Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

On the self-assembly of a tryptophan labeled deoxycholic acid

by

Leana Travaglini, Marta Gubitosi, Maria C. di Gregorio, Nicolae V. Pavel, Andrea D'Annibale, Mauro Giustini, Victor H. Soto Tellini, José Vázquez Tato, Marc Obiols-Rabasa, Solmaz Bayati and Luciano Galantini

Contents:

1. Supporting figures S2

2. Supporting tables S9

1. Supporting Figures

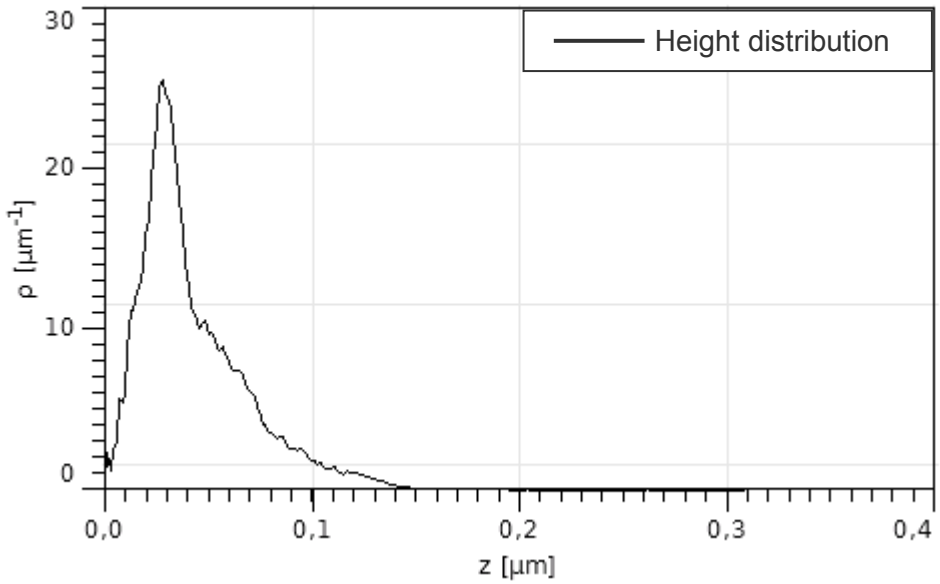

Fig. S1 AFM height distribution of the tubules observed for a 4.0 x 10^{-3} M β-L-TrpDC (pH 11.0) sample at 20 °C.

