

Supporting Information for

Transfer Hydrogenation of Aldehydes on Amphiphilic Catalyst Assembled at the Interface of Emulsion Droplets

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Contents

General experimental details	S2-3
Results of recycling of PTsEN	S3
Photographs of catalyst Ir-PTsEN under reaction conditions	S4
Fluorescence Measurements	S4
¹ H NMR of ligand PTsEN	S5

General experimental details: ^1H NMR spectrum was recorded on a Bruker AV500 (500 MHz) instrument using D_2O as the solvent at $85\text{ }^\circ\text{C}$. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (H_2O , 4.18 ppm for ^1H NMR).¹ Fluorescence spectra were recorded at room temperature on an Edinburgh FLS920 fluorescence spectrometer. The emission spectra were recorded by excitation at 340 nm.

Monomer **2** (4-vinylbenyl)-trimethyl ammonium chloride and $[(\text{Cp}^*\text{IrCl}_2)_2]$ ($\text{Cp}^*=\text{C}_5\text{Me}_5$) was obtained from Aldrich Chemical Co. DMF was dried and distilled before use following standard procedures. Benzaldehyde and furfural were freshly distilled before use. All other reagents were used without purification as commercially available.

General procedure for the preparation of PTsEN

Monomer **1** (150 mg, 0.66 mmol) and monomer **2** (168 mg, 0.84 mmol) were added to a solution of anhydrous DMF (5 mL) with AIBN (10 mg, 0.06 mmol). The mixture was degassed for three times of freeze–thaw under liquid nitrogen. Polymerization was carried out at $60\text{ }^\circ\text{C}$ for 24 h under argon. After filtration, the residue was washed by DMF and CH_2Cl_2 in turn, and dried in vacuo to give **PTsEN** (299 mg, 94% yield).as white solid. δ_{H} (500 MHz, D_2O , $85\text{ }^\circ\text{C}$) 1.66 ppm (br, CH, CH_2 , the backbone of polymer), 2.88 (br, CH_2N), 3.11 (br, $\text{N}(\text{CH}_3)_3$), 4.46 (br, CH_2Ph), 6.49-7.10, 7.10-7.48, 7.50-7.91 (br, Ar – H). The molar ratio of the monomers was determined by ^1H NMR analysis (monomer **1** : monomer **2** = 0.43 : 0.57).

Typical procedure for transfer hydrogenation of aldehydes

The reduction of benzaldehyde at $\text{S}/\text{Ir} = 10000:1$ was carried out as following: **PTsEN** (9 mg, containing 0.018 mmol monomer **1**) and $[(\text{Cp}^*\text{IrCl}_2)_2]$ (1.6 mg, 0.002 mmol) were suspended in degassed

distilled water (15 mL) under argon. After stirred at 80 °C for 1 h, Benzaldehyde (4.2 g, 40 mmol) and HCOONa (5.4 g, 80 mmol) were quickly added to the resulting solution. The conversion was monitored by GC (equipped with HP 19091G-B213 column). The reaction mixture was cooled to room temperature after completion, and the product was extracted with ethyl ether (3×10 mL). The ethereal phase was removed with syringe. A new reaction could be conducted by adding benzaldehyde (40 mmol) and a equiv formic acid in turn.

Table S1 Catalytic activities of transfer hydrogenation of benzaldehyde using **Ir-PTsEN** in three consecutive cycles.^a

Cycles	Conv (%)
1	99
2	67
3	39

^a Product is extracted with diethyl ether. Reaction conditions: 80 °C, HCOONa (2.0 equiv), water (15 mL), S/Ir 1 × 10⁴:1, reaction time 6 min.

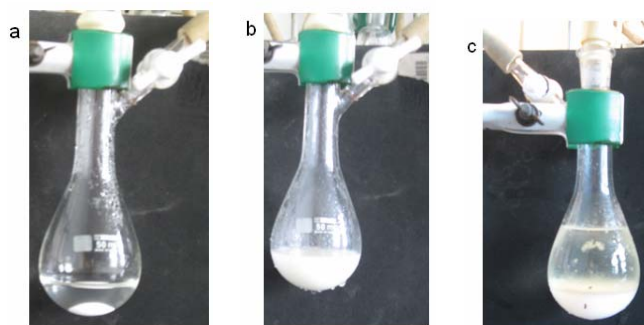


Fig. S1. Photographs of catalyst **Ir-PTsEN** under the reaction conditions. a) **Ir-PTsEN** in water (15 mL). b) **Ir-PTsEN** in the emulsion system consisting of benzaldehyde (40 mmol), water (15 mL) and HCOONa (2 equiv). c) After reaction completion, ethyl ether is added to the mixture of reaction.

