

Monitoring photoswitching of azobenzene-based self-assembled monolayers on ultrathin platinum films by UV-Vis spectroscopy in the transmission mode

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Supplementary Information

Chemicals and general procedures. 4-(phenylazo)phenol (98%), 11-Br-1-undecene (95%), 1-dodecanethiol (98%), 9-borabicyclo[3.3.1]nonane (9-BBN) (99%) and sodium carbonate were purchased from Sigma-Aldrich (Milan) and used as received. All solvent used (from Carlo Erba, Milan) were analytical grade. Syntheses were carried out under a low intensity level of vis light.

Instrumentation. ¹H NMR spectra were recorded on a VARIAN INOVA 500 spectrometer, using TMS as internal standard. ESI-MS spectra were recorded on an Agilent 1100 Series ESI/MSD spectrometer. Experimental conditions were as follows: capillary voltage, 3.5 KV; fragmentor, 100 V; source temperature, 350 °C; drying gas, N₂ (10 L/min), carrier solvent, methanol (0.4 mL/min). The samples were dissolved in methanol containing trifluoroacetic acid. UV/vis absorption spectra were recorded with a Jasco V-560 spectrophotometer. AFM measurements were carried out in air by using a Dimention 3100S-1 (Digital Instruments). Aqueous contact angles were measured using a goniometer (KERNCO) under ambient conditions.

Synthesis of phenyl-(4-undec-10-enyloxy)phenyl-diazene (A)

4-(phenylazo)phenol (0.40 g, 2.0 mmol), 11-Br-1-undecene (1.7 ml, 8.0 mmol) and sodium carbonate (3.0 g) were refluxed in 100 ml of acetonitrile for 3 days. The reaction mixture was filtered to eliminate the sodium carbonate suspension and then cooled at -18 °C for 3 hours. A yellow precipitate was obtained. The solid was filtered, washed and dried in vacuo (yield 45 %). Anal. calcd (%) for C₂₃H₃₁N₂O: C, 78.81; H, 8.63; N, 7.99; found: C, 78.57; H, 8.50; N, 7.75. ESI-MS *m/z*: [M+H]⁺ 351 (100%).

Synthesis of 4-(11-dodecylsulfanyl-undecyloxy)-phenyl]-phenyl-diazene (1). The synthesis of **1** was achieved by using a general method to obtain unsymmetrical sulfides.^{1S} 1-dodecanthiol (0.18 g, 0.90 mmol) was added to 10 mL of THF solution of **A** (0.32 g, 0.90 mmol) containing a catalytic amount of 9-BBN (60 μL). The reaction mixture was stirred at 0 °C for 12 hours, under nitrogen atmosphere. Addition of methanol (5 mL) at room temperature led to the precipitation of a yellow solid. The precipitate was collected by filtration, washed several times with small amounts of THF,

and dried under vacuum (yield 90%). Anal. calcd (%) for $C_{35}H_{56}N_2OS$: C, 75.96; H, 10.21; N, 5.06; S, 5.80; found: C, 75.50; H, 10.05; N, 4.89; S, 5.92. ESI-MS m/z : $[M+H]^+$ 553 (100%). 1H -NMR ($CDCl_3-d_1$): δ 7.9 (4H, d, $J=8.0$ Hz, $C_5H_4N=N-C_6H_4-O-$); 7.5 (3H, d, $J=7.7$ Hz, C_5H_4N); 7.0 (2H, d, $J=8.0$ Hz, $-C_5H_4-O-$); 4.0 (2H, t, $J=7.3$ Hz, azo-O-CH₂-(CH₂)₁₀-S-(CH₂)₁₁-CH₃); 2.48 (4H, t, $J=7.4$ Hz, azo-O-(CH₂)₁₀-CH₂-S-CH₂-(CH₂)₁₀-CH₃); 1.76 (2H, t, $J=7.5$ Hz, azo-O-CH₂-CH₂-(CH₂)₉-S-(CH₂)₁₁-CH₃); 1.52 (4H, q, $J=7.4$ Hz, azo-O-(CH₂)₉-CH₂-CH₂-S-CH₂-CH₂-(CH₂)₉-CH₃); 1.24 (34H, broad s, azo-O-CH₂-(CH₂)₈-CH₂-CH₂-S-CH₂-CH₂-(CH₂)₉-CH₃); 0.86 (3H, t, $J=7.5$ Hz, azo-O-(CH₂)₉-CH₂-CH₂-S-CH₂-CH₂-(CH₂)₉-CH₃).

Photoisomerization of 1. Figure 1S shows the absorption spectra of a 26 μM CH_2Cl_2 solution of **1** recorded before (solid line) and after (dashed line) UV (350 nm) irradiation. The spectra were recorded under ambient conditions using a quartz cell with an optical pathway of 10 mm.

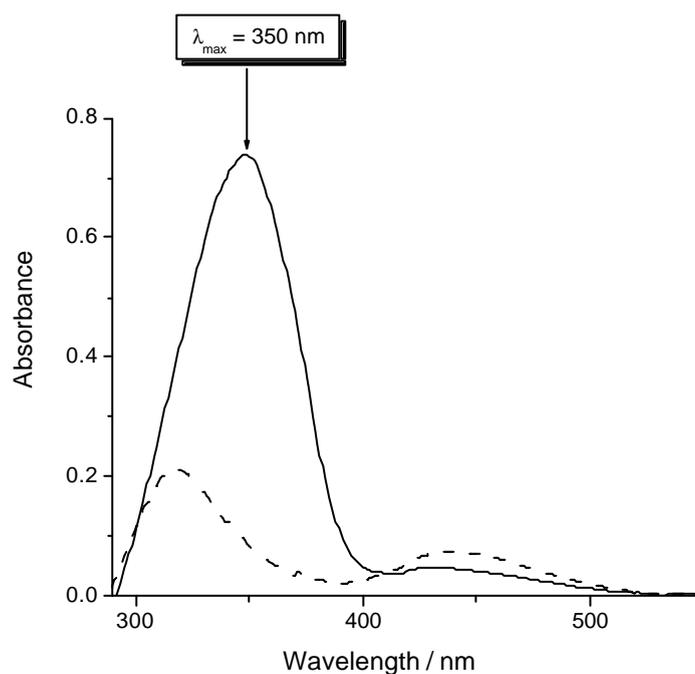


Fig. 1S

References

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