Electronic Supplementary Information (ESI)

for

Temperature-responsive self-assembled nanostructures from lysine-based surfactants with high chain length asymmetry: from tubules and helical ribbons to micelles and vesicles

Isabel S. Oliveira, Mikail Lo, Maria J. Araújo, Eduardo F. Marques*

Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, nº 687, P-4169-007 Porto, Portugal
**efmarque@fc.up.pt.*

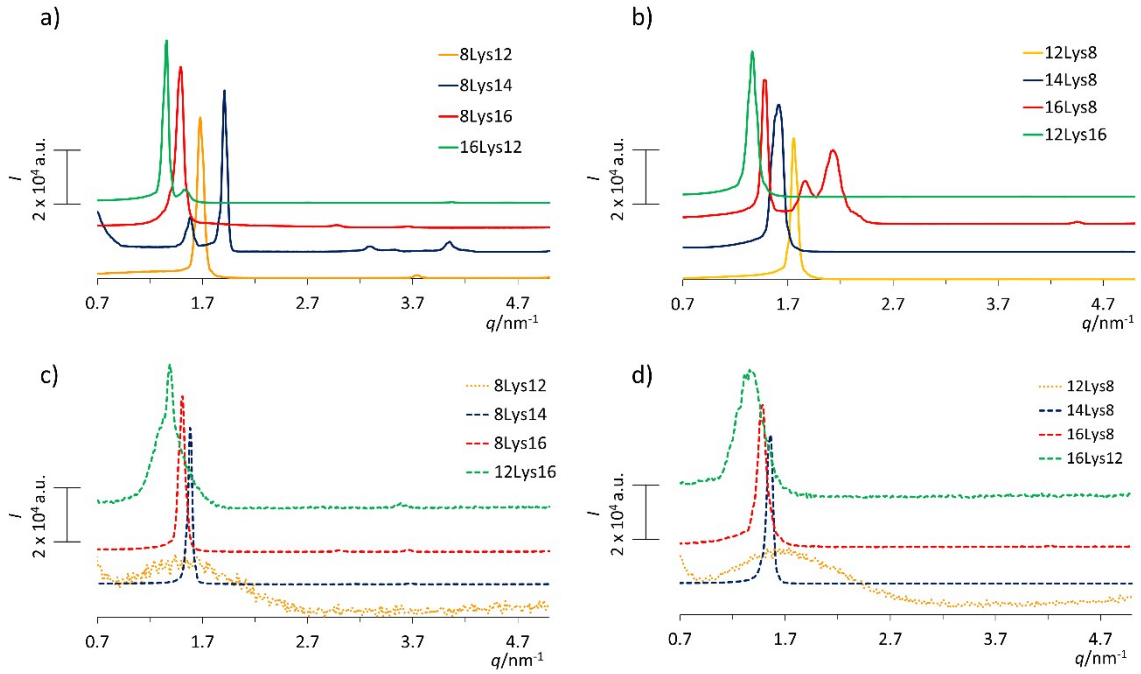
1. Thermodynamic parameters of phase transitions

Table S1. Thermodynamic parameters associated with the phase transitions of the 8Lys*n* and *m*Lys8 lysine-derived surfactants in water, as obtained from de DSC scans.