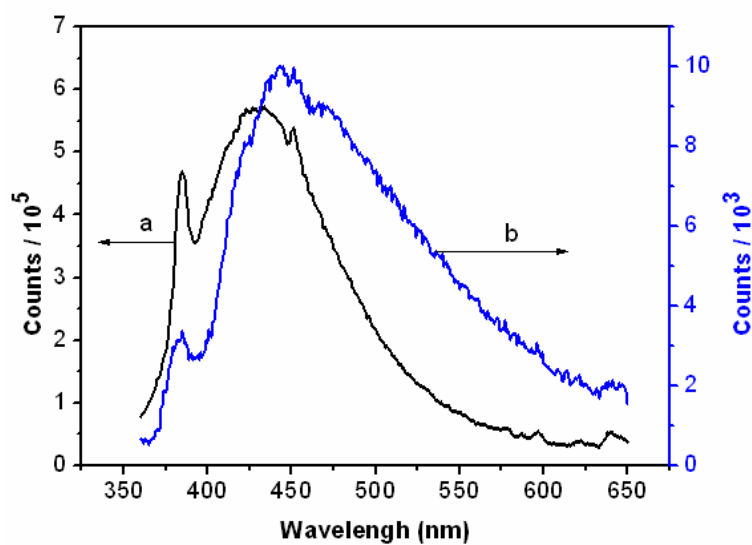
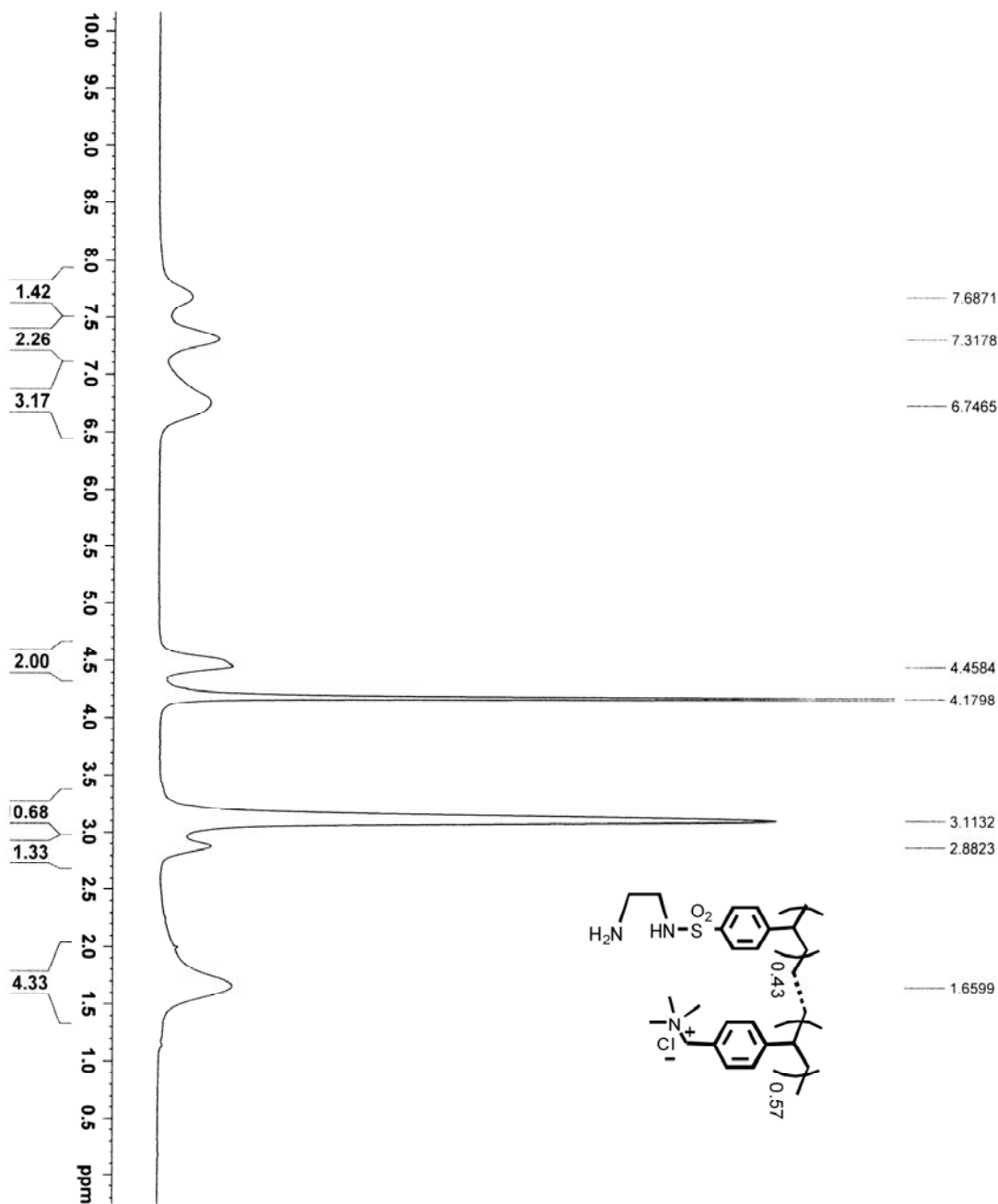


Fig. S2. Fluorescence spectra a) **Ir-PTsEN** in water (15 mL). b) **Ir-PTsEN** in the emulsion system consisting of benzaldehyde (40 mmol) and water (15 mL).

References:

- [1] H. E. Gottlieb, V. Kotlyar, and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515.

1H sample: 1ljun in D2O



Current Data Parameters
 NAME 1ljun
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070712
 Time 9.36
 INSTRUM AV500
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 32768
 SOLVENT D2O
 NS 64
 DS 2
 SWH 13020.833 Hz
 FIDRES 0.397364 Hz
 AQ 1.2583796 sec
 RG 181
 DK 38.400 usec
 DE 8.00 usec
 TR 358.2 K
 DI 2.00000000 sec
 T10 1

===== CHANNEL f1 =====
 NUCL1 1H
 P1 10.25 usec
 PL1 0.00 dB
 SFO1 500.1330008 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1302965 MHz
 WTM EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00