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Supporting Information

Low melting mixtures based on β-cyclodextrin derivatives and *N*,*N'*-dimethylurea as solvents for sustainable catalytic processes.

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1) Materials

All chemicals were purchased from Fisher Scientific and Aldrich Chemicals in their highest purity, excepted β-CD and CRYSME-β-CD provided by Roquette Frères and RAME-β-CD furnished by Wacker. HTMAP-β-CD was obtained by a chemical modification of β-CD described by Deratani et al. [1]. HP-β-CD was purchased from Aldrich Chemicals. All chemicals were used as supplied without further purification. Organic layers obtained after catalysis experiments were analyzed by ^{1}H-NMR on a Bruker DRX300 spectrometer (300 MHz for ^{1}H nuclei) and by gas chromatography on a Shimadzu GC-17A gas chromatograph equipped with a polydimethylsiloxane capillary column (30 m x 0.32 mm) and a flame ionization detector. Perkin–Elmer DSC Pyris 1 apparatus was used for differential scanning calorimetry analysis. A Brookfield Model LVDVII+Pro viscometer with the SC4-25 spindle at 200 rpm was used to determine the LMMs viscosities. An ATAGO AP-300 automatic polarimeter was used for polarimetric measurements on the mixtures “1-decene + aldehydes” obtained from hydroformylation experiments (no optical rotation were obtained indicating, that the branched aldehyde is racemic).

2) DSC measurements

Cyclodextrin and DMU were firstly finely grinded in a mortar. The mixture was then heated at 110°C until a clear solution was formed. A portion of each mixture (about 17mg) was transferred in a sealed aluminium pan which was directly introduced in the differential scanning calorimeter (Perkin–Elmer DSC Pyris 1). An empty pan of the same type was employed as a reference. All experiments were performed in the temperature range 65–105°C, at a heating/cooling rate of 5 $°C.min^{-1}$. Three successive cycles were done following the same program. Temperature and heat flow rates were calibrated with very pure indium standard, whose melting temperature and enthalpy are well known. Data acquisition (onsets of the (solid + liquid) equilibria temperatures) and processing were done with Perkin–Elmer’s Pyris TM software. The mass of the samples was determined with a precision ±0.0002 g using a Sartorius M2P balance.

3) Viscosity measurements

Viscosity was measured at 90°C into a SC4-13RPY sample chamber with embedded RTD temperature probe. The temperature was controlled with a TC502 circulating bath refrigerated using a programmable controller. The sample volume was slightly adapted to the volume of the sample chamber. The program parameters and results analysis were controlled with the Rheocalc@ PC Software.

4) Catalytic experiments

3.1) Hydroformylation experiments

In a typical hydroformylation experiment, $Rh(acac)(CO)_2$ (5.5 mg; 21 μmol; 1 eq.), TPPTS (60mg; 105 μmol; 5 eq.) and solvent constituents at solid state (4.2 g of *N*,*N*'-dimethylurea and 1.8 g of RAME-β-CD (w/w (%) = 70/30) for example) were charged into a 25 mL autoclave. Air was replaced by 20 bar of CO/H_2 (1/1) and after heating at 90°C, the mixture was stirred using a multipaddle unit (1500 rpm) for 1 hour for an incubation period. The stirring was then stopped and after cooling and depressurization, 1-decene (6g; 42 mmol; 2000 eq.) was introduced under nitrogen in the autoclave. The medium was heated at 90°C and then stirred (1500 rpm) for 1 hour at this temperature under 50 bar of CO/ H_2 (1/1).

3.2) Trost Tsuji experiments

For the Trost Tsuji experiment, $Pd(OAc)_2$ (1.75 mg; 8 μmol; 1 eq.), TPPTS (40 mg; 70 μmol; 9 eq.), *N*,*N*'-dimethylurea (0.98 g) and RAME-β-CD (0.42 g) (w/w (%) = 70/30) were introduced into a Schlenk tube. Then, the reaction mixture was stirred under nitrogen for 1 hour in an oil bath at 90°C and at 1200 rpm for an incubation period during which the medium became fluid and limpid. After cooling at room temperature, this catalytic layer became quickly solid and allyloctylcarbonate (0.167 g; 800 μmol; 100 eq.) and diethylamine (0.171 g, 2.4 mmol; 300 eq.) dissolved in heptane (1.4 g) were added on it. After immersion of the Schlenk tube in the oil bath at 90°C, the solid catalytic layer became quickly liquid again and the biphasic system was then stirred for 5 minutes at 90°C. After cooling, the organic layer was very easily recovered under air-atmosphere without special caution and the solid catalytic layer was then recycled after introduction under nitrogen of a new solution of allyloctylcarbonate and diethylamine in heptane.

