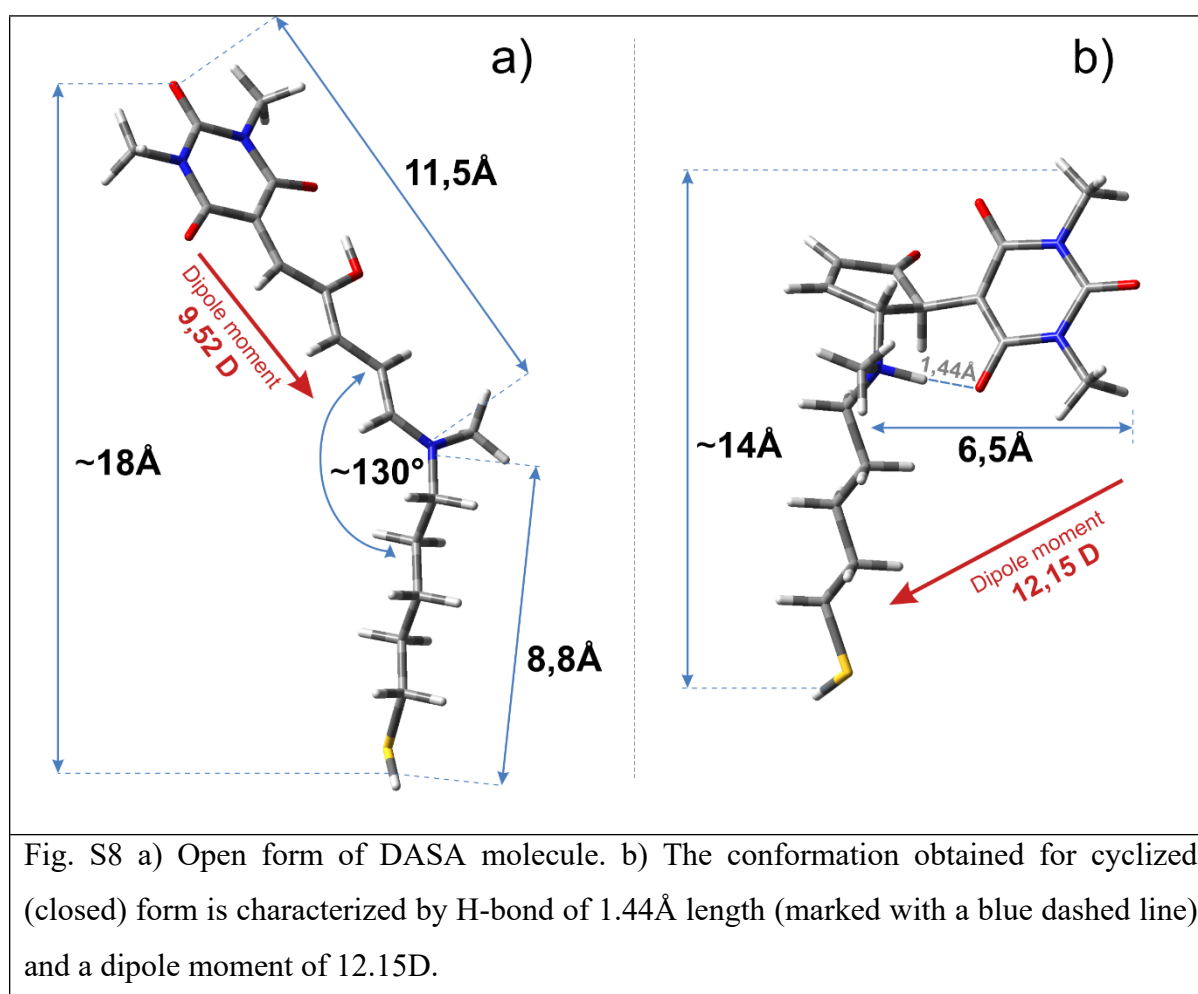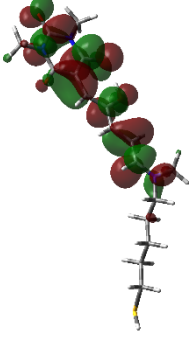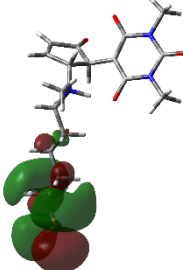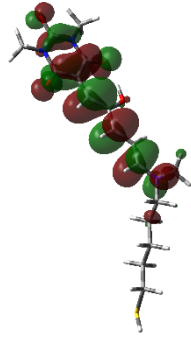

