Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary information for

Tunable detection range ion-selective nano-optodes by controlling solvatochromic dye transducer lipophilicity

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Contents

Experimental Section

Reagents. *para*-Toluenesulfonyl chloride (TsCl), 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde, 2,2'-oxydiethanol, tetrabutylammonium chloride (TBAC), stearoyl chloride, 4-methylpyridine, 1-iodooctadecane, 1,4-dimethylpyridinium iodide, 4-dimethylaminopyridine (DMAP), triethylamine (Et_3N), piperidine, diethylene glycol, tetraethylene glycol, acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), 4-dimethylpyridinium iodide, methanol (CH_3OH), bis(2-ethylhexyl) sebacate (DOS), polyurethane (PU), polyvinyl chloride (PVC), tetrahydrofuran (THF), sodium tetrakis- [3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), potassium ionophore I (valinomycin), alginic acid sodium salt from brown algae (bioreagent, suitable for immobilization of micro-organisms), calcium chloride ($CaCl_2$), sodium chloride (NaCl), were purchased from Sigma-Aldrich. All solutions were prepared by dissolving appropriate salts into deionized water (Milli-Q). All salts used were analytical grade or higher.

Preparation of K^+-selective emulsion sensors

PU-DOS emulsion sensors. 0.23 mg of SD-PEG2 (0.20 mg of SD-C1, 0.21 mg of SD-C4, 0.27 mg of SD-C18, and 0.25 mg of SD-PEG4), 0.6 mg of NaTFPB, 6.0 mg of DOS, 3.0 mg of PU were dissolved in 3.0 mL of THF and get a homogeneous solution. 0.2 mL of the solution was pipetted and injected into 2 mL of deionized water on a vortex at the speed of 1000 rpm. Compressed air was blown on the surface of emulsion for 30 min to remove THF and reduce the solution volume back to 2 mL. Fluorescence response measurements were performed with 100-fold diluted stock solution.

PVC-DOS emulsion sensors and DOS emulsion sensors. They are prepared with the same recipe and procedure but replace PU with the same amount of PVC or remove PU.

Preparation of alginate particles

Sodium alginate (10 mg) was dissolved in 1 mL PU-DOS nanosphere stock solutions (SD-PEG4, SD-C1, SD-C18). 1.0 g $CaCl_2$ was dissolved in 100 mL milli-Q water. Disposable syringes (1 mL, NORM-JECT®) were used to make alginate particles by dropping emulsion contained sodium alginate solution to $CaCl_2$ solution. 5 alginate particles were prepared for each kind of SD-based sensor.

Instrumentation

Fluorescence signals were measured with a fluorescence spectrometer (Fluorolog-3, Horiba Jobin Yvon) using disposable cuvette. Fluorescence intensity was recorded at the wavelength of 600 nm. The emulsion fluorescence response measurements were performed by adding known aliquots of corresponding potassium solutions.

Alginate particle photos were taken with a digital camera (Canon EOS 5D Mark II, Lens: Canon EF f/2.8L 100mm Macro IS USM)

The size and ζ-potential of the particles were measured on ZetaSizer Nano ZS (Malvern Instruments) at 25 °C.[1] At least 3 measurements were carried out for each data point.

Supplementary results (Figure S1-S4 and Table S1-S2)

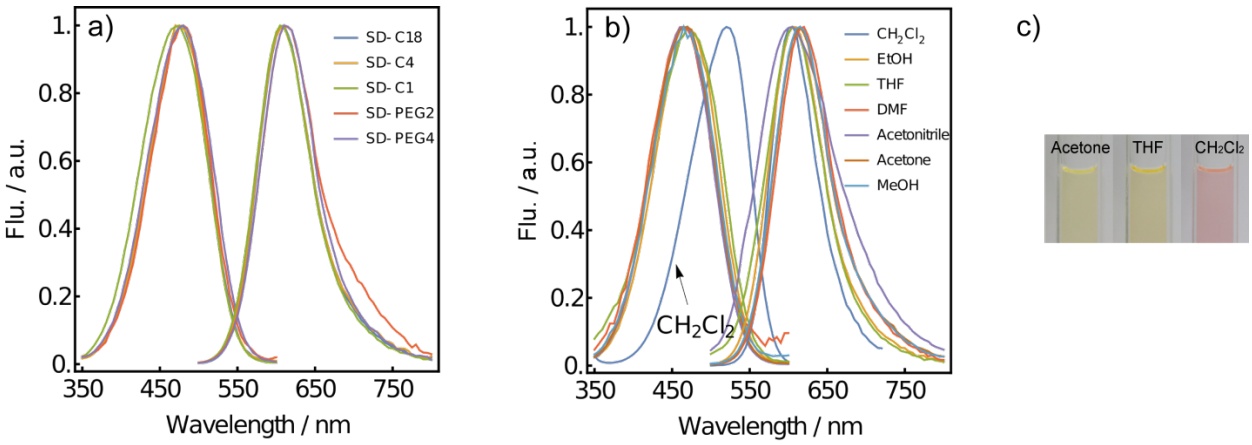


Figure S1. a) Normalized excitation and emission spectra of SDs in EtOH. b) Normalized excitation and emission spectra of SD-C1 in different solvents. c) Images of cuvettes with SD-C1 in acetone, THF and CH_2Cl_2.

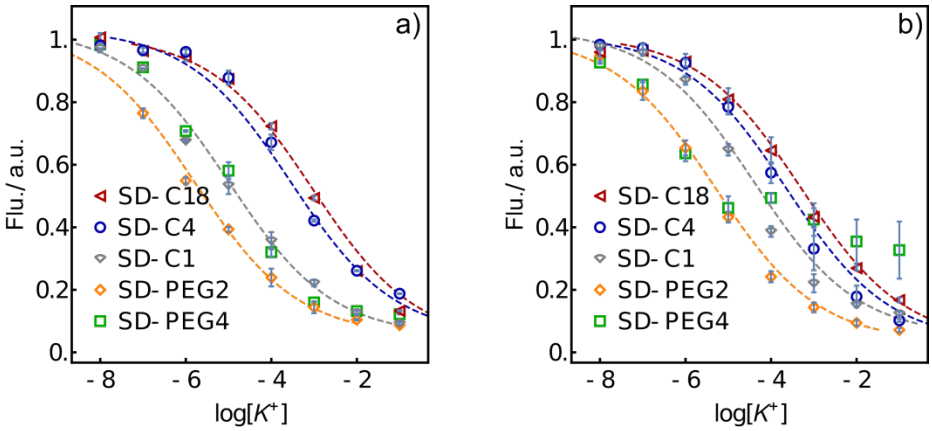


Figure S2. Fluorescence response for the emulsion sensors fabricated a) with or b) without PVC. Standard deviations were calculated from three parallel experiments.

Table S1. Theoretical lipophilicity of different SDs, expected calibration curve shift and practically gained shift value of the K^+-selective emulsions with different matrix.

	SD-PEG4	SD-PEG2	SD-C1	SD-C4	SD-C18
Theoretical shift	0.15	0.14	0.68	1.99	
Practical shift (PVC-DOS)	-1.4	0.8	1.45	0.5	
Practical shift (DOS)	N/A	0.9	0.45	0.45	

Table S2. Diameters and ζ-potentials of the K^+-selective emulsion with different SDs

Emulsion sensors	SD-PEG4	SD-PEG2	SD-C1	SD-C4	SD-C18
Dia. / nm	135.4 ± 0.9	132.9 ± 0.4	136.9 ± 1.0	140.0 ± 0.7	138.6 ± 0.9
ζ-potential / mV	-46.64 ± 1.19	-42.84 ± 0.60	-42.78 ± 1.84	-43.86 ± 1.67	-47.08 ± 1.27

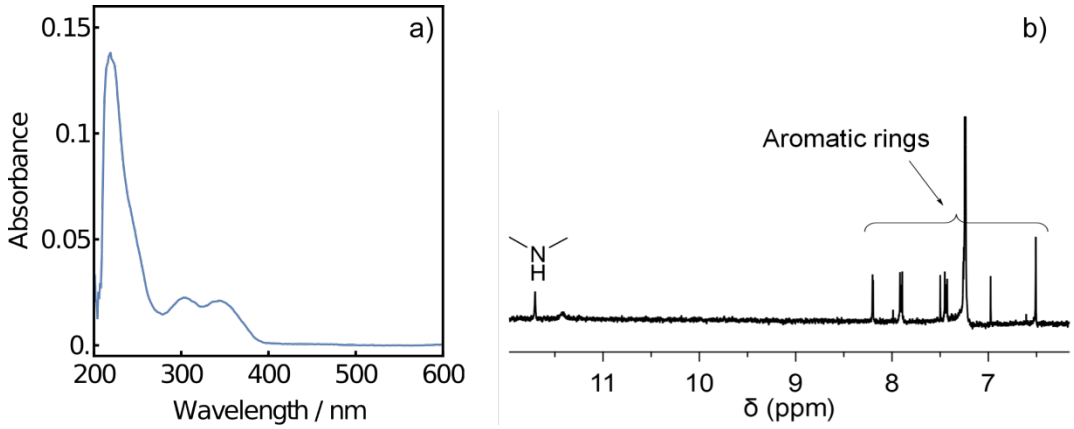


Figure S3. a) Absorbance spectrum of polyurethane in THF. The peaks at 280 nm to 390 nm are due to the benzene vibration. b) ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polyurethane.

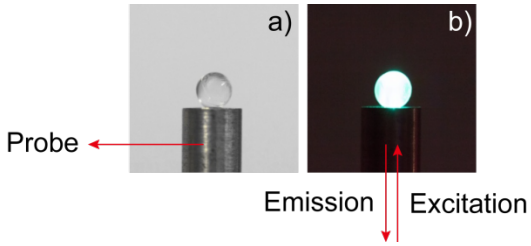
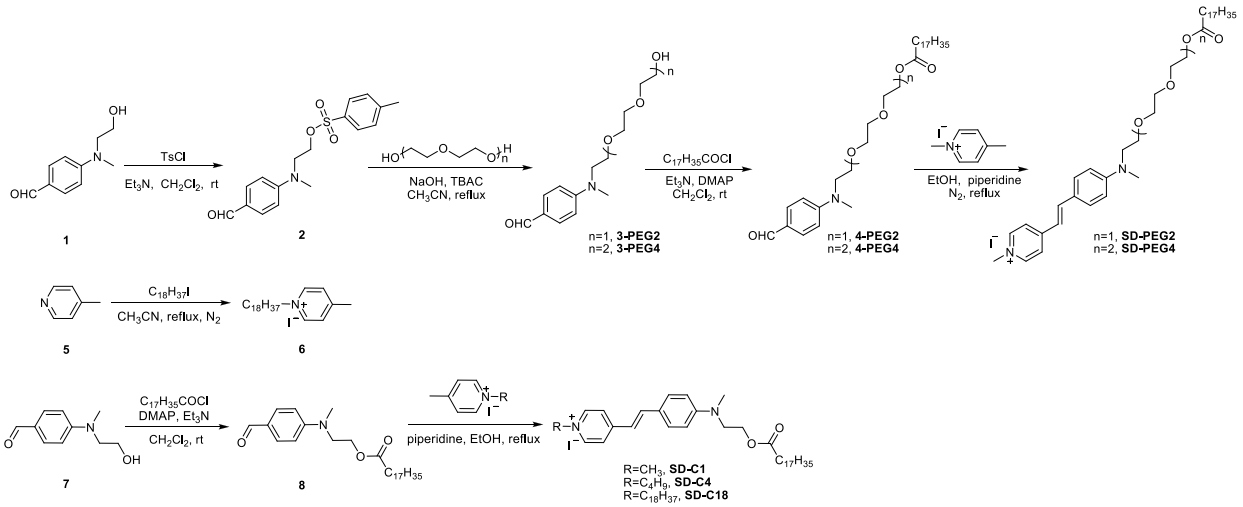


Figure S4. An alginate particle on the optical fiber probe a) under room light and b) under the excitation beam (500 nm) in the dark (without optical filter). Both the excitation and emission beams could pass through the probe.

General procedure for the synthesis of SD-PEG4, SD-PEG2, SD-C4, SD-C18



Scheme S1. Synthesis of the SDs (SD-PEG2, SD-PEG4, SD-C1, SD-C4, SD-C18).

