

Electronic Supplementary Information

Reversible photochromism of a *N*-salicylidene aniline anion

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Synthesis

Starting materials

Solvents (HPLC grade methanol from Prolabo; DMSO d_6 99.98% D) and reagents (sulfanilic acid from Sigma-Aldrich and salicylaldehyde 99% from Acros Organic) were obtained commercially and use as received. Diallyl hexyl amine is synthesized as described in [1].

Synthesis of 1: In a round flask of 25 mL, 0.552 mmol (100 mg) of diallyl hexyl amine is dissolved in 10 mL of MeOH. 0.607 mmol (105.1 mg, 1.1 eq.) of sulfanilic acid is added to the solution and stirring is maintained until most of the acid has disappeared. The solution is then filtered to remove the excess of sulfanilic acid and the solvent is evaporated under vacuum at room temperature. NMR: ^1H NMR (300 MHz, d^6 -DMSO) δ ppm: 0.1 (m, 2 H) 0.5 (m, 3 H) 0.9 (m, 1 H) 3.0 (d, J = 7.0 Hz, 2 H) 4.8 (s, 1 H) 4.8 (d, J = 4.7 Hz, 1 H) 5.1 (m, J = 17.3, 10.0, 7.2, 7.0 Hz, 1 H) 5.9 (d, J = 8.8 Hz, 1 H) 6.7 (d, J = 8.8 Hz, 1 H). ^{13}C -NMR (300 MHz, d^6 -DMSO) δ ppm: 5.0, 14.2, 15.6, 18.0, 23.1, 38.9, 39.2, 39.5, 39.8, 40.0, 40.4, 44.3, 46.8, 105.6, 117.6, 118.2, 119.1, 125.6, 141.9. Melting point: 87°C. *Anal.* Calc for $\text{C}_{18}\text{H}_{30}\text{N}_2\text{O}_3\text{S}$: C 60.98, H 8.53, N 7.90, Found: C 60.59, H 8.91, N 7.87 %.

Synthesis of 2: 0.282 mmol (100 mg) of diallyl ammonium sulfanilate is dissolved in 10 mL MeOH. 0.282 mmol (34.4 mg) of salicylaldehyde is added to the solution. The reaction is followed by ^1H -NMR and at the end of the reaction; the solvent is removed under vacuum at room temperature. The crude product is then recrystallized in hot MeOH for purification. **2** is obtained as yellow-orange crystals. NMR: ^1H NMR (300 MHz, d^6 -DMSO) δ ppm: 0.8 (m, 3 H) 1.3 (m, 6 H) 1.6 (m, 2H) 3.0 (m, 2 H) 3.7 (d, J = 7.0 Hz, 4 H) 5.5 (m, 4 H) 5.9 (m, J = 17.0, 10.0, 7.1, 7.1 Hz, 2 H) 7.0 (t, J = 7.8 Hz, 2 H) 7.4 (m, 3 H) 7.7 (d, J = 8.5 Hz, 3 H) 9.0 (s, 1 H). ^{13}C -NMR (300 MHz, d^6 -DMSO) δ (ppm): 13.8, 16.6, 21.8, 22.9, 25.6, 30.6, 51.4, 54.0, 63.6, 119.1, 120.6, 125.3, 126.7, 127.0, 132.6, 133.3, 147.9, 160.3, 163.6. IR $\bar{\nu}$ (cm^{-1}): 1614 s, 1591 s, 1570 s, 1491 m, 1456 s, 1429 m, 1404 m, 1375 m, 1302 m, 1279 s, 1219 vs, 1184 vs, 1177 vs, 1153 s, 1121 vs, 1030 vs, 1007 vs, 949 s, 922 m, 910 m, 845 s, 526 m, 779 m, 762 s, 716 s, 638 vs, 573 s, 550 m, 501 m, 463 w, 444 w, 413 vw. TGA-TDA: melting point: 112°C. degradation: 283°C. *Anal.* Calc for $\text{C}_{25}\text{H}_{34}\text{N}_2\text{O}_4\text{S}$: C 65.47, H 7.47, N 6.11, Found: C 65.21, H 7.37, N 5.89 %

Instrumentation

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 MHz spectrometer with DMSO as internal standard. Infrared spectra were obtained using a Equinox 55 from Bruker on KBr disks. Diffuse reflectance spectra were recorded on a Varian Cary 5E spectrophotometer using PTFE as reference. Spectra were measured on pure solids to avoid matrix effects and presented as normalized Kubelka-Munk function to allow meaningful comparisons. Light irradiation was carried out with a LOT-ORIEL 200 W high-pressure mercury arc lamp (LSN261). Melting point of **1** was measured on a Heizbank System Kofler Type WME from Wagner and Munz. Melting point and degradation of **2** were measured on a SDT 2960 simultaneous DSC-TGA from TA Instruments using Al_2O_3 reference.

X-ray data for **2** were collected on a MAR345 image plate, with Mo-K_α radiation (Zr filter) generated by a Rigaku UltraX 18 rotating anode. The reflections on the images were indexed and integrated using the CrysAlisPro package (Agilent Technologies).² Data were scaled and corrected for absorption using the integrated scale3 abspack procedure. The structures were solved by direct methods (SHELXS-97)² and refined first isotropically and then anisotropically using SHELXL-97.³ Hydrogen atoms were placed at calculated positions and refined in riding mode with respect to the parent atoms.

