

Supplementary Electronic Information for:

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**Self-assembly of cyclodextrin-oil inclusion complexes at the oil-water
interface: a route to surfactant free emulsions**

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In Figure S1, we present Transmission Electron Microscope (TEM) images of microcrystals of α -CD-tetradecane inclusion complexes (ICs) produced by dispersing small amount of tetradecane into an aqueous solution of α -CD (see the main text for more details and discussion). Figure S2 shows the effect of the CD type on the formation precipitates of microcrystals from ICs with tetradecane. The result depends on the size of the CDs hydrophobic cavity and its geometric match with the guest molecule, tetradecane. Figures S3 and S4 show the evolution in the formation of microcrystals from α -CD-tetradecane and β -CD-tetradecane ICs in solution of different pH and times after homogenisation. Figure S5 represents the effect of urea (chaotropic agent) on the formation of aggregates of ICs of β -CD and tetradecane at different times. The urea affects the formation of hydrogen bonds between the CD molecules and also influences the hydrophobic effect which drives the formation of the IC with the tetradecane molecules.

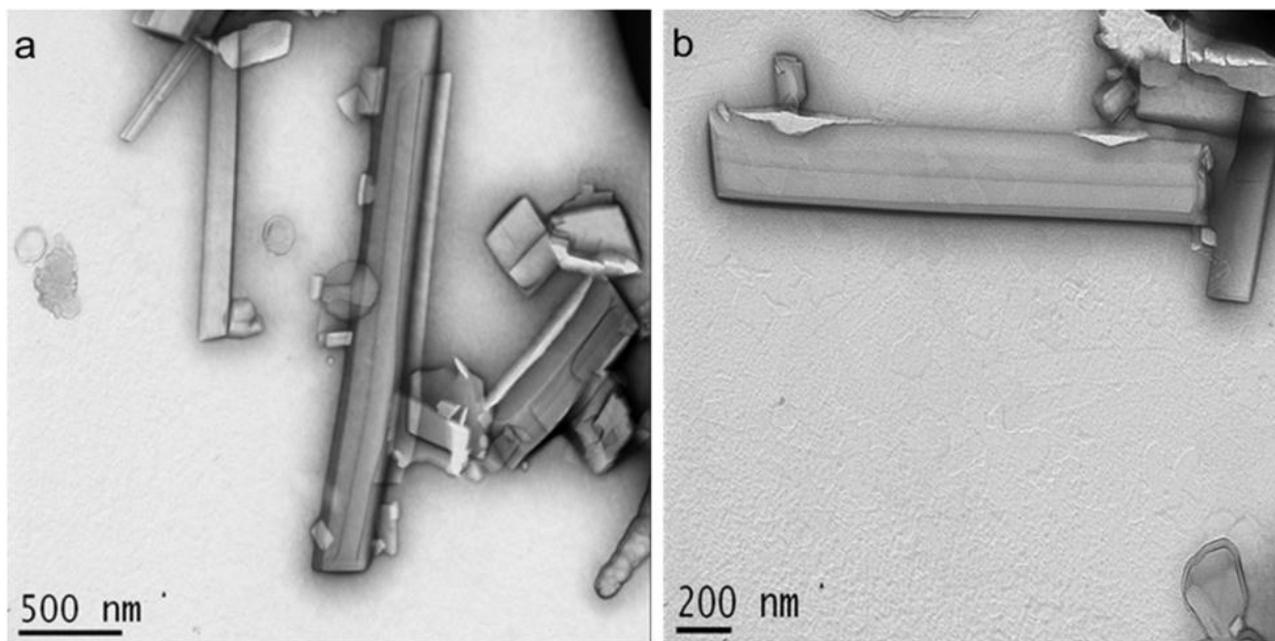


Figure S1: TEM images for α -CD/tetradecane ICs (a) and (b).

