Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information

New supramolecular amphiphiles based on renewable resources

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General.

β-Cyclodextrin (kleptose) and isosorbide were generous gifts from Roquette Freres (Lestrem, France) and were used as received. Span 85 and oleoyl chloride were purchased from Sigma-Aldrich and other organic compounds were purchased from Acros and used without further purifications.

Differential Scanning Calorymetry (DSC) Measurements.

The thermograms of various complexes were recorded on a differential scanning calorimeter Perkin Elmer Pyris 1. About 15 mg of sample was placed in a aluminium pan and heated at a rate of 20°C per min in a range of -40 to 220°C under a stream of nitrogen.

Tensiometry.

The processor tensiometer Sigma 70 (KSV) and the Wilhelmy plate method for air–water interface have been used for the surface tension measurements at 298 K. A concentrated solution is installed in a syringe and the addition of small volumes to ultrapure water enhances the solution concentration. After each addition, the solution is gently stirred for 30 s. Equilibrium surface tension is measured for each concentration. All surface tension values were mean quantities of at least three measurements. The standard deviation of the mean never deviated ±1.5% of the mean. The precision of the force transducer of the surface tension apparatus was 0.1 mN/m and before each experiment, the platinum plate was cleaned in flame.

^{1}H NMR Analysis.

The ^{1}H spectra were recorded at 300.13 MHz on a Bruker Avance DRX300 spectrometer.^{1}H chemicals shifts are given in ppm.

Synthesis of isosorbide dioleate

1,4:3,6-dianhydro-D-glucitol (0.02 mol) and the oleoyl chloride (0.05 mol) were dissolved in pyridine (15mL) and DMF (15mL). The solution was heated for 6h at 50°C with stirring. Methanol (50mL) was added to the mixture to stop the reaction. Water was added to solubilize excess isosorbide and the oleic ester was extracted with diethyl ether. The organic phase was dried and subjected on a silica gel column. The purous isosorbide dioleate was obtained with diethyl ether / hexane (1:1) as eluant.

R_f=0.48 (hexane/diethyl ether 9:1); δ_H(300 MHz, DMSO-d_6, 25°C, TMS): 5.4 (4H, m, **H**C=C**H**), 5.1 (2H, m, C**H** isosorbide), 4.8 (1H, t, C**H** isosorbide), 4.5 (1H, d, C**H** isosorbide), 3.8-4.0 (4H, m, C**H$_2$** isosorbide), 2.2-2.4 (4H, m, -C**H$_2$**CO-), 2.0 (8H, t, - C**H$_2$**-HC=CH-), 1.6 (4H, q, -C**H$_2$**-CH_3), 1.3 (40H, s, 20 C**H$_2$**), 0.9 ppm (6H, t, C**H$_3$**); IR: ν_{max} / cm^{-1}=1740 (C=O).

Preparation of inclusion complexes (compound 1 and 2).

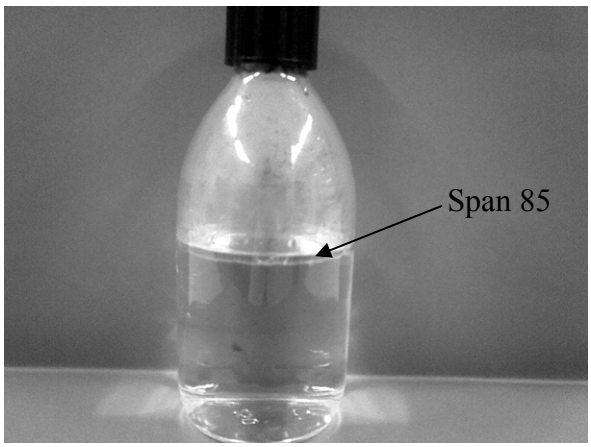
The inclusion complexes were prepared using the suspension method. An aqueous solution of β-CD (12 mmol/L) was prepared (Figure S1a) and polyol esters in equimolar proportion added. Before stirring, fatty esters float on the surface of the clear cyclodextrin solution (Figure S1b). The solution was then mechanical stirring for 24h. After a few minutes, the solution becomes trouble and a white solid rapidly appears even if the cyclodextrin was introduced below its limit of solubility (Figure S1c). The resulting suspension was filtered and the white powder obtained was washed with water then diethylether before drying at 40°C during 2 hours.

Elemental analysis (%) calcd for compound **1** ($C_{126}H_{335}O_{80}$; Dioleate isosorbide/2βCD/4H_2O): C 50.17; H 7.42. Found: C 50.14; H 8.01.

Elemental analysis (%) calcd for compound **2 (**$C_{186}H_{335}O_{121}$; Span85/3βCD/8H_2O): C 49.58; H 7.47. Found: C 49.39; H 7.46.

