Electronic Supplementary Information

A self-emulsifying catalytic system for the aqueous biphasic hydroformylation of triglycerides

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Materials and methods

All chemicals were purchased from Acros, Strem or Aldrich Chemicals in their highest purity. Olive oil was purchased from Aldrich while Very High Oleic Sunflower Oil (VHOSO) was provided by Oleon. Roquette Frères (Lestrem, France) was gratefully acknowledged for generous gifts of β -CD and CRYSMEB (β -CD randomly substituted by methyl groups). RAME- β -CD was purchased from Wacker-Chemie GmbH (Germany). Deionized water was used in all experiments. NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300 MHz for ¹H nuclei and 75 MHz for ¹³C nuclei. CDCl₃ (99.50% isotopic purity), D₂O (99.50% isotopic purity) were purchased from Eurisotop.

Triolein (**T**) was used as model triglyceride. Compared to technical grade triglycerides, its purity and symmetrical structure derived from glycerol and oleic acid has the significant advantage of facilitating the analysis of the reaction products. The phase diagrams were elaborated by mixing a well-known quantity of CDs, **T** and water in a test tube. The solution was stirred at the appropriate temperature using an oil bath for 20 min at 1400 rpm. The stirring was then switched off and the system is allowed to stand for a given period at a given temperature. The phase diagrams of CD/**T**/water systems were obtained by visual and microscopic observations. The benchmark chromophore Red 1 has been used to help visualizing the multiphase systems and determining the type of emulsion.

Nephelometric measurements were realized using a Turbiscan MA 2000 in backscattering mode. The detector is placed at 135° from the 850 nm light source. All experiment were performed using a cylindrical 5mL glass vessel thermostated at 20°C.

GC-MS analysis were performed using a Shimadzu GC-17A gas chromatograph using a Varian capillary column (length 30 m, internal diameter 0.025 μ m) and a Shimadzu GCMS-QP500 mass spectrometer. The product were analyzed using a temperature gradient from 250 °C to 300 °C at 1.5 °C/min.

Tensiometric measurements were performed using the hanging drop technic (drop of the CD solution in air or in oil) with a Dataphysics OCA 15 instrument.

All the hydroformylation experiments were carried out in laboratory reactors from Parr Instrument Company (USA). To prevent oxidation of the catalyst precursors, the reaction mixture was transferred into the reactor using the standard Schlenk technique.



supramolecular amphiphile

Figure S1. Equilibriums existing between free CD and triolein (**T**) and their 1:1 and 2:1 CD/**T** supramolecular complexes.



Figure S2. Linearization of the Gibbs equation calculated from the variation of the interfacial tension at the triolein/water interface. Only data recorded at low CD concentrations were considered to ensure a monomolecular adsorption of the CDs at the T/water interface. RAME- β -CD (\diamond), HP- β -CD (\bigcirc) and CRYSMEB (\Box) at RT.



Figure S3. Surface tension variation at the air/water interface for RAME- β -CD (\blacklozenge), HP- β -CD (\bigcirc) and CRYSMEB (\Box) at RT. Only data recorded at low CD concentrations were considered to ensure a monomolecular adsorption of the CDs at the air/water interface.



Figure S4. Linearization of the Gibbs equation calculated from the variation of the surface tension at the air/water interface for RAME- β -CD (\diamond), HP- β -CD (\circ) and CRYSMEB (\Box) at RT. Only data recorded at low CD concentrations were considered to ensure a monomolecular adsorption of the CDs at the air/water interface.

The surface concentration of the modified CD/T complexes at the interface of a two-phase system could be expressed as:

$$\Gamma_{T \,\subset\, CD} = \frac{-1}{RT \,\partial ln C_{CD}} \,\,(1)$$

where $\Gamma_{T \subset CD}$ is defined as the interfacial excess of the CD (mol.cm⁻²) and γ the surface tension (mN.m⁻¹). From $\Gamma_{T \subset CD}$, the interfacial area (surface occupied by the modified CD or the supramolecular CD/triglyceride complex) could be expressed as:

$$A_{T \,\subset\, CD} = \frac{10^{16}}{\Gamma_{T \,\subset\, CD} N_A} \left(\,\text{\AA}^2 \right) \ (2)$$

where N_A is the Avogadro constant.

