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# **Supplementary Information for**

## Photolysis-driven coalescence of microdroplets in microfluidic chambers

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### **General experimental details**

All solvents and reagents were purchaised from commercial sources (Krytox 157-FSH (Dupont), PEG-600 (Sigma-Aldrich), HFE 7500 (3M)) and used without purification unless otherwise noted. Thin layer chromatography was performed on aluminium-backed Merck Kieselgel 60 F 254 pre-coated plates. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded on a Bruker 250 spectrometer (250 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual proton in the NMR solvent (CDCl<sub>3</sub>:  $\delta$  7.26, CD<sub>3</sub>OD:  $\delta$  3.31). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd =double doublet, t = triplet, m = multiplet), coupling constants in Hertz (Hz), integration.

The material used for UV irradiation consisted of an IX73 Olympus inverted microscope and a ps-pulsed tripled frequency Nd:YAG laser (model PNV-M02510, Teem Photonics) working at 355 nm wavelength with a pulse width of about 400 ps and emitting 20  $\mu$ J/pulse energy. The pulse repetition rate was set to 1 kHz for all experiments. The width of the laser spot was estimated from a direct microscope image to about 35  $\mu$ m. Images of droplets were taken in the microchannel using a standard CCD camera (uEye) at 30 frames per second rate. The droplet size distribution and image processing were realized using ImageJ software.

### Synthesis of surfactants



**Scheme 1.** Synthesis of surfactants **3** and **4**. Reagents and conditions: i) piperazine,  $K_2CO_3$ , DMSO, 120 °C, 16 h (98%); ii) Pd/C, H<sub>2</sub>, MeOH, rt, 10h, (quant.); iii) crotonaldehyde, 6M HCl, toluene, 120 °C, 4 h, (24%); iv) Boc<sub>2</sub>O, DMAP, DCM, rt, 2h, (93%); v) SeO<sub>2</sub>, dioxane, 80 °C, 3h, (quant.); vi) NaBH<sub>4</sub>, MeOH, rt, 1 h, (87%); vii) MeO-PEG600-CH<sub>2</sub>CO<sub>2</sub>H, DCC, DMAP, DCM, rt, 16h, (70%); viii) 4M HCl/dioxane, rt, 2 h, (89%); ix) Krytox-COCl, Et<sub>3</sub>N, THF/HFE7100, rt, 24 h; x) 4M HCl/dioxane, rt, 2 h, (quant.); xi) MeO-PEG-CH<sub>2</sub>CO<sub>2</sub>H, DCC, DMAP, Et<sub>3</sub>N, DMF, rt, 24 h, (75%); xii) Krytox-COCl, Et<sub>3</sub>N, THF/HFE7100 rt, 24 h.

**1-(2-nitrophenyl)piperazine**<sup>1</sup>: A mixture of 1-fluoro-2-nitrobenzene (10.00 g, 70.87 mmol, 1.0 equiv), piperazine (30.52 g, 354.35 mmol, 5.0 equiv) and  $K_2CO_3$  (48.97 g, 354.35 mmol, 5.0 equiv) in DMSO (150 mL) was stirred at 120°C for 16 h. After cooling to room temperature a solution of NaHCO<sub>3</sub> 10% was added and the product was extracted with DCM. The organic layer was washed twice with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to provide a

dark orange oil (14.38 g, 98%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.76 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.48 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.15 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.04 (td, *J* = 8.3, 1.3 Hz, 1H), 3.03 (s, 8H).

**2-(piperazin-1-yl)aniline:** 1-(2-nitrophenyl)piperazine (7.42 g, 35.81 mmol, 1.0 equiv) was added to a suspension of Pd/C 10% (185 mg) in MeOH (150 mL) under hydrogen atmosphere (1atm) at rt. The reaction was charged with hydrogen until the disappearance of the yellow starting product. The mixure was then filtered on cellite and concentrated under reduced pressure to afford a brown oil (6.35 g, quant.). The crude product was used without further purification for the next step.

**2-methyl-8-(piperazin-1-yl)quinoline:** 2-(piperazin-1-yl)aniline (6.45 g, 36.39 mmol, 1.0 equiv) was dissolved in 6M HCl (75 mL), after addition of crotonaldehyde (9.0 mL, 109.17 mmol, 3.0 equiv) the mixture was stirred for 1h at rt. Toluene (40 mL) was added and the reaction was heated at 120°C for 4 h. After cooling to rt, the organic layer was removed, and the aqueous layer was neutralized by addition of NaOH. The solution was extracted with DCM and the organic layer was washed twice with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (DCM $\rightarrow$ DCM/MeOH 9/1 $\rightarrow$ DCM/MeOH 4/1). Yellow oil (1.98 g, 24 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 8.3 Hz, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.10 (d, *J* = 1.8 Hz, 1H), 3.12 (s, 8H), 2.75 (s, 3H), 1.58 (br s, 1H).

