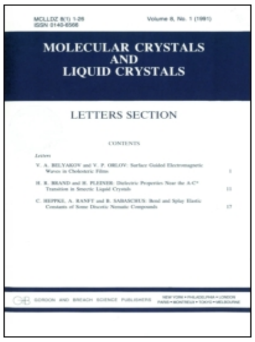

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A conjugated polymer electrolyte for quasi-solid state dye-sensitized solar cell applications

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A conjugated polymer electrolyte for quasi-solid state dye-sensitized solar cell applications

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ABSTRACT
A new conjugated ionic polymer was applied for DSSCs. Poly(2-ethynyl-N-methylpyridinium iodide) (PEMPI) was prepared by the non-catalyst polymerization of 2-ethynylpyridine using iodomethane without any additional initiator or catalyst. The polymerization proceeded homogeneously to give a high yield of polymer (87%). The photoluminescence peak was observed at 568 nm corresponding to a photon energy of 2.19 eV. Quasi-solid-state DSSCs with a SnO_2:F/TiO_2/D719 dye/solid-state electrolyte/Pt device was fabricated with PEMPI, which shows the maximum power conversion efficiency (PCE) of 6.01%.

KEYWORDS
polyacetylene; iodomethane; 2-ethynylpyridine; quasi-solid-state DSSC; cyclic voltammogram

Introduction

Numerous experimental and theoretical studies on the conjugated polymers have been performed over past decades [1–5]. Conjugated polymers are especially attractive for electric and opto-electronic applications because of (i) electrical conductivity; (ii) fast and high nonlinear optical responses; (iii) inherent synthetic flexibility; (iv) chemical reactivity and complex formation ability; and (iv) ease of processing into ultrathin films [6–10].

These conjugated polymers are of high interest due to their potential as promising materials for photovoltaics, displays, lasers, nonlinear optical materials, membranes for gas separation and for liquid-mixture separation, and chemical sensors [2,3,11–13]. Organic semiconducting materials are finding broad applications in areas of organic field-effect transistors (OTFTs), light emitting diodes (OLEDs), nonvolatile memory devices, photovoltaic cells, chemical sensors, and radio frequency identification (RF-ID) tags for integration into low-cost, large-area electronics [14–25].

The pyridine-based ionic conjugated polymers have been used as material candidates for the fabrication of ultrathin amphiphilic films [26,27], cationic polyacetylene-silica nanohybrids [28], hybrid polymer gels [29], nanocrystalline CdS polymer sensitizer [30,31], SERS (surface-enhanced Raman spectroscopy) active pi-conjugated polymer-Ag nanocomposites [32], unipolar write-once-read-many-times (WORM) memory devices [33], etc.

Since the report from the Grätzel group [34], dye-sensitized solar cells (DSSCs) have obtained much attention among researchers. The Grätzel group reported power conversion

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efficiency (PCE) of 12% using a liquid electrolyte and its efficiency was very close to the amorphous silicon-based inorganic solar cells [35]. Although DSSCs based on liquid electrolytes have reached as high as 12% under AM 1.5G 1 sun light intensity (100 mW/cm^2), it has a demerit that the liquid electrolytes lost due to leakage and/or volatility of the electrolyte solution, a major drawback that limits DSSCs stability. Several significant research works has been carried out to minimize this problem. These approaches include employing a polymeric electrolyte, solid-state or quasi-solid-state hole conductors and ionic liquid electrolytes for replacing the liquid electrolytes [36–39].

In our previous paper [24], we synthesized an ionic conjugated polyacetylene (PEMPI) via the non-catalyst polymerization of 2-ethynylpyridine using iodomethane. Herein, we report the new ionic polymer (PEMPI) as a polymer matrix to trap liquid electrolyte to form a quasi-solid-state electrolyte. The DSSCs architecture was a SnO_2:F/TiO_2/D719 dye/quasi-solid-state electrolyte/Pt device. The DSSCs performance of PEMPI was also examined for the first time.

Experimental

2-Ethynylpyridine (Aldrich Chemicals, 98%) was vacuum distilled after drying with CaH_2 (85°C/12 mmHg) [40]. Iodomethane (Aldrich Chemicals., 99%) was used as received. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled. Poly(2-ethynyl-N-methylpyridinium iodide) (PEMPI) was prepared by the non-catalyst polymerization of 2-ethynylpyridine with iodomethane in DMF solvent without any additional initiator or catalyst according to our previous paper [24]. The cyclic voltammetry (CV) analysis was carried out with CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mV/s in 0.1 M solution of tetrabutylammonium tetrafluoroborate in acetonitrile. A platinum wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode.

DSSCs were fabricated as follows. Screen-printable nc-TiO_2 pastes were prepared using ethyl cellulose (Aldirich), lauric acid (Fluka) and terpineol (Fluka). The prepared nc-TiO_2 paste was coated on a FTO conducting glass (TEC8, Pilkington, 8 Ω/cm, glass thickness of 2.3 mm), dried in air at ambient temperature for 5 min and sintered at 500°C for 30 min. The power conversion efficiency of DSSCs was dependent on the particle size of each layer. Particle size of blocking TiO_2 layer, single TiO_2 layer, and scattering TiO_2 layer was 40, 20, and 400 nm, respectively. Several crystal forms of TiO_2 occur naturally: rutile, anatase, and brookite. Rutile is the thermodynamically most stable form. Anatase is the preferred structure in DSSCs, because it has a larger band gap (3.2 vs 3.0 eV for rutile) and a higher conduction band edge energy. This leads to a higher Fermi level and Voc in DSSCs for the same conduction band electron concentration. So, we used the anatase structure of TiO_2 in for the evaluation of polymer electrolyte.

For dye adsorption, the annealed nc-TiO_2 electrodes were immersed in absolute ethanol containing 0.5 mM N719 dye