

Use of degradable cationic surfactants with cleavable linkages for enhancing the  
chemiluminescence of acridinium ester labels

Supplementary Material

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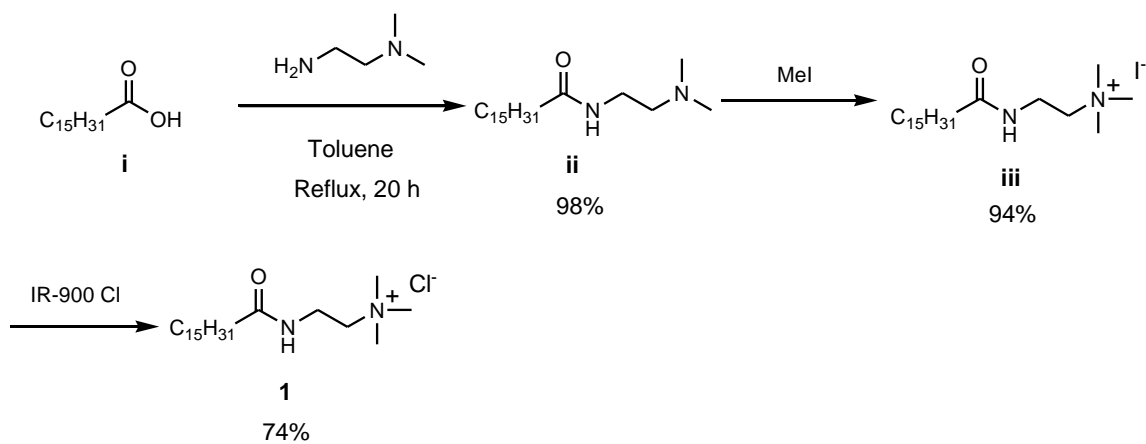


Figure S1. Synthetic scheme for cationic surfactant **1** with cleavable amide linkage.

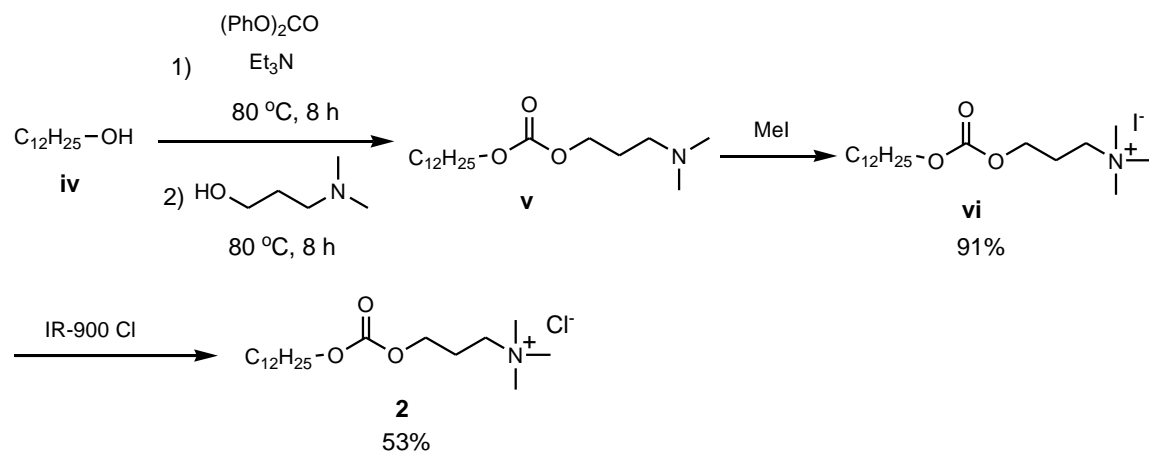


Figure S2. Synthetic scheme for cationic surfactant **2** with cleavable carbonate linkage.

### *Synthesis of cationic amide surfactant 1 (Figure S1)*

#### Compound ii

Palmitic acid (**i**, 2.564 g, 10.00 mmoles), toluene (100 mL) and N,N-dimethylethylenediamine (1.147 mL, 10.50 mmoles) were combined and refluxed for 20 hours. The reaction mixture was concentrated to dryness which gave 3.21 g of a slightly yellow solid. The crude solid was re-crystallized from dry acetone (75 mL). The desired product **ii** (1.83g) was obtained as white, needle-like crystals.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ), 0.87 (t, 3H,  $J = 6.5$ ), 1.20-1.35 (m, 24H), 1.55-1.70 (m, 2H), 2.17 (t, 2H,  $J = 7.5$ ), 2.30 (s, 6H), 2.49 (t, 2H,  $J = 5.5$ ), 3.36 (dt, 2H,  $J = 5.5, 5.5$ ), 6.25 (br s, 1H). MALDI-TOF MS  $m/z$  327.4 ( $\text{M} + \text{H}^+$ ); HRMS  $m/z$  327.3376 ( $\text{M} + \text{H}^+$ ) (327.3375 calculated).

#### Compound iii

Compound **ii** (1.41 g, 4.32 mmoles), acetone (50 mL) and iodomethane (0.309 mL, 4.97 mmoles) were refluxed at 80°C under an argon atmosphere for 6 hours. The reaction mixture was cooled to room temperature and the precipitated white solid was collected by filtration. The filter cake was washed with dry acetone (10 mL x 4) and dried over  $\text{P}_2\text{O}_5$  under high vacuum. The desired product **iii** (1.904 g) was obtained as a white solid.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ) 0.88 (t, 3H,  $J = 6.5$ ), 1.21-1.38 (m, 22H), 1.57-1.70 (m, 4H), 2.29 (t, 2H,  $J = 7.3$ ), 3.42 (s, 9H), 3.78-3.89 (m, 4H), 7.96 (br s, 1H). MALDI-TOF MS  $m/z$  282.36 ( $\text{M-NMe}_3^+$ ); HRMS  $m/z$  341.3528 ( $\text{M}^+$ ) (341.3532 calculated).

#### Compound 1

Compound **iii** (1.50 g, 3.20 mmoles) was dissolved in absolute ethanol (400 mL) at room temperature and IR-900 chloride resin (76.2 g, 3.20 mmoles) was added and stirred at room temperature for 1 hour. Then, the mixture was passed through an IR-900 chloride resin column (80 g pre-washed with absolute ethanol). The column was eluted with absolute ethanol (600 mL). The eluent was concentrated under reduced pressure which gave 1.51 g of a slightly brown solid. This material was re-crystallized from

anhydrous acetone/ethanol. The desired product, surfactant **1** (0.895 g), was obtained as a white solid.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ) 0.86 (t, 3H,  $J = 6.3$ ), 1.17-1.38 (m, 22H), 1.55-1.68 (m, 4H), 2.27 (t, 2H,  $J = 7.3$ ), 3.43 (s, 9H), 3.70-3.85 (m, 4H), 8.72 (br s, 1H). MALDI-TOF MS  $m/z$  282.36 ( $\text{M-NMe}_3^+$ ); HRMS  $m/z$  341.3529 ( $\text{M}^+$ ) (341.3532 calculated).

#### *Synthesis of cationic carbonate surfactant **2** (Figure S2)*

##### Compound **v**

A mixture of dodecanol (**iv**, 2.236 mL, 10.00 mmoles), triethylamine (1.394 mL, 10.00 mmoles) and diphenyl carbonate (2.142 g, 10.00 mmoles) was heated to  $80^\circ\text{C}$  for 16 hours. Then, 3-dimethylamino-1-propanol (2.366 mL, 20.00 mmoles) was added and heated to  $80^\circ\text{C}$  for an additional 16 hours. The reaction mixture was then concentrated under reduced pressure to give 3.92 g of a dark yellow oil. It was purified by silica gel column chromatography using methanol/ethyl acetate (1:9) as eluent. The desired product **v** (2.63 g) was obtained as a yellow oil.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ) 0.88 (t, 3H,  $J = 6.5$ ), 1.20-1.42 (m, 18H), 1.61-1.71 (m, 2H), 1.87-1.98 (m, 2H), 2.33 (s, 6H), 2.49 (br t, 2H,  $J = 7.0$ ), 4.12 (t, 2H,  $J = 6.5$ ), 4.19 (t, 2H,  $J = 6.3$ ). MALDI-TOF MS  $m/z$  316.3 ( $\text{M+H}^+$ ); HRMS  $m/z$  316.2855 ( $\text{M+H}^+$ ) (316.2852 calculated).

##### Compound **vi**

Compound **v** (1.500 g, 4.75 mmoles), acetone (50 mL) and iodomethane (0.340 mL, 5.47 mmoles) were combined and refluxed for 6 hours. After cooling to room temperature, the desired product precipitated out as a white solid. It was collected by filtration and washed with ethyl acetate (10 mL x 4). The solid was dried over  $\text{P}_2\text{O}_5$  under high vacuum. The desired product **vi** (1.988 g) was obtained as a white solid.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ) 0.87 (t, 3H,  $J = 7.0$ ), 1.60-1.72 (m, 18H), 2.05-2.34 (m, 2H), 3.49 (s, 9H), 3.76 (t, 2H,  $J = 7.3$ ), 4.12 (t, 2H,  $J = 6.5$ ), 4.29 (m, 2H). MALDI-TOF MS  $m/z$  316.3 ( $\text{M+H}^+$ ); HRMS  $m/z$  316.2855 ( $\text{M+H}^+$ ) (316.2852 calculated).

## Compound 2

Compound **vi** (1.50 g, 3.28 mmoles) was dissolved in absolute ethanol (200 mL) at room temperature and IR-900 chloride resin (78 g, 328 mmoles) was added and stirred at room temperature for 1 hour. Then, the mixture was passed through an IR-900 chloride resin column (80 g pre-washed with absolute ethanol). The column was eluted with absolute ethanol (400 mL). The eluent was concentrated under reduced pressure which gave 1.5 g of a white solid. The crude product was re-crystallized from anhydrous acetone. The desired product **2** (0.637 g) was obtained as a white solid. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) 0.86 (t, 3H, *J* = 6.5) 1.60-1.70 (m, 18H), 2.18-2.30 (m, 2H), 3.49 (s, 9H), 3.72 (t, 2H, *J* = 7.8), 4.11 (t, 2H, *J* = 6.8), 4.25 (m, 2H). HRMS *m/z* 330.3013 (M<sup>+</sup>) (330.3008 calculated).