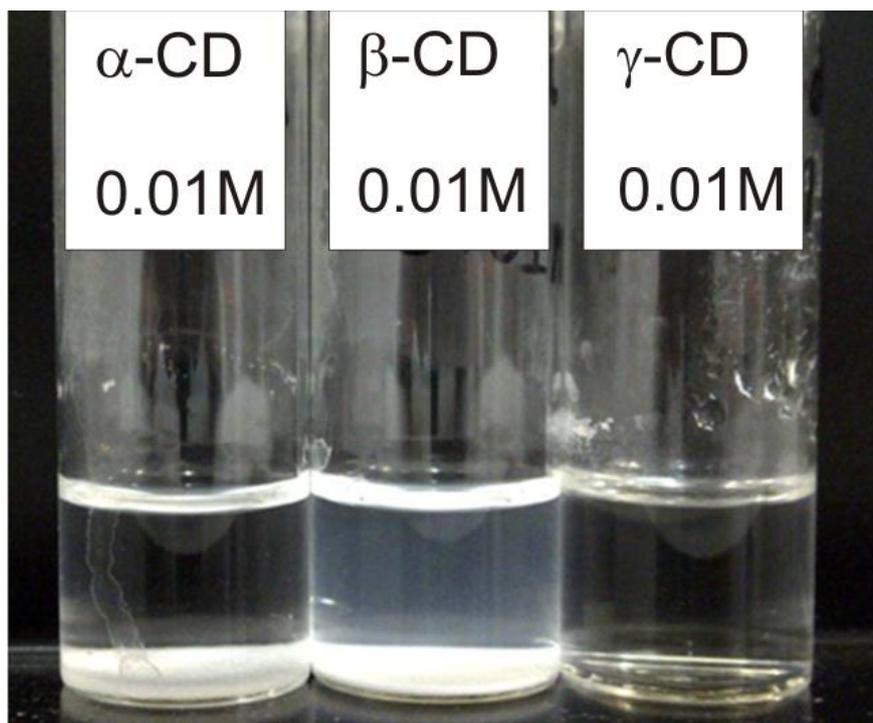


Figure S2: Effect of CD hydrophobic cavity on the formation of CD/tetradecane ICs. Only α -CD and β -CD with smaller hydrophobic cavities were able to form ICs with tetradecane while γ -with a larger cavity could not. Images were captured after 3 days of preparation.

