

# Synthesis and Characterization of Photomodulable Amphiphiles

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## Abstract

Synthesis and characterization of new amphiphilic azobenzenes with non ionic character is presented. The synthetic methodology is simple and versatile which allow the generation of molecular diversity from the same precursors in an easy way.

## Introduction

Chemistry has created a wide range of ever more sophisticated molecules and materials and has developed a very powerful arsenal of procedures for constructing them from atoms linked by covalent bonds. Beyond the molecule, supramolecular chemistry offers unique opportunities directed towards the fabrication of new supramolecular structures and materials. These have dynamic characteristics mainly because their constituents are bonded by reversible interactions which are, in some cases, possible to manipulate in an external manner<sup>1,2</sup>

In this context we are interested in the design, synthesis and characterization of new amphiphilic systems which morphology or function would be possible to manipulate in response to an external stimulus.

## Results and Discussion

Ionic Azobenzenes amphiphiles have been previously reported in order to investigate the physicochemical properties of biomimetic membranes<sup>3, 4, 5</sup>. The charged headgroup on these surfactants have such large effective cross-sectional areas that the conformation change taken by the tails as a result of the illumination has little effect on the packing of the amphiphile in the absorbed interfacial layer<sup>6</sup>.

In order to obtain systems with potential application as membrane modulators; the synthesis and characterization of new artificial amphiphiles was performed. The simple and versatile synthetic methodology presented was designed in order to achieve molecular diversity from the same precursors in an easy way. These amphiphiles possess a general chemical structure that can be grouped in four structural components: a long hydrophobic tail, a rigid core segment which is also photomodulable, a polar non ionic head and a spacer between the rigid segment and the head. Supramolecular characterizations of these systems are currently in progress.