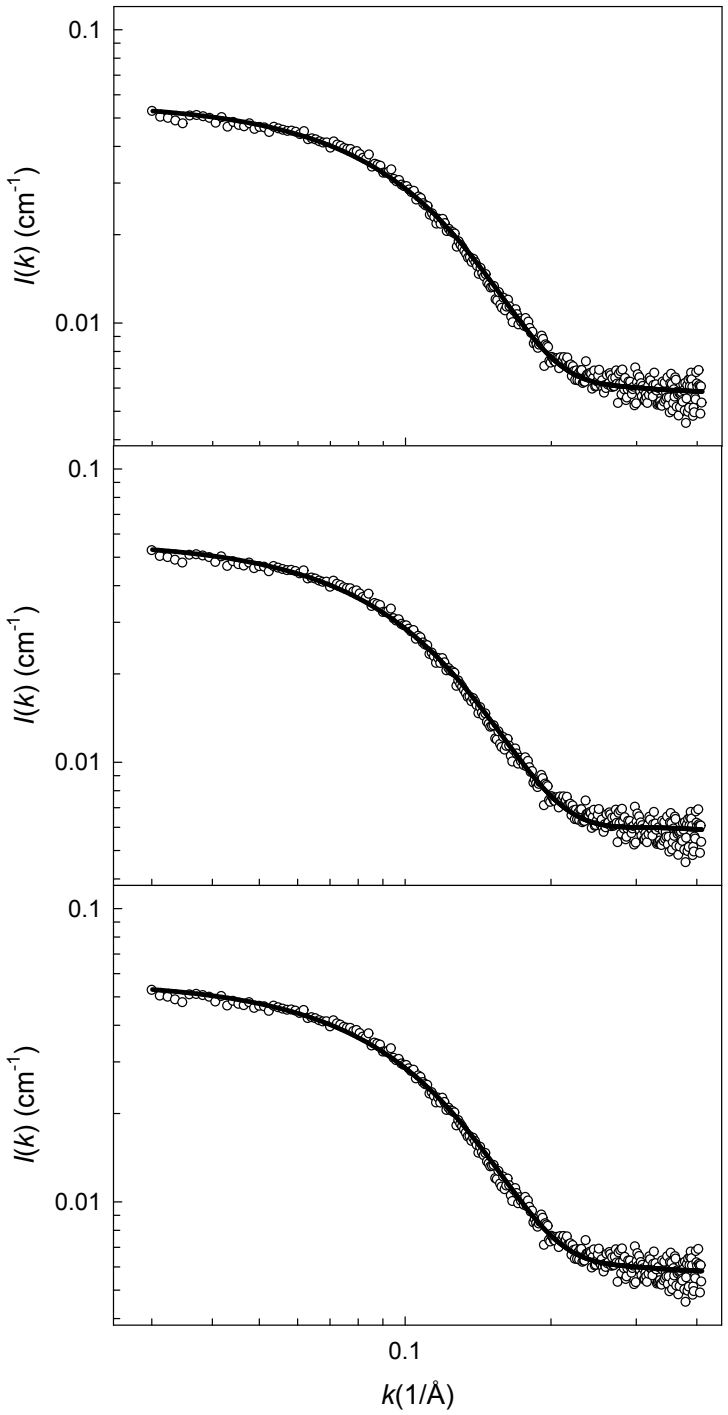

Fig. S2 Model-based fits carried out assuming different geometries of the micelles formed at 55 °C. Experimental (circles) and theoretical (full line) SAXS intensities curves of a 4.00 x 10^{-2} M β-L-TrpDC sample in carbonate/bicarbonate buffer 6.00 x 10^{-2} M (pH 11.0) assuming a prolate ellipsoidal (a), oblate ellipsoidal (b) and spherical (c) geometry.

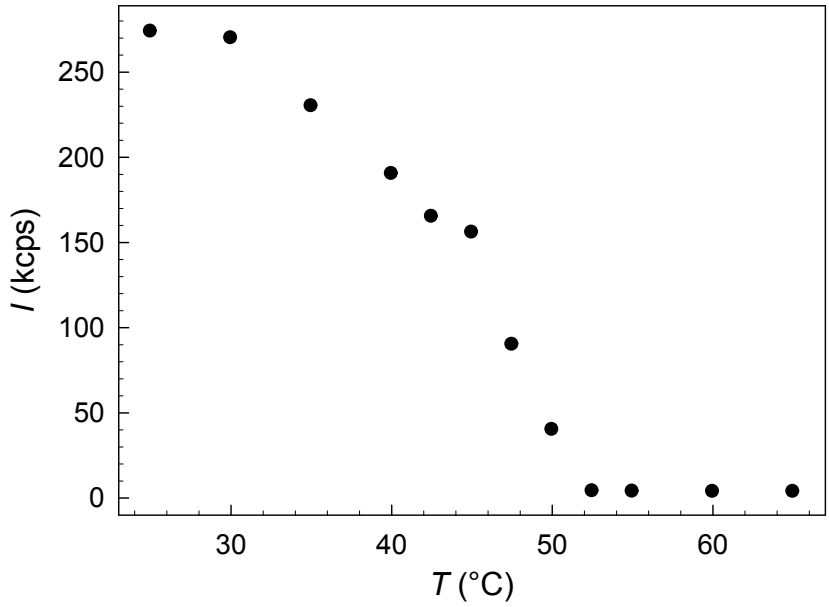

Fig. S3 Light scattering average intensities as a function of temperature for a 4.0 x 10^{-3} M β-L-TrpDC sample (pH 11.0).

