

## Supporting information

### Azobenzene thiols experimental part

#### 1. 4-(3 mercaptopropyloxy)-azobenzene (AZO1) synthesized in a 4 step reaction a, b, c, d.

##### a. 4-(3 hydroxypropyloxy)-azobenzene

7.92 g (40 mmol) of 4-phenyl-azophenol and 5 g of 3-chloropropanol-1 (53 mmol) were dissolved in 50 ml of DMF. 6 g of anhydrous potassium carbonate were added and the mixture refluxed for 4 hours with. It was then poured into cold water, filtered, washed neutral, dried and re-crystallised from cyclohexane. The yield was 9.8 g (96% theory), Mp 97°

Elemental analysis: Calculated for  $C_{15}H_{16}N_2O_2$ : C, 70.29; H, 6.29; N, 10.92. Found: C, 70.20; H, 6.27; N, 10.90%.

b. 8.3 g (32 mmol) of the above compound was dissolved in 50 ml pyridine, cooled to -7°, then 7 g of tosylchloride was added. After 1 hour some crystals appeared. The solution was kept at room temperature for 1 hour and then put into an ice-only bath for 2 hours. Water was then added in 1 ml portions to keep the temperature between 0° and +2°. After the addition of ~8 ml of cool water at ~-2°, 100 ml was added and the precipitate filtered and washed 3 times with 1 mM of  $H_2SO_4$  and finally with water. The yield was 12.3 g (93% theory) and the product was crystallised from cyclohexane. Mp 114°

Elemental analysis: Calculated for  $C_{22}H_{22}N_2O_4S$ : C, 64.37; H, 5.40; N, 6.82. Found: C, 64.44; H, 5.44; N, 6.84%.

##### c. 4-(3-thioaceto-propyloxy)-azobenzene

6.15 g (15 mmol) of the above tosylate in 80 ml of ethanol was refluxed with 3 g (100% excess) of potassium thiol acetate for 2 hours. The solution was then cooled to room temperature, filtered and washed with ethanol (2 x 50 ml) The volume of filtrate was reduced to one third and 100 ml of warm water was added (~40°), then filtered and dried. The yield was 4.43 g (94% theory).

Elemental analysis: Calculated for  $C_{17}H_{18}N_2O_2S$ : C, 64.94; H, 5.77; N, 8.90; S, 10.19. Found: C, 64.80; H, 5.73; N, 8.92; S, 10.43%.

##### d. 4-(3-mercaptopropyloxy)-azobenzene

All operations were carried out under nitrogen. 0.13 g of potassium hydroxide was dissolved in 4 ml methanol and 0.25 g (0.7 mmol) of the above thiolacetate was added with an additional 2 ml of methanol and left for 48 hours at room temperature. 2 ml of water and 4 drops of concentrated HCl were added, filtered, washed and crystallised from acetone/methanol 1:2. The yield was 0.15 g, Mp 93.5-94.5°.

Elemental analysis: Calculated for  $C_{15}H_{16}N_2OS$ : N, 10.28. Found: N, 9.99%

#### 2. Acetylated 4,4'-Bis(2-mercaptoethyl)-azobenzene (AZO2-acetyl) synthesized in a 3 step reaction a, b, c.

a. 4,4'-Bis(2-hydroxyethyl)-azobenzene

90 ml of ethanol was added to a solution of 3.9 g of sodium hydroxide in 18 ml of water and then 15 g (0.09 mol) 4-hydroxyethyl nitrobenzene. It was brought to reflux and 48.3 g of Zn powder was added in small portions. After this addition, the solution was refluxed for 1 hour. It was then hot filtered, washed with ethanol and air was bubbled through the filtrate for 2 hours. The liquid was then rotary evaporated to a small volume and water was added. The oil which separated was washed with water, crystallised from ethanol (~50 ml) and then again from toluene. The yield was 2.34 g (56.4% theory), Mp 138°

Elemental analysis: Calculated for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.08; H, 6.71; N, 10.36. Found: C, 71.27; H, 6.73; N, 10.42%.

b. Tosylation of compound a.

2.34 g (8.6 mmol) of bishydroxyethyl-azobenzene was dissolved in 40 ml of pyridine. The solution was cooled to -7° and 4.2 g of tosyl chloride was added and kept at -7° for 1 hour with stirring. The solution was then kept at 0° for 24 hours. Water was added in portions of ~1 ml whilst keeping the temperature at ~0 to +5°. Then 100 ml of water was added, then filtered and washed once with a 0.5 mM solution of H<sub>2</sub>SO<sub>4</sub> followed by washing 4 times with water and finally the product was dried. The yield was 4 g (80% theory), Mp 118°

Elemental analysis: Calculated: S, 11.08. Found: S, 11.51%

c. Bis-thiolacetate of compound a.

2.5 g of potassium thiolacetate was added to a hot solution of 3.6 g of tosylate in ethanol and refluxed for 1.5 hours. The solution was left at room temperature overnight, then filtered and washed 3 times with water and finally dried. The yield was 1.2 g of bis-thiolacetate of hydroxyethyl-azobenzene, Mp 136.4-137.7°

Elemental analysis: Calculated for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 62.14; H, 5.73; N, 7.24; S, 16.59. Found: C, 62.00; H, 5.76; N, 7.25; S, 16.38%