(a)

(b)



(c)

Figure S1: Preparation of compound **2** by suspension method. *a)* Initial aqueous solution of β-CD (12 mM), *b)* solution of Span 85 and β-CD before stirring, *c)* Suspension obtained after stirring of the Span 85/β-CD solution.

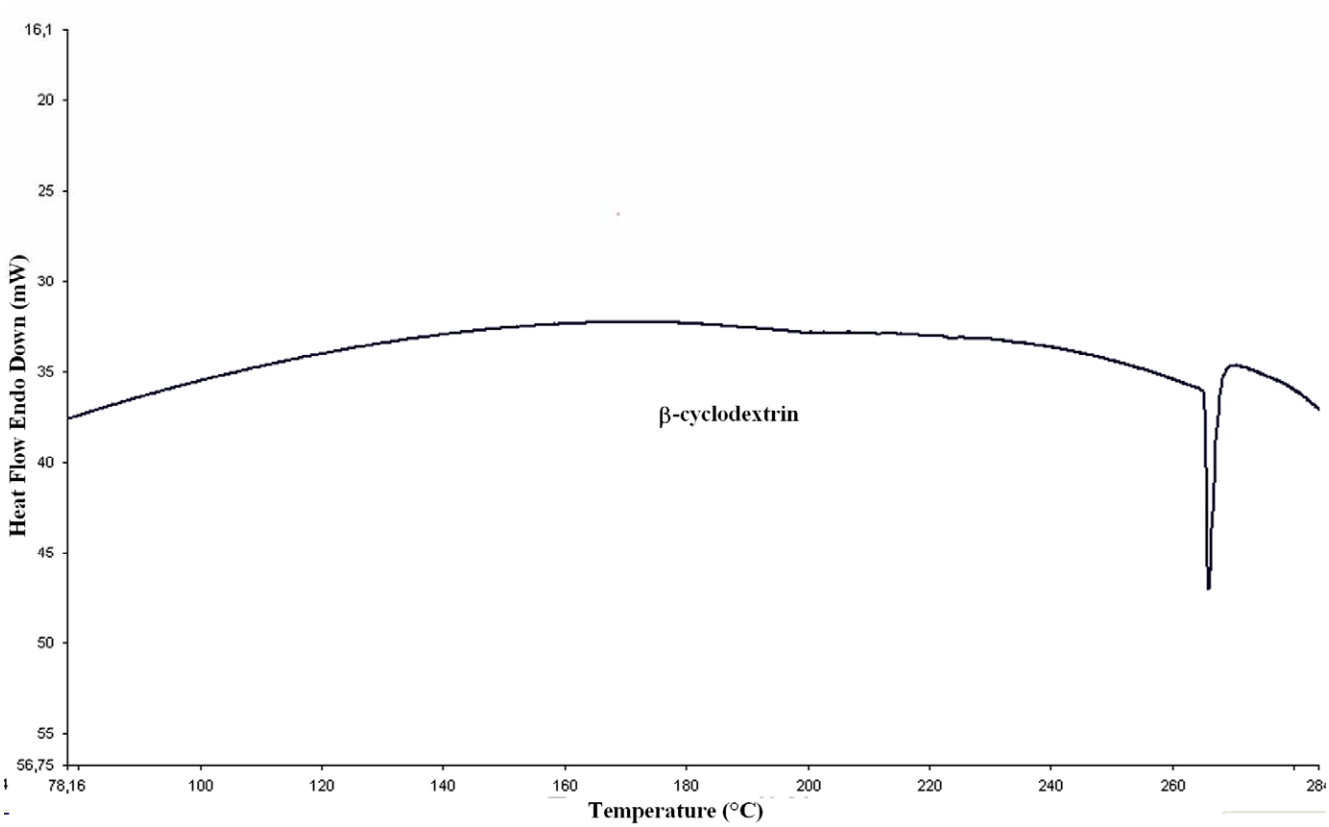


Figure S2: DSC curve of β-CD (second cycle of heating).