Crystallographic data (CCDC 947429) can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

[1] F. Rullens, M. Devillers and A. Laschewsky, *Macromol. Chem. Phys.*, 2004, **205**, 1155.

[2] Agilent Technologies XRD (2010). Agilent Technologies, Xcalibur CCD system, CrysAlisPro Software system, Version 1.171.35.15

[3] G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

Crystal Data of 2:

$C_{25}H_{34}N_2O_4S$, $M = 458.6 \text{ g.mol}^{-1}$, Monoclinic space group $P2_1$, $a = 11.7222(3)$, $b = 8.40571(17)$, $c = 12.7175(3) \text{ \AA}$, $\beta = 101.724(3)^\circ$, $V = 1226.96(5) \text{ \AA}^3$, $D_c (Z = 2) = 1.241 \text{ mg.m}^{-3}$; $\mu = 0.165 \text{ mm}^{-1}$, $T = 150 \text{ K}$, $\theta_{max} = 25.6^\circ$, $R_1 [I > 2\sigma(I)] = 0.0381 [4199]$, $wR_2 = 0.0857$.

Table 1: selected bonds, angles and torsion angles

<i>Bonds (Å)</i>					
S(1)-O(2)	1.4492(18)	C(6)-C(7)	1.384(3)	C(16)-C(17)	1.374(4)
O(19)-C(18)	1.347(3)	C(12)-C(13)	1.444(3)	S(1)-C(5)	1.774(2)
C(5)-C(10)	1.388(3)	C(15)-C(16)	1.385(3)	C(5)-C(6)	1.388(3)
C(9)-C(10)	1.379(3)	S(1)-O(4)	1.4617(17)	C(8)-C(9)	1.391(3)
C(14)-C(15)	1.379(3)	N(11)-C(12)	1.285(3)	C(13)-C(18)	1.413(3)
S(1)-O(3)	1.4458(17)	C(7)-C(8)	1.394(3)	C(17)-C(18)	1.378(4)
N(11)-C(8)	1.412(3)	C(13)-C(14)	1.402(3)		
<i>Angles (°)</i>					
O(2)-S(1)-O(3)	113.51(10)	O(2)-S(1)-O(4)	111.48(10)	O(2)-S(1)-C(5)	105.02(11)
O(3)-S(1)-O(4)	112.62(10)	O(3)-S(1)-C(5)	106.83(11)	O(4)-S(1)-C(5)	106.74(10)
C(8)-N(11)-C(12)	120.2(2)	S(1)-C(5)-C(6)	118.25(17)	S(1)-C(5)-C(10)	121.82(18)
C(6)-C(5)-C(10)	119.9(2)	C(5)-C(6)-C(7)	120.0(2)	C(6)-C(7)-C(8)	120.8(2)
N(11)-C(8)-C(7)	124.9(2)	N(11)-C(8)-C(9)	116.9(2)	C(7)-C(8)-C(9)	118.2(2)
C(8)-C(9)-C(10)	121.5(2)	C(5)-C(10)-C(9)	119.5(2)	N(11)-C(12)-C(13)	122.0(2)
C(12)-C(13)-C(14)	119.1(2)	C(12)-C(13)-C(18)	122.5(2)	C(14)-C(13)-C(18)	118.4(2)
C(13)-C(14)-C(15)	121.1(2)	C(14)-C(15)-C(16)	119.3(2)	C(15)-C(16)-C(17)	120.8(2)
C(16)-C(17)-C(18)	120.7(2)	O(19)-C(18)-C(13)	121.1(2)	O(19)-C(18)-C(17)	119.2(2)
C(13)-C(18)-C(17)	119.8(2)				
<i>Torsion angles (°)</i>					
N(11)-C(8)-C(9)-C(10)	179.5(2)	Γ_2	C(15)-C(16)-C(17)-C(18)	-0.5(4)	
N(11)-C(12)-C(13)-C(18)	-1.1(4)	Γ_3	C(14)-C(15)-C(16)-C(17)	1.0(4)	
N(11)-C(12)-C(13)-C(14)	-178.2(2)		C(13)-C(14)-C(15)-C(16)	-0.4(4)	
C(9)-C(8)-N(11)-C(12)	-163.1(2)		C(13)-C(12)-N(11)-C(8)	178.8(2)	
C(7)-C(8)-N(11)-C(12)	17.8(4)	Γ_1	C(12)-C(13)-C(18)-O(19)	2.9(4)	
C(6)-C(7)-C(8)-N(11)	-179.8(2)		C(12)-C(13)-C(18)-C(17)	-176.0(2)	
C(18)-C(13)-C(14)-C(15)	-0.7(4)		C(12)-C(13)-C(14)-C(15)	176.6(2)	

Table 2: Hydrogen bonds present in the crystal structure of 2

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	type
O(19)-H(19)...N(11)	0.84	1.89(1)	2.632(3)	147	intra
N(20)-H(20)...O(2a)	0.93	2.51(1)	3.226(2)	134	inter
N(20)-H(20)...O(4a)	0.93	1.98(1)	2.854(2)	156	inter