SUPPORTING INFORMATION

An Amphiphilic Ionic Liquid Stabilizing Palladium Nanoparticles for Highly Efficient Catalytic Hydrogenation

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1. Synthesis of ILs

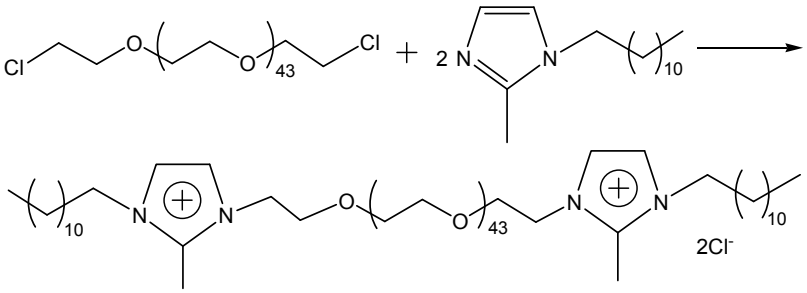
Preparation of 1-Dodecyl-2-Methylimidazole

A solution of 2-methylimidazole (1.314 g, 17 mmol) in 10 mL of anhydrous THF was added to a stirred suspension of NaH (0.504 g, 21 mmol) in 8 mL of THF at room temperature. The mixture was stirred for 1 h and then a mixed solution of 1-bromododecane (4.0 g, 16 mmol) and tetrabutylammonium bromide (0.258 g, 0.8 mmol) in 10 mL THF was added. After 6 h at 40 °C, the precipitate was filtered and washed with CH_2Cl_2 (2×15 mL), and then evaporating the solvent gave 1-dodecyl-2-methylimidazole (3.8 g, Yield: 95%). δ_H(500 MHz; $CDCl_3$; Me_4Si) 6.89 (1H, s, CH), 6.80 (1H, s, CH), 3.80 (2H, t, CH_2), 2.36 (3H, s, CH_3), 1.71 (2H, m, CH_2), 1.30-1.26 (18H, m, CH_2), 0.88 ppm (3H, t, CH_3).

Preparation of the Poly(ethylene glycol) Functionalized Dicationic Ionic Liquid (C_{12}Im-PEG IL)

The PEG-2000 chloride was synthesized according the our previously reported

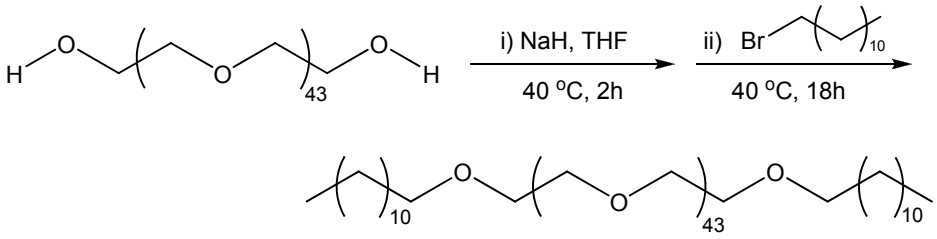
procedure.[1] A mixture of chlorinated PEG-2000 (3.5 g, 1.7 mmol) and 1-dodecyl-2-methylimidazole (0.88 g, 3.5 mmol) was stirred at 90 °C for 72 h under 1.0 MPa nitrogen at autoclave. After the quaterization reaction of 1-dodecyl -2-methylimidazole with chlorinated PEG, then the product was washed with diethyl ether (3×2 mL) and then the solvent was evaporated at 70 °C for 2 h under vacuum to afford slightly yellow and highly viscous liquid (Scheme 1S, Yield: 99%). δ_H(500 MHz, $CDCl_3$; Me_4Si) 8.05 (2H, s, CH), 7.37 (2H, s, CH), 4.62 (4H, t, CH_2), 4.15 (4H, t, CH_2), 3.92 (4H, t, CH_2), 3.46-3.81 (m, PEG), 1.78 (4H, m, CH_2), 1.33-1.25 (36H, m, CH_2), 0.88 ppm (6H, t, CH_3). Found: C, 56.16; H; 9.06, N; 1.87. Calc. for $C_{122}H_{240}O_{44}N_4Cl_2$: C, 57.75; H, 9.47; N, 2.21%.



Scheme 1S Synthesis of the poly(ethylene glycol) functionalized dicationic C_{12}Im-PEG IL.

2. Preparation of C_{12}-PEG-C_{12} Surfactants

A solution of PEG-2000 (3.4 g, 1.7 mmol) in 10 mL of anhydrous THF was added to a stirred suspension of NaH (0.096 g, 4.0 mmol) in 8 mL of THF at 40 °C. The mixture was stirred for 2 h and then a solution of 1-bromohexane (1.0 g, 4.0 mmol) in 10 mL THF was added. After 18 h at 40 °C, the precipitate was filtered and washed with CH_2Cl_2 (2×15 mL); and then evaporation of the solvent gave C_{12}-PEG-C_{12} surfactant (Scheme 2S, Yield: 83%). δ_H(500 MHz; $CDCl_3$; Me_4Si) 3.44-3.58 (m, PEG), 1.57 (4H, m, CH_2), 1.24-1.28 (36H, m, CH_2), 0.88 ppm (6H, t, CH_3). Found: C, 57.73; H, 9.84. Calc. for $C_{114}H_{230}O_{46}$: C, 58.61; H, 9.85%.



Scheme 2S Synthesis of C_{12}-PEG-C_{12} Gemini surfactants.

3. Conductivity Measurements of the Poly(ethylene glycol) Functionalized Dicationic Ionic Liquid (C_{12}Im-PEG IL)

Generally, the critical micelle concentration (CMC) of surfactants can also be measured by conductivity measurements.[2,3] In this paper, the conductivity of different solutions as a function of concentration was also measured using an electrical conductivity meter (DDS-307) at room temperature. As shown in Fig. 1S, the CMC of C_{12}Im-PEG IL (about 3.8×10^{-3} molL^{-1}) determined from conductivity measurements is close to the value from surface tension measurements (Fig. 5).

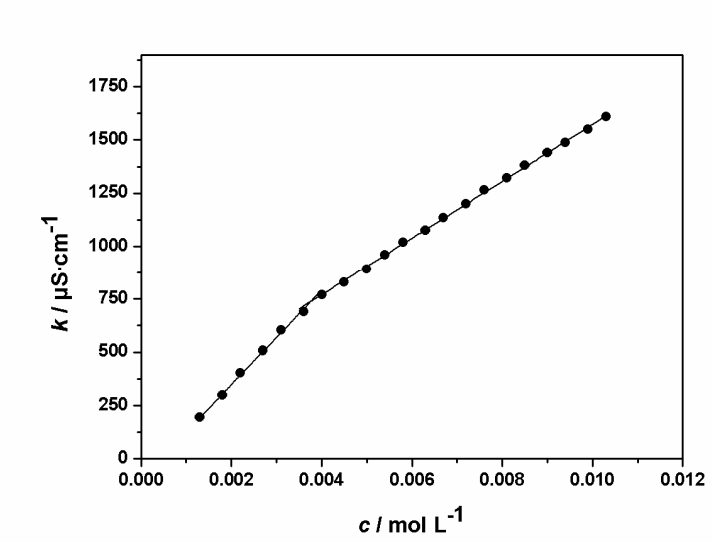


Fig. 1S The plots of specific conductivity *vs* the concentration of C_{12}Im-PEG IL at 25 °C.

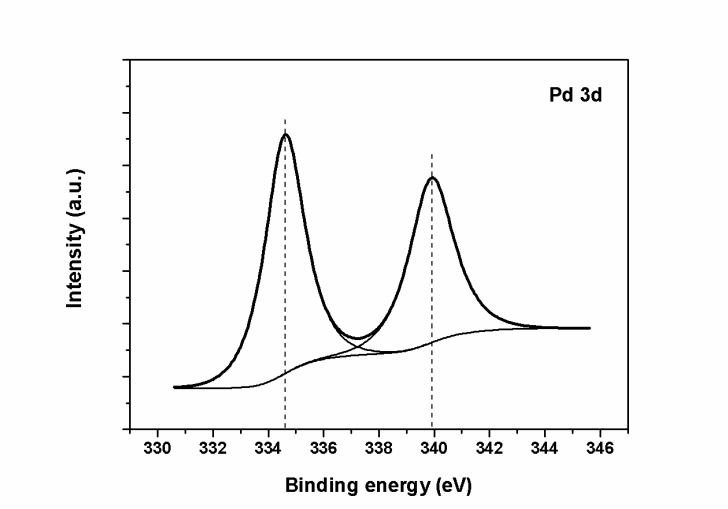


Fig. 2S X-ray photoelectron spectra of the isolated palladium NPs.

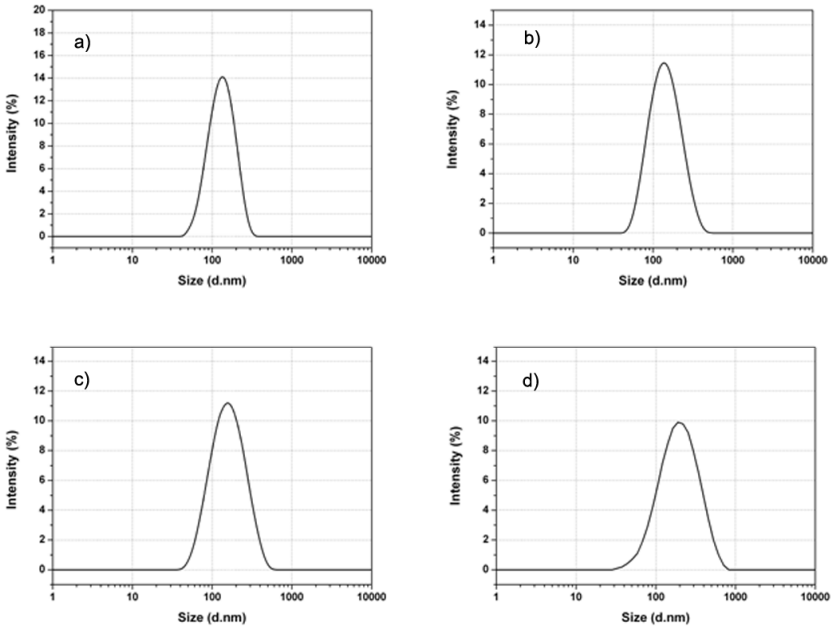
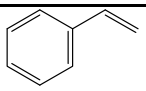
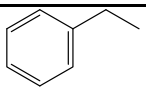
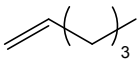
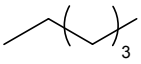
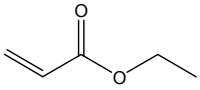
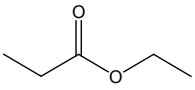
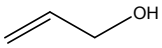
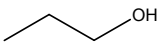
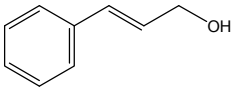
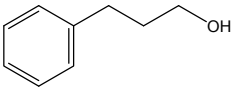
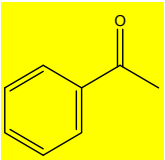
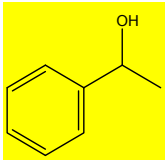
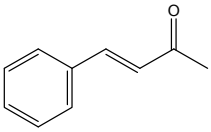
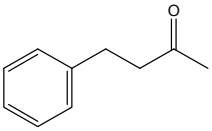
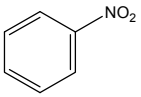
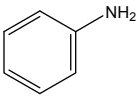
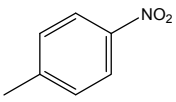
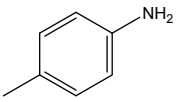
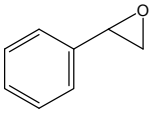
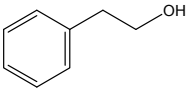


Fig. 3S Hydrodynamic diameter of C_{12}Im-PEG IL micelles formed in the aqueous solution at the concentration of a) 4.73×10^{-3} molL^{-1}; b) 7.0×10^{-3} molL^{-1}; c) 1.03×10^{-2} molL^{-1}; d) 1.31×10^{-2} molL^{-1}, respectively. The distribution of hydrodynamic diameter was calculated from the CONTIN algorithm.

Table 1S Hydrogenation of various substrates catalyzed by the aqueous colloidal suspension of palladium NPs[a]

Entries	Substrates	Sub/Pd	Products	*t* [h]	Yield [%]	TOF [h^{-1}]
1		10,000		1.5	100	12300
2		10,000		4	100	5200
3		10,000		3	100	6800
4		10,000		4	95	4750
5		10,000		1	100	17200
6		2,000		3	100	1430
7		5,000		4	100	2850
8		1,000		5	<1	nd[b]
9		5,000		10	93.3	1200
10		1,000		2	>99	1280
11		1,200		3	100	1050
12		1,000		3.5	90.6	640

[a]Reaction conditions: 1.5 mL of aqueous colloidal suspension containing 2.25×10^{-6} mol Pd catalyst; room temperature (25 °C); hydrogen pressure (1.0 MPa); [b]Not determined.

Reference

1 H. Li, Y. Qiao, L. Hua and Z. Hou, *ChemCatChem*, 2010, **2**, 1165–1170.

2 K. Din, M. S. Sheikh and A. A. Dar, *J. Phys. Chem. B*, 2010, **114**, 6023–6032.

3 P. Carpena, J. Aguiar, P. Bernaola-Galván and C. C. Ruiz, *Langmuir*, 2002, **18**, 6054–6058.