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Photoelectrochemical Solar Cells based on Polyterthiophenes Containing Porphyrins using Ionic Liquid Electrolyte

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A copolymer of 5,15-bis([2′2″:5″,2‴-terthiophen]-3″-yl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin with 2,2′:5′2″-terthiophene was successfully electrosynthesized by cyclic voltammetry, galvanostatic, and potentiostaic methods. This conducting copolymer was then incorporated into photovoltaic devices using liquid electrolyte and tested for photovoltaic responses. An ionic liquid, ethyl-methylimidazolium dicyanamide, containing iodine (I_2, 60 mM) and tetrapropylammonium iodide (TPAI, 500 mM) has been employed as liquid electrolyte in photoelectrochemical solar cells based on polyterthiophenes containing porphyrins with an overall conversion efficiency of 0.14% at a solar simulated light intensity of 500 W m^{-2}.
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It is widely felt that the commercial viability of inorganic solar cells based on crystalline silicon is limited by the high cost of fabrication leading to long payback times. Owing to their attractive conductivity and stable chemical and physical properties, inherently conducting polymers have become leading contenders for the development of organic-based photovoltaic devices.[1-5] They provide the possibility of creating extremely lightweight, easily prepared, low-cost, and flexible photoelectrochemical solar cells. One of the limitations on the performance of photoelectrochemical cells is the mediocre stability of the liquid electrolyte in the cell. A possible answer to this problem is the use of ionic liquids.

Since the discovery of the first ambient temperature ionic liquid (a *N*-ethylpyridinuim bromide-aluminium chloride melt) in 1951,[6] many classes of molten salts have been investigated. Ionic liquids are attractive due to their chemical and thermal stability, nonflammability, high ionic conductivity, and a wide electrochemical window. In recent years, room-temperature ionic liquids have also been investigated as potential candidate electrolytes for use in batteries, photoelectrochemical cells, electroplating, and capacitors.[7-10] The presence of normal organic liquid electrolytes in photoelectrochemical solar cells can result in some practical limitations with sealing, long-term operation, and thermal stability. Hence, ionic liquid electrolytes have been employed as iodine and iodide-based liquid electrolytes to replace organic solvent-based liquid electrolytes in photoelectrochemical solar cells in this study. Thus, ionic liquid-based electrolyte was prepared by dissolving iodine (60 mM) and tetrapropylammonium iodide (TPAI, 500 mM) in ethyl-methylimidazolium dicyanamide (EMI^+dca^-, shown in Fig. 1a). In addition, a traditional organic liquid electrolyte was prepared by dissolving iodine (60 mM) and tetrapropylammonium iodide (TPAI, 500 mM) in ethylene carbonate/propylene carbonate (1:1 by weight).

In our previous studies, porphyrin containing light harvesting conducting polymers showed better photovoltaic performance than those without porphyrin moieties.[11,12]

Here we also present work done in developing photoelectrochemical solar cells based on a range of novel porphyrin functionalised terthiophene building blocks (Fig. 1b), such as 5,15-bis([2′2″:5″,2‴-terthiophen]-3″-yl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (BisTTh-Por), and BisTTh-copper coordinated porphyrin (BisTTh-Cu-Por).

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Experimental

5,15-Bis([2′2″:5″,2‴-terthiophen]-3″-yl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (BisTTh-Por), and BisTTh-copper coordinated porphyrin (BisTTh-Cu-Por) were synthesized by Officer and co-workers.[12] Ethyl-methylimidazolium dicyanamide (EMI^+dca^-) was synthesized by MacFarlane and co-workers.[12] 2,2′:5′2″-Terthiophene (Aldrich), tetrabutylammonium perchlorate (TBAP, Fluka), iodine (Univar, Ajax or Aldrich 99.8%), tetrapropylammonium iodide (Aldrich, ⩾98%), dichloromethane (DCM, Univar, Ajax), ethylene carbonate (Aldrich 99%), propylene carbonate (Aldrich 99%).

Electrosynthesis and testing of copolymers were achieved using an electrochemical hardware system comprised of an EG&G PAR 363 Potentiostat/Galvanostat, a Bioanalytical Systems CV27 voltammograph, a MacLab 400 with Chart v3.5.7/EChem v 1.3.2 software (ADInstruments), and a PC computer. A three-electrode electrochemical cell was used which comprised a working electrode (ITO-coated glass), a platinum mesh auxiliary electrode, and a Ag/Ag^+ reference electrode with salt bridge.

The device was assembled by sandwiching a liquid electrolyte between the copolymer coated ITO coated glass electrode and the Pt sputtered ITO coated glass electrode. This work was done with a border of parafilm as spacer between these two electrodes. The photovoltaic devices were tested by linear sweep voltammetry (LSV).

Results and Discussion

Initial attempts to electrodeposit polymers from the above novel monomers onto platinum and ITO-coated glass electrodes to form a homopolymer film were unsuccessful; which is probably due to steric hindrance given the large size of the molecule. Therefore, the copolymerization of the above monomers with terthiophene (TTh) was considered. These new copolymer structures couple light harvesting capabilities and electronic properties that result in unprecedented energy conversion efficiencies for these types of photoelectrochemical systems.

