

Supporting Information

Selective and sensitive chromo-fluorogenic sensing of anionic surfactants in water using functionalised silica nanoparticles

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1. Experimental procedures

Chemicals

30 % suspension of ludox silica nanoparticles AS-30 Colloidal Silica were purchased from Sigma-Aldrich and the nanoparticles were used without any further purification. The solvents were absolute grade and were purchased from Scharlab. Anions chloride, bromide sulfate, nitrite, nitrate, phosphate, pyrophosphate and carbonate solutions were prepared from sodium salts purchased from Scharlab. Sodium lauryl sulphate (LS, $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$) was purchased from Merck. Sodium tetradecyl sulfate (STS, $\text{CH}_3(\text{CH}_2)_{13}\text{OSO}_3\text{Na}$), sodium decyl sulfate (SDeS) and sodium hexyl sulfate (SHS) were purchased from Acros Organics, mono-*n*-dodecyl phosphate (DP) was purchased from Lancaster, sodium dodecyl benzenesulfonate (LAS) was obtained from Fluka and sodium octyl sulfate (SOS) was purchased from Chempur. The cationic surfactant hexadecyltrimethylammonium bromide (CTAB, $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$) was provided by Fluka. *t*-Octylphenoxypolyethoxyethanol (Tx) surfactant was purchased from Sigma-Aldrich. Methylene Blue (MB) was purchased from Riedel-de Haen. Sodium acetate, sodium butyrate, sodium hexanoate, sodium octanoate, sodium decanoate, sodium dodecanoate, myristic acid, sodium palmitate and sodium oleate were obtained from Sigma Aldrich. Chemical structures for all surfactants and carboxylates are showed in Figure SI-1. For the imidazolium derivative, *N*-methylimidazole was provided by Acros Organics and 3-(chloropropyl)trimethoxysilane was

purchased from Fluka. The spectroscopic inhibitor, 3-(mercaptopropyl)triethoxysilane (MPTS) for the synthesis of the solid **S1** was provided by Aldrich.

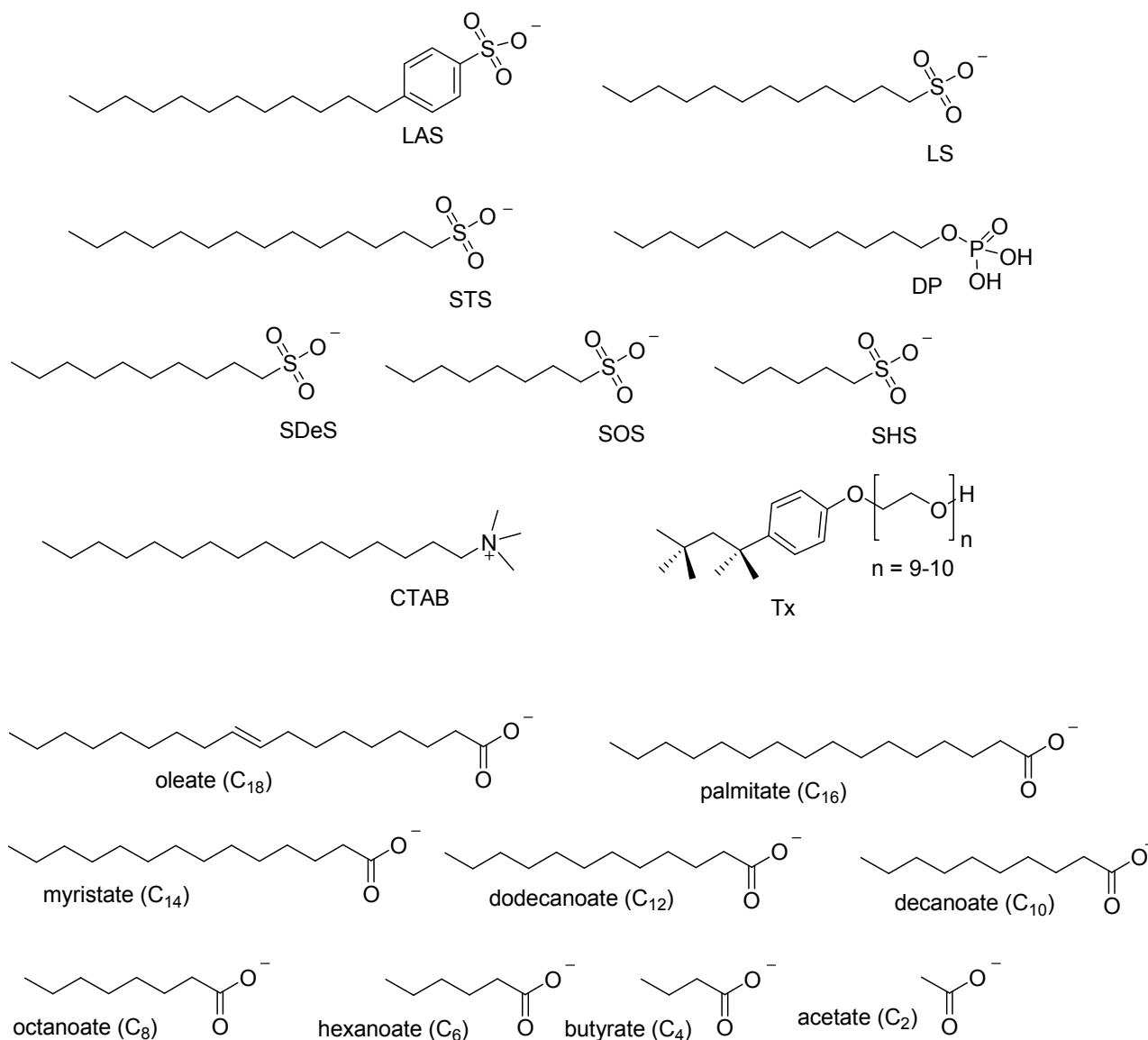


Figure SI-1. Chemical structures of surfactants and carboxylates tested.