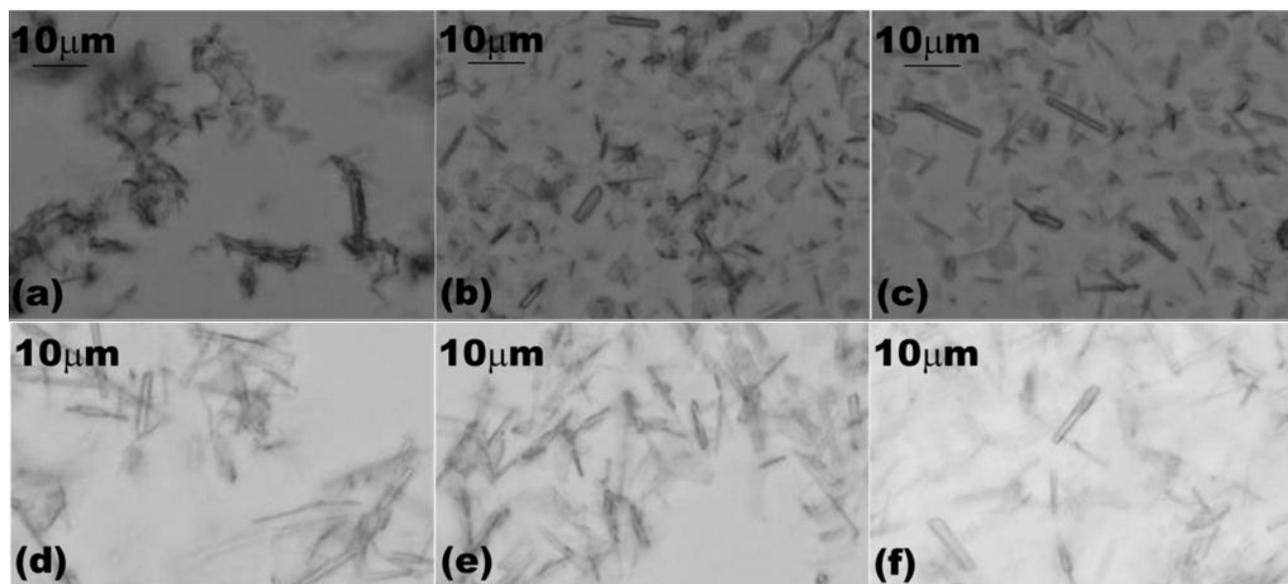


Fig. S3 microscope micrographs showing α -CD-tetradecane ICs formed under different pH of the aqueous solutions but captured at different days. (a) pH 1.98 24 hours (b) pH 7.16 24 hours (c) pH 11.60 24 hours (d) pH 1.98 after 7 days (e) pH 7.16 after 7 days (f) pH 11.60 after 7 days.

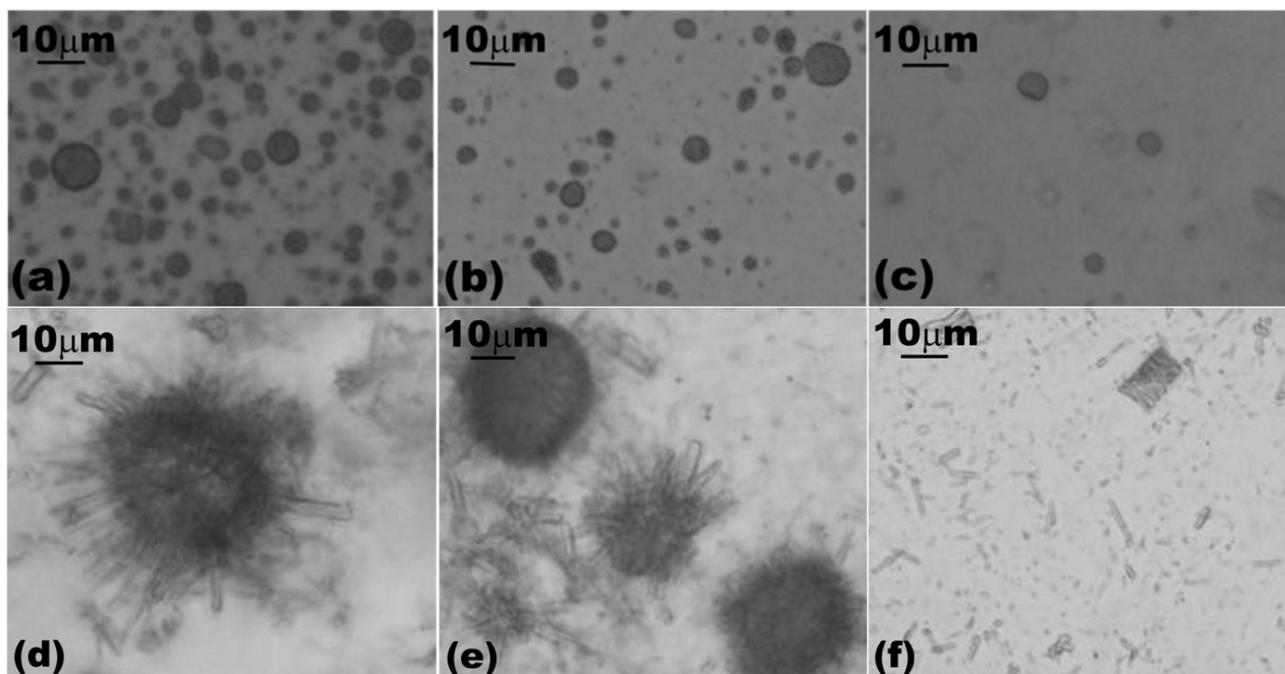


Fig. S4 Optical micrographs showing β -CD/tetradecane ICs formed under different pH of the aqueous solutions but captured at different days. (a) pH 1.98 24 hours (b) pH 7.16 24 hours (c) pH 11.60 24 hours (d) pH 1.98 after 7 days (e) pH 7.16 after 7 days (f) pH 11.60 after 7 days.