Surfactant	$T_{m,onset}$/˚C		T_m/˚C		$\Delta_{tr}H_m$/kJ·mol^{-1}		$\Delta_{tr}S_m$/J·K^{-1}·mol^{-1}	
	1st heating	reheating	1st heating	reheating	1st heating	reheating	1st heating	reheating
8Lys12	14.6 ± 1.0		17.2 ± 0.8		0.5 ± 0.3		1.8 ± 0.9	
8Lys14	23.1 ± 0.2	20.9 ± 0.6	30.7 ± 0.6	30.2 ± 0.4	54.2 ± 1.1	42.0 ± 0.9	178.4 ± 3.7	138.1 ± 2.8
8Lys16	33.5 ± 1.3	23.9 ± 0.2	36.0 ± 0.9	30.4 ± 0.4	60.6 ± 3.0	51.4 ± 1.2	186 ± 19	169.4 ± 4.1
12Lys8	27.7 ± 0.1		28.8 ± 0.1		10.3 ± 1.3		32.3 ± 2.2	
14Lys8	31.7 ± 0.8	13.3 ± 0.6	35.6 ± 0.6	18.6 ± 1.9 31.4 ± 0.6	58.3 ± 1.1	50.9 ± 4.9	182.0 ± 8.6	175 ± 24
16Lys8	25.8 ± 0.4	30.8 ± 2.0	37.5 ± 1.1	30.8 ± 2.0	62.6 ± 3.2	53.3 ± 1.4	201 ± 10	176.6 ± 4.6

Table S2. Thermodynamic parameters associated with the phase transitions of the 12Lys16 and 16Lys12 lysine-derived surfactants in water, as obtained from de DSC scans.

Surfactant	$T_{m,onset}$/˚C			T_m/˚C			$\Delta_{tr}H_m$/kJ·mol^{-1}			$\Delta_{tr}S_m$/J·K^{-1}·mol^{-1}		
	1st heating	reheating	cooling	1st heating	reheating	cooling	1st heating	reheating	cooling	1st heating	reheating	cooling
12Lys16	48.6 ± 0.7	36.5 ± 0.1	26.1 ± 2.5	51.1 ± 0.6	39.2 ± 0.2 43.1 ± 0.2	28.1 ± 0.2	63.4 ± 3.8	46.9 ± 6.2	-43.3 ± 2.9	195.6 ± 12.0	159.3 ± 5.3	-143.2 ± 9.6
16Lys12	49.8 ± 0.1	44.8 ± 0.3	27.0 ± 0.4	53.57 ± 0.07	46.8 ± 0.2	25.3 ± 0.1	65.0 ± 1.5	55.0 ± 1.1	-54.1 ± 2.8	199.6 ± 2.8	171.8 ± 3.3	-180.4 ± 9.2



2. SAXS data

Fig. S1 Diffractograms obtained by SAXS for all surfactants studied: a) and b) powder; c) and d) tubule dispersions.

3. Tubule-vesicle transition

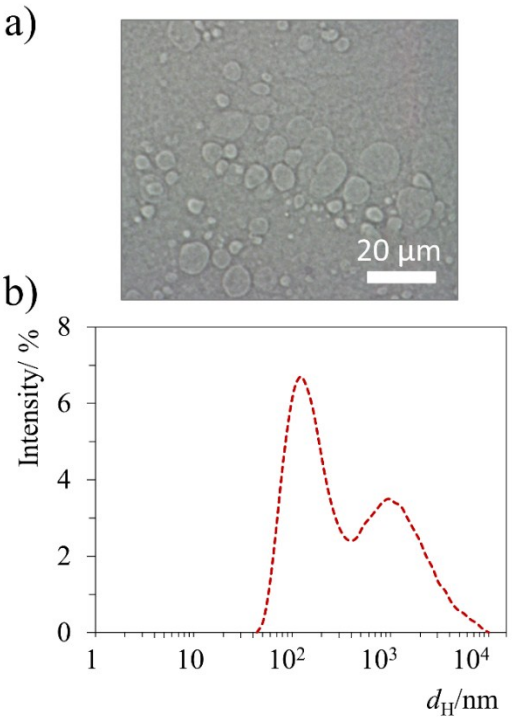


Fig. S2 Evidence for polydisperse vesicle formation for 16Lys12: a) light micrograph; b) mean size distribution obtained by DLS, both for 0.50 wt% dispersions.