2-((4-Formylphenyl)(methyl)amino)ethyl 4-methylbenzenesulfonate (**2**)

A solution of 4-[(2-hydroxyethyl)(methyl)amino]-benzaldehyde **1** (5 g, 27.9 mmol) and Et_3N (5.75 mL, 36.5 mmol) in anhydrous CH_2Cl_2 (200 mL) was stirred for 10 min at room temperature. TsCl (7.95 g, 41.9 mmol) was then added to the mixture and stirred at room temperature for 3 days. The reaction mixture was washed twice with water and twice with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using gradient elution with ethyl acetate/hexane (1:2 to 2:1) as the mobile phase. The desired product **2** was obtained as a yellow solid (7.2 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.70 – 7.67 (m, 4H), 7.25 – 7.23 (m, 2H), 6.61 – 6.57 (m, 2H), 4.21 (t, J = 4.2 Hz, 2H), 3.72 (t, J = 4.5 Hz, 2H), 3.00 (s, 3H), 2.39 (s, 3H) ppm.

2-(2-(2-((4-Formylphenyl)(methyl)amino)ethoxy)ethoxy)ethyl stearate (**4-PEG2**)

NaOH (0.5 g, 12.5 mmol), diethylene glycol (1.16 mL, 12.0 mmol), **2** (1 g, 3.0 mmol), tetrabutylammonium chloride (TBAC) (0.08 g, 0.3 mmol) and activated molecular sieves (4 Å, 10 pellets, dia.: 1.6 mm) was added to the dry CH_3CN (40 mL). The mixture was then heated to reflux for 24 h. After cooling to room temperature, the suspension was filtered, and the solvent was removed by evaporation. The residue was purified by flash silica gel column chromatography with ethyl acetate/hexane (1:1 to 4:1) as the eluent to obtain crude **3-PEG2**.

Crude **3-PEG2** (204.71 mg, 0.77 mmol) and stearoyl chloride (350.03 mg, 1.16 mmol) were dissolved in 30 mL of dry CH_2Cl_2 and stirred for 30 min. DMAP (50 µL) and Et_3N (50 µL) were added and the mixture was stirred at room temperature overnight. The reaction mixture was washed twice with water and twice with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The crude compound was purified by silica gel column chromatography using gradient elution with ethyl acetate/hexane (1:5 to 1:1) as the mobile phase. The desired product **4-PEG2** was obtained as a yellow solid (280 mg, 68% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.72 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 9.0 Hz, 2H), 4.20 (t, J =4.8 Hz, 2H), 3.68 – 3.61 (m, 10H), 3.10 (s, 3H), 2.31 (t, J = 7.5 Hz, 2H), 1.63 – 1.58 (m, 2H), 1.30 – 1.25 (m, 28H), 0.88 (t, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.36, 173.96, 152.72, 132.13, 126.93, 112.66, 72.43, 70.92, 70.67, 69.43, 69.34, 68.26, 63.37, 61.89, 53.04, 40.09, 34.36, 32.07, 29.84, 29.80, 29.76, 29.62, 29.50, 29.43, 29.29, 25.06, 22.83, 14.26 ppm. m/z (ESI): $[M+1]^+$ 534.5.

2-(4-Formylphenyl)-5,8,11,14-tetraoxa-2-azahexadecan-16-yl stearate (**4-PEG4**)

NaOH (0.5 g, 12.5 mmol), tetraethylene glycol (1.04 mL, 6.0 mmol), **2** (2 g, 6.0 mmol), TBAC (0.08 g, 0.3 mmol) and activated molecular sieves (4 Å, 10 pellets, dia.: 1.6 mm) was added to the dry CH_3CN (50 mL). The mixture was then heated to reflux for 24 h. After cooling to the room temperature, the suspension was filtered, and the solvent was removed by evaporation. The residue was purified by flash silica gel column chromatography with ethyl acetate/hexane (1:1 to 2:1) as the eluent to obtain crude **3-PEG4**.

Crude **3-PEG4** (652 mg, 1.83 mmol) and stearoyl chloride (556 mg, 1.83 mmol) were dissolved in 30 mL of dry CH_2Cl_2 and stirred for 30 min DMAP (50 µL) and Et_3N (50 µL) were added and the mixture was stirred at room temperature overnight. The reaction mixture was washed twice with water and twice with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The crude compound was purified by silica gel column chromatography using gradient elution with ethyl acetate/hexane (1:5 to 2:1) as the mobile phase. The desired product **4-PEG4** was obtained as a yellow solid (700 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.73 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.22 (t, *J* = 4.8 Hz, 2H), 3.69 – 3.61 (m, 18H), 3.10 (s, 3H), 2.32 (t, *J* = 8.0 Hz, 2H), 1.65 – 1.57 (m, 2H), 1.27 – 1.25 (m, 28H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 190.35, 173.99, 153.66, 132.20, 125.46, 111.19, 70.97, 70.81, 70.80, 70.78, 70.73, 70.70, 69.36, 68.57, 63.47, 52.18, 39.37, 34.36, 32.07, 29.84, 29.80, 29.76, 29.62, 29.50, 29.43, 29.29, 25.06, 22.83, 14.27 ppm. m/z (ESI): $[M+1]^+$ 621.5.

(E)-1-methyl-4-(4-(methyl(2-(2-(2-(stearoyloxy)ethoxy)ethoxy)ethyl)amino)styryl)pyridinium iodide (**SD-PEG2**)

To a solution of **4-PEG2** (111 mg, 0.21 mmol) and 1,4-dimethylpyridinium iodide (48.8 mg, 0.21 mmol) in 20 mL of dry ethanol was added piperidine (10 µL). The mixture was heated to reflux under N_2 atmosphere overnight. After cooling, the solid precipitate was then filtered and washed 3 times with cold ethanol. The desired product **SD-PEG2** was obtained as a dark red solid (100 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.78 (d, *J* = 6.0 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 15.6 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.42 (s, 3H), 4.21 (t, *J* = 4.8 Hz,, 2H), 3.69 – 3.61 (m, 10H), 3.09 (s, 3H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.62 – 1.57 (m, 2H), 1.31 – 1.24 (m, 28H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 173.99, 154.29, 150.56, 144.32, 142.97, 130.96, 123.20, 117.58, 113.72, 70.92, 70.69, 69.42, 68.27, 63.41, 53.20, 47.80, 40.17, 34.37, 32.07, 29.84, 29.81, 29.77, 29.63, 29.51, 29.44, 29.30, 25.08, 22.84, 14.27 ppm. m/z (ESI): $[M - I]^+$ 623.3.

(E)-1-methyl-4-(4-(methyl(16-oxo-3,6,9,12,15-pentaoxatritriacontyl)amino)styryl)pyridinium iodide (**SD-PEG4**)

To a solution of **4-PEG4** (436 mg, 0.70 mmol) and 1,4-dimethylpyridinium iodide (165 mg, 0.70 mmol) in 20 mL of dry ethanol was added 10 µL of piperidine. The mixture was heated to reflux under N_2 atmosphere overnight. After cooling, the solid precipitate was then filtered and washed 3 times with cold ethanol. The desired product **SD-PEG4** was obtained as a red solid (424 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.76 (d, *J* = 6.8 Hz, 2H), 7.82 (d, *J* = 5.6 Hz, 2H), 7.61 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 4.42 (s, 3H), 4.23 – 4.20 (m, 2H), 3.70 – 3.61 (m, 18H), 3.09 (s, 3H), 2.31 (t, *J* = 8.0 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.27 – 1.25 (m, 28H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 173.99, 154.40, 151.68, 144.01, 143.27, 131.04, 122.73, 122.43, 116.36, 112.08, 70.94, 70.77, 70.71, 70.69, 69.33, 68.64, 63.45, 52.15, 47.80, 39.30, 34.35, 32.05, 29.83, 29.79, 29.75, 29.61, 29.49, 29.42, 29.28, 25.05, 22.82, 14.26 ppm. m/z (ESI): $[M - I]^+$ 711.5.

4-Methyl-1-octadecylpyridinium iodide (**6**)

To a solution of 4-methylpyridine **5** (380 µL, 4.2 mmol) in acetonitrile (20 mL) was added dropwise a solution of 1-iodooctadecane (1.6 g, 4.2 mmol) in acetonitrile (20 mL). The mixture was refluxed under N_2 overnight. Upon cooling to room temperature, the solvent was removed under reduced pressure and the desired product **6** was obtained as a white solid after recrystallization from ethyl acetate (1.65 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.18-9.17 (m, 2H), 7.87 (d, *J* = 6.0 Hz, 2H), 4.86 (t, *J* = 7.6 Hz, 2H), 2.68 (s, 3H), 2.04 – 1.96 (m, 2H), 1.33 - 1.22 (m, 30H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.14, 144.11, 128.99, 61.61, 32.04, 31.86, 29.83, 29.78, 29.73, 29.64, 29.48, 29.18, 26.14, 22.81, 22.52, 14.25 ppm. m/z (ESI): $[M - I]^+$ 345.4.

(E)-1-methyl-4-(4-(methyl(2-(stearoyloxy)ethyl)amino)styryl)pyridinium iodide (**SD-C1**), (E)-1-butyl-4-(4-(methyl(2-(stearoyloxy)ethyl)amino)styryl)pyridinium (**SD-C4**), (E)-4-(4-(methyl(2-(stearoyloxy)ethyl)amino)styryl)-1-octadecylpyridinium iodide (**SD-C18**) were synthesized according to the ref. S1.

SD-C1 was obtained as an orange solid.[2]

SD-C4 was obtained as a brick-red solid (35% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, J = 6.8 Hz, 2H), 7.86 (d, J = 6.4 Hz, 2H), 7.63 (d, J = 16.0 Hz, 1H), 7.53 (t, J = 9.2 Hz, 2H), 6.88 (d, J = 16.0 Hz, 1H), 6.75 (d, J = 8.8 Hz, 2H), 4.64 (t, J = 7.2 Hz, 2H), 4.28 (t, J = 6.0 Hz, 2H), 3.68 (t, J = 6.0 Hz, 2H), 3.09 (s, 3H), 2.26 (t, J = 7.6 Hz, 2H), 2.01 – 1.96 (m, 2H), 1.58 – 1.56 (m, 4H), 1.45 – 1.38 (m, 2H), 1.31 – 1.24 (m, 26H), 0.98 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.86, 154.51, 151.52, 143.45, 143.40, 131.02, 123.12, 122.86, 116.68, 112.22, 61.09, 60.68, 50.90, 39.00, 34.33, 33.65, 32.07, 29.85, 29.81, 29.76, 29.61, 29.51, 29.41, 29.27, 24.97, 22.84, 19.64, 14.27, 13.70 ppm. m/z (ESI): $[M - I]^+$ 576.8.

SD-C18 was obtained as a dark red solid (74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, J = 6.8 Hz, 2H), 7.86 (d, J = 6.8 Hz, 2H), 7.63 (d, J = 16.0 Hz, 1H), 7.53 (t, J = 8.8 Hz, 2H), 6.88 (d, J = 15.6 Hz, 1H), 6.74 (d, J = 8.8 Hz, 2H), 4.63 (t, J = 7.8 Hz, 2H), 4.28 (t, J = 6.0 Hz, 2H), 3.68 (t, J = 6.4 Hz, 2H), 3.09 (s, 3H), 2.26 (t, J = 8 Hz, 2H), 2.00 – 1.96 (m, 2H), 1.59 – 1.56 (m, 2H), 1.34 – 1.25 (m, 58H), 0.88 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.84, 154.42, 151.32, 143.39, 143.20, 131.00, 123.16, 123.07, 116.86, 112.36, 61.05, 60.81, 50.99, 39.12, 34.32, 32.06, 31.72, 29.84, 29.80, 29.75, 29.65, 29.60, 29.50, 29.40, 29.26, 29.21, 26.27, 24.96, 22.83, 14.26 ppm. m/z (ESI): $[M - I]^+$ 774.0.