Figure S1: DSC thermograms (exothermicity up/endothermicity down) for the determination of melting temperature of:

(a) Pure DMU
(b) DMU/β-CD (w/w(%): 70/30)
(c) DMU/CRYSME-β-CD (w/w(%): 70/30)
(d) DMU/RAME-β-CD (w/w(%): 70/30)
(e) DMU/HP-β-CD (w/w(%): 70/30)
(f) DMU/HTMAP-β-CD (w/w(%): 70/30).

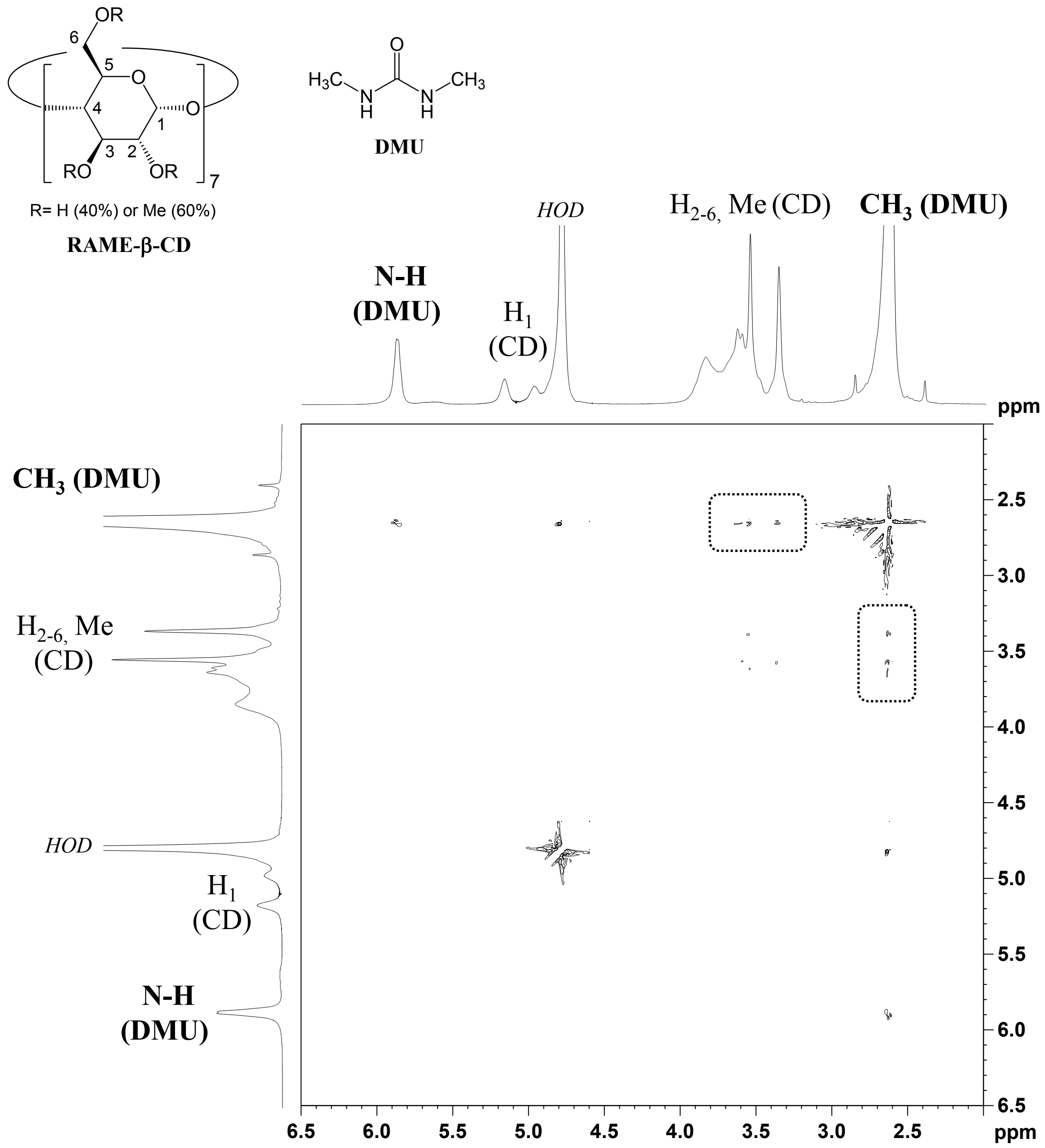

Figure S2: T-ROESY NMR spectrum of a mixture of DMU / RAME-β-CD / D_2O (weight ratios: 70/30/50) (300 MHz, 25°C).