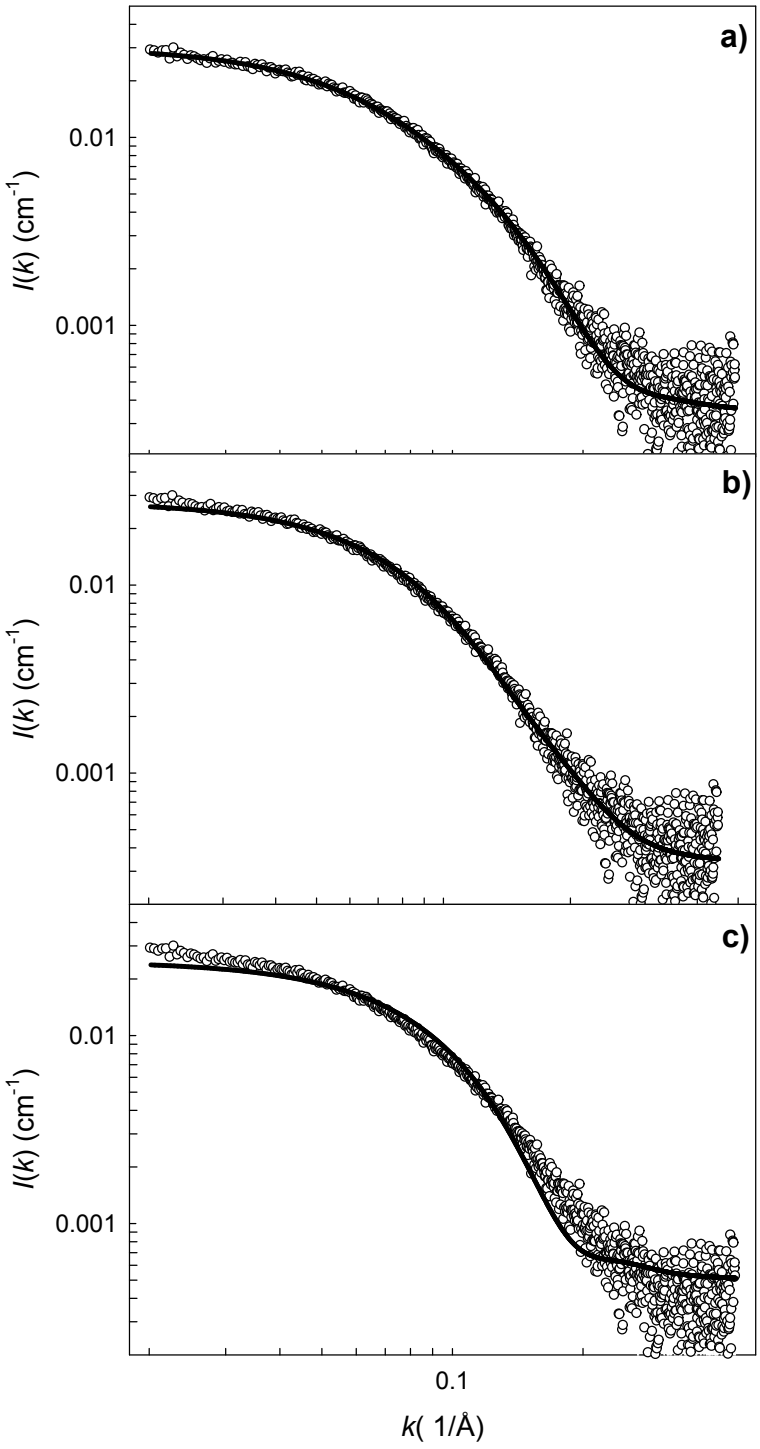

Fig. S4 Experimental (circles) and theoretical (full line) SAXS intensities curves of a 1.00 x 10^{-2} M β-L-TrpDC sample (pH 1.8) at 20 °C assuming a prolate ellipsoidal (a), an oblate ellipsoidal (b) and a spherical (c) geometry.