Theoretical calculations

Calculation of relationship between the lipophilicity and lifetime

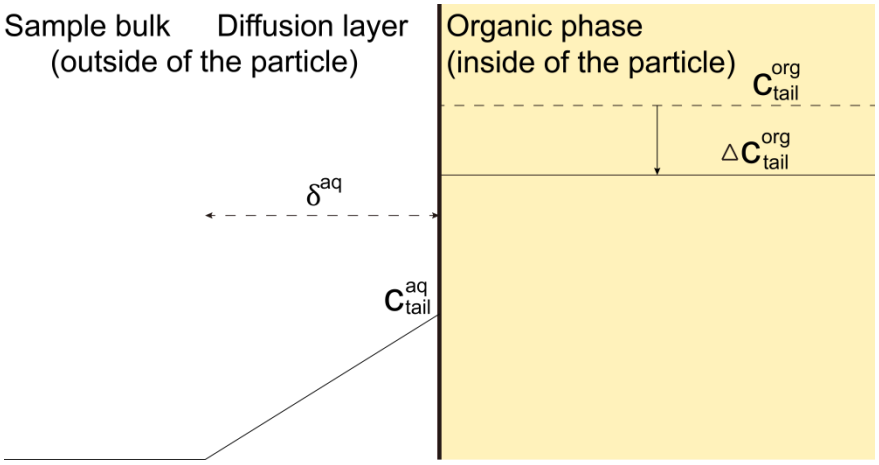


Figure S5. Kinetic model used to describe the leaching behavior from the nanoparticles.

The partition equilibrium constant could be written as following:

$$P_{tail} = \frac{c_{tail}^{org}}{c_{tail}^{aq}} \quad (1)$$

Figure S5 shows the kinetic procedure of the leaching behavior. The rate is sufficiently slow that the concentration of the compound in the particle phase remains uniform. The flux *J* of the compound from a particle into a contacting aqueous phase void of the compound and placed under hydrodynamic control (constant diffusion layer thickness, δ_{aq}) described for a one-dimensional system as:

$$J = -D_{tail}^{aq} \frac{c_{tail}^{aq}(0)}{\delta^{aq}} = -D_{tail}^{aq} \frac{c_{tail}^{org}}{P_{tail}\delta^{aq}} \quad (2)$$

We recall that flux is related to the number of moles Δn_{tail} transported per unit time and unit area, which is related to the concentration and particle radius as follows:

$$J = \frac{\Delta n_{tail}}{4\pi r^2 \cdot t} = \frac{\Delta c_{tail}^{org} \frac{4}{3}\pi r^3}{4\pi r^2 \cdot t} = \frac{\Delta c_{tail}^{org} \cdot r}{3t} \quad (3)$$

Eq 2 and eq 3 are combined and give the fraction of the organic compound lost during time.

$$\frac{\Delta c_{tail}^{org}}{c_{tail}^{org}} = -D_{tail}^{aq} \frac{3t}{P_{tail}\delta^{aq} r} \quad (4)$$

If one tolerates a loss of 10% ($\Delta c_{tail}^{org}(t) / c_{tail}^{org}$ = -0.1) during one day (t = 8.64 × 10^4 s) of continuous contact of a 140 nm-diameter (result from DLS) particles (*r* = 7.0 × 10^{-6} cm) with a flowing aqueous sample with δ_{aq} ≈ 1.0 × 10^{-2} cm, and assuming a typical diffusion coefficient of D_{tail}^{aq} ≈ 10^{-5} cm^2s^{-1}, one calculates a required lipophilicity $\log P_{tail}$ > 8.56.

Theory of the ion-exchange process – relationship between equilibrium constant and calibration curve.

The overall phase transfer equilibrium can be expressed with eq 5 with subscripts (org), (aq) and (sur) designating the organic phase, the aqueous phase and the surface of emulsion particles respectively.

$$SD^+_{org} + L_{org} + R^-_{org} + K^+_{aq} \rightleftharpoons KL^+_{org} + R^-_{org} + SD^+_{sur} \quad (5)$$

$$K = \frac{\Gamma_{SD^+}[KL^+]_{org}}{[SD^+]_{org}\, a_{K^+}[L]_{org}} = K_{K^+/SD^+}\beta_{KL} \quad (6)$$

The equilibrium constant K is expressed by eq 6, while Γ_{SD^+} is the molar concentration of the SDs on the surface. $[KL^+]_{org}$, $[SD^+]_{org}$ and $[L]_{org}$ are the molar concentrations of the complexed K^+ ionophore I, SD and K^+ ionophore I in the organic phase. In eq 6, β_{KL} is the complex formation constant while K_{K^+/SD^+} is the constant for the ion-exchange of potassium and SD between the surface and inside of the particles. This constant is inversely proportional to the partition coefficient of the SD.

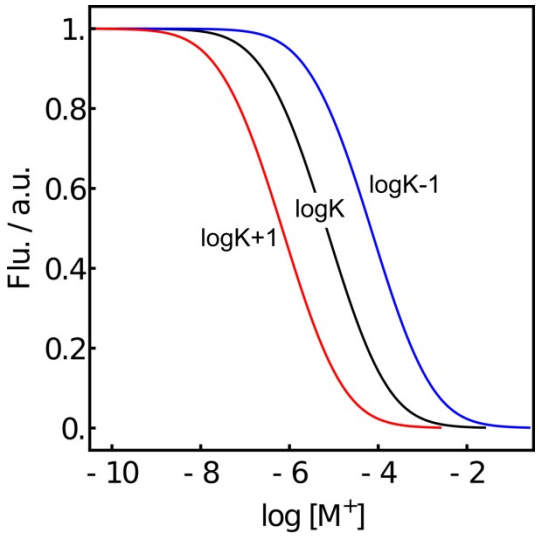
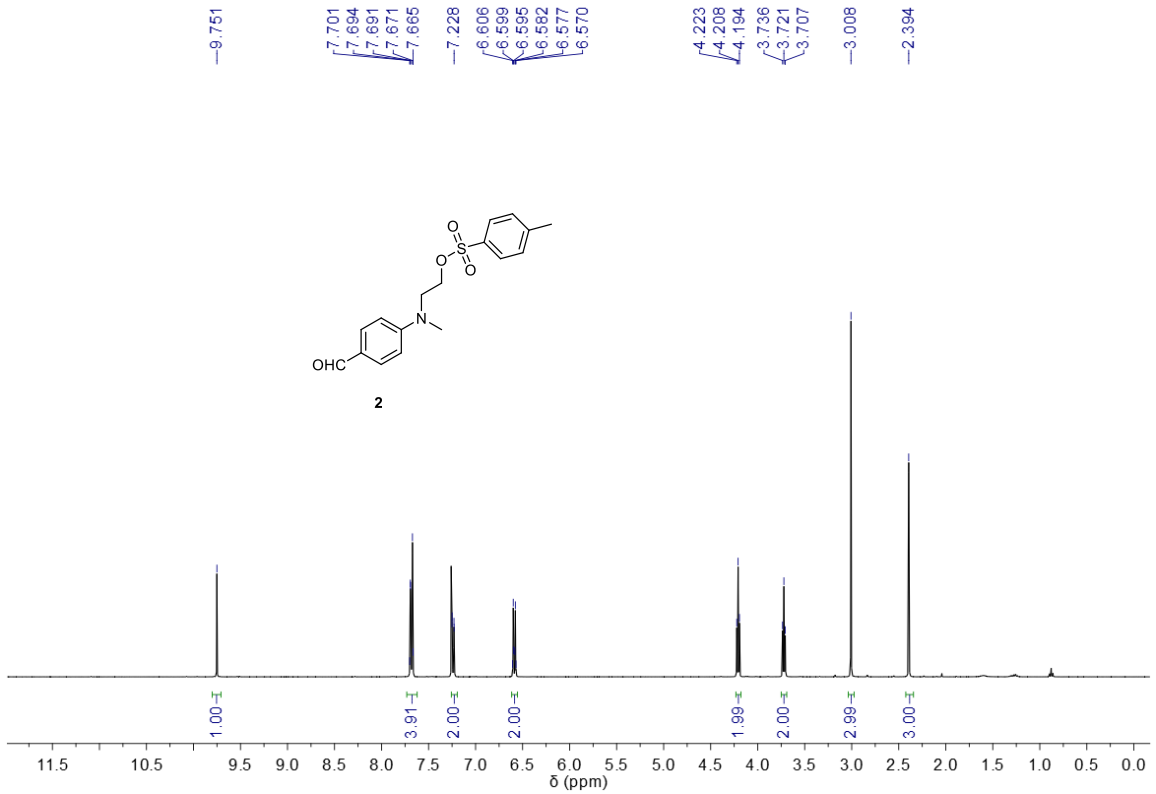
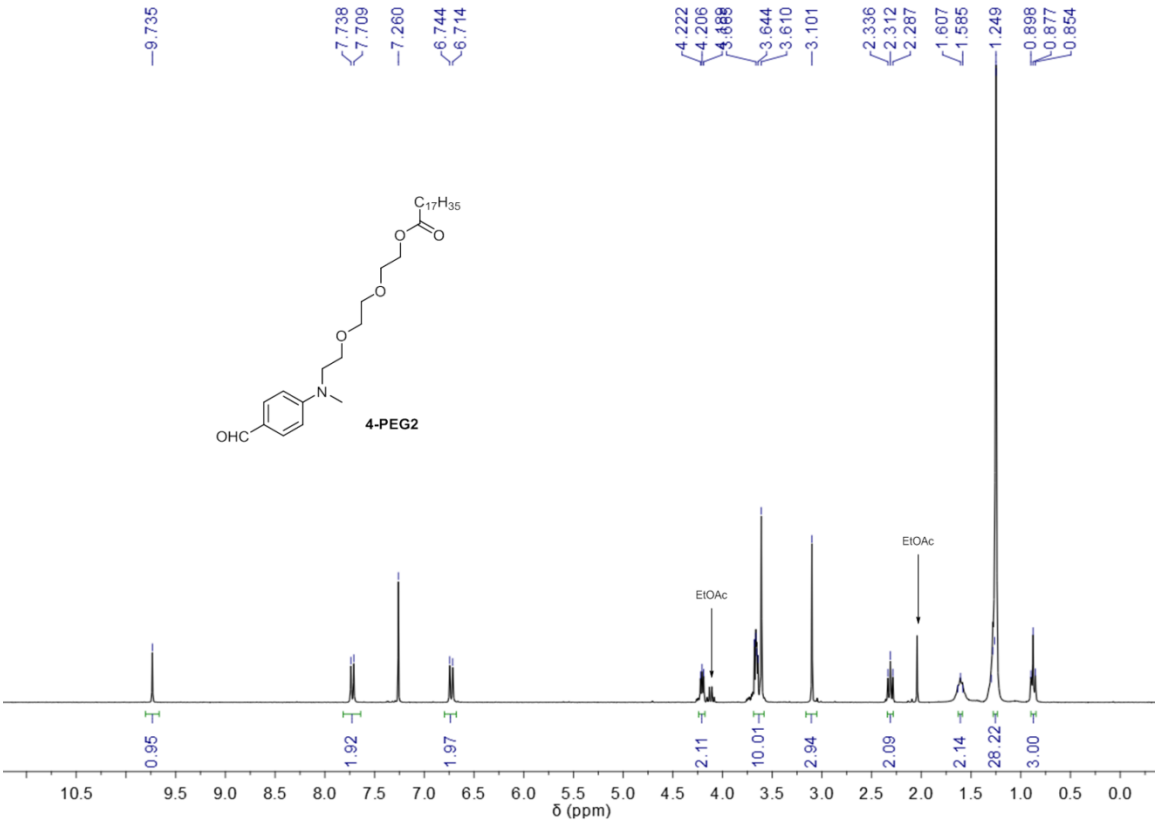
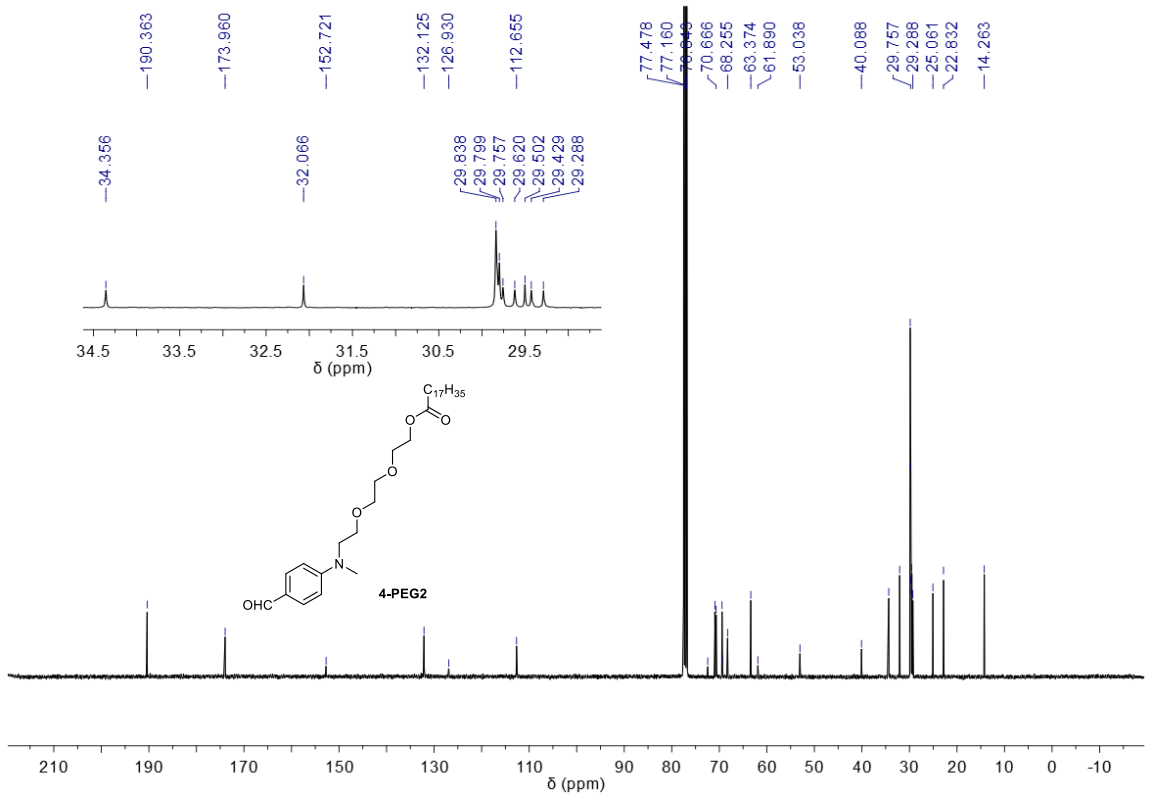