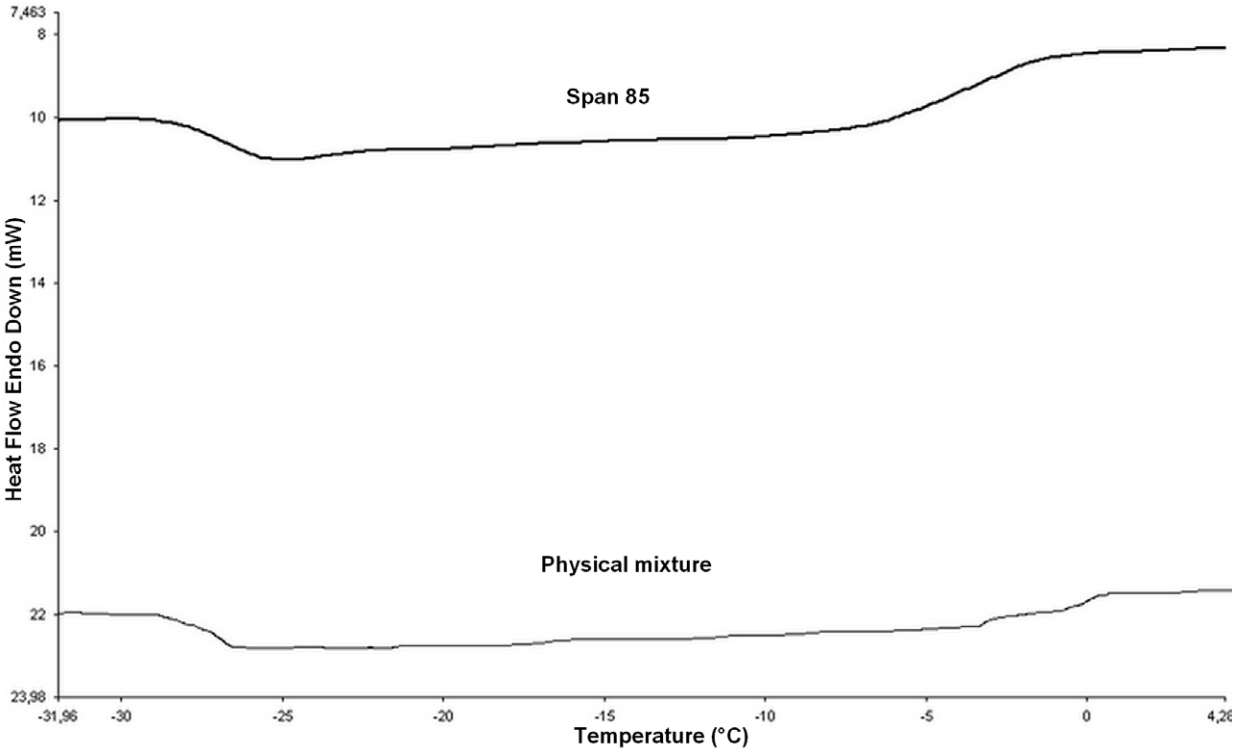


Figure S3: DSC curve of Span 85 and physical mixture of Span 85/β-CD (T: -32°C – 5°C), second cycle of heating.

