Supporting information

Dye-Sensitized Solar Cells with Solvent-Free Ionic Liquid Electrolytes

Yiming Cao, † Jing Zhang, † Yu Bai, † Renzhi Li, † Shaik M. Zakeeruddin, ‡

Michael Grätzel, ‡ and Peng Wang †,*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (CAS), Changchun 130022, China and Laboratory for Photonics and Interfaces, Swiss Federal Institute of Technology, CH 1015, Lausanne, Switzerland

*Corresponding author. E-mail: peng.wang@ciac.jl.cn.

†Changchun Institute of Applied Chemistry, CAS.

‡Swiss Federal Institute of Technology.
**Synthesis of 1,3-dimethylimidazolium iodide.** A 100-mL flask equipped with a dropping funnel, thermometer, water-cooled condenser, and magnetic stirrer was charged with 20.53 g (0.25 mol) of freshly distilled N-methylimidazole. The solution was cooled and maintained at 5 °C while 42.58 g (0.3 mol) of iodomethane was added dropwise under Ar to avoid the oxidation of iodide. After that, the mixture was refluxed for 2 h under Ar. The crude compound was dissolved in 200 ml water and extracted with CH$_2$Cl$_2$ at least three times to remove unreacted iodomethane. After the removal of water on a rotary evaporator, the resulting solid was dried in vacuo at 100 °C for 6 h. Yield: 95%. $^1$H NMR (400 MHz, $d_6$-DMSO, δ$_H$): 9.02 (s, 1H), 7.67 (d, 2H), 3.84 (s, 6H).

**Synthesis of 1-ethyl-3-methylimidazolium iodide.** The same procedure was used except that the mixture was refluxed for 5 h. Yield: 96%. $^1$H NMR (400 MHz, $d_6$-DMSO, δ$_H$): 9.10 (s, 1H), 7.78 (t, 1H), 7.69 (t, 1H), 4.18 (q, 2H), 3.84 (s, 3H), 1.41 (t, 3H).

**Synthesis of 1-propyl-3-methylimidazolium iodide.** The same procedure was used except that the mixture was refluxed for 8 h. Yield: 97%. $^1$H NMR (400 MHz, $d_6$-DMSO, δ$_H$): 9.12 (s, 1H), 7.77 (t, 1H), 7.71 (t, 1H), 4.13 (t, 2H), 3.85 (s, 3H), 1.82-1.75 (m, 2H), 0.85 (t, 3H).

**Synthesis of 1-butyl-3-methylimidazolium iodide.** The same procedure was used except that the mixture was refluxed overnight. Yield: 96%. $^1$H NMR (400 MHz, $d_6$-DMSO, δ$_H$): 9.11 (s, 1H), 7.77 (t, 1H), 7.69 (t, 1H), 4.16 (t, 2H), 3.85 (s, 3H), 1.81-1.71 (m, 2H), 1.32-1.20 (m, 2H), 0.90 (t, 3H).

**Synthesis of 1-hexyl-3-methylimidazolium iodide.** The same procedure was used except that the mixture was refluxed for 16 h. Yield: 96%. $^1$H NMR (400 MHz, $d_6$-DMSO, δ$_H$): 9.11 (s, 1H), 7.77 (t, 1H), 7.70 (t, 1H), 4.15 (t, 2H), 3.85 (s, 3H), 1.82-1.72 (m,2H), 1.27 (m, 6H), 1.86 (t, 3H).

**Synthesis of 1-allyl-3-methylimidazolium iodide.** The same procedure was used except that the reaction was performed for 30 min at room temperature Yield: 95%. $^1$H NMR (400 MHz, $d_6$-DMSO, δ$_H$): 9.10 (s, 1H), 7.71 (dd, 2H), 6.09-6.00 (m, 1H), 5.38-5.27 (m, 2H), 4.85 (d, 2H), 3.86 (s, 3H).
The general synthesis of 1,3-dialkylimidazolium thiocyanates. Silver thiocyanate was precipitated by mixing aqueous solutions of silver nitrate and potassium thiocyanate (1/1, molar ratio), washed well with water to remove any unreacted reagents, and used immediately. An aqueous solution of the iodide was added to an aqueous slurry of the excess silver thiocyanate and the solution heated gently with stirring for 1 h. Silver iodide was removed by filtration and the water removed from the filtrate under vacuum. To ensure complete removal of silver salts from the product, dichloromethane or water was added and the solution was cooled in a refrigerator or freezer for a day, before filtration and removal of the solvent to give the clean product. The Ag⁺ and I⁻ contents were confirmed with ICP-MS, being below 0.5% w/w.

1,3-Dimethylimidazolium thiocyanate. Yield: 79%. ¹H NMR (400 MHz, d₆-DMSO, δH): 9.02 (s, 1H), 7.67 (d, 2H), 3.85 (s, 6H).

1-Ethyl-3-methylimidazolium thiocyanate. Yield: 81%. ¹H NMR (400 MHz, d₆-DMSO, δH): 9.10 (s, 1H), 7.78 (t, 1H), 7.96 (t, 1H), 4.22-4.16 (q, 2H), 3.84 (s, 3H), 1.41 (t, 3H).

1- Allyl-3-methylimidazolium thiocyanate. Yield: 80%. ¹H NMR (400 MHz, d₆-DMSO, δH): 9.10 (s, 1H), 7.72 (m, 2H), 6.09-6.00 (m, 1H), 5.39-5.26 (m, 2H), 4.84 (d, 2H), 3.87 (s, 3H).

1-Propyl-3-methylimidazolium thiocyanate. Yield: 83%. ¹H NMR (400 MHz, d₆-DMSO, δH): 9.10 (s, 1H), 7.77 (t, 1H), 7.71 (t, 1H), 4.13 (t, 2H), 3.85 (s, 3H), 1.84-1.76 (m, 2H), 0.86 (t, 3H).
Figure S1. Plots of density of 1,3-alkylimidazolium thiocyanate versus temperature.
**Figure S2.** Plots of specific conductivity of 1,3-alkylimidazolium thiocyanate versus temperature in the Arrhenius coordinate.
Figure S3. Plots of fluidity of 1,3-alkylimidazolium thioyanate versus temperature in the Arrhenius coordinate.
Figure S4. Plots of density versus temperature. a–d, melts I–IV.
Figure S5. Plots of specific conductivity versus temperature in the Arrhenius coordinate. a–d, melts I–IV.
Figure S6. Plots of fluidity versus temperature in the Arrhenius coordinate. a–d, melts I–IV.
Figure S7. Plots of diffusion coefficient of triiodide versus temperature in the Arrhenius coordinate. a–d, melts I–IV.