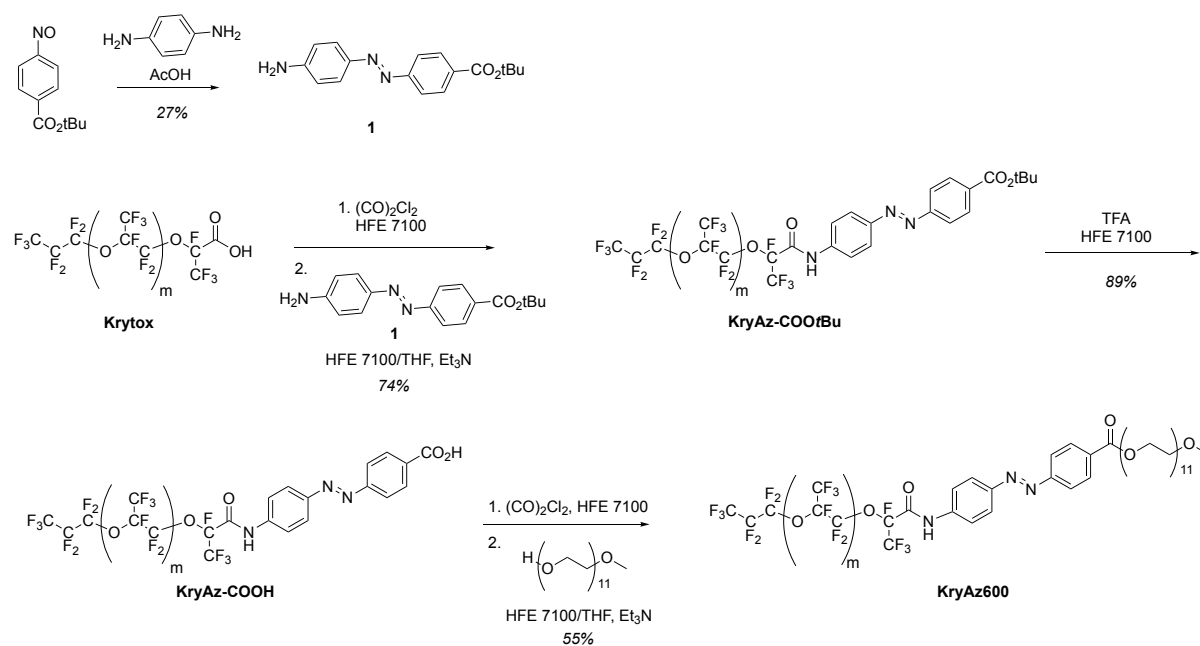


Supporting information (S1) : Chemical synthesis procedure of KryAz600 surfactant.

General Procedures

All purchased reagents were used without further purification. HFE7100 was dried on molecular sieves 4Å. ^1H and ^{13}C NMR spectra were recorded on a JEOL 400 spectrometer and referenced to the resonance of the solvent used. Infrared (IR) spectra were recorded with a Nicolet Nexus FT-IR spectrometer equipped with an ATR-Germanium unit and are reported as wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were performed on a Bruker maXis mass spectrometer by the "Fédération de Recherche" ICOA/CBM (FR2708) platform.

Synthetic scheme



Synthetic procedures

1: To a solution of *t*-butyl 4-nitrosobenzoate (95 mg, 0.46 mmol) in AcOH (4 mL) was added 4-phenylenediamine (49 mg, 0.45 mmol, 1 equiv). After stirring at 60°C for 12 h, the mixture was evaporated under reduced pressure. The residue was dissolved in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (1/1, 50 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL), the combined organic layers were washed with a saturated aqueous solution of NaHCO_3 , dried over anhydrous Na_2SO_4 , filtered and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel-PE/EA: 7/3) to afford **1** (37 mg, 0.12 mmol, 27%) as an orange solid; ^1H NMR (400 MHz, CDCl_3): δ ppm 8.10 (d, $J = 8.2$ Hz, 2H), 7.84 (m, 4H), 6.75 (d, $J = 8.7$ Hz, 2H), 4.14 (br s, 2H, NH_2), 1.63 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 165.6, 155.5, 150.3, 145.7, 132.7, 130.5, 125.7, 122.1, 114.7, 81.4, 28.4; HRMS (ESI): calc. for $\text{C}_{17}\text{H}_{20}\text{N}_3\text{O}_2^+$, $[\text{M}+\text{H}]^+ m/z$ 298.1550, found m/z 298.1550.