General Techniques

TG analysis, transmission electron microscopy, elemental analysis, nuclear magnetic resonance, UV-visible spectroscopy and fluorescence spectroscopy techniques were employed to characterize the materials. Thermo-gravimetric analysis were carried out on a TGA/SDTA 851e Mettler Toledo equipment, using an oxidant atmosphere (Air, 80 mL/min) with a heating program consisting on a heating ramp of 10 °C per minute from 393 K to 1273 K and an isothermal heating step at this

temperature during 30 minutes. Transmission Electron Microscopy (TEM) images of the particles were obtained with a Philips CM10 operating at 20 KeV. Samples for TEM were prepared by spreading a drop of nanoparticles solution in H₂O onto standard carbon-coated copper grids (200 mesh). UV-visible spectroscopy was carried out with a Lambda 35 UV/Vis Spectrometer Perkin Elmer Instruments. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were acquired with Varian 300 spectrometer (Sunnyvale, CA, USA).

Synthesis of N-methyl-N'-propyltrimethoxysilylimidazolium chloride

The *N*-methyl-*N'*-propyltrimethoxysilylimidazolium chloride was prepared as follows. A mixture of *N*-methylimidazole (6.6 g, 80 mmol) and 3-(chloropropyl)trimethoxysilane (15.9 g, 80 mmol) were stirred in a dry 100 ml flask under nitrogen flow at 95 °C for 24 h. After cooling at room temperature, the resulting liquid product was washed with ether. The final compound was obtained as a yellow liquid. ¹H NMR (DMSO-D₆): δ (ppm) = 0.55 (m, 2H, -CH₂-Si-), 1.81 (m, 2H, CH₂-CH₂-Si-), 3.46 (s, 9H, CH₃-O-), 3.83 (s, 3H, -N-CH₃), 4.11 (t, 2H, -N-CH₂-CH₂-), 7.69 (d, 1H, Me-N-CH-CH-), 7.75 (d, 1H, CH-CH-N-CH₂-), 9.11 (s, 1H, N-CH-N-). ¹³C NMR (DMSO-d₆): δ (ppm) = 5.4 (-CH₂-Si-), 23.4 (-CH₂-CH₂-Si-), 35.7 (CH₃-O-), 50.1 (-N-CH₃), 50.9 (-N-CH₂-) 122.2 (-CH-CH-N-CH₂-), 123.6 (Me-N-CH-CH-), 136.6 (-N-CH-N-).

2. Preparation, characterization and use of functionalised silica nanoparticles S1.

Coated silica nanoparticles **S1** were prepared using the corresponding trialkoxysilyl derivatives following reported procedures by Montalti and coworkers. Ludox silica nanoparticles AS-30, 17 nm average diameter, (12 mL) were added to a solution containing acetic acid (60 mL), water (60 mL) and ethanol (100 mL). Then a mixture of 3-(mercaptopropyl)trimethoxysilane (**MPTS**, 2.5 mmol) and *N*-methyl-*N'*-propyltrimethoxysilylimidazolium chloride (12.5 mmol) were added to the nanoparticle suspension. The crude reaction was heated at 80 °C for 48 hours, the ethanol was evaporated and then the acetic acid solution neutralized with a saturated solution of ammonium acetate. The solvent was removed and nanoparticles were washed with acetone. The functionalised nanoparticles (**S1**) were precipitated and isolated by filtration, washed with water and acetone and dried at 70 °C.

Thermogravimetric analyses were carried out under a flow of air and with a heating rate of 10 °C/minute in the 30-1000 °C interval. The final solid was maintained at 1000 °C for 30 minutes. In the obtained thermograms of **S1** three clearly defined zones are observed; (i) from 30 °C to 150 °C which was assigned to loss of water and organic solvents (6.11 %), (ii) from 150 °C to 800 °C which was assigned to the organic matter attached into the nanoparticle surface (25.11 %) and, finally (iii) from

800° to 1000° C a third step was assigned to condensation of silanol groups (0.16 %). The silica residue amounts to 68.6 %. The diameter of **S1** nanoparticles was determined by TEM that shows a very homogenous particle size of 17.0 ± 2.6 nm.

Solid **S1** contains 2.07 mmol of imidazolium per gram of SiO₂. A further characterization of the interaction of the solid **S1** with the anionic surfactant LAS can be estimated from Figure 3 that shows that the saturation of the calibration curve was observed at a LAS concentration of 1.80×10^{-3} mol dm⁻³. From the amount of nanoparticles used in these experiments the saturation of the curve corresponds to a 1:1 molar ratio between imidazolium binding sites and LAS molecules. This indicated that each imidazolium cation coordinates with one molecule of LAS most likely resulting in the formation of a highly regular hydrophobic monolayer on the surface of the **S1** nanoparticles.

Signalling experiments using nanoparticles **S1** were carried out at pH 5.5. The pH was fixed using diluted HCl or NaOH solutions when appropriate.