Supplementary Material (ESI) for New Journal of Chemistry

Electronic Supplementary Information (ESI)

Experimental procedure and characterization of products 5a-c, 6a-c, and 7a-d.

***N*-Butylfurfurylimine 5a.** Freshly distilled furfural **1** (4.30 cm^3, 52 mmol) is charged in a two necked round bottom flask under N_2; then anhydrous $MgSO_4$ (3.13 g, 26 mmol) is added, followed by butylamine (5.14 cm^3, 52 mmol). The exothermic reaction is monitored by means of TLC and GC-MS; after 2 hours the conversion is complete. Imine **5a** is obtained by distillation under reduced pressure (T_{eb} =60°C, p = 10 mbar) as a colourless liquid (7.7 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, ^3J (H, H) = 7.2 Hz, 3H, $N(CH_2)_3CH_3$), 1.33-1.42 (m, 2H, $N(CH_2)_2CH_2CH_3$), 1.66-1.71 (m, 2H, $NCH_2CH_2CH_2CH_3$), 3.58 (t, ^3J (H, H) = 6.8 Hz, 2H, $NCH_2(CH_2)_2CH_3$), 6.47 (dd, ^3J (H, H) = 1.8 Hz, ^3J (H, H) = 3.2 Hz, 1H, 4-H furan), 6.72 (d, ^3J (H, H) = 3.2 Hz, 1H, 3-H furan), 7.50 (d, ^3J (H, H) = 1.8 Hz, 1H, 5-H furan), 8.08 ppm (s, 1H, N=C*H*); GC rt 17.4 min; MS (70 eV, EI): m/z 151 (20) [M^+]; 122 (75) [M^+- CH_3CH_2]; 108 (100) [M^+- $CH_3(CH_2)_2$]; 94 (25) [M^+- $CH_3(CH_2)_3$]; 81 (100) [M^+- $CH_3(CH_2)_3N$]; 67 (6) [M^+- $CH_3(CH_2)_3$ NCH]; 53 (20).

***N*-Octylfurfurylimine 5b.** The imine is prepared from **1a** and octylamine in 98% yield after distillation under reduced pressure (T_{eb} = 95°C, p = 9 10^{-2} mbar) with the same procedure of compound **5a**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J (H, H) = 6.2 Hz, 3H, $N(CH_2)_7CH_3$), 1.28-1.31 (m, 10H, $N(CH_2)_2(CH_2)_5CH_3$), 1.68-1.75 (m, 2H, $NCH_2CH_2(CH_2)_5CH_3$), 3.58 (t, ^3J (H, H) = 7.4 Hz, 2H, $NCH_2(CH_2)_6CH_3$), 6.47 (dd, ^3J (H, H) = 1.6 Hz, ^3J (H, H) = 3.2 Hz, 1H, 4-H furan), 6.72 (d, ^3J (H, H) = 3.2 Hz, 1H, 3-H furan), 7.51 (d, ^3J (H, H) = 1.6 Hz, 1H, 5-H furan), 8.08 (s, 1H, N=C*H*); GC rt 18.2 min; MS (70 eV, EI): m/z 207 (5) [M^+]; 192 (3) [M^+- CH_3]; 178 (15) [M^+- CH_3CH_2]; 164 (30) [M^+- $CH_3(CH_2)_2$]; 150 (100) [M^+- $CH_3(CH_2)_3$]; 136 (10) [M^+- $CH_3(CH_2)_4$]; 122 (45) [M^+- $CH_3(CH_2)_5$]; 108 (60) [M^+- $CH_3(CH_2)_6$]; 94 (25) [M^+- $CH_3(CH_2)_7$]; 80 (50) [M^+- $CH_3(CH_2)_7N$]; 67 (5) [M^+- $CH_3(CH_2)_7$ NCH]; 53 (15).

