Supplementary Information for Hierarchical assembly of pH-responsive surfactant-cyclodextrin complexes

Larissa dos Santos Silva Araújo^{a,b}, Leah Watson^b, Daouda A. K. Traore^{b,c}, Giuseppe Lazzara^{*a}, Leonardo Chiappisi^{*b}

^aDipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze pad 17, 90128 Palermo, Italy ^bInstitut Max von Laue - Paul Langevin, 71 avenue des Martyrs, 38042 Grenoble, France ^cSchool of Life Sciences, Keele University, Staffordshire ST5 5BG, United Kingdom.

S1. Thermogravimetry



Figure S1: Thermogravimetric analysis of α -cyclodextrin and β -cyclodextrin.

Email addresses: giuseppe.lazzara@unipa.it (Giuseppe Lazzara*), chiappisil@ill.eu (Leonardo Chiappisi*)

S2. Phase behaviour



Figure S2: Phase behaviour of $C_{12}E_5Ac$ - βCD before (a) and after (b) heating $C_{12}E_5Ac$ - βCD



Figure S3: $C_{12}E_{10}Ac-\alpha CD$ before (a) and after heating (c) and $C_{12}E_{10}Ac-\beta CD$ before (b) and after heating (d).

S3. Thermodynamic parameters obtained from volumetric studies

Table T1: Thermodynamic parameters of different surfactant-cyclodextrin complexes obtained from the volumetric fit.

Surfactant	Cyclodextrin	$\alpha = 0$			$\alpha = 1$		
		n	K $(10^3 \text{ kg mol}^{-1})$	$\Delta V (cm^3 mol^{-1})$	n	K $(10^3 \text{ kg mol}^{-1})$	$\Delta V (cm^3 mol^{-1})$
C ₁₂ E ₅ Ac	αCD	1.17 ± 0.1	6.23 ± 0.46	-8.16 ± 0.1	1.50 ± 0.1	3.49 ± 0.12	-10.67 ± 0.23
$C_{12}E_{10}Ac$		1.71 ± 0.2	7.62 ± 0.31	-8.29 ± 0.1	0.54 ± 0.2	5.76 ± 0.2	-8.87 ± 0.16
C ₁₂ E ₅ Ac	βCD	0.8 ± 0.1	5.68 ± 0.08	5.30 ± 0.1	1.47 ± 0.1	11.25 ± 1.04	14.45 ± 1.93
$C_{12}E_{10}Ac \\$		1 ± 0.1	8.50 ± 0.96	5.34 ± 0.3	0.85 ± 0.1	15.1 ± 0.42	14.16 ± 1.13

S4. Small-angle Neutron Scattering (SANS)



Figure S4: SANS curves of Ratio [CD]/[Surfactant] = 1, degree of ionization α =0 and α =1. (a) C₁₂E₅Ac- α CD, (b) C₁₂E₅Ac- β CD, (c) C₁₂E₁₀Ac- α CD and (d) C₁₂E₁₀Ac- β CD. Measurements recorded on D22 at ILL.



Figure S5: SANS curves profiles of $C_{12}E_5Ac - \beta CD$ (Ratio [CD]/[Surfactant] = 2) at different concentrations:(a) α =0 (nonionized), (c) α =1 (ionized). Comparison of βCD with ionized $C_{12}E_5Ac$ (green) and $C_{12}E_{10}Ac$ (blue) with different surfactant concentrations. Different degree of ionization (α) scattering profile curves of $C_{12}E_{10}Ac$ with αCD (c) and βCD (f). Curves are scaled by successive factors of 7 for readability. Measurements a and c were recorded on D11 and b and d on D22 at ILL.



Figure S6: SANS curves of different concentrations of the $C_{12}E_{10}Ac-\alpha CD$ (Ratio [CD]/[Surfactant] = 2), at (a) $\alpha = 0$ (nonionized) and (b) $\alpha = 1$ (ionized). Curves are scaled by successive factors of 5 for readability. Measurements were recorded on D11 at ILL.



Figure S7: SANS curves: Highlight of the structure factor in the SANS curves of $C_{12}E_5Ac$ at different degree of ionization (Ratio [CD]/[Surfactant] = 2): (a) α CD and (b) α CD systems: Curves intensity normalized by $\alpha = 0$. (c) β CD and (d) β CD systems: Curves intensity normalized by $\alpha = 0$. Measurements were recorded on D22 at ILL.



Figure S8: SANS curves: Highlight of the structure factor in the SANS curves of $C_{12}E_{10}Ac$ at different degree of ionization (Ratio [CD]/[Surfactant] = 2): (a) α CD and (b) α CD systems: Curves intensity normalized by $\alpha = 0$. (c) β CD and (d) β CD systems: Curves intensity normalized by $\alpha = 0$. Measurements were recorded on D22 at ILL.