*tert*-butyl 4-(2-methylquinolin-8-yl)piperazine-1-carboxylate: To a solution of 2-methyl-8-(piperazin-1-yl)quinoline (500 mg, 2.20 mmol, 1.0 equiv) in DCM (5 mL), di-*tert*-butyl dicarbonate (528 mg, 2.42 mmol, 1.1 equiv) and DMAP (54 mg, 0.44 mmol, 0.2 equiv) were added and the mixture was stirred at rt for 2 h. The solution was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The product was used without further purification. Yellow oil (670 mg, 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.97 (d, *J* = 8.3 Hz, 1H), 7.40-7.30 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.06 (dd, *J* = 6.8, 2.3 Hz, 1H), 3.80-3.72 (m, 4H), 3.37-3.30 (m, 4H), 2.72 (s, 3H), 1.50 (s, 9H).

*tert*-butyl 4-(2-formylquinolin-8-yl)piperazine-1-carboxylate: To a mixture of selenium dioxide (303 mg, 2.73 mmol, 1.3 equiv) in dioxane (35 mL), *tert*-butyl 4-(2-methylquinolin-8-yl)piperazine-1-carboxylate (688 mg, 2.1 mmol, 1.0 equiv) was added and the mixture was stirred for 3 h at 80 °C. After cooling to rt, the mixture was filtered through cellite, eluted with DCM. After removing the solvents under reduced pressure, the crude product was used without further purification. Yellow oil (717 mg, quant). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  10.18 (s, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.21 (dd, *J* = 7.5 Hz, 1.3 Hz, 1H), 3.84-3.77 (m, 4H), 3.48-3.42 (m, 4H), 1.52 (s, 9H).

*tert*-butyl **4-(2-(hydroxymethyl)quinolin-8-yl)piperazine-1-carboxylate:** To *tert*-butyl 4-(2-formylquinolin-8-yl)piperazine-1-carboxylate (400 mg, 1.17 mmol, 1.0 equiv) in MeOH (5 mL), NaBH<sub>4</sub> (89 mg, 2.34 mmol, 2.0 equiv) was added at 0°C and the mixture was stirred at rt for 0.5 h before being quenched with 1M HCl. After removing the MeOH under reduced pressure, water was added to the residue, followed by extraction with DCM. The combined organic phases were washed twice with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to dryness. The crude product was used without further purification. Yellow oil (350 mg, 87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.06 (d, *J* = 8.5 Hz, 1H), 7.47–7.36 (m, 2H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.11 (dd, *J* = 6.1, 2.8 Hz, 1H), 4.89 (s, 2H), 3.81–3.66 (m, 4H), 3.36–3.21 (m, 4H), 1.49 (s, 9H).

**Compound 5:** To a solution of *tert*-butyl 4-(2-(hydroxymethyl)quinolin-8-yl)piperazine-1-carboxylate (100 mg, 0.29 mmol, 1.0 equiv) in DCM (5 mL), MeO-PEG600-CH<sub>2</sub>CO<sub>2</sub>H<sup>\*</sup> (240 mg, 0.35 mmol, 1.2 equiv), DMAP (106 mg, 0.87 mmol, 3.0 equiv) and DCC (120 mg, 0.58 mmol, 2.0 equiv) were added and the mixture was stirred at rt overnight. After evaporation to dryness, the crude product was purified by column chromatography on silica gel (DCM/MeOH 95/5) to afford the product as a yellow oil (206 mg, 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.13 (d, *J* = 8.5 Hz, 1H), 7.48-7.40 (m, 3H), 7.11 (tm, *J* = 4.5 Hz, 1H), 5.46 (s, 2H), 4.29 (s, 2H), 3.80-3.60 (m, 46H), 3.55-3.50 (m, 4H), 3.35 (s, 3H), 3.37-3.30 (m, 4H), 1.48 (s, 9H).

<sup>\*</sup>Prepared in three steps (i) MeI, NaH, THF, rt; ii) *tert*-butyl bromoacetate, NaH, THF, rt; iii) HCl, THF, rt) from commercially available PEG600.

**Compound 6:** To the Boc-protected amine **5** (206 mg, 0.20 mmol, 1.0 equiv) 4M HCl/dioxane (3 mL) was added at 0°C and the mixture was stirred at rt for 3 h in the dark. After completion of the reaction, the mixture was concentrated under reduced pressure. The crude product was used without further purification. Yellow oil (172 mg, 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.14 (d, *J* = 8.5 Hz, 1H), 7.47-7.40 (m, 3H), 7.14 (dd, *J* = 6.8, 1.5 Hz, 1H), 5.44 (s, 2H), 4.28 (s, 2H), 3.80-3.40 (m, 46+4H), 3.35 (br s, 3+4H).