Figure S6. Theoretical simulation of the response of the ion-exchange based ion-selective optode sensor with different equilibrium constants. Curves are plotted with equations derived by ion-exchange equilibrium, charge conservation, and mass conservation.[2]

^{1}H and ^{13}C NMR spectra



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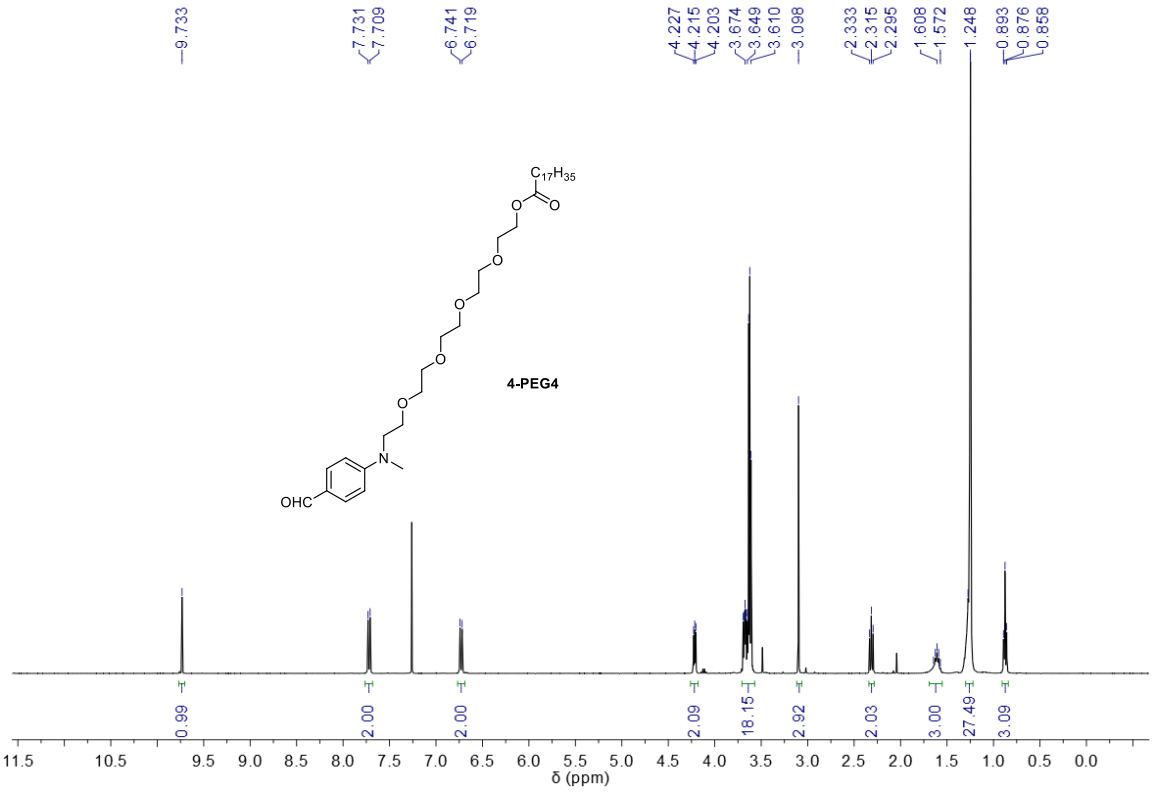
δ (ppm)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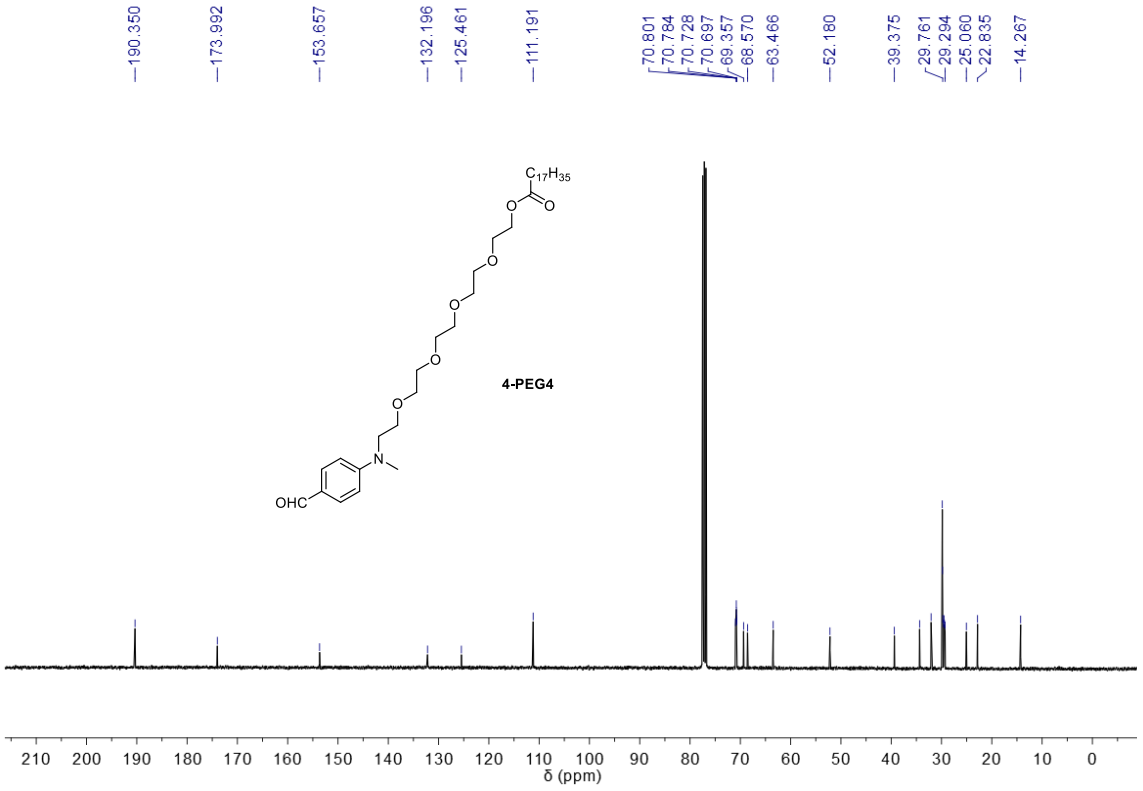
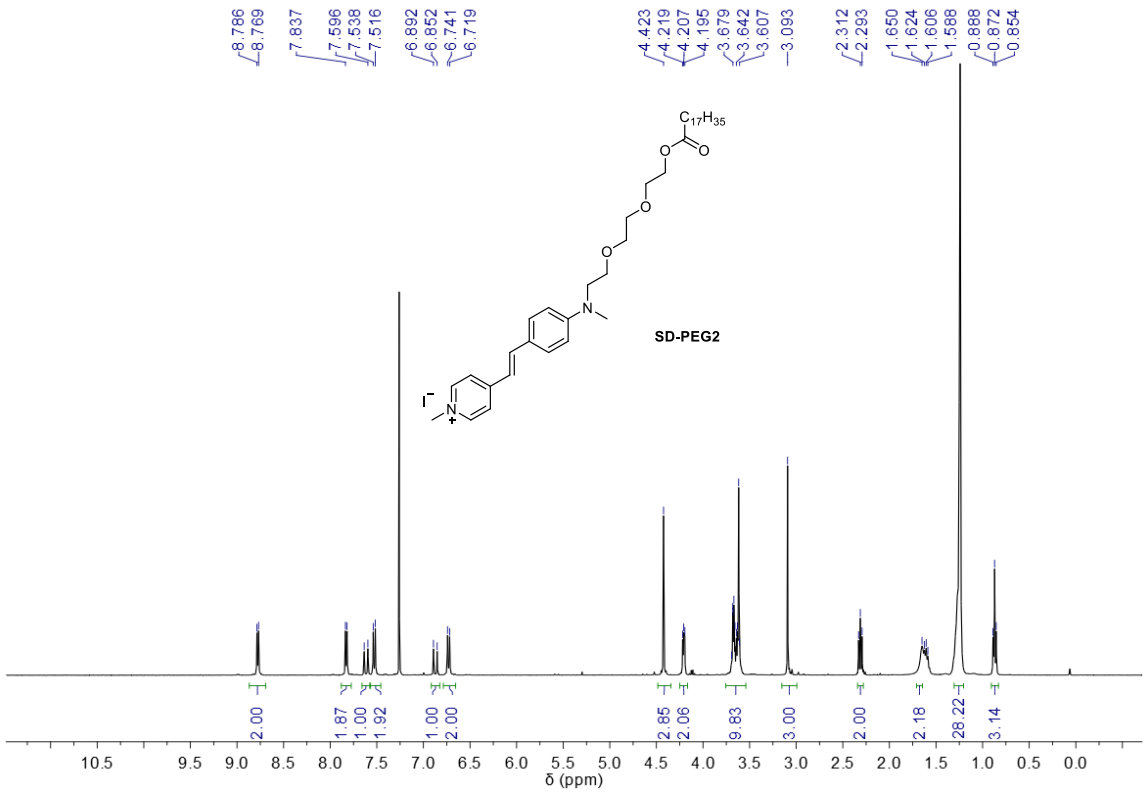
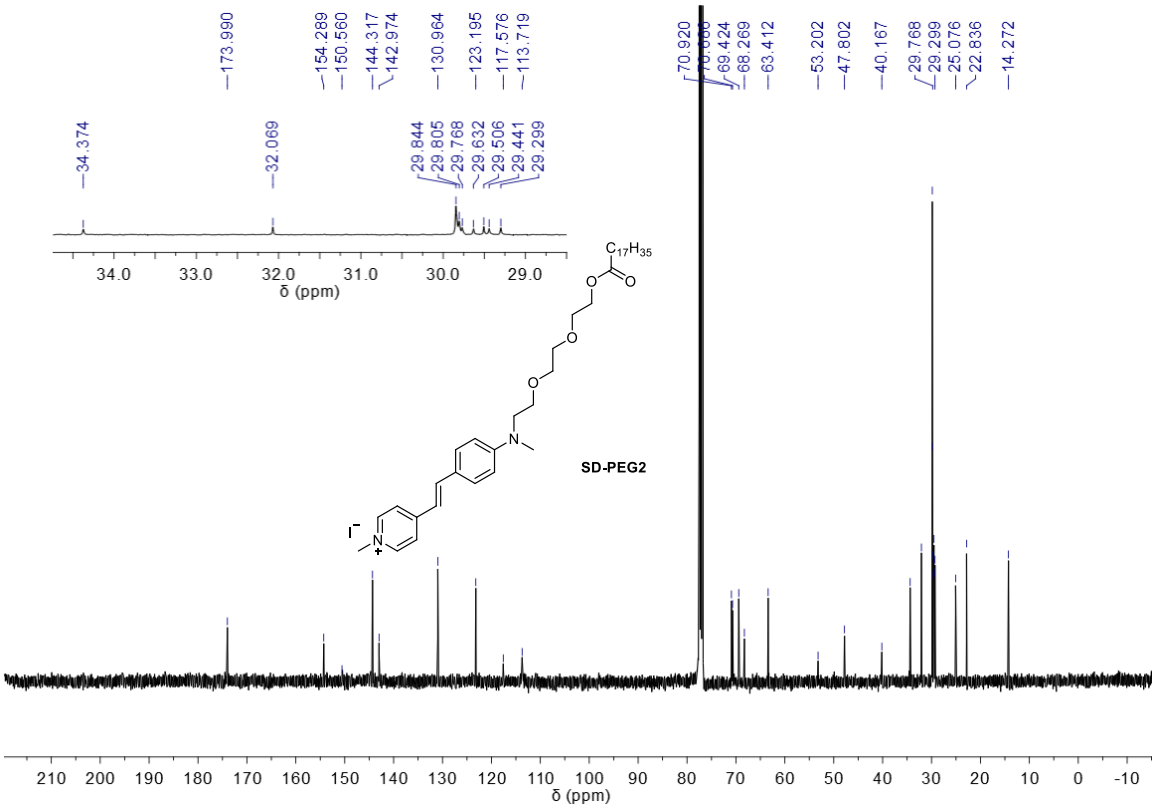
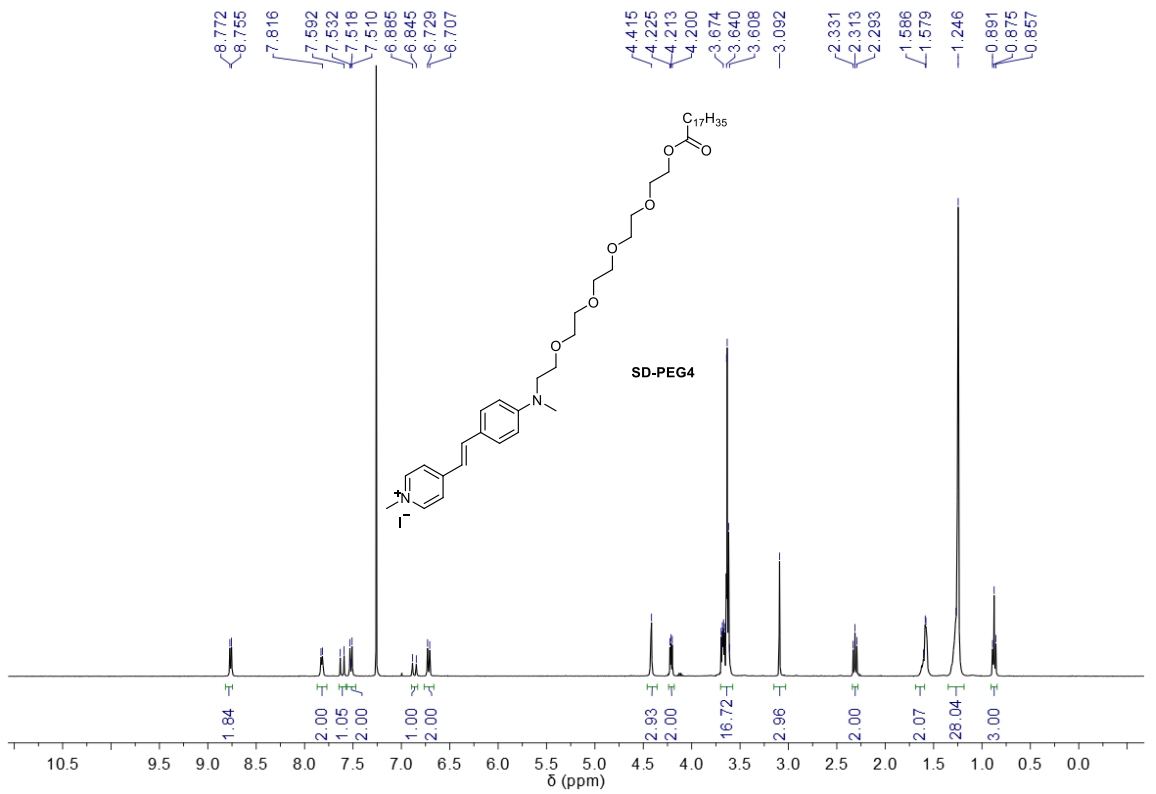
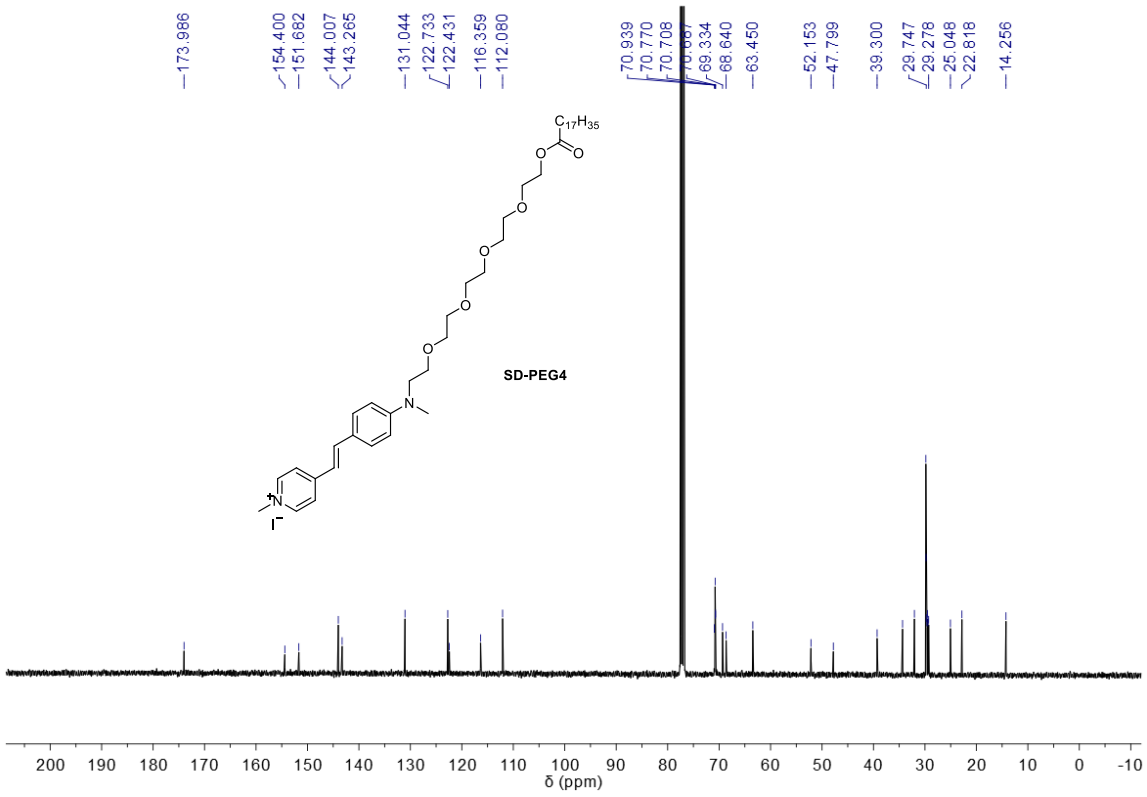
6.719
4.227
4.215
4.203
3.674
3.649
3.610
3.098
2.333
2.315
2.295
1.608
1.572
1.248
0.893
0.876
0.858
4-PEG4
OHC
0.99
2.00
2.00
2.09
18.15
2.92
2.03
3.00
27.49
3.09
δ (ppm)