Both $\Gamma_{T \subset CD}$ and $A_{T \subset CD}$ were calculated from the above γ variations (Figure 3). Low concentrations of CDs were considered to ensure a monomolecular adsorption of the CDs at the interface, in line with the curve profiles depicted in Figure 3. Upon addition of **T** to the CD solutions, $\Gamma_{T \subset CD}$ were calculated to be 8.3 $\cdot 10^{-11}$, 5.9 $\cdot 10^{-11}$ and 5.4 $\cdot 10^{-11}$ mol.cm⁻² for RAME- β -CD, HP- β -CD and CRYSMEB, respectively. To the interfacial excesses corresponded interfacial areas of 199, 280 and 305 Å², respectively.

The CD/**T** stoichiometry was determined from the following equation (3):

$$N_T \subset CD = \frac{A_T \subset CD}{A_{CD,ref}}$$
(3)

Surfacic areas of CDs (in the absence of **T**) were determined using the same equations at the air/water interface in the presence of various CDs concentration. $A_{CD,ref}$ were 197 Å², 183 Å², 147 Å² for RAME- β -CD, HP- β -CD and CRYSMEB, respectively. These values are coherent with the surfacic area measured for the native β -CD (183 Å²). The $A_{T \subset CD}$ values were higher than the maximum surface occupied by the CD alone and corroborated the existence of **T** \subset CD supramolecular complexes at the aqueous/organic interface.

Conversely, the N_{TCCD} stoichiometry was 1, 1.5 and 2 for RAME- β -CD, HP- β -CD and CRYSMEB, respectively. A high CD/**T** molar ratio of 3 was found for native CDs, thus explaining the rapid precipitation of the native CD/**T** supramolecular complexes when the CD concentration raised.

In a typical experiment, $Rh(CO)_2(acac)$ (3.9 mg, 0.015 mmol, 1 eq) TPPTS (42 mg, 0.075 mmol, 5 eq) and CRYSMEB (2.3 g, 2 mmol) were degassed by vacuum-N₂ cycles three times and were dissolved in degassed deionized water (3.4 mL). The resting solution was stirred at room temperature until all the rhodium complex was dissolved (4 h). 1 mL of triolein (0.91 g, 1 mmol) was poured into the autoclave and N₂-purged. The catalytic solution was then cannulated under nitrogen into the autoclave. Once a temperature of 80 °C has been reached, the autoclave was pressurized under CO/H₂ pressure (80 bar) and the solution was vigorously stirred (2500 rpm). When the reaction was over, the apparatus was allowed to cool to room temperature and depressurized. The organic phase was extracted directly after opening the autoclave thank to products decantation. The products were analyzed by ¹H and ¹³C NMR experiments. All runs have been performed at least twice in order to ensure reproducibility. Additionally, no trace of TPPTS could be detected in the organic phase by ¹H and ³¹P NMR measurements.

Procedure for the synthesis of HRh(CO)TPPTS₃

In a Schlenk tube were dissolved 150 mg Rh(CO)₂acac and 1.2 g TPPTS in 3 mL degassed water. The mixture was stirred under H₂ pressure (1 bar) for 4 h. A green-yellow solution was obtained. 25 mL ethanol were then added and a yellow precipitate was obtained. The precipitate was filtrated under nitrogen atmosphere and rinsed three times with hot ethanol to eliminate unreacted products. The resulting HRh(CO)TPPTS₃ complex was dried under vacuum for 2 h. Yield: 73% (752 mg).



Figure S5. ¹H NMR spectrum of triolein (**T**) in CDCl₃ at 25 °C.



Figure S6. ¹H NMR spectrum of hydroformylated triolein (**T**) in CDCl₃ at 25 °C.