**Compound 3:** Krytox-acid chloride<sup>2,3,4</sup> (0.18 mmol, 1.0 eq) was dissolved in HFE7100 and was added to a solution of the free amine (**6**) (172 mg, 0.18 mmol, 1.0 equiv) and triethylamine (63  $\mu$ L, 0.45 mmol, 2.5 equiv) in dry THF and HFE7100. The mixture was stirred at room temperature overnight under argon. After evaporation to dryness, the residue was taken up in FC3283 ((C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>N)), filtered through a plug of silica and washed subsequently with methanol and toluene. After removal of the solvent, the product\* was obtained as a yellow oil, that was used without further purification. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.97 (d, J=7.5 Hz, 1H), 7.46-7.37 (3H), 6.90 (d, J=7.0 Hz, 1H), 5.27 (s, 2H), 4.08 (s, 2H), 3.40-3.20 (m, 46+4H), 3.20-3.10 (m, 3+4H).

(8-(piperazin-1-yl)quinolin-2-yl)methanol: To the Boc-protected amine 2 (100 mg, 0.29 mmol, 1.0 equiv), 4M HCl/dioxane (3 mL) was added at 0°C and the mixture was stirred at rt for 2 h in the dark. After completion of the reaction, the mixture was concentrated under reduced pressure. The crude product was used without further purification. Yellow oil (71 mg, quant.). <sup>1</sup>H NMR (MeOD):  $\delta$  9.21 (d, *J* = 8.8 Hz, 1H), 8.24-8.14 (m, 3H), 7.99 (t, *J* = 7.8 Hz, 1H), 5.36 (s, 2H), 3.69-3.63 (m, 4H), 3.51-3.45 (m, 4H).

**Compound 7:** To a solution of (8-(piperazin-1-yl)quinolin-2-yl)methanol (100 mg, 0.41 mmol, 1.0 equiv) in DMF (5 mL), MeO-PEG600-CH<sub>2</sub>CO<sub>2</sub>H (340 mg, 0.49 mmol, 1.2 equiv), DMAP (150 mg, 1.23 mmol, 3.0 equiv) and DCC (169 mg, 0.82 mmol, 2.0 equiv) were added and the mixture was stirred at rt 24 h. After evaporation to dryness, the crude product was purified by column chromatography on silica gel (DCM/MeOH 98/2) to afford the product as a yellow oil (280 mg, 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.14 (d, *J* = 8.5 Hz, 1H), 7.50-7.42 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.17 (dd, *J* = 7.0, 1.5 Hz, 1H), 4.92 (s, 2H), 4.29 (s, 2H), 3.74-3.50 (m, 46+8H), 3.37 (s, 3H).

**Compound 4:** Krytox-acid chloride was dissolved in HFE7100 and was added to a solution of the free alcohol (7) (100 mg, 0.10 mmol, 1.0 equiv) and triethylamine (35  $\mu$ L, 0.25 mmol, 2.5 equiv) in dry THF and HFE7100. The mixture was stirred at room temperature overnight under argon. After evaporation to dryness, the residue was taken up in FC3283 ((C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>N)), filtered through a plug of silica and washed subsequently with methanol and toluene. After removal of the solvent, the product\* was obtained as a yellow oil, that was used without further purification.

\*formation of products **3** and **4** was confirmed by <sup>1</sup>H and <sup>19</sup>F NMR<sup>5,6</sup> and FT-IR spectroscopy<sup>5,7</sup>. For NMR analysis, a sample of the product was dissolved in hexafluorobenzene, transferred to an NMR tube and sealed with an internal capillary tube containing benzene- $d_6$  as a lock signal. Change of the peak (-132 ppm) corresponding to the CF group next to the terminal Krytox carbonyl was detected. By FT-IR analysis, the absorbance peak at 1775 cm<sup>-1</sup> corresponding to the carboxylic acid C=O stretch of Krytox-COOH and appearance of a novel carbonyl C=O stretch due to product formation were monitored. Due to disappearance of the acid absorbance peak of 1775 cm<sup>-1</sup>, the conversion was estimated to be near total (Fig. 1, 2).



**Figure 1.** (left) Full-scale FT-IR spectra of compounds **6**, **3** and Krytox-COOH; (right) comparison of FT-IR spectra of compound **3** and Krytox-COOH (zoom in 1850-1500 cm<sup>-1</sup> region).



**Figure 2.** (left) Full-scale FT-IR spectra of compounds **7**, **4** and Krytox-COOH; (right) comparison of FT-IR spectra of compound **4** and Krytox-COOH (zoom in 1850-1500 cm<sup>-1</sup> region).

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