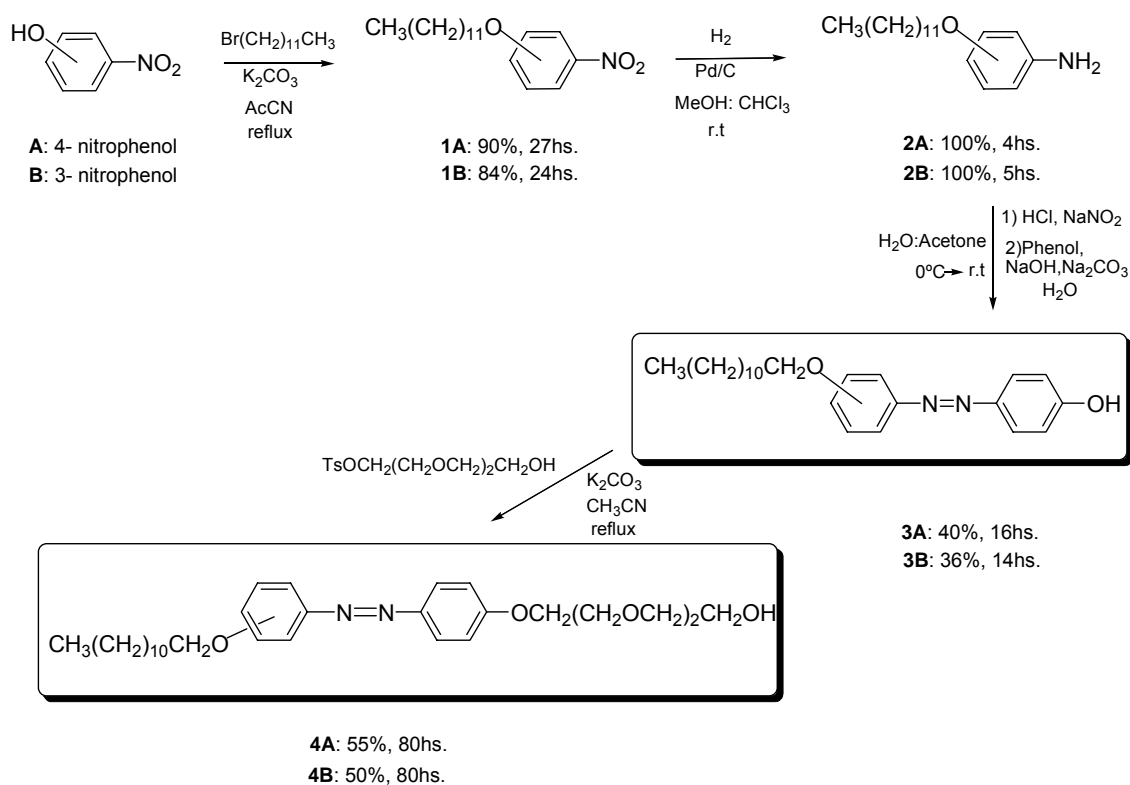


Fig. 1- Synthetic Methodology

## General Experimental Procedure

All manipulations were carried out under an atmosphere of nitrogen. Acetonitrile was dried over K<sub>2</sub>CO<sub>3</sub> and distilled immediately before use.

**Compound 1:** To a solution containing 886.3 mg (6.38 mmol) of nitrophenol and 5.28 g (38.28 mmol) K<sub>2</sub>CO<sub>3</sub> in 20 ml acetonitrile under stirring was added 1.84 mL (7.66 mmol) dodecyl bromide in 10 ml acetonitrile. The reaction mixture was refluxed for 27 hours and subsequently filtered through Celite. The solvent was removed by reduced pressure and the crude product was obtained as a solid. This solid was further purified by column chromatography on neutral aluminum oxide (hexane: diethyl ether) and **1** was recovered as a white solid.

**Compound 1A** (90%) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 0.88 (t, 3H, CH<sub>3</sub>), 1.27-1.47 (m, 18H, CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 4.05 (t, 2H, OCH<sub>2</sub>), 6.93 (d, 2H, Ar-H), 8.19 (d, 2H, Ar-H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 14.072 (CH<sub>3</sub>), 22.67, 25.91, 28.98, 29.29, 29.32, 29.52, 29.56, 29.62, 29.63, 31.91 (CH<sub>2</sub>), 68.93 (OCH<sub>2</sub>), 114.41, 125.8, 141.4, 164.26 (Ar-C).

**Compound 1B** (84%) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 0.81 (t, 3H, CH<sub>3</sub>), 1.10-1.40 (m, 18H, CH<sub>2</sub>), 1.73 (m, 2H, CH<sub>2</sub>), 3.96 (t, 2H, OCH<sub>2</sub>), 7.16 (d, 1H, Ar-H), 7.41 (d, 1H, Ar-H) 7.70-7.75 (m, 2H, Ar-H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 14.072 (CH<sub>3</sub>), 22.67, 25.91, 28.98, 29.29, 29.32, 29.52, 29.56, 29.62, 29.63, 31.91 (CH<sub>2</sub>), 68.93 (OCH<sub>2</sub>), 114.41, 125.8, 141.4, 164.26 (Ar-C).

**Compound 2:** To a solution of 300 mg (0.98 mmol) dodecyl dodecyloxy nitrophenol dissolved in 10 ml anhydrous CHCl<sub>3</sub> was added 8.6 ml methanol. The reaction was stirred in the presence of 50 mg of 10% Pd/C under hydrogen atmosphere for 4-6 hours at room

temperature. Then it was filtered off and the solvent was removed under reduced pressure. The bright grey solid **2** was used without further purification in the following step.

**Compound 3:** To 271.46 mg (0.98 mmol) of **2** in 4.51 mL of 1:1 aqueous acetone was added 0.45 mL of hydrochloric acid concentrated. To this mixture 2.25 mL of aqueous NaNO<sub>2</sub> (93.15 mg, 1.35 mmol) was added and the solution was maintained at 0°C for 1 h. The resulting diazonium slurry was then added to the following mixture: phenol 131.6 mg (1.40 mmol), NaOH 52.86 mg (1.32 mmol), Na<sub>2</sub>CO<sub>3</sub> 228.96 mg (2.16 mmol) in 3.78 mL of MilliQ water maintaining the temperature at 0°C for an additional 1 h. Then, the mixture was stirred for further 16 h at room temperature. After this, it was neutralized with acetic acid and the precipitate containing compound **3** was well washed with MilliQ water. Further purification was not necessary.