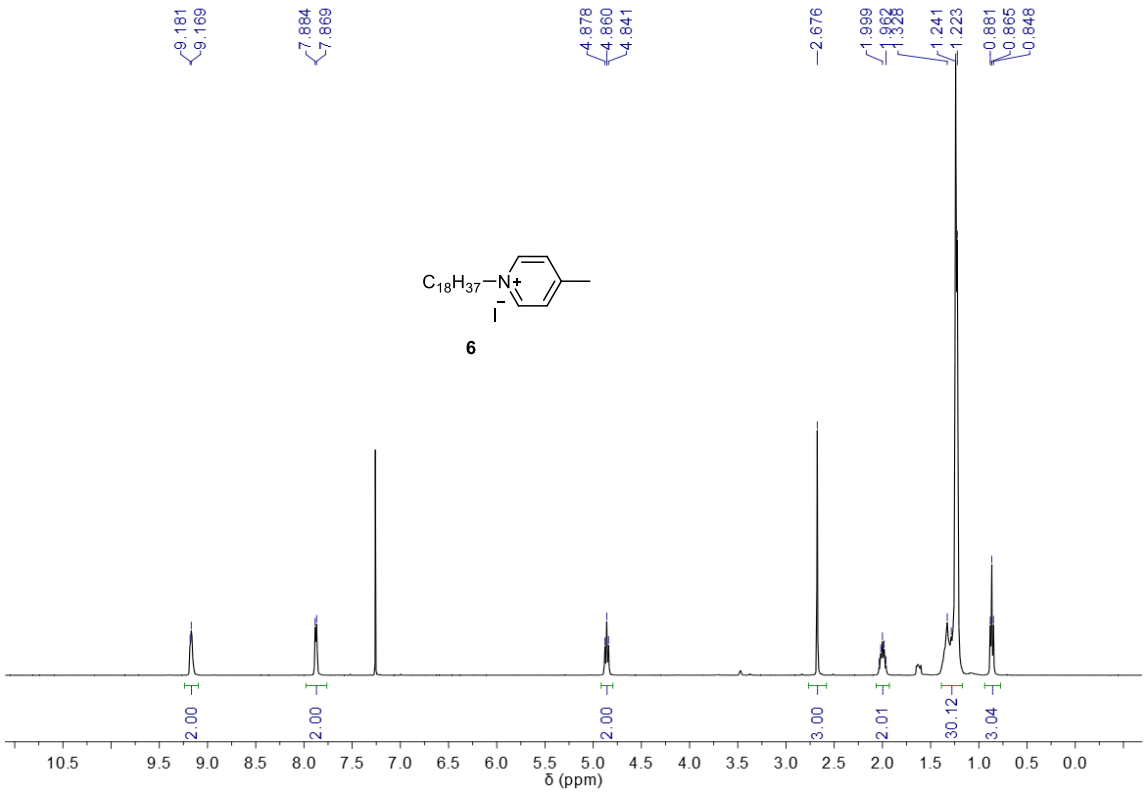

190.350
173.992
153.657
132.196
125.461
111.191
70.801
70.784
70.728
70.697
69.357
68.570
63.466
52.180
39.375
29.761
29.294
25.060
22.835
14.267
C17H35
4-PEG4
OHC
δ (ppm)