KryAz-COOtBu: To a solution of Krytox® (2.22 g, 0.32 mmol) in anhydrous HFE7100 (7 mL) under argon was added oxalyl chloride (0.2 mL, 10 equiv). After stirring at 60°C for 12 h, the mixture was evaporated under reduced pressure. To a solution of the crude product in anhydrous HFE7100 (8 mL) under argon was added a solution of **1** (95 mg, 0.32 mmol, 1 equiv) and Et_3N (0.2 mL) in anhydrous THF (8 mL). After stirring at r.t. for 12 h, the supernatant was removed and the orange oil was washed with THF (3 x 15 mL) to afford **KryAz-COOtBu** (1.62 g, 0.24 mmol, 74%) as an orange oil. IR (ATR): 1705, 1693 cm^{-1} .

KryAz-COOH: To a solution of **KryAz-COOtBu** (1.62 g, 0.24 mmol) in HFE7100 (5 mL) was added trifluoroacetic acid (100 μ L, 1.35 mmol, 5.6 equiv). After stirring at r.t. for 12 h, the mixture was evaporated under reduced pressure. The crude product was washed with H₂O (4 x 5 mL), acetone (2 x 5 mL) and CH₂Cl₂ (2 x 5 mL) to afford **KryAz-COOH** (1.43 g, 0.21 mmol, 89%) as an orange oil. **IR (ATR):** 1784, 1708, 1690 cm^{-1} .

KryAz600: To a solution of **KryAz-COOH** (930 mg, 0.138 mmol) in anhydrous HFE7100 (6 mL) under argon was added oxalyl chloride (225 μ L, 1.38 mmol, 10 equiv). After stirring at 60°C for 12 h, the mixture was evaporated under reduced pressure. The crude residue in solution in anhydrous HFE7100 (6 mL) was added to a solution of *O*-methyl-undecaethylene glycol (80 mg, 0.15 mmol, 1.2 equiv) and Et₃N (37 μ L, 0.28 mmol, 2 equiv) in anhydrous THF (6 mL). After stirring at r.t. for 12 h, the supernatant was removed and the yellow oil was washed with H₂O (2 x 5 mL) acetone (2 x 5 mL) and CH₂Cl₂ (2 x 50 mL) to afford **KryAz600** (920 mg, 0.127 mmol, 92%) as a yellow oil. **IR (ATR):** 1707, 1693 cm^{-1} .

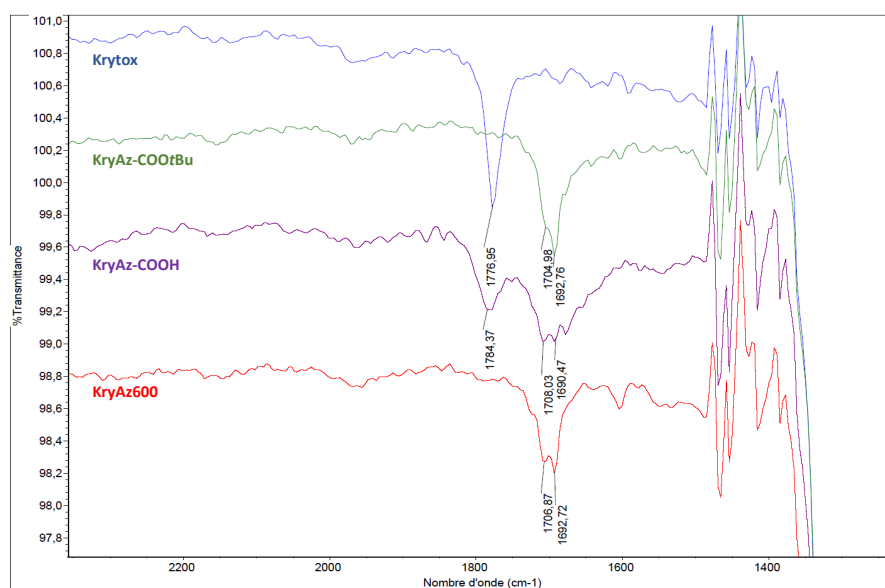


Figure S1. Portion of the infrared spectra of the different surfactants synthesized.