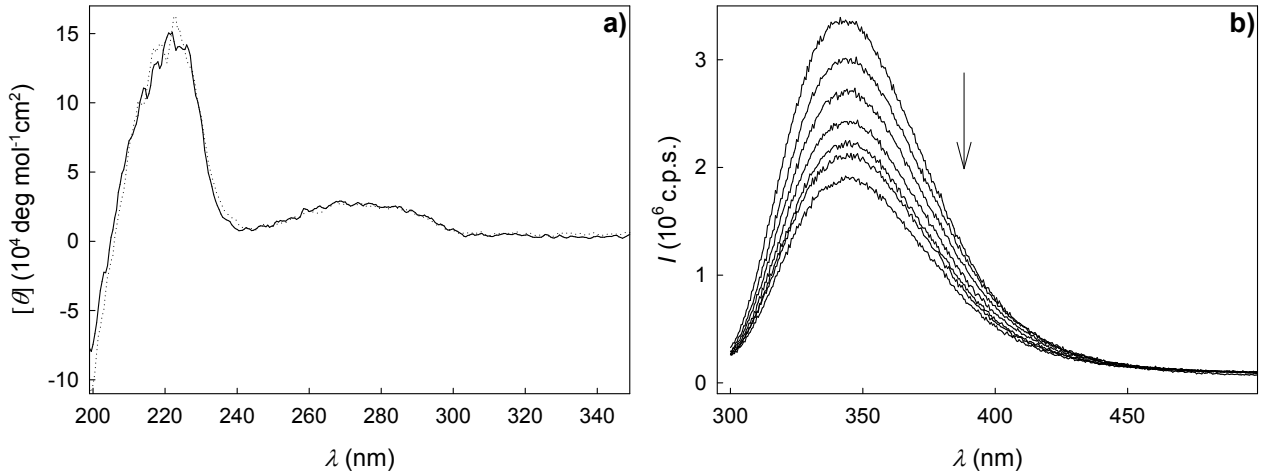

Fig. S5 (a) CD profile recorded on a 1.00 10^{-2} M β-L-TrpDC sample (pH 1.8) in the presence of NaCl 1.00 x 10^{-2} M, at 25 (full line) and 60 °C (dotted line). (b) Fluorescence spectra (λ_{ecc}= 290 nm, 0.1 mm path length quarz cell, slits 2/2 nm; 0.5 nm resolution; 0.25 s integration time) recorded at 25, 35, 40, 45, 50, 55 and 60 °C, the arrow indicates the profile evolution upon heating.