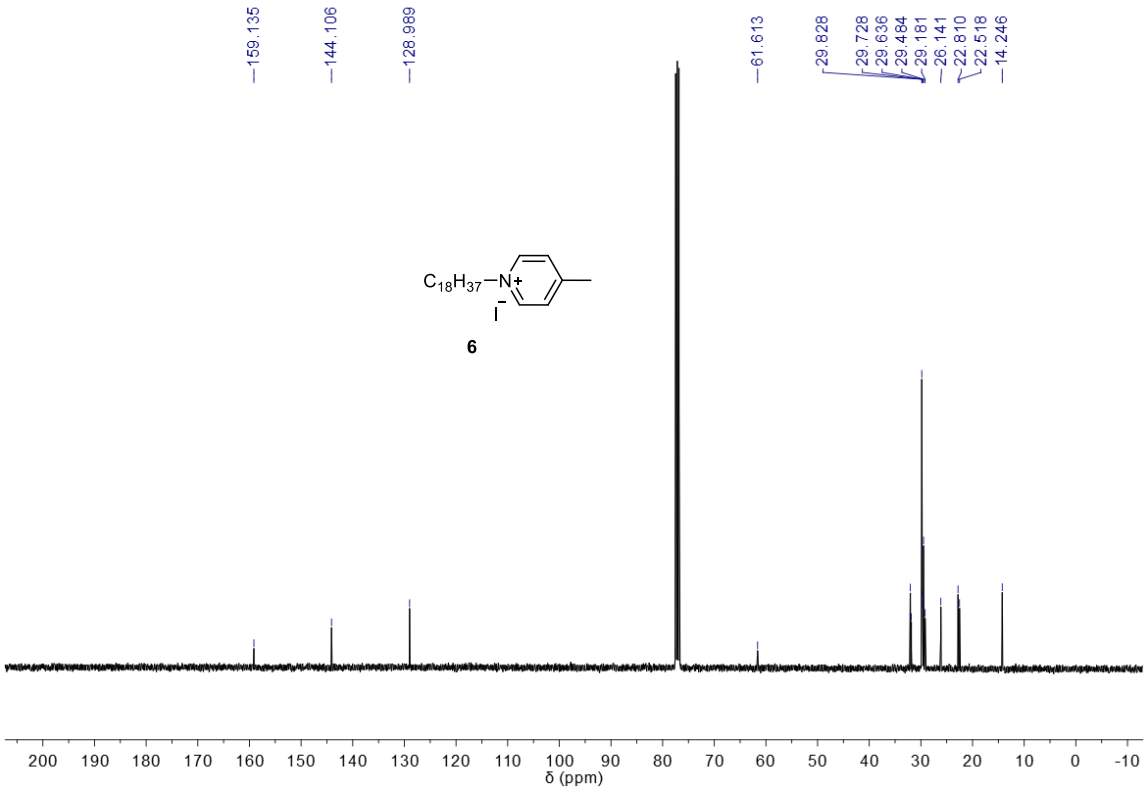

8.786
8.769
7.837
7.596
7.538
7.516
6.892
6.852
6.741
6.719
4.423
4.219
4.207
4.195
3.679
3.642
3.607
3.093
2.312
2.293
1.650
1.624
1.606
1.588
0.888
0.872
0.854
C17H35
SD-PEG2
I−
2.00
1.87
1.00
1.92
1.00
2.00
2.85
2.06
9.83
3.00
2.00
2.18
28.22
3.14
δ (ppm)

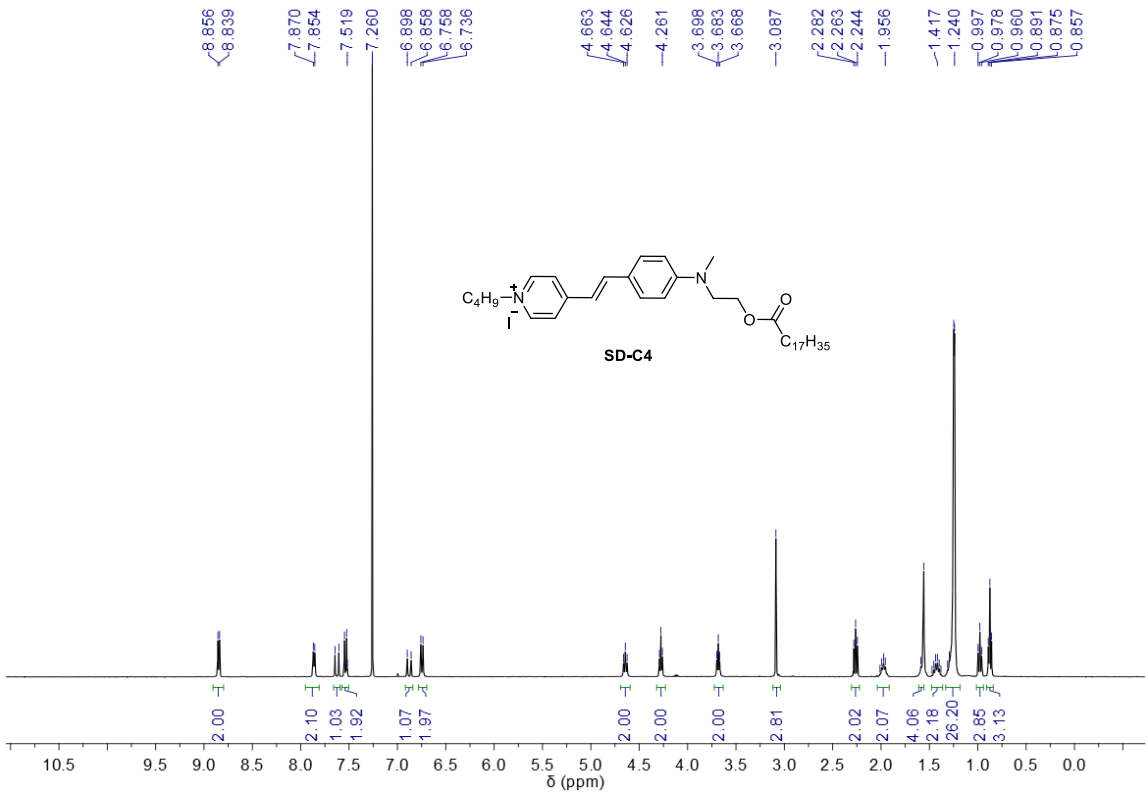

173.990
154.289
150.560
144.317
142.974
130.964
123.195
117.576
113.719
70.920
69.424
68.269
63.412
53.202
47.802
40.167
29.768
29.299
25.076
22.836
14.272
34.374
32.069
29.844
29.805
29.768
29.632
29.506
29.441
29.299
δ (ppm)
SD-PEG2
δ (ppm)

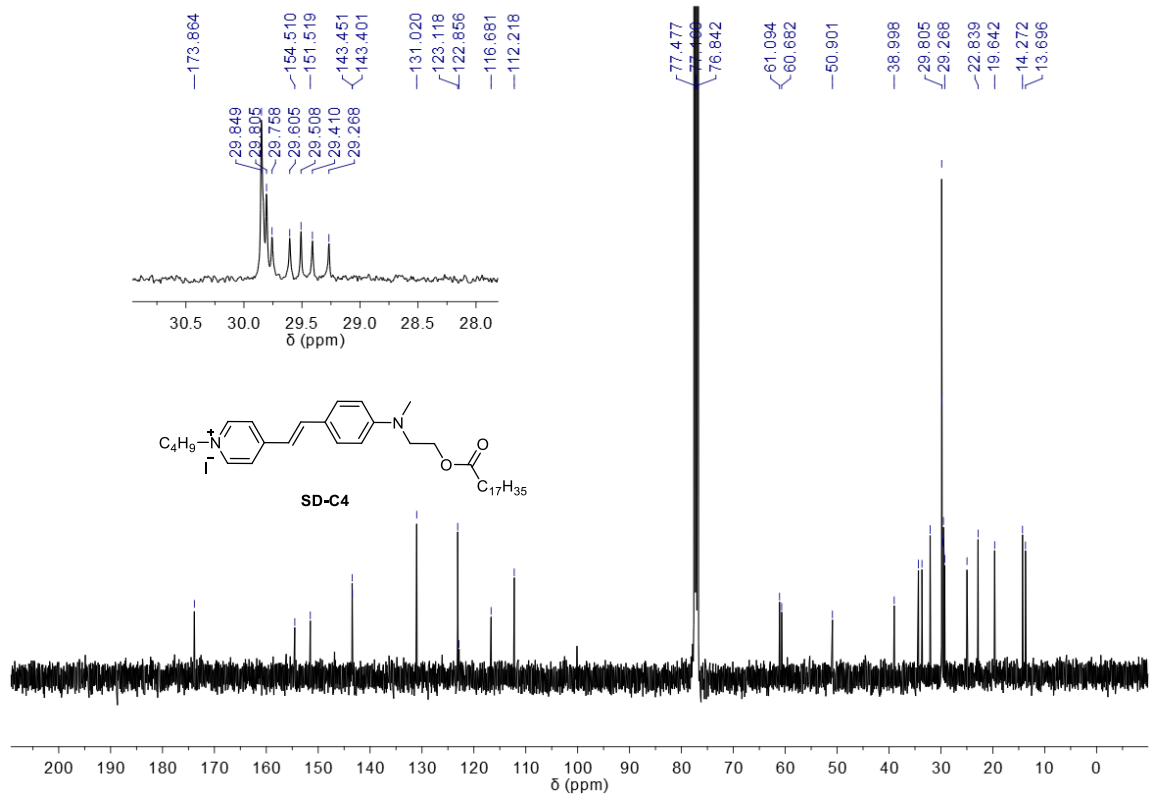

8.772
8.755
7.816
7.592
7.532
7.518
7.510
6.885
6.845
6.729
6.707
4.415
4.225
4.213
4.200
3.674
3.640
3.608
3.092
2.331
2.313
2.293
1.586
1.579
1.246
0.891
0.875
0.857
SD-PEG4
1.84
2.00
1.05
2.00
1.00
2.00
2.93
2.00
16.72
2.96
2.00
2.07
28.04
3.00
δ (ppm)

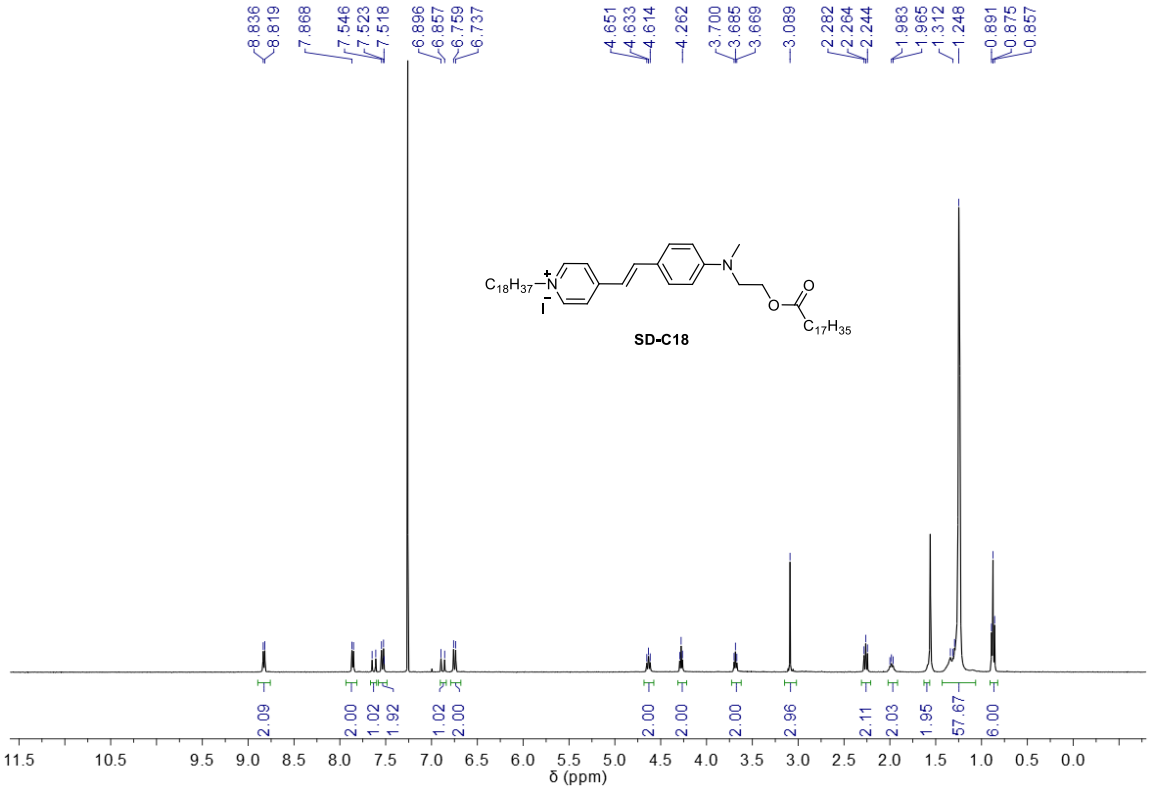

173.986
154.400
151.682
144.007
143.265
131.044
122.733
122.431
116.359
112.080
70.939
70.770
70.708
69.334
68.640
63.450
52.153
47.799
39.300
29.747
29.278
25.048
22.818
14.256
SD-PEG4
δ (ppm)