4. Phase scanning data

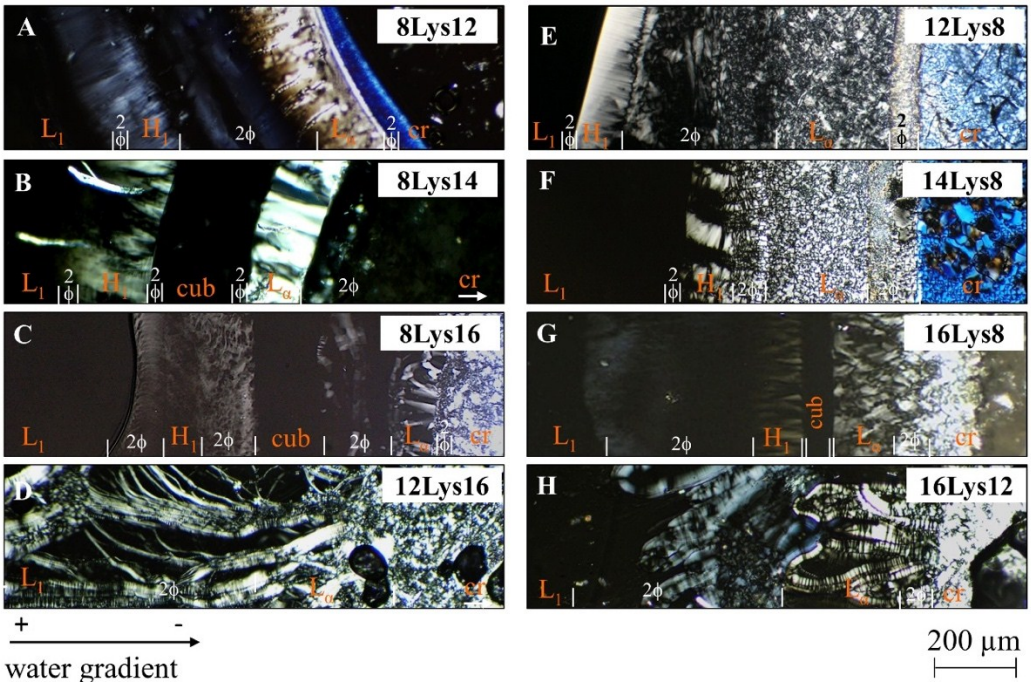


Fig. S3. Phase scanning imaging of 8Lys12 (A), 8Lys14 (B), 8Lys16 (C), 12Lys8 (E), 14Lys8 (F), 16Lys8 (G), 12Lys16 (D), and 16Lys12 (H) at 25 ˚C (A, E), 40 ˚C (B, C, F, G) and 55 ˚C (D, H). The images were obtained under polarized light. Abbreviations: Lα, lamellar liquid crystalline phase; L1, isotropic phase; H1, hexagonal phase; cub, isotropic cubic phase; cr, hydrated crystals.

Table S3 Summary of the phase sequence observed for the anionic lysine-based surfactants studied. The textures observed under polarized light are described under the respective assigned liquid-crystalline phase.

Surfactant	Phase Sequence
8Lys12	L_1 *isotropic (liquid)* → H_1 *marble texture* → L_α *mosaic texture* → cr
8Lys14	L_1 *isotropic* → H_1 *marble texture* → cub *isotropic (very viscous)* → L_α *mosaic texture* → cr
8Lys16	L_1 *isotropic* → H_1 *striated texture* → cub *isotropic* → L_α *mosaic texture* → cr
12Lys8	L_1 *isotropic* → H_1 *granulated marble texture* → L_α *mosaic texture* → cr
14Lys8	L_1 *isotropic* → H_1 *marble texture* → L_α *mosaic texture* → cr
16Lys8	L_1 *isotropic* → H_1 *marble texture* → cub *isotropic* → L_α *mosaic texture* → cr
12Lys16	L_1 *isotropic* → L_α *oily-streaks* → cr
16Lys12	L_1 *isotropic* → L_α *oily-streaks* → cr