***N*-Hexylfurfurylimine 5c.** The imine is prepared from **1a** hexylamine in 97% yield after distillation under reduced pressure (T_{eb} = 90°C, p = 1 10^{-1} mbar) with the same procedure of compound **5a**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J (H, H) = 3.2 Hz, 3H, $N(CH_2)_5CH_3$), 1.23-1.38 (m, 6H, $N(CH_2)_2(CH_2)_3CH_3$), 1.65-1.75 (m, 2H, $NCH_2CH_2(CH_2)_3CH_3$), 3.56 (t, ^3J (H, H) = 4.6 Hz, 2H, $NCH_2(CH_2)_4CH_3$), 6.46 (dd, ^3J (H, H) = 1.2 Hz, ^3J (H, H) = 2.2 Hz, 1H, 4-H furan), 6.71(d, ^3J (H, H) = 2.2 Hz, 1H, 3-H furan), 7.50 (d, ^3J (H, H) = 1.2 Hz, 1H, 5-H furan), 8.07 (s, 1H, N=C*H*); GC rt 15.6 min; MS (70 eV, EI): m/z 179 (5) [M^+]; 164 (10) [M^+- CH_3]; 150 (100) [M^+- CH_3CH_2]; 136 (10) [M^+- $CH_3(CH_2)_2$]; 122 (60) [M^+- $CH_3(CH_2)_3$]; 108 (70) [M^+- $CH_3(CH_2)_4$]; 94 (35) [M^+- $CH_3(CH_2)_5$]; 80 (75) [M^+- $CH_3(CH_2)_5N$]; 67 (5) [M^+- $CH_3(CH_2)_5$ NCH]; 53 (15).

***N*-Butylfurfurylamine 6a**. Freshly distilled imine **5a** (7.55 g, 50 mmol) is charged in a two necked round bottom flask with Pd/C 10 wt % (750 mg) and connected to a rubber balloon filled with H_2 (1 atm); the reaction is stirred at room temperature and checked by means of TLC and GC-MS. After 24 hours Pd/C is filtered off on Celite and the amine is obtained by distillation under reduced pressure (T_{eb} =40°C, p = 8.10^{-2} mbar) as a colourless liquid (7.5 g, 98%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, ^3J (H, H) = 7.0 Hz, 3H, $N(CH_2)_3CH_3$), 1.25-1.52 (m, 4H, $NCH_2(CH_2)_2CH_3$), 2.60 (t, ^3J (H, H) = 6.6 Hz, 2H, $NCH_2(CH_2)_2CH_3$), 3.78 (s, 2H, NCH_2-furan), 6.17 (d, ^3J (H, H) = 3.2 Hz, 1H, 3-H furan), 6.31 (dd, ^3J (H, H) = 1.8 Hz, ^3J (H, H) = 3.2 Hz, 1H, 4-H furan), 7.33 (d, ^3J (H, H) = 1.8 Hz, 1H, 5-H furan); GC rt 17.1 min; MS (70 eV, EI): m/z 153 (15) [M^+]); 110 (30) [M^+- $CH_3(CH_2)_2$]; 96 (15) [M^+- $CH_3(CH_2)_3$]; 81 (100) [M^+- $CH_3(CH_2)_3$ NH]; 53 (15).

***N*-Octylfurfurylamine 6b**. The amine is prepared in 98% yield as a pale yellow oil after distillation under reduced pressure (T_{eb} =90°C, p = 7.10^{-2} mbar) starting from imine **5b** as described for compound **6a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, ^3J (H, H) = 6.4 Hz, 3H, $N(CH_2)_7CH_3$), 1.26-1.27 (m, 10H, $N(CH_2)_2(CH_2)_5CH_3$), 1.44-1.50 (m, 2H, $NCH_2CH_2(CH_2)_5CH_3$), 2.59 (t, ^3J (H, H) = 6.8 Hz, 2H, $NCH_2(CH_2)_6CH_3$), 3.76 (s, 2H, NCH_2-furan), 6.15 (d, ^3J (H, H) = 3.2 Hz, 1H, 3-H furan), 6.30 (dd, ^3J (H, H) = 2.2 Hz, ^3J (H, H) = 3.2 Hz, 1H, 4-H furan), 7.35 (d, ^3J (H, H) = 2.2 Hz, 1H, 5-H furan); GC rt 17.1 min; MS (70 eV, EI): m/z 209 (25) [M^+]; 180 (5) [M^+- CH_3CH_2]; 166 (5) [M^+- $CH_3(CH_2)_2$]; 152 (5) [M^+- $CH_3(CH_2)_3$]; 110 (100) [M^+- $CH_3(CH_2)_6$]; 96 (20) [M^+- $CH_3(CH_2)_7$]; 81 (100) [M^+- $CH_3(CH_2)_7$ NH]; 53 (15).