Poly(BisTTh-Por-*co*-TTh) was successfully electrodeposited onto ITO-coated glass electrode using either cyclic voltammetry (CV), constant potential, or constant current from a solution consisting of BisTTh-Por (5 mM)/TTh (5 mM) in 0.1 M tetrabutylammonium perchlorate (TBAP)/dichloromethane (DCM). Before the fabrication of photovoltaic devices, all polymers were fully reduced at −0.8 V. In the fabrication of photoelectrochemical solar cells, poly(BisTTh-Por-*co*-TTh) modified ITO-coated glass electrodes are assembled with platinum film (1 nm) modified ITO-coated glass counter electrodes, and the intervening space filled with liquid electrolyte.

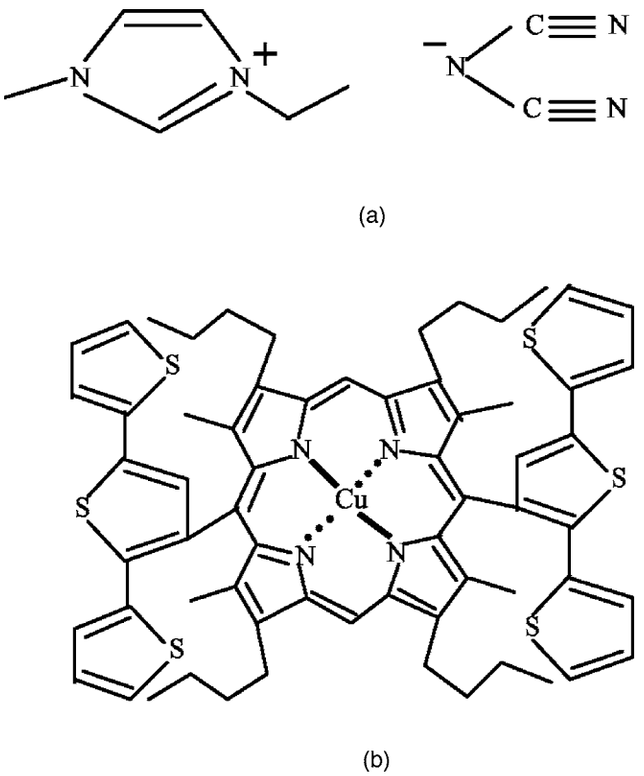

Figure 1. (a) Chemical structures of ionic liquid, EMI^+dca^- and (b) BisTTh-Cu coordinated porphyrin.

This poly(BisTTh-Por-*co*-TTh) based photoelectrochemical cell using ionic liquid electrolyte shows a very similar photovoltaic response curve compared with that using traditional organic liquid electrolyte. The short-circuit photo-current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor of this poly(BisTTh-Por-*co*-TTh) based photoelectrochemical solar cell with the EMI^+dca^--based ionic liquid electrolyte are 0.412 mA cm^{-2}, 256 mV, and 0.315, respectively, yielding an energy conversion efficiency (η) of 0.065%. The identical results obtained from the same cell with the traditional organic liquid electrolyte (J_{sc} = 0.384 mA cm^{-2}, V_{oc} = 266 mV, FF = 0.315, η = 0.064%) indicate that this ionic liquid electrolyte offers the same level of photovoltaic performance as traditional organic liquid electrolyte in this type of photovoltaic device.

Further investigations were carried out by copolymerizing a novel monomer, BisTTh-Cu-Por which has better light harvesting than BisTT-Por, with terthiophene from a solution consisting of BisTTh-Cu-Por (5 mM)/TTh (5 mM) in 0.1 M TBAP/DCM. These polymers were electrodeposited onto ITO-coated glass electrodes using cyclic voltammetry between the potential limits −0.8 and +1.2 V at a scan rate of 50 mV s^{-1}. The thickness of the polymer films was varied by controlling the different charge passed through the ITO-coated glass working electrodes during polymer growth. All poly(BisTTh-Cu-Por-*co*-TTh) film modified ITO-coated glass electrodes were fully reduced at −0.8 V in 0.1 M TBAP/DCM solution before they were assembled into photoelectrochemical solar cells.

Both ionic liquid and traditional organic liquid electrolytes were studied in this novel poly(BisTTh-Cu-Por-*co*-TTh) based photoelectrochemical solar cell. Figure 2 displays the energy conversion efficiency results vs charge density during copolymer growth and the comparison of energy conversion efficiency results using ionic liquid (EMI^+dca^-) electrolyte (curve a) or traditional organic liquid electrolyte (curve b). It shows that photoelectrochemical solar cells using ionic liquid (EMI^+dca^-) electrolyte initially show similar results for energy conversion efficiency compared with those using traditional organic liquid electrolyte. However, with the increase of polymer film thickness, photoelectrochemical cells with ionic liquid electrolyte produced higher energy conversion efficiency than those with organic liquid electrolyte. This is probably due to the high conductivity of the ionic liquid electrolyte which helps the electron transfer between the two electrodes in thicker films while the traditional organic liquid electrolyte is less conductive. Both kinds of devices show similar influence of film thickness on energy conversion efficiency.[11]