 $FN = \frac{B}{4}$. The B signal represents four protons The normalization integration factor is given by of the glycerol moiety of the triglyceride. They are not involved in the hydroformylation reaction and can be used as a reference signal. The number of initial C=C double bonds (DB_i) is calculated from the pure initial substrate:

$$DB_i = \frac{A - FN}{2}$$

with A the peak integration of oléfinic proton added to one of glycerol moiety.

For example, $DB_i = 3$ for triolein.

Once the reaction is complete, the conversion is given by:

$$Conv.(\%) = \frac{DB_i - DB_f}{DB_i} \times 100 = \frac{A_i - A_f}{A_i - FN} \times 100$$

where A_i and A_f represent the integration values of the A signal before and after reaction, respectively.

The aldehyde selectivity is given by:

$$HF \ selec.(\%) = \frac{H/_{NF}}{DB_i - DB_f} \times 100$$

where H is the integration value of the H signal attributed to the formyl proton.

The hydrogenation selectivity is determined from the hydroformylation selectivity by:

hydrogenation selec. (%) = 100 - selec.HF(%)

Table S1. Fatty acids distributions of the studied naturally occurring vegetable oils.

The distributions were determined after a 36 h transesterification in methanol using 1 mol% of MeONa as catalyst. The resulting mixtures consisting of fatty acids methyl esters were analyzed by GC and GC-MS.

Entry	Fatty acids (mol%)	Formula	Olive	VHOSO	Rapeseed	Sesame	Soybean
1	Palmitic	C _{16:0}	11	3.4	4.6	9.2	10
2	Palmitoleic	C _{16:1}	0.7	0.1	0.2	nd	nd
3	Stearic	C _{18:0}	4.2	3.2	1.5	5.5	4.3
4	Oleic	C _{18:1}	77	84	62	41	22
5	Linoleic	C _{18:2}	3.2	7.3	20	31	50
6	Linolenic	C _{18:3}	0.7	0.1	9.1	1.5	6.7
7	Arachidic	C _{20:0}	2.5	0.3	0.6	5.8	3.1
8	Eicosenoïc	C _{20:1}	nd	0.3	1.3	0.1	0.1
9	Behenic	C _{22:0}	0.6	1.1	0.3	nd	1.1
10	Erucic	C _{22:1}	nd	nd	0.7	nd	nd

Nephelometric measurements

Emulsions with different CDs were formulated as follows: 10 mL water, 2 mL **T** and 620 mg of CD (water/oil/CD in 80/15/5 wt%). The emulsions were vigorously shaken and put in the analysis device. Nephelometric measurements along the vessel and with time are depicted Figure S7.



Figure S7. Nephelometric measurements of different CD-based emulsions with time.

Decantation rates were determined by the variation of the height at 10% backscattering. The decantation rate of the different emulsions are given by the slope of the height variations (in mm.min⁻¹) described in Figure S8.



Figure S8. Decantation rate determination.

Stokes' equations

For a small spherical droplet moving in a viscous fluid, the force of viscosity applied on the sphere is given by:

 $F = 6\pi\mu Rv$

where μ is the dynamic viscosity of the continuous phase (10⁻³ Pa.s), *R* the radius of the droplet, *v* its velocity. Assuming a constant decantation rate (no acceleration), the forces applied on the droplet are its weight, the Archimede's force and frictional forces. Using the second mechanics principle:

$$0 = \rho_{H_20} V_{drop} g - \rho_{oil} V_{drop} g - 6\pi\mu R v$$

where ρ_{H2O} and ρ_{oil} are the densities of the aqueous and the oil phases, respectively, and V_{drop} is the volume of the droplet.

$$6\pi\mu Rv = \frac{4}{3}\pi R^3 g(\rho_{H_20} - \rho_{oil})$$

Reformulating the previous equation gives:

$$R = \sqrt{\frac{2g(\rho_{H_2O} - \rho_{oil})}{9\mu\nu}}$$