***N*-Hexylfurfurylamine 6c**. The amine is prepared in 95% yield as a pale yellow oil after distillation under reduced pressure (T_{eb} = 70°C, p = 7.10^{-2} mbar) starting from imine **5c** as described for compound **6a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, ^3J (H, H) = 6.2 Hz, 3H, $N(CH_2)_5CH_3$), 1.23-1.27 (m, 6H, $N(CH_2)_2(CH_2)_3CH_3$), 1.47-1.52 (m, 2H, $NCH_2CH_2(CH_2)_3CH_3$), 2.61 (t, ^3J (H, H) = 7.2 Hz, 2H, $NCH_2(CH_2)_4CH_3$), 3.77 (s, 2H, NCH_2-furan), 6.19 (d, ^3J (H, H) =

3.0 Hz, 1H, 3-H furan), 6.32 (dd, ^3J (H, H) = 2.2 Hz, ^3J (H, H) = 3.0 Hz, 1H, 4-H furan), 7.34 (d, ^3J (H, H) = 2.2 Hz, 1H, 5-H furan); GC rt 15.4 min; MS (70 eV, EI): m/z 181 (5) [M^+]; 110 (40) [M^+- $CH_3(CH_2)_4$]; 96 (10) [M^+- $CH_3(CH_2)_5$]; 81 (100) [M^+- $CH_3(CH_2)_5$ NH]; 53 (10).

***N,N*-dibutylfurfurylamine 7a.** Freshly distilled amine **6a** (1.53 g, 10 mmol), K_2CO_3 (1.38 g, 10 mmol) and bromobutane (1.07 cm^3, 10 mmol) are charged in a two necked round bottom flask and stirred at room temperature for 24 hours. The reaction is monitored by GC-MS, when the conversion is completed, K_2CO_3 is filtered off and the product is purified by distillation under reduced pressure (T_{eb} = 70°C, p = 8.10^{-2} mbar) giving a pale yellow oil (1.24 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (m, 6H, 2 × CH_3(CH$_2$)$_3$N), 1.27-1.33 (m, 4H, 2 × CH_3CH_2CH_2(CH$_2$)$_2$N), 1.43-1.49 (m, 4H, 2 × $CH_3CH_2CH_2$CH_2N), 2.42 (m, 4H, 2 × CH_3(CH$_2$)$_2$CH_2N), 3.64 (s, 2H, NCH_2-furan), 6.15 (d, ^3J (H, H) = 3.0 Hz, 1H, 3-H furan), 6.31 (dd, ^3J (H, H) = 1.8 Hz, ^3J (H, H) = 3.0 Hz, 1H, 4-H furan), 7.36 (d, ^3J (H, H) = 1.8 Hz, 1H, 5-H furan); GC rt 20.6 min; MS (70 eV, EI): m/z 209 (10) [M^+]; 166 (45) [M^+- $CH_3(CH_2)_2$]; 81 (100) [M^+- $CH_3(CH_2)_3$N $CH_3(CH_2)_3$]; 53 (10).