**Compound 3A** (40%), mp 96-97°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 0.88 (t, 3H, CH<sub>3</sub>), 1.27-1.47 (m, 18H, CH<sub>2</sub>), 1.81 (m, 2H, CH<sub>2</sub>), 4.03 (t, 2H, OCH<sub>2</sub>), 4.63 (s, 1H, OH), 6.93 (d, 2H, Ar-H), 6.98 (d, 2H, Ar-H), 7.81 (d, 2H, Ar-H), 7.85 (d, 2H, Ar-H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 14.078 (CH<sub>3</sub>), 22.67, 26.025, 29.22, 29.33, 29.38, 29.56, 29.58, 29.62, 29.65, 31.91 (CH<sub>2</sub>), 68.40 (OCH<sub>2</sub>), 114.72, 115.76, 124.33, 124.51, 146.91, 147.23, 161.27 (Ar-C).

**Compound 3B** (36%), mp 67-69°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 0.81 (t, 3H, CH<sub>3</sub>), 1.10-1.40 (m, 18H, CH<sub>2</sub>), 1.73 (m, 2H, CH<sub>2</sub>), 3.96 (t, 2H, OCH<sub>2</sub>), 4.50 (s, 1H, OH), 6.79-7.00 (m, 3H, Ar-H), 7.14-7.22 (m, 3H, Ar-H), 7.73-7.88 (d, 2H, Ar-H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 12.4 (CH<sub>3</sub>), 21.00, 24.40, 27.70-28.00 (CH<sub>2</sub>), 75.30 (OCH<sub>2</sub>), 110.5, 114.2, 114.8, 115.9, 123.3, 123.4, 127.9, 146.9, 148.0, 158.2 (Ar-C).

**Compound 4:** To 75 mg (0.197 mmol) of dodecyloxy-hydroxyl azobenzene and 300 mg (2.17 mmol) K<sub>2</sub>CO<sub>3</sub> suspension was added 63 mg (0.207 mmol) triethylene glycol p-toluenesulfonate in 10 mL of dry acetonitrile. The reaction mixture was allowed to react at reflux for 80 hours and then filtered out. The solid was further purified by column chromatography on neutral aluminum oxide (hexane: diethyl ether) and pure **4** was obtained.

**Compound 4A** (55%) Yellow solid, mp 105-106°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 0.88 (t, 3H, CH<sub>3</sub>), 1.27-1.47 (m, 18H, CH<sub>2</sub>), 1.81 (m, 2H, CH<sub>2</sub>), 2.08 (s, 1H, OH); 3.61-3.74 (m, 8H, CH<sub>2</sub>); 3.90 (t, 2H, CH<sub>2</sub>); 4.03 (t, 2H, OCH<sub>2</sub>), 4.22 (t, 2H, CH<sub>2</sub>); 6.99 (m, 4H, Ar-H), 7.86 (m, 4H, Ar-H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 14.1 (CH<sub>3</sub>), 22.68, 26.00, 29.22, 29.33, 29.40, 29.50, 29.60, 29.63, 29.65, 31.91 (CH<sub>2</sub>), 61.8, 69.15, 69.71, 70.45, 70.59, 70.90, 72.50 (OCH<sub>2</sub>), 114.71, 114.85, 124.26, 124.32, 146.97, 147.32, 160.65, 161.275 (Ar-C).

**Compound 4B** (50%) Red solid, mp 60-62°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 0.81 (t, 3H, CH<sub>3</sub>), 1.05-1.45 (m, 16H, CH<sub>2</sub>), 1.63-1.67 (m, 4H, CH<sub>2</sub>), 3.74-3.96 (m, 8H, CH<sub>2</sub>); 3.90 (t, 2H, CH<sub>2</sub>); 3.84 (t, 2H, OCH<sub>2</sub>), 4.22 (t, 2H, CH<sub>2</sub>); 6.81-7.19 (m, 2H, Ar-H), 7.26-7.46 (m, 4H, Ar-H), 7.79-7.91 (m, 2H, Ar-H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 13.1 (CH<sub>3</sub>), 21.70, 25.10, 28.30, 28.60, 30.90 (CH<sub>2</sub>), 60.80, 67.20, 68.71, 69.45, 70.30, 71.40, 76.40 (OCH<sub>2</sub>), 105.40, 115.40, 115.50, 116.6, 123.70, 128.6, 153.00, 153.10, 158.90, 160.20 (Ar-C).

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