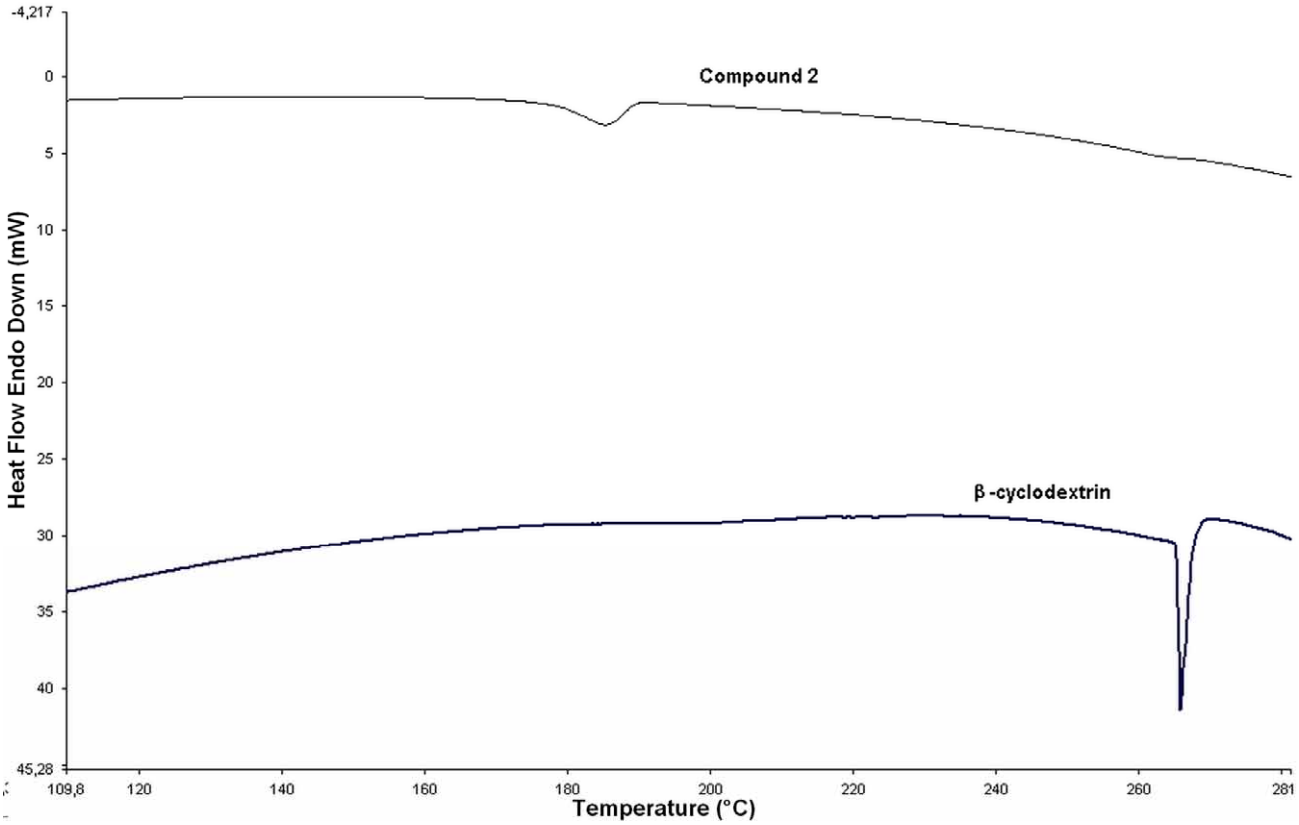


Figure S4: DSC curve of β-CD and compound **2** (second cycle of heating).

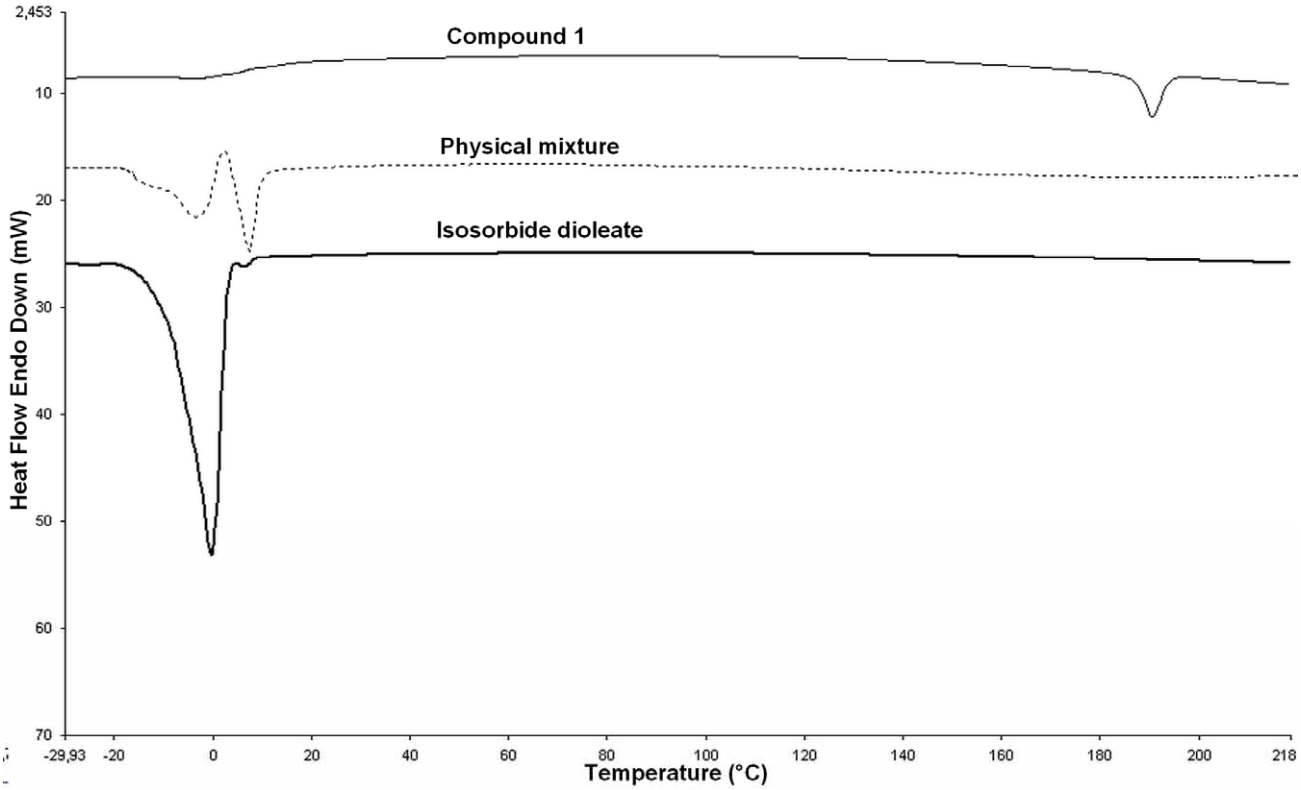


Figure S5: DSC curve of isosorbide dioleate, physical mixture of isosorbide dioleate/β-CD and compound **1** (second cycle of heating).

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