***N*-butyl-*N*-dodecylfurfurylamine 7b** is obtained with the same procedure of **7a** starting from **6a** and bromododecane,70% yield after flash chromatography (cyclohexane/AcOEt 8/2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86-0.94 (m, 6H, CH_3(CH$_2$)$_{11}$N, CH_3(CH$_2$)$_3$N), 1.26-1.35 (m, 20H, CH_3(CH_2)$_9$(CH$_2$)$_2$N, CH_3CH_2(CH$_2$)$_2$N), 1.50-1.52 (m, 4H, CH_3(CH$_2$)$_9$CH_2CH$_2$N, CH_3CH_2CH_2CH_2N), 2.44-2.49 (m, 4H, CH_3(CH$_2$)$_{10}$CH_2N, CH_3(CH$_2$)$_3$CH_2N), 3.72 (s, 2H, NCH_2-furan), 6.22 (d, ^3J (H, H) = 3.2 Hz, 1H, 3-H furan), 6.33 (dd, ^3J (H, H) = 2.2 Hz, ^3J (H, H) = 3.2 Hz, 1H, 4-H furan), 7.38 (d, ^3J (H, H) = 2.2 Hz, 1H, 5-H furan); GC rt 26.5 min; MS (70 eV, EI): m/z 321 (10) [M^+]; 278 (40) [M^+- $CH_3(CH_2)_2$]; 166 (65) [M^+- $CH_3(CH_2)_{10}$]; 81 (100) [M^+- $CH_3(CH_2)_{11}$ N $CH_3(CH_2)_3$].

***N*-Butyl-*N*-octylfurfurylamine 7c.** The amine **7c** is prepared from amine **6b** with the same procedure described for compound **7a**, obtained as a pale yellow oil in 90% yield after distillation under reduced pressure (T_{eb} =100°C, p = 9 10^{-2} mbar). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, ^3J (H, H) = 6.4 Hz, 3H, CH_3(CH$_2$)$_7$N), 0.93 (t, ^3J (H, H) = 7.2 Hz, 3H, N(CH$_2$)$_3$CH_3), 1.24-1.36 (m, 12H, CH_3(CH_2)$_5$(CH$_2$)$_2$N, CH_3CH_2(CH$_2$)$_2$N), 1.75-1.79 (m, 4H, CH_3(CH$_2$)$_5$CH_2CH_2N, CH_3CH_2CH_2CH_2N), 2.72-2.77 (m, 4H, CH_3(CH$_2$)$_6$CH_2N, CH_3(CH$_2$)$_2$CH_2N), 4.08 (s, 2H, NCH_2-furan), 6.40 (dd, ^3J (H, H) = 1.8 Hz, ^3J (H, H) = 3.2 Hz, 1H, 3-H furan), 6.52 (d, ^3J (H, H) = 3.2 Hz, 1H, 4-H furan), 7.45 (d, ^3J (H, H) = 1.8 Hz, 1H, 5-H furan); GC rt 20.3 min; MS (70 eV, EI): m/z 265 (10) [M^+]; 222 (30) [M^+- $CH_3(CH_2)_2$]; 166 (50) [M^+- $CH_3(CH_2)_6$]; 81 (100) [M^+- $CH_3(CH_2)_3$ N $CH_3(CH_2)_7$], 53 (5).

***N*-Dodecyl-*N*-octyl-furfuryl amine 7d.** The amine is prepared from octyl-furfuryl amine **6b** as described for compound **7b,** in a 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85-0.88 (m, 6H, CH_3(CH$_2$)$_{11}$N, CH_3(CH$_2$)$_7$N), 1.24-1.28 (m, 28H, CH_3(CH_2)$_9$(CH$_2$)$_2$N, CH_3(CH_2)$_5$(CH$_2$)$_2$N), 1.71-1.73 (m, 4H, CH_3(CH$_2$)$_9$CH_2CH_2N, CH_3 (CH$_2$)$_5$CH_2CH_2N), 2.67 (m, 4H, CH_3(CH$_2$)$_{10}$CH_2N, CH_3(CH$_2$)$_6$CH_2N), 4.00 (s, 2H, NCH_2-furan), 6.38 (dd, ^3J (H, H) = 1.6 Hz, ^3J (H, H) = 3.2 Hz, 1H, 4-H furan), 6.38 (d, ^3J (H, H) = 3.2 Hz, 1H, 3-H furan), 7.43 (d, ^3J (H, H) = 1.6 Hz, 1H, 5-H furan); GC rt 27.3; MS (70 eV, EI): m/z 377 (10) [M^+]; 278 (75) [M^+- $CH_3(CH_2)_6$]; 264 (10) [M^+- $CH_3(CH_2)_7$]; 222 (80) [M^+- $CH_3(CH_2)_{10}$]; 208 (10) [M^+- $CH_3(CH_2)_{11}$]; 81 (100) [M^+- $CH_3(CH_2)_{11}$ N $CH_3(CH_2)_7$].