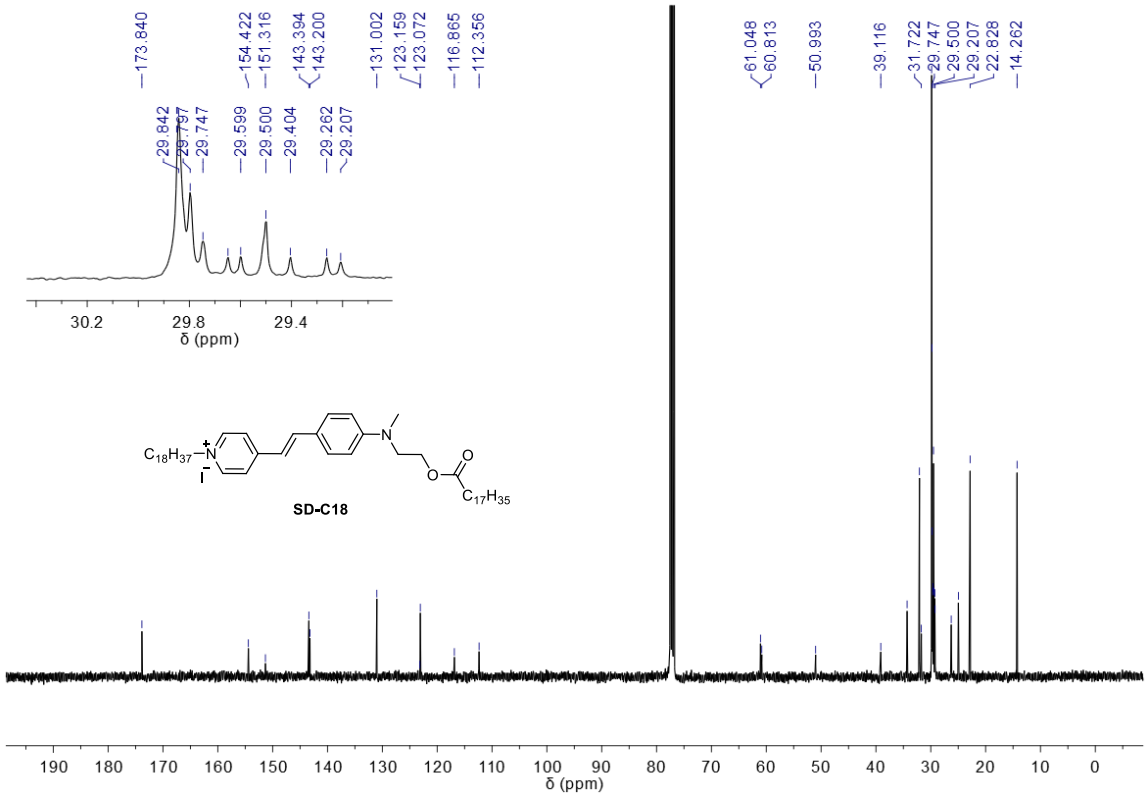

9.181
9.169
7.884
7.869
4.878
4.860
4.841
2.676
1.999
1.241
1.223
0.881
0.865
0.848
6
2.00
2.00
2.00
3.00
2.01
30.12
3.04
δ (ppm)


159.135
144.106
128.989
61.613
29.828
29.728
29.636
29.484
29.181
26.141
22.810
22.518
14.246
$C_{18}H_{37}$–N+
I-
6
δ (ppm)

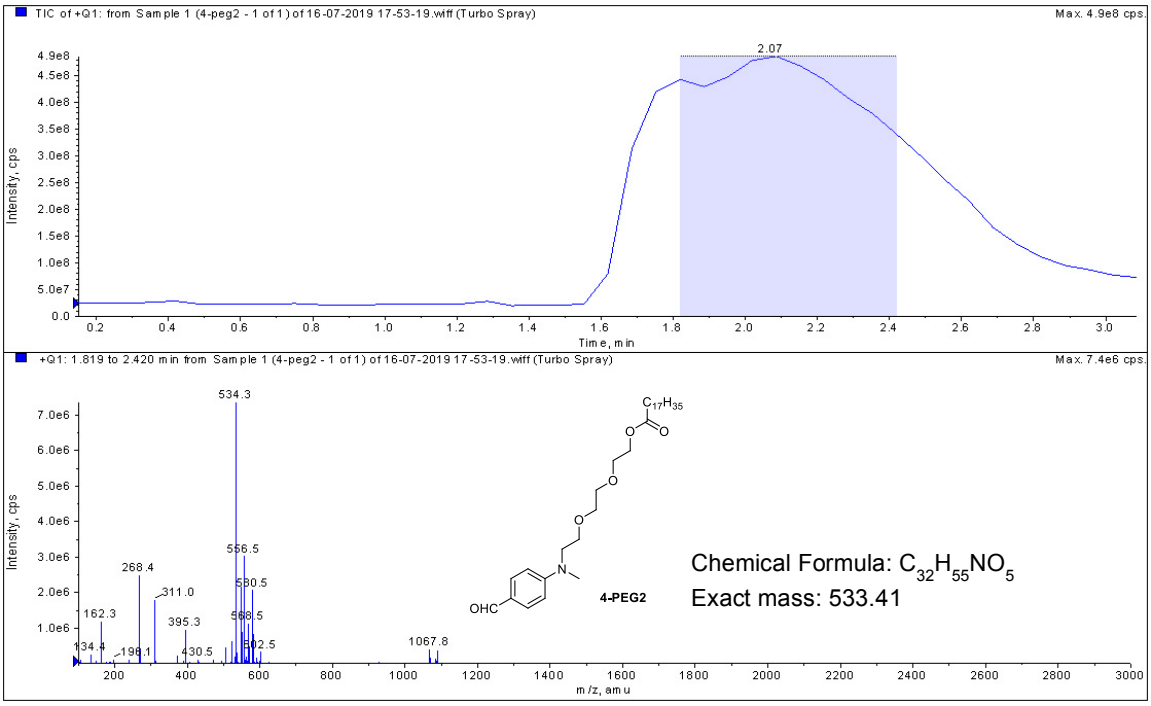

8.856
8.839
7.870
7.854
7.519
7.260
6.898
6.858
6.758
6.736
4.663
4.644
4.626
4.261
3.698
3.683
3.668
3.087
2.282
2.263
2.244
1.956
1.417
1.240
0.997
0.978
0.960
0.891
0.875
0.857
C_4H_9–N+
I-
N
O
O
$C_{17}H_{35}$
SD-C4
2.00
2.10
1.03
1.92
1.07
1.97
2.00
2.00
2.00
2.81
2.02
2.07
4.06
2.18
26.20
2.85
3.13
δ (ppm)

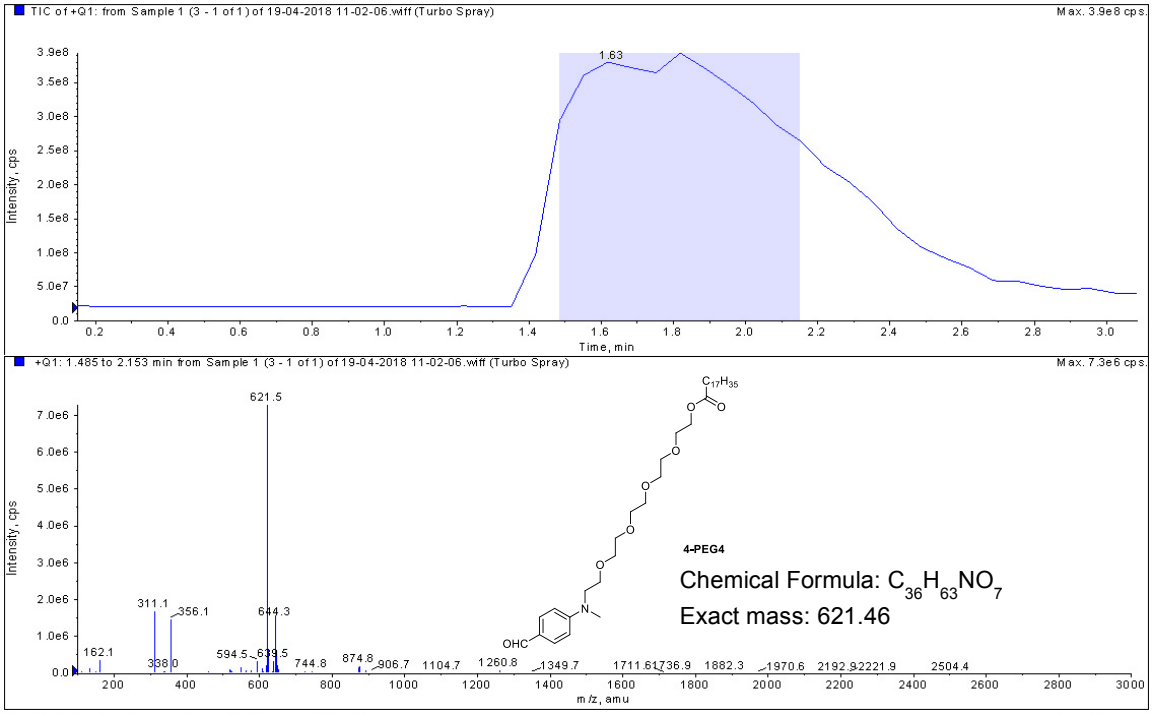

173.864
154.510
151.519
143.451
143.401
131.020
123.118
122.856
116.681
112.218
77.477
77.160
76.842
61.094
60.682
50.901
38.998
29.805
29.268
22.839
19.642
14.272
13.696
29.849
29.805
29.758
29.605
29.508
29.410
29.268
30.5 30.0 29.5 29.0 28.5 28.0
δ (ppm)
C4H9
N
I
O
C17H35
SD-C4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

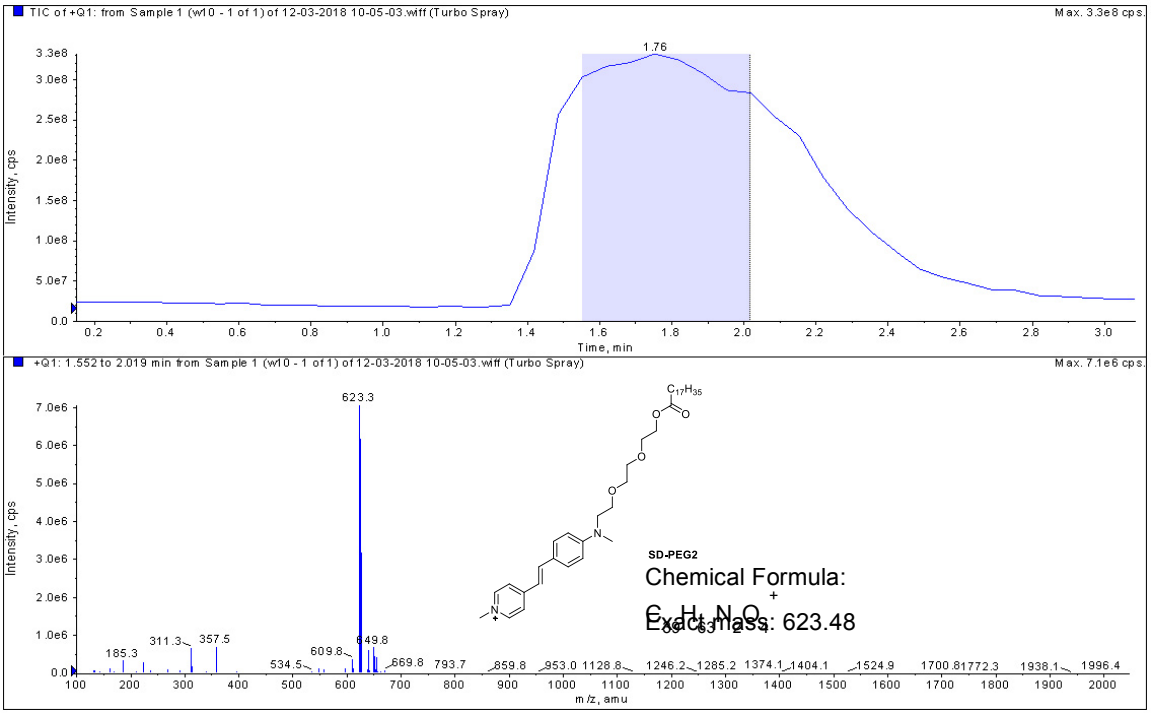

8.836
8.819
7.868
7.546
7.523
7.518
6.896
6.857
6.759
6.737
4.651
4.633
4.614
4.262
3.700
3.685
3.669
3.089
2.282
2.264
2.244
1.983
1.965
1.312
1.248
0.891
0.875
0.857
C18H37
N
I
O
C17H35
SD-C18
2.09
2.00
1.02
1.92
1.02
2.00
2.00
2.00
2.00
2.96
2.11
2.03
1.95
57.67
6.00
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