Fig. S8 a) Open form of DASA molecule. b) The conformation obtained for cyclized (closed) form is characterized by H-bond of 1.44Å length (marked with a blue dashed line) and a dipole moment of 12.15D.
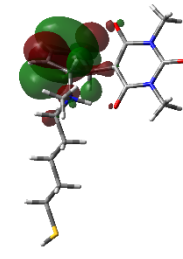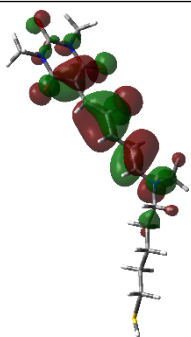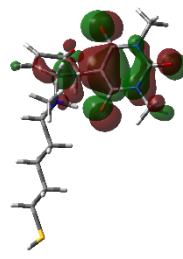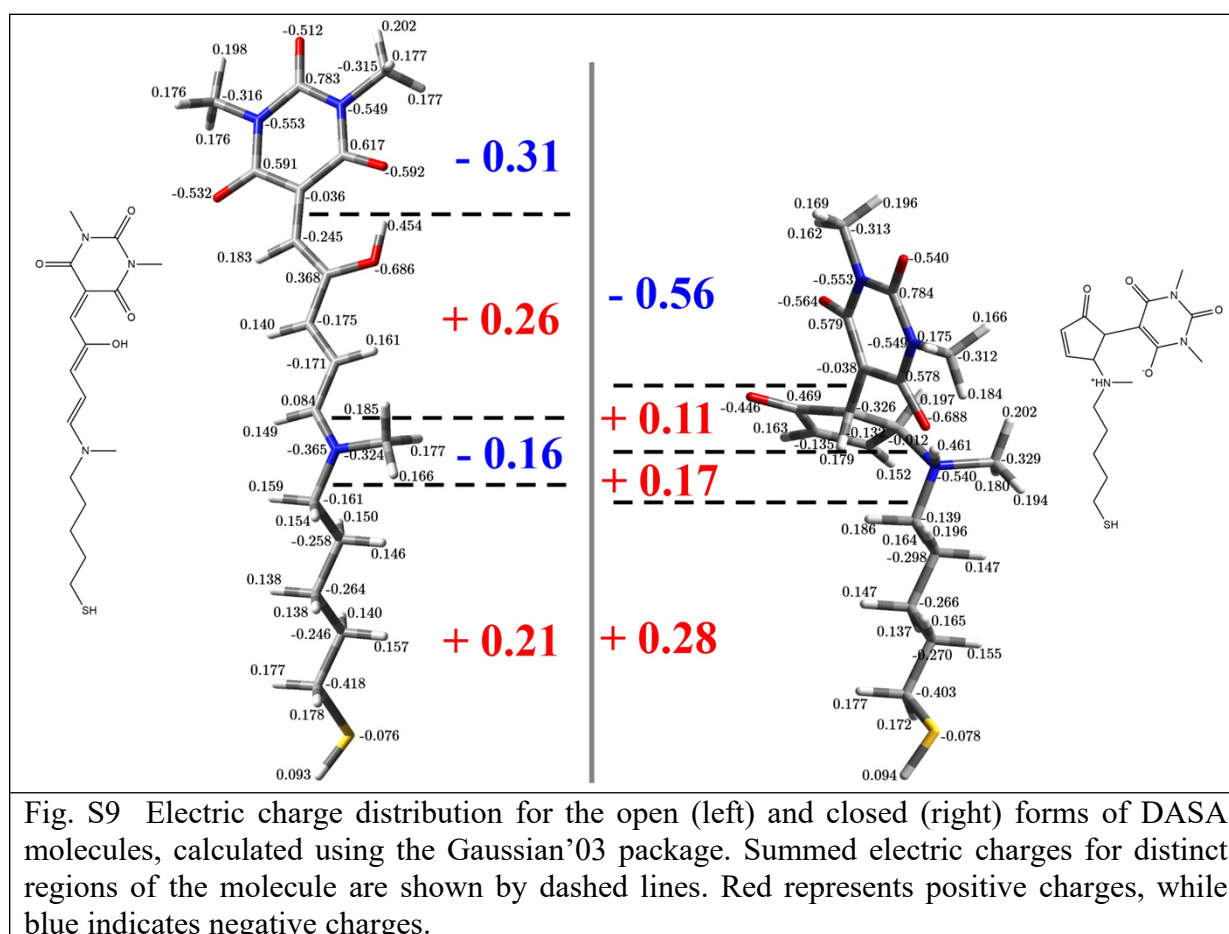
Table S1. Shapes and energies (in eV) of two frontier HOMOs and LUMOs wave functions calculated at B3LYP/6–31G* level for neutral molecules in the gas phase. Different colors of the molecular orbital surfaces represent a phase of the wave functions (red for positive, green for negative).