In the presence of D_2O, this low melting mixtures tend to become a simple solution of DMU and RAME-β-CD upon dilution and so, the potential specific interactions offered by low melting mixtures in its pure state might be (at least partially) missed. In this context, this T-ROESY NMR experiment highlighted dipolar contacts between RAME-β-CD protons and methyl protons of DMU.

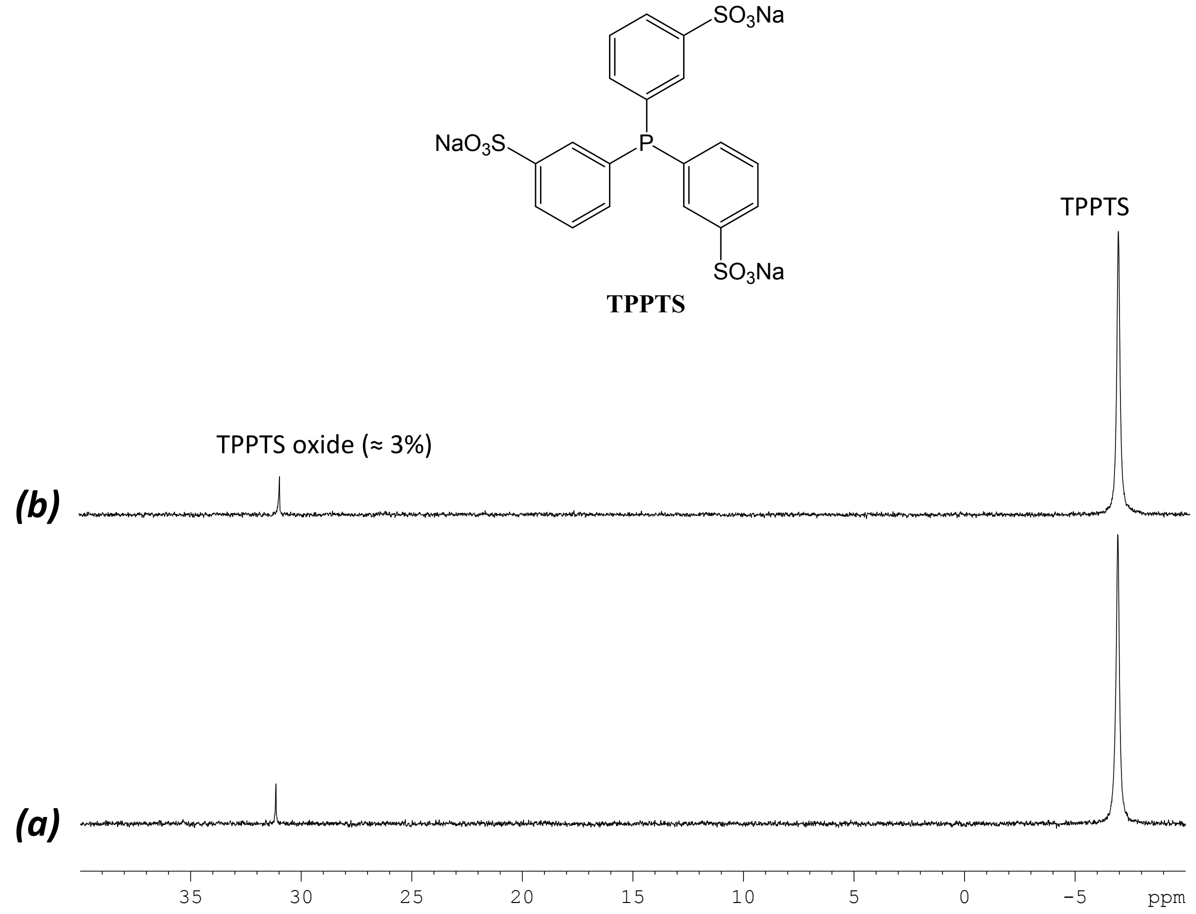

Figure S3: $^{31}P\{^{1}H\}$ NMR spectra of TPPTS in a DMU / RAME-β-CD mixture (weight ratios: 70/30; 20 mg of TPPTS /g of mixture; 25 °C, 121.5 MHz)

(a) after dissolution in D_2O (33% of D_2O)

(b) after 10 heating-cooling cycles under nitrogen (from room temperature to 90°C then room temperature) followed by a dissolution in D_2O (33% of D_2O).

[1] A. Deratani, G. Lelièvre, T. Maraldo and B. Sébille, *Carbohydr. Res.*, 1989, **192**, 215-222.