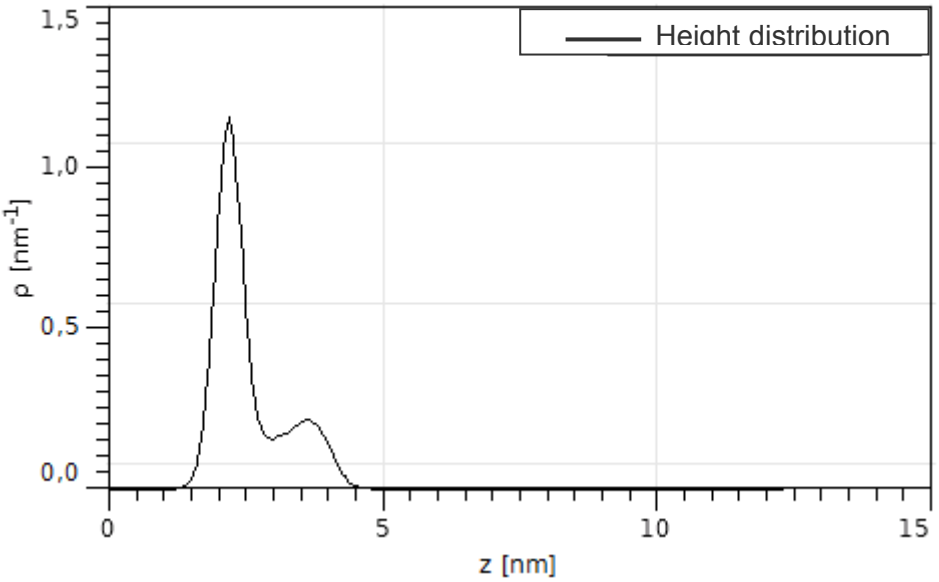

Fig. S6 AFM height distribution of the gel worm-like structure observed for a 1.00 x 10^{-2} M β-L-TrpDC sample (pH 1.8) containing NaCl 1.00 x 10^{-2} M at 20 °C.

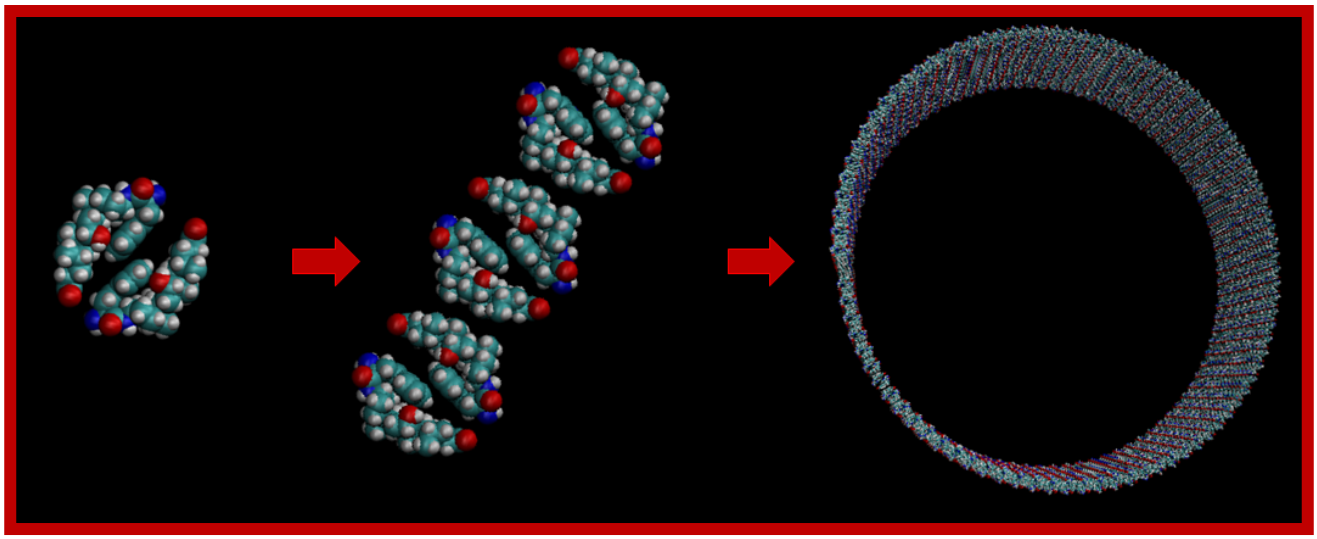

Fig. S7 A possible aggregation model for the β-L-TrpDC tubule in alkaline conditions. The different colors in the molecule represent H (white), C (cyan), N (blue) and O (red). An antiparallel face-to-face supramolecular organization may be hypothesized. The building block, constituted by two molecules with a face-to-face disposition, is characterized by a slightly truncate wedge shape that ensures the wall curvature. The packing results in both the carboxylate and the amine group laying on the tubule wall surfaces and thus reinforcing the whole structure by intermolecular hydrogen bonding. The hydrophobic Trp indole moieties are oriented towards the wall interior. Consequently, it is likely that the π–π interactions involving such moieties stabilize in the first place the building blocks and the whole tubular structure, taking place between molecules of different building blocks along the tubules.