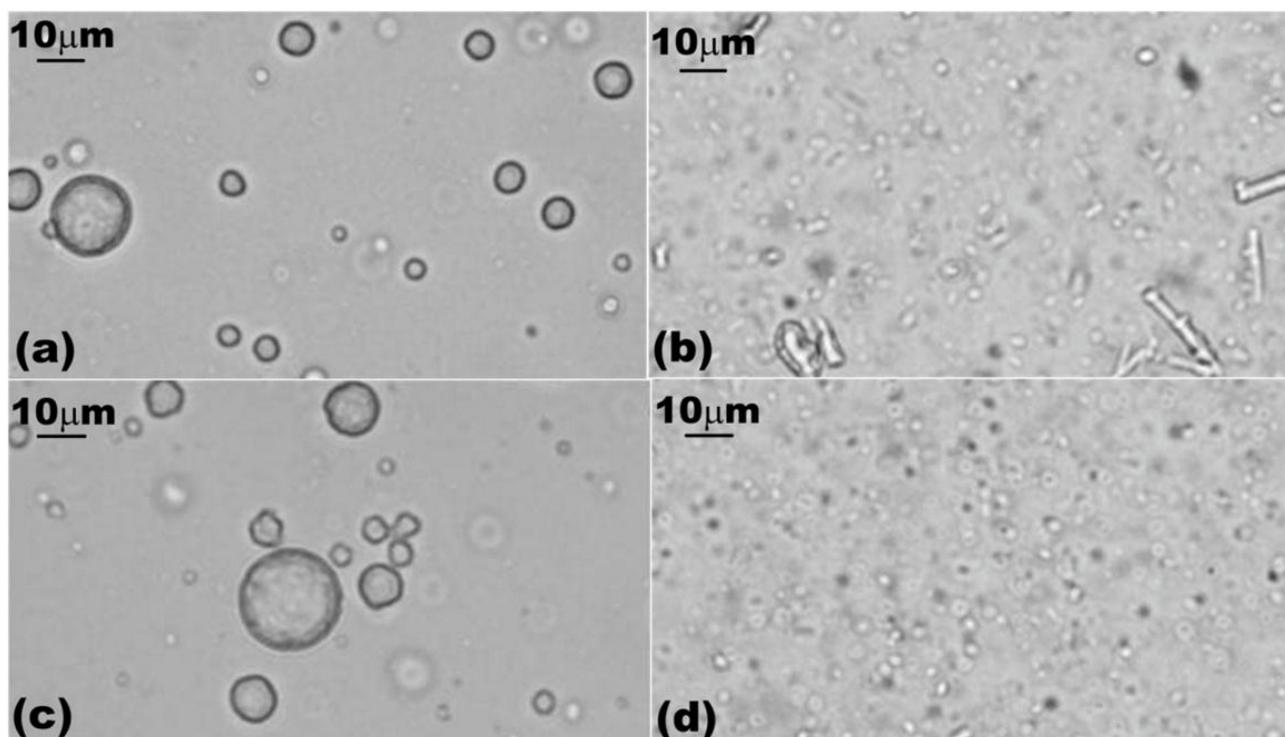


Fig. S5. Images showing the effect of urea concentration on the size of β -CD/tetradecane ICs as a function of time. (a) in 0.5 M urea immediately after dispersion; (b) in 0.5 M urea after 3 days. (c) in 1 M urea immediately after dispersion; (d) in 1 M urea after 3 days.

Calculations to determine the possible number of tetradecane molecules that can be accommodated in γ -CD cavity.

Here we estimate whether more than one molecule of TD can fit in the γ -CD cavity in a stretched state. To estimate the effective diameter of the stretched tetradecane molecule we treated it as a sequence of 14 spherical segments of approximately the same volume v , as shown in the diagram below. In addition we assumed that the stretched tetradecane molecule has a zig-zag structure with 109° between C-C-C bonds, as illustrated below:

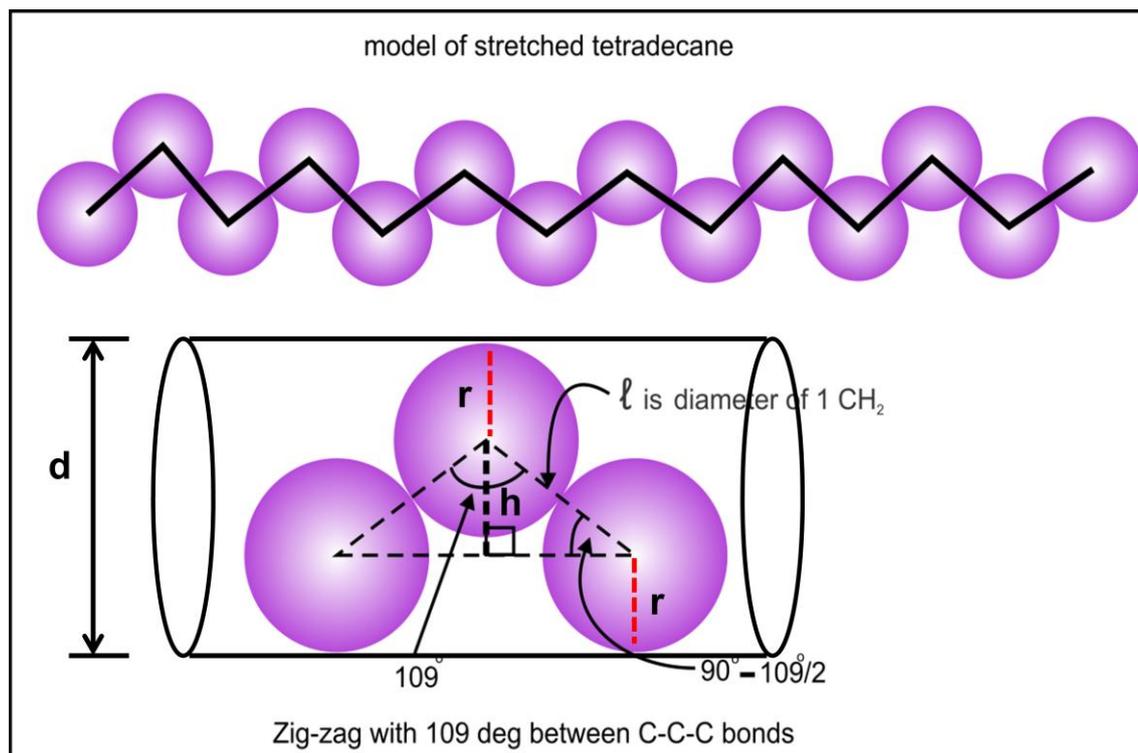


Fig. S6. Model of the stretched tetradecane molecule.

The volume, v of one segment of tetradecane (cm^3) is given by;

$$v \approx \frac{14M_{TD}}{14N_A\rho_{TD}} \quad (1)$$

Here, M_{TD} is the molar mass ($198.39 \text{ g mol}^{-1}$) of tetradecane, N_A ($6.022 \times 10^{23} \text{ mol}^{-1}$) is the Avogadro's number and ρ_{TD} is the density (0.763 g cm^{-3} at 298 K) of tetradecane and 14 accounts for the number of segments. Therefore $v = 3 \times 10^{-23} \text{ cm}^3$. The diameter, l , of one segment of TD (cm) is found by assuming that CH_2 is approximately spherical and then substituting the value of volume (v) from Eq. (1). To get size in nm the values are divided by a factor of 10^9 .

$$\ell = 2 \left(\sqrt[3]{\frac{3v}{4\pi}} \right) \quad (2)$$

Hence the size of the sphere (ℓ) is 0.39 nm. $\sin(35.5) = h/0.39$, therefore $h = 0.22$ nm. The diameter of the stretched TD molecule is $d = h + \ell = (0.22 + 0.39) = 0.61$ nm. The diameters of γ -CD are: larger opening = 0.95 nm and smaller opening = 0.79 nm. 2 stretched molecules of tetradecane lying side by side will have a cross sectional diameter of $2d = 2 \times 0.609 = 1.22$ nm. Since this value is greater than diameters of γ -CD, this means only 1 TD molecule can be accommodated into the γ -CD cavity i.e. from these calculations, it is not possible to have two tetradecane molecules in γ -CD cavity.