

Synthesis and characterisation of SP_{Im}

NMR spectra were carried out on a Bruker AVANCE instrument using XWINMR software processed on a Silicon Graphics O2 workstation. The instrument operated at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR. Mass spectra were recorded on Bruker ESQUIRE LCMS instrument. TGA analysis was conducted using a Perkin-Elmer Pyris TGA in a flowing dry nitrogen atmosphere (50 mL / min.) between 25 and 800 °C with a heating rate of 10 °C / min. DSC traces are presented using the convention of endothermic as up and exothermic as down. All scans were carried out at a heating/cooling rate of 10 °C /min in the range of -150 °C – 200 °C using a TA Q100 series calorimeter.

A. **1-(3-bromoethyl)-2,3,3-trimethylindolenium bromide** was synthesized according to previously published procedure.¹

B. **1 - (3''-bromoethyl) - 3,3' - dimethyl - 6 -nitrospiro -[2*H*-1-benzopyran-2,2'-indoline] (SP-Br)**

A solution of 1-(3-bromoethyl)-2,3,3-trimethylindolenium bromide (2g, 5.76 mmol) and ethanol (15 ml) was added slowly to a suspension of 5-nitrosalicylaldehyde (1g, 5.76 mmol) in ethanol (5 ml). To the reaction mixture was added triethyl amine (0.63g, 5.76 mmol). The reaction mixture was stirred and refluxed over 4 h under nitrogen. The solvent was removed under vacuum and the resulting crude dark brown compound was purified by silica/hexane:ethylacetate 10:1 to afford a bright light yellow compound, 0.23g, yield-10%. Analytical data; ¹H NMR (400 MHz) δ (CDCl₃):

Analytical data; ^1H NMR (400 MHz) δ (CDCl_3): 1.11 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 3.31-3.61 (m, 4H, 2 x CH_2), 5.86 (d, H, $J = 10.4$ Hz, CH), 6.52 (d, H, $J = 7.6$ Hz, Ar-H), 6.67 (d, H, $J = 9.2$ Hz, CH), 6.85 (m, H, Ar-H), 7.04 (d, H, $J = 7.2$ Hz, Ar-H), 7.12-7.16 (m, 3H, Ar-H), 7.95 (m, 2H, Ar-H), ^{13}C NMR (CDCl_3) δ (ppm): 19.83, 25.88, 29.83, 45.60, 53.00, 106.29, 106.54, 115.61, 118.48, 120.24, 121.75, 122.13, 122.88, 126.06, 127.90, 128.58, 135.84, 141.19, 145.95, 159.16. (m/z ion) calculated for 415.06 ($\text{M}+\text{H}$) $^+$ and found 415.2 ($\text{M}+\text{H}$) $^+$.

C. 1' - (3''-methylimidazolioethyl) - 3,3' - dimethyl - 6 -nitrospiro -[2H-1-benzopyran-2,2'-indoline] bromide (SP-Imidazolium)(9).

1' - (3''-bromoethyl) - 3,3' - dimethyl - 6 -nitrospiro -[2H-1-benzopyran-2,2'-indoline] (SP-Br) (1.11g, 2.67 mmol) was treated with 1-methyl imidazole (0.87g, 10.69 mmol) in (acetonitrile: DMF, 1:1) (15 ml). The reaction solution was heated to 100 °C, and left to stir over 15 h. The resulting dark red solution was cooled down and washed with ether several times to remove starting material. The resulting light brown solid was filtered off and purified by silica/chloroform:methanol, 3:1, to afford a red neat compound, 0.8 g, yield -60 %. Analytical data; ^1H NMR (400 MHz) δ (CDCl_3): 1.07 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 3.64 (t, 2H, CH_2), 3.93 (s, 3H, CH_3), 4.50-4.65 (m, 2H, CH_2), 5.78 (d, H, $J = 12$ Hz, CH), 6.37 (d, H, $J = 4$ Hz, Ar-H), 6.63 (d, H, $J = 8$ Hz, CH), 6.76 (m, H, Ar-H), 6.92 (d, H, $J = 8$ Hz, Ar-H), 6.98-7.02 (m, 3H, Ar-H), 7.52 (s, H, Ar-H), 7.61 (s, H, Ar-H), 7.85-7.89 (m, 2H, Ar-H), 10.01 (s, H, Ar-H). ^{13}C NMR (CDCl_3) δ (ppm): 19.92, 26.02, 36.65, 44.38, 49.22, 52.61, 106.24, 106.48, 115.47, 118.44, 120.83, 121.13, 122.12, 122.97, 123.20, 123.54, 125.92, 127.83, 129.07, 135.71, 137.33, 141.04, 146.03,

158.99. (m/z ion) calculated for 497.11 (M+H)⁺ and found 497.00 (M+H)⁺, 417 (M-Br)⁺, 335.20 (M-Imidazolium ring)⁺.

Differential scanning calorimetry: m.p: 138.6°C

Thermogravimetric analysis: degradation temperature: 292°C, water content: 4.4%

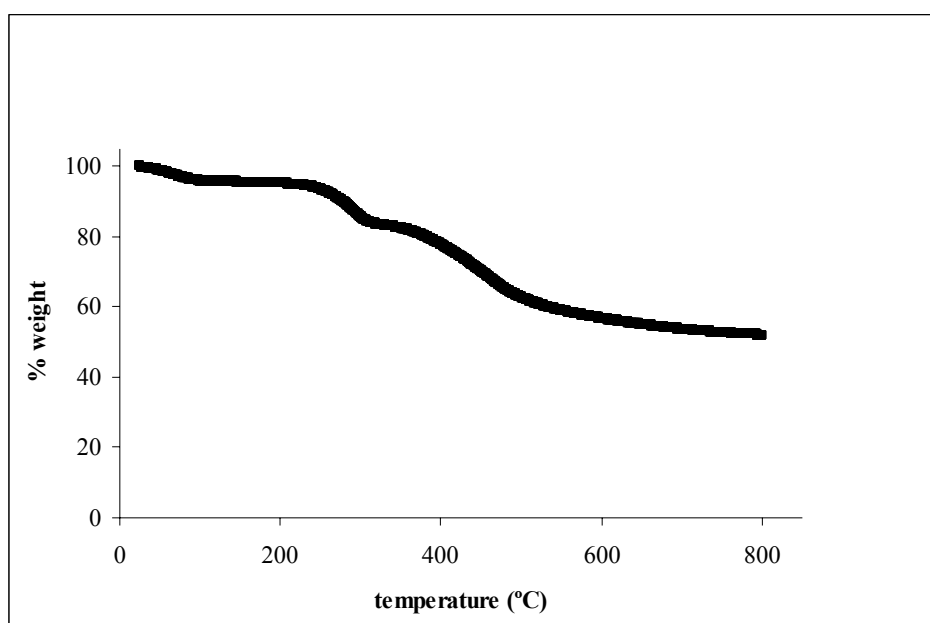


Fig. 1 Thermogravimetric analysis of SP_{1m}

References

1. Y. Hirshberg, *Journal of the American Chemical Society*, 1956, **78**, 2304-2312.