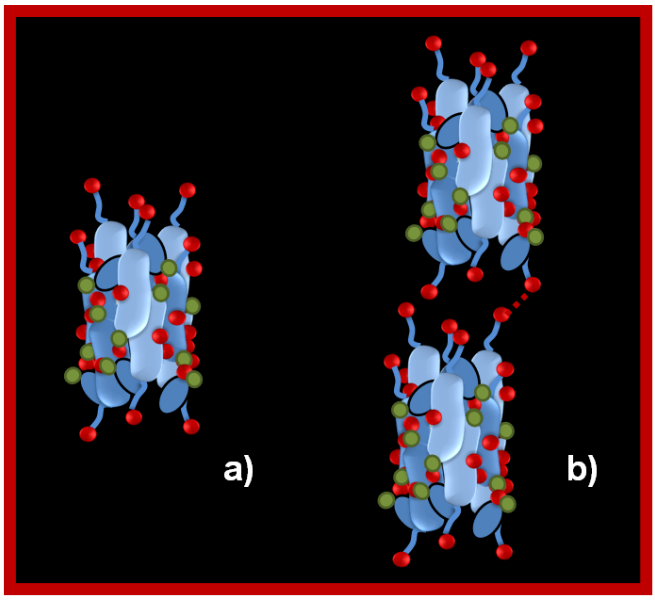

Fig. S8 A possible aggregation model for the β-L-TrpDC micelles. Carboxyl, carbonyl or hydroxyl groups are reported as red spheres; amine NH_2 and amide NH groups are reported in green. The Trp lateral group is represented as a darker blue ellipse with a black contour. Primary micelles (a) with Trp partially embedded in the hydrophobic core are formed in basic conditions. The micelles can grow due to the formation of hydrogen bonds involving the carboxyl groups (red dotted line) in acidic conditions (b).

2. Supporting tables

Table S1 Best fitting semi-major (a_e) and semi-minor (b_e) axes (a_e = b_e for the sphere) and agreement factor(χ^2_N) of the SAXS data collected on a 4.00 x 10^{-2} M β-L-TrpDC sample(pH 11.0) at 55 °C, for different geometries of the scattering particles. The estimated standard deviations are given in parentheses.

	a_e(Å)	b_e(Å)	χ^2_N
Prolate ellipsoid	23.0(4)	12.0(3)	1.27
Oblate ellipsoid	19.2(2)	14.2(3)	1.41
Sphere	16.1(4)	-	1.36

Table S2 Aggregation number (n_{agg}) and hydration number per monomer (N_{Hyd}) values calculated for ellipsoidal prolate micelles of a 4.00 x 10^{-2} M β-L-TrpDC sample (pH 11.0) at 55 °C, assuming different ionization degree (α). The estimated standard deviations are reported in parentheses.

α	n_{agg}	N_{hyd}
0.0	9.4(2)	22(3)
1.0	11.6(2)	13(3)

Table S3 Best fitting semi-major (a_e) and semi-minor (b_e) axes (a_e = b_e for the sphere) and agreement factor (χ^2_N) of the SAXS data collected on a 1.00 x 10^{-2} M β-L-TrpDC sample(pH 1.8) at 20 °C. The estimated standard deviations are reported in parentheses.

	a_e (Å)	b_e (Å)	χ^2_N
Prolate ellipsoid	45.8(5)	14.0(5)	0.79
Oblate ellipsoid	10.0(5)	27.9(5)	1.02
Sphere	20.0(5)	-	3.28

Table S4 Aggregation number (n_{agg}) estimated from the IFT extrapolated $I(0)$ value and hydration number per monomer (N_{Hyd}) by assuming the ellipsoidal prolate geometry and different ionization degree (α) values estimated for the micelles formed by a 1.00 x 10^{-2} M β-L-TrpDC sample (pH 1.8) at 20 °C. The estimated standard deviations are reported in parentheses.

α	n_{agg}	N_{hyd}
0.0	19(1)	37(6)
0.5	24(1)	25(4)
1.0	31(1)	14(4)