MO	Open form	Closed form
LUMO+1		
	0.22 eV	0.40 eV
LUMO		
	−2.25 eV	−1.73 eV
HOMO-LUMO gap	2.59 eV	3.36 eV
HOMO		
	−4.84 eV	−5.09 eV

| HOMO–1 | | |
| | **−6.64 eV** | **−6.02 eV** |

Fig. S9 Electric charge distribution for the open (left) and closed (right) forms of DASA molecules, calculated using the Gaussian'03 package. Summed electric charges for distinct regions of the molecule are shown by dashed lines. Red represents positive charges, while blue indicates negative charges.
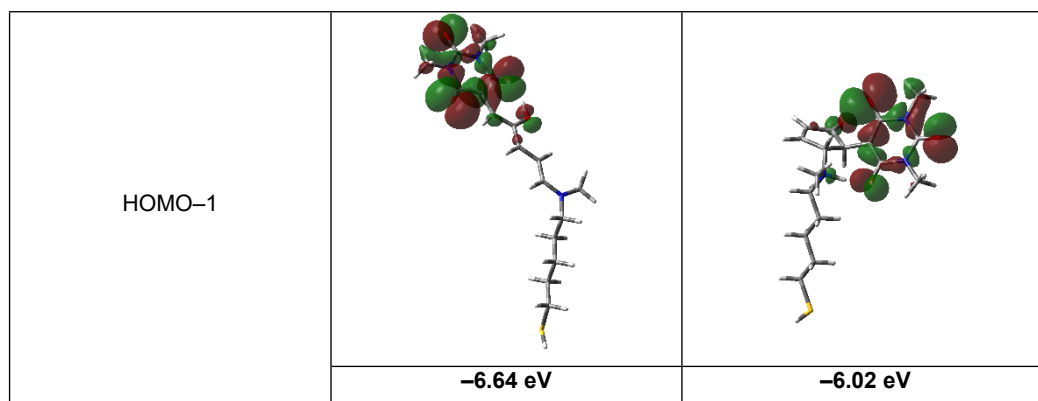
References

(1) Helmy, S.; Leibfarth, F. A.; Oh, S.; Poelma, J. E.; Hawker, C. J.; de Alaniz, J. R. Photoswitching Using Visible Light: A New Class of Organic Photochromic Molecules. *J. Am. Chem. Soc.* **2014**, 136, 8169.

(2) Mallo, M.; Foley, E. D.; Iranmanesh, H.; Kennedy, A. D.; Luis, E. T.; Ho, J.; Harper, J. B.; Beves, J. B. Structure-function relationships of donor-acceptor Stenhouse adduct photochromic switches. *Chem. Sci*. **2018**, *9*, 8242-8252.

(3) Voigtländer, B.; Meyer, G.; Amer, M. N. Epitaxial growth of the magnetic cobalt film on Au(111) studied by scanning tunneling microscopy. *Phys. Rev. B.* **1991**, V.44, (18) 10354-10357.

(4) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993,** 98, 5648-5652.

(5) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron-Density. *Phys. Rev. B* **1988**, 37, 785.