

## Electronic Supplementary Information

# Ammonium based zwitterions showing both LCST- and UCST-type phase transitions with water in a very narrow temperature range

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### Preparation of zwitterions

Two types of zwitterions, *N,N,N*-tripentyl-3-sulfonyl-1-propaneammonium (N<sub>555</sub>C3S) and *N,N,N*-trihexyl-3-sulfonyl-1-propaneammonium (N<sub>666</sub>C3S), were prepared in this paper. Trialkylamine and 1,3-propanesultone were dissolved into acetone, and the resulting solution was mixed under dry nitrogen gas atmosphere. The obtained solution was stirred for two days at 80 °C. After removal of acetone by evaporation, the residual liquid was repeatedly washed with excess amounts of anhydrous diethylether. A resultant solid was dissolved in dichloromethane, and the solution was passed through a column filled with aluminum oxide. After then, it was purified by recrystallisation from ethylacetate/methanol, and obtained white powder was dried *in vacuo* at 60°C for 24 h. Chemical structure and purity of N<sub>555</sub>C3S and N<sub>666</sub>C3S were confirmed by <sup>1</sup>H-NMR spectroscopy and elemental analysis.

### N<sub>555</sub>C3S: *N,N,N*-Tripentyl-3-sulfonyl-1-propaneammonium

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>;  $\delta$ /ppm relative to TMS): 0.93 (9H, t,  $J=7.02$ ), 1.37 (12H), 1.70 (6H), 2.16 (2H), 2.92 (2H, t,  $J=5.83$ ), 3.19 (6H), 3.72 (2H). Elemental analysis (%) for C<sub>18</sub>H<sub>39</sub>O<sub>3</sub>NS: Found: C, 61.66; H, 11.79; N, 3.92; C/N, 15.75. Calcd: C, 61.84; H, 11.25; N, 4.01; C/N, 15.43.

### N<sub>666</sub>C3S: *N,N,N*-Trihexyl-3-sulfonyl-1-propaneammonium

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>;  $\delta$ /ppm relative to TMS): 0.89 (9H, t,  $J=6.57$ ), 1.33 (18H), 1.69 (6H), 2.15 (2H), 2.93 (2H, t,  $J=5.90$ ), 3.16 (6H), 3.75 (2H). Elemental analysis (%) for C<sub>21</sub>H<sub>45</sub>O<sub>3</sub>NS: Found: C, 64.17; H, 12.17; N, 3.47; C/N, 18.49. Calcd: C, 64.40; H, 11.58; N, 3.58; C/N, 18.01.

**Table S1** Thermal properties of prepared zwitterions (ZIs)

ZI	$T_{\text{m}}^{*1}/^{\circ}\text{C}$	$T_{\text{d}}^{*2}/^{\circ}\text{C}$
N <sub>555</sub> C2S	157	253
N <sub>666</sub> C3S	202	250

\*<sup>1</sup>Melting temperature \*<sup>2</sup>Decomposition temperature