



Bis-imidazolium iodide organic ionic plastic crystals and their applications to solid state dye-sensitized solar cells



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ARTICLE INFO

Article history:

Received 1 March 2017

Received in revised form

3 May 2017

Accepted 2 June 2017

Available online 3 June 2017

Keywords:

Organic ionic plastic crystals

OIPCs

Solid state electrolyte

DSSCs

ABSTRACT

Novel dicationic bis-imidazolium iodide salts have been discovered as new organic ionic plastic crystalline materials. Most of them show multiple solid-solid phase transitions below their melting temperatures. Their phase transition temperatures are dependent on the imidazolium cation structure. According to Timmermans' definition of plastic crystals, bis-imidazolium iodide salts with either *n*-heptyl or *n*-octyl side arms can be classified as "true plastic crystals" because of their low ΔS_f values ($< 20 \text{ J mol}^{-1} \text{ K}^{-1}$). The bis-imidazolium iodide salts are stable up to 260 °C under thermal gravimetric analysis. The ionic conductivities, investigated using dielectric relaxation spectroscopy, follow the Arrhenius temperature dependence with discontinuities and changes in slopes at the observed solid–solid phase transition temperature. Dye-sensitized solar cells (DSSCs) fabricated by a whole solid-state electrolyte consisting of *n*-hexyl side-armed bis-imidazolium iodide (**BIH-6**) show a 4.93% power conversion efficiency (η): a remarkable result for the solid-state electrolyte system compared to that obtained using an liquid electrolyte with 1-butyl-3-methylimidazolium iodide ($\eta = 8.00\%$) as a reference composition.

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1. Introduction

Organic ionic plastic crystals (OIPCs) have been attractive to materials chemists because of their unique physical, chemical, and electrical properties, including multiple crystalline phases, high ionic conductivity, and large electrochemical windows [1–3]. Therefore, their potential applications as highly conductive solid-state electrolytes in fuel cells, batteries, and solar cells have been widely studied [1–3]. Typically, these classical "plastic crystals" were defined by Timmermans as having a low entropy of fusion (ΔS_f) $< 20 \text{ J K}^{-1} \text{ mol}^{-1}$ [4]. Usually plastic crystal materials with lower ΔS_f values exhibit larger heat absorptions during one or multiple solid–solid phase transitions below melting temperature. OIPCs usually show long-range order but short-range disorder, typically arising from rotational motions of the molecules [5,6]. A highly conductive plastic crystal, tetraethylammonium dicyanamide ([Et₄N][DCA]), has a ΔS_f of $4 \pm 0.5 \text{ J K}^{-1} \text{ mol}^{-1}$, which is one of the lowest known ΔS_f values in OIPCs [7]. Pyrrolidinium salts with

different alkyl substituents and a wide range of anions display plastic crystalline behaviors [8–13]. High ionic conductivities were also observed in ammonium [14] and phosphonium OIPCs [15]. The mechanism of the ion conduction of OIPCs is still not completely understood; however, it may be directly related to the disorder that originates from rotational and transition motions of the molecules in the partially crystalline matrix [16]. For OIPCs based on imidazolium, Lee *et al.* found that the bis-imidazolium salts of Br[−] or PF₆[−] with alkyl side arms show multiple solid–solid phase transitions and some compounds have a small ΔS_f ($\leq 12 \text{ J K}^{-1} \text{ mol}^{-1}$), which fulfills Timmermans' definition [17]. Also, NMR observations of PF₆[−] anions at various temperatures showed that the bis-imidazolium PF₆[−] salt with *n*-hexyl side chains can align in an external magnetic field during cooling from its melting phase [18].

In previous studies, some OIPCs with iodide anions were applied to dye-sensitized solar cells (DSSCs). Grätzel and his coworkers suggested all solid-phase electrolyte system composed of *N*-methyl-*N*-butylpyrrolidinium iodide (P_{1,4}I) iodine (I₂) and succinonitrile (non-ionic plastic crystal material) [19]. A mixture of *N*-methyl-*N*-propylpyrrolidinium iodide (P_{1,3}I) and imidazolium iodide ionic liquids was also used as an electrolyte for DSSCs [20].

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Both electrolyte compositions show relatively low melting temperatures (<80 °C). For other types of iodide salts, choline iodide ($T_m = 160$ °C) was reported as a DSSC electrolyte [21]. Most recent reported new ionic plastic crystal for DSSCs is *N,N*-dimethyl-2-(methylsilyloxy)ethaniminium iodide [22]. However, still few ionic plastic crystalline materials have been reported for solar cell applications. In this work, we found that bis-imidazolium iodide (**BII**) salts exhibit plastic crystal properties and can also be applied to the solid electrolyte of DSSCs. The structure–property relationship is also studied for these new plastic crystal materials.

2. Experimental

2.1. Materials

Acetonitrile (MeCN) was dried with anhydrous K_2CO_3 and then distilled. Tetrahydrofuran (THF) was distilled with benzoinquinone and sodium. All other chemicals and solvents were used as received.

2.2. Instruments

1H and ^{13}C NMR spectra were obtained on Varian VNMRS 500 MHz spectrometer. DSC results were obtained on a TA Instrument Q200 differential scanning calorimeter with a scan rate of 10 K/min under N_2 . TGA results were obtained on a TA Instrument SDT Q600 Simultaneous TGA/DSC with a heating rate of 10 K/min under N_2 . Melting points were observed on Electrothermal 9300 melting point apparatus with a 1 K/min heating rate. Ionic conductivity was measured on a Novocontrol GmbH Concept 40 broad band dielectric spectrometer. Samples for dielectric relaxation spectroscopic measurements were placed on a 30 mm diameter polished brass electrode and dried in vacuo at 100 °C for 24 h, after which a second polished brass electrode with a 15 mm diameter was placed on top of the sample. 50 μm silica-rod spacers were used to control the sample thickness. Data were collected in isothermal frequency sweeps every 5 K from 220 to 0 °C under a dry N_2 flow. Frequency sweeps were performed isothermally from 10 MHz to 0.01 Hz for every measurement.

2.3. DSSC device fabrication

FTO glass substrates were cleaned with acetone and ethanol (v/v, 50:50) using an ultra-sonicator. FTO glass substrates were immersed in 40 mM titanium tetrachloride ($TiCl_4$, Aldrich) solution with 70 °C for 30 min for preparing TiO_2 blocking layer on the cleaned FTO glass substrate. Nanocrystalline transparent TiO_2 electrodes (Dyesol, 18NR-T) were doctor bladed on the previously prepared FTO glass substrates and sintered at 500 °C for 30 min in air. The resulting TiO_2 electrodes were immediately immersed in 0.3 mM solution of N719 dye in ethanol for 18 h. Dye-absorbed nanocrystalline TiO_2 electrodes were rinsed with ethanol, then dried by nitrogen gas blow. Pt CE was prepared simultaneously by spin-coating the Pt precursor solution (10 mM H_2PtCl_6 in isopropanol) on FTO glass substrate and subsequently sintered at 450 °C for 20 min. The as prepared TiO_2 electrodes and CE were sandwiched by using 60 μm thick surllyn spacer (surllyn-1702, Dupont). The formulation electrolyte solution was filled into the sandwiched cell through the hole drilled in the CE and then dried at 70 °C for 2 h in vacuum. The formulation was prepared by dissolving 0.600 M **BII-6** (or **BII-8**), 0.0300 M I_2 , 0.100 M guanidinium thiocyanate, and 0.500 M 4-*tert*-butylpyridine in MeCN. As a reference experiment, a liquid electrolyte was filled into the sandwiched cell and the hole was sealed by surllyn spacer and cover glass; the liquid electrolyte composed of 0.600 M 1-butyl-3-

methylimidazolium (BMI) iodide ionic liquid, 0.0300 M I_2 , 0.100 M guanidinium thiocyanate, and 0.500 M 4-*tert*-butylpyridine in mixture of MeCN.

2.4. Synthetic procedures for **BII** salts

1,2-Bis[*N*-(*N'*-methylimidazolium)]ethane diiodide (**BII-1**)

A solution of 1-methylimidazole (2.46 g, 30 mmol) and 1,2-diiodoethane (4.23 g, 15 mmol) in THF (20 mL) was stirred for 2 weeks at room temperature. The precipitate was filtered and washed with tetrahydrofuran (THF) three times. Drying in a vacuum oven gave a colorless crystalline iodide salt **BII-1** (0.870 g, 13%). MP 236–237 °C. 1H NMR (500 MHz, $DMSO-d_6$, 23 °C): δ 3.84 (s, 6H), 4.68 (s, 4H), 7.59 (t, $J = 1.5$, 2H), 7.72 (t, $J = 1.5$, 2H), 8.99 (s, 2H). ^{13}C NMR (125 MHz, $DMSO-d_6$, 23 °C): δ 36, 48, 122, 124, 137.

1,2-Bis[*N*-(*N'*-ethylimidazolium)]ethane diiodide (**BII-2**)

A solution of 1-ethylimidazole (2.88 g, 30 mmol) and 1,2-diiodoethane (4.23 g, 15 mmol) in THF (20 mL) was stirred for 2 weeks at room temperature. The precipitate was filtered and washed with tetrahydrofuran (THF) three times. Drying in a vacuum oven gave a colorless crystalline iodide salt **BII-2** (1.21 g, 17%). MP 213–214 °C. 1H NMR (500 MHz, $DMSO-d_6$, 23 °C): δ 1.40 (t, $J = 8$, 6H), 4.20 (m, $J = 8$, 4H), 4.67 (s, 4H), 7.61 (t, $J = 1.5$, 2H), 7.83 (t, $J = 1.5$, 2H), 9.09 (s, 2H). ^{13}C NMR (125 MHz, $DMSO-d_6$, 23 °C): δ 15, 39, 49, 122, 123, 136.

1,2-Bis[*N*-(*N'*-butylimidazolium)]ethane diiodide (**BII-4**)

A solution of 1-butylimidazole (2.73 g, 22 mmol) and 1,2-dibromoethane (2.07 g, 11 mmol) in MeCN (20 mL) was refluxed for 3 days. After cooling to room temperature, the precipitate was filtered and washed with THF three times. Drying in a vacuum oven gave colorless crystalline bromide salt (0.478 g, 12%). A solution of the bromide salt (0.478 g, 1.3 mmol) and NaI (4 equiv.) in deionized water (5 mL) was stirred for 24 h at ambient temperature. The precipitate was filtered and drying in a vacuum oven gave a colorless crystalline solid **BII-4** (0.411 g, 60% from the bromide salt). MP 134–139 °C. 1H NMR (500 MHz, $DMSO-d_6$, 23 °C): δ 0.89 (t, $J = 8$, 6H), 1.22 (m, $J = 8$, 4H), 1.73 (m, 4H), 4.15 (t, $J = 8$, 4H), 4.69 (s, 4H), 7.66 (t, $J = 1.5$, 2H), 7.83 (t, $J = 1.5$, 2H), 9.10 (s, 2H). ^{13}C NMR (125 MHz, $DMSO-d_6$, 23 °C): δ 13, 19, 31, 48, 49, 122, 123, 136.

1,2-Bis[*N*-(*N'*-hexylimidazolium)]ethane diiodide (**BII-6**)

A solution of 1-hexylimidazole (3.35 g, 22 mmol) and 1,2-dibromoethane (2.07 g, 11 mmol) in MeCN (20 mL) was refluxed for 3 days. After cooling to room temperature, the precipitate was filtered and washed with THF three times. Drying in a vacuum oven gave colorless crystalline bromide salt (3.51 g, 65%). A solution of the bromide salt and NaI (4 equiv.) in deionized water was stirred for 24 h at ambient temperature. The precipitate was filtered and drying in a vacuum oven gave a colorless crystalline solid **BII-6** (3.92 g, 93% from the bromide salt). MP 208–209 °C. 1H NMR (500 MHz, $CDCl_3$, 23 °C): δ 0.89 (t, $J = 8$, 6H), 1.34 (m, 12H), 1.96 (m, 4H), 4.26 (t, $J = 8$, 4H), 5.29 (s, 4H), 7.47 (t, $J = 1.5$, 2H), 8.51 (t, $J = 1.5$, 2H), 10.1 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C): δ 14, 22, 26, 30, 31, 48, 51, 122, 124, 136.

1,2-Bis[*N*-(*N'*-heptylimidazolium)]ethane diiodide (**BII-7**)

A solution of 1-heptylimidazole (3.66 g, 22 mmol) and 1,2-dibromoethane (2.07 g, 11 mmol) in MeCN (20 mL) was refluxed for 3 days. After cooling to room temperature, the precipitate was filtered and washed with THF three times. Drying in a vacuum oven gave colorless crystalline bromide salt (3.88 g, 68%). A solution of the bromide salt and NaI (4 equiv.) in deionized water was stirred for 24 h at ambient temperature. The precipitate was filtered and

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