Figure 1. Relationship between quaternary ammonium salts concentration in water and number of active individuals of *Daphnia magna*, after a 48 h exposure. Points: observed values (mean of two replicates); lines: logistic model fitted to the observed data.

Fig. 1

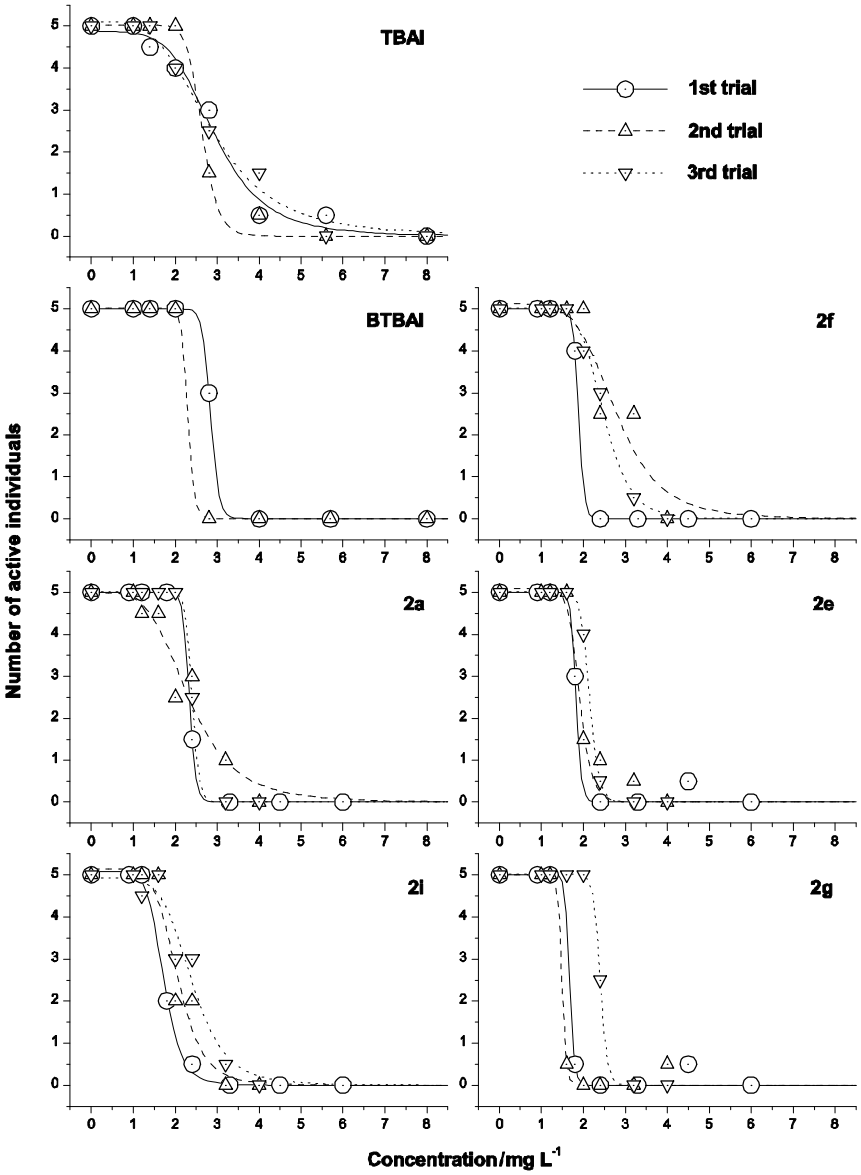

Figure 2. Relationship between quaternary ammonium salts concentration in water and bioluminescence of *Vibrio fischeri*, after a 15 min exposure. Points: observed values; lines: logistic model fitted to the observed data.

Fig. 2