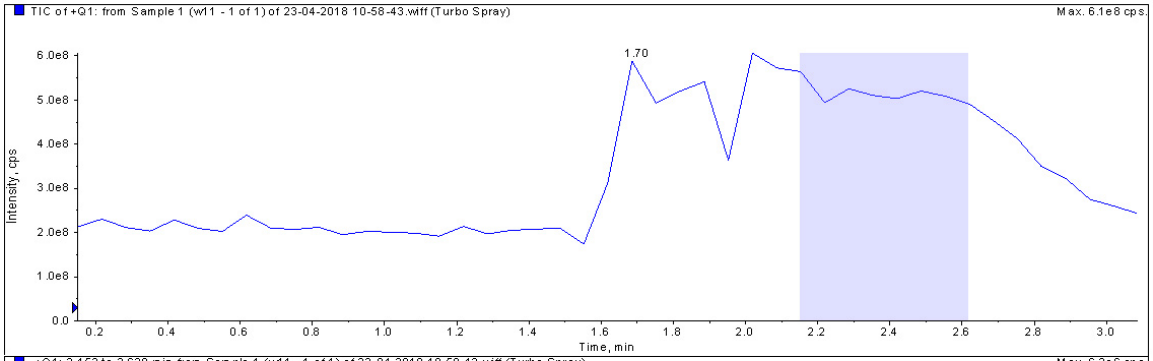


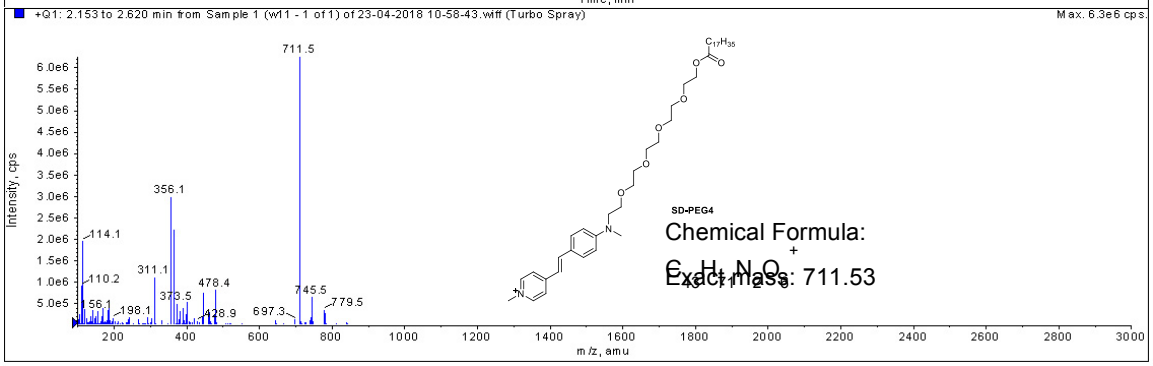
Mass spectra

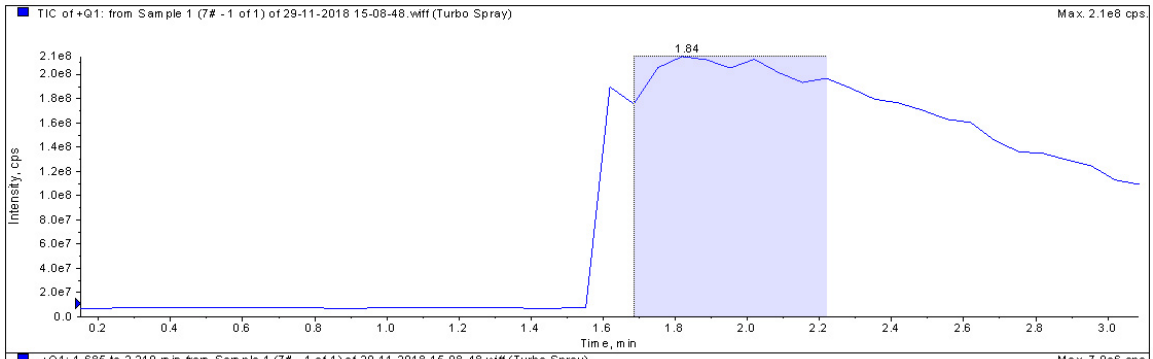


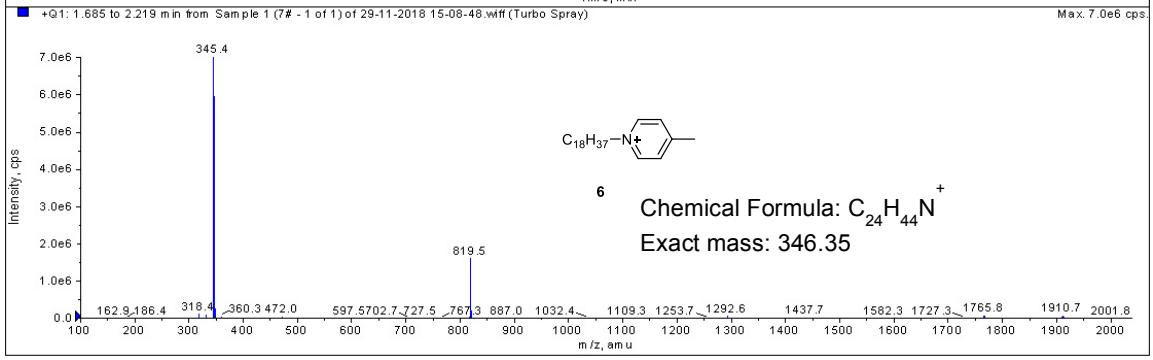

TIC of +Q1: from Sample 1 (3 - 1 of 1) of 19-04-2018 11-02-06.wiff (Turbo Spray)
Max. 3.9e8 cps.
Intensity, cps
Time, min
1.63
+Q1: 1.485 to 2.153 min from Sample 1 (3 - 1 of 1) of 19-04-2018 11-02-06.wiff (Turbo Spray)
Max. 7.3e6 cps.
m/z, amu
621.5
311.1
356.1
644.3
4-PEG4
Chemical Formula: C36H63NO7
Exact mass: 621.46

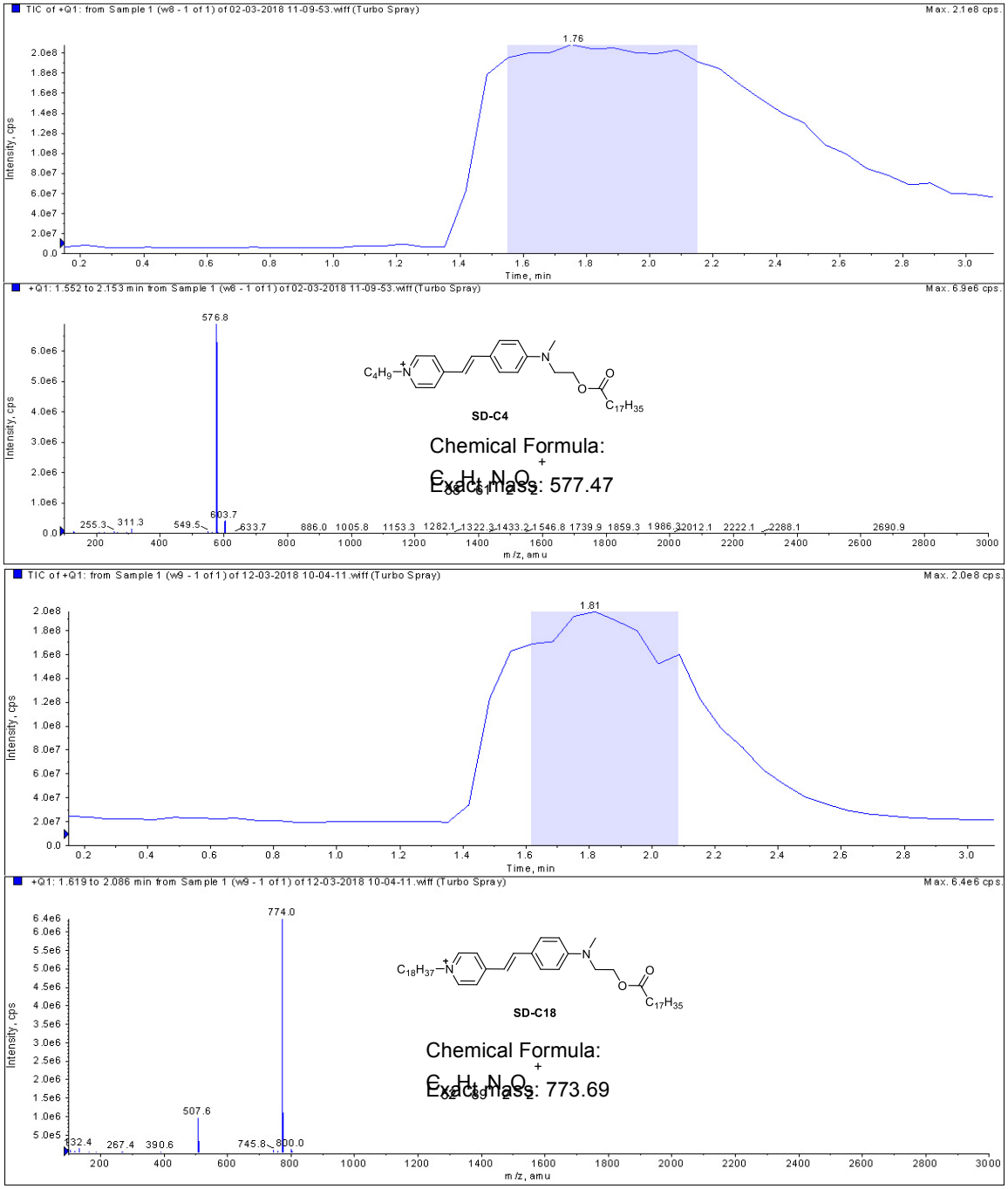

TIC of +Q1: from Sample 1 (w10 - 1 of 1) of 12-03-2018 10-05-03.wiff (Turbo Spray)
Max. 3.3e8 cps.
Intensity, cps
Time, min
1.76
+Q1: 1.552 to 2.019 min from Sample 1 (w10 - 1 of 1) of 12-03-2018 10-05-03.wiff (Turbo Spray)
Max. 7.1e6 cps.
m/z, amu
623.3
311.3
357.5
609.8
649.8
SD-PEG2
Chemical Formula:
Exact mass: 623.48


TIC of +Q1: from Sample 1 (wl1 - 1 of 1) of 23-04-2018 10-58-43.wiff (Turbo Spray)
Max. 6.1e8 cps.
Intensity, cps
Time, min
1.70


+Q1: 2.153 to 2.620 min from Sample 1 (wl1 - 1 of 1) of 23-04-2018 10-58-43.wiff (Turbo Spray)
Max. 6.3e6 cps.
Intensity, cps
m/z, amu
711.5
356.1
114.1
110.2
311.1
373.5
478.4
745.5
779.5
SD-PEG4
Chemical Formula: $C_{45}H_{91}NO_5^+$
Exact mass: 711.53


TIC of +Q1: from Sample 1 (7# - 1 of 1) of 29-11-2018 15-08-48.wiff (Turbo Spray)
Max. 2.1e8 cps.
Intensity, cps
Time, min
1.84


+Q1: 1.685 to 2.219 min from Sample 1 (7# - 1 of 1) of 29-11-2018 15-08-48.wiff (Turbo Spray)
Max. 7.0e6 cps.
Intensity, cps
m/z, amu
345.4
819.5
$C_{18}H_{37}-N^+$
6
Chemical Formula: $C_{24}H_{44}N^+$
Exact mass: 346.35



References

S1. L. Wang, S. Sadler, T. Cao, X. Xie, J. M. Von Filseck and E. Bakker, *Anal. Chem.*, 2019, **91**, 8973.

S2. L. Wang, X. Xie, J. Zhai and E. Bakker, *Chem. Commun.*, 2016, **52**, 14254.