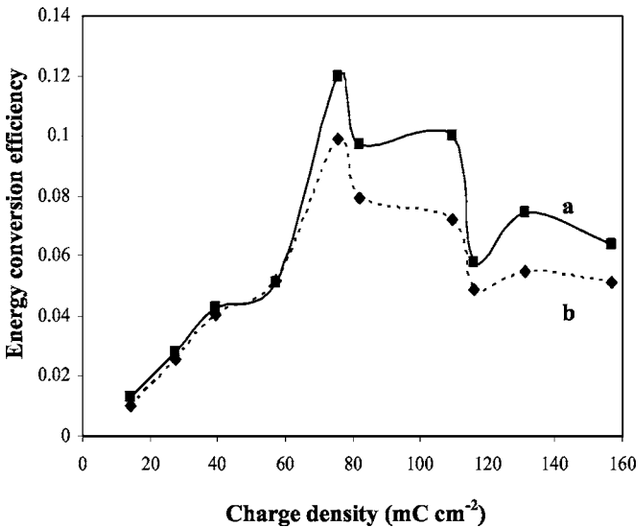

Figure 2. Energy conversion efficiency results vs charge density during poly(BisTTh-Cu-Por-*co*-TTh) copolymer growth, using ionic liquid-based (EMI^+dca^-) electrolyte (solid line) and traditional liquid electrolyte (dashed line) under a halogen white light intensity of 500 W m^{-2}. Cell active area: 0.04 cm^2. The polymer film thickness on the ITO-coated glass electrodes is a function of charge (mC) passed during copolymer growth.

The short-circuit photocurrent density (J_{sc}), open-circuit voltage

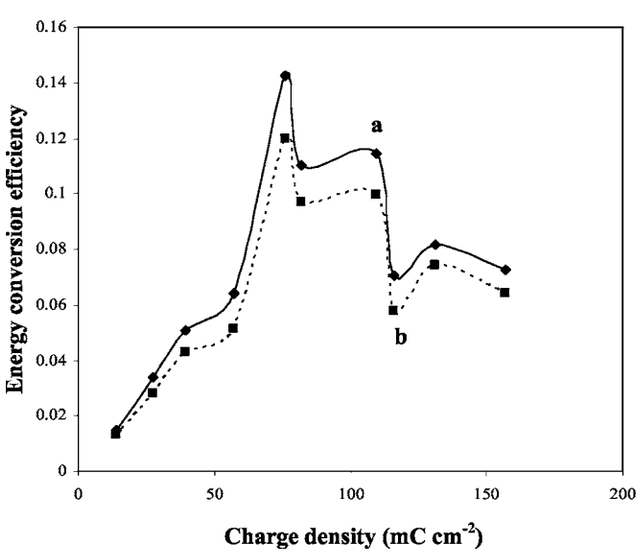

Figure 3. Energy conversion efficiency results vs charge density during poly(BisTTh-Cu-Por-*co*-TTh) copolymer growth using ionic liquid-based (EMI^+dca^-) electrolyte under a halogen white light intensity of 500 W m^{-2} at different testing temperatures: (a) 80°C (solid line) and (b) room temperature (dashed line). Cell active area: 0.04 cm^2.

(V_{oc}), and fill factor of the best poly(BisTTh-Cu-Por-*co*-TTh) (charge density = 75.81 mC cm^{-2}) based photoelectrochemical solar cell are 0.983 mA cm^{-2}, 188 mV, and 0.324, respectively, yielding an energy conversion efficiency (η) of 0.120% with the EMI^+dca^--based ionic liquid electrolyte, and 0.894 mA cm^{-2}, 198 mV, and 0.280, respectively, yielding an energy conversion efficiency (η) of 0.099% with the traditional organic liquid electrolyte. Further preliminary investigation on these devices was performed at high temperature (80°C) with ionic liquid electrolyte (thermally stable) (Fig. 3). It displayed an average 20% increase of energy conversion efficiency when compared with those results obtained at room temperature. This is possibly due to the increase of ionic movement under high temperature which improves the conductivity of ionic liquid. It can be concluded that ionic liquid electrolyte offers an advantage over traditional organic liquid electrolyte when these photovoltaic devices are operated under high temperature.

Conclusion

Photoelectrochemical solar cells based on polyterthiophenes containing porphyrins produced higher photovoltaic response than those based on polyterthiophenes without porphyrin moieties.[3-5] For the first time we successfully employed ionic liquid electrolyte in high efficiency polymer-based photovoltaic devices. Copper-coordinated porphyrin containing bisterthiophene based photoelectrochemical solar cell using ionic liquid electrolyte displayed higher photovoltaic response than those using traditional organic liquid electrolyte. Ionic liquid electrolyte shows advantages over traditional organic liquid electrolyte in these photoelectrochemical solar cells and offers increased photovoltaic performance, chemical and thermal stability, and the added opportunity for developing long-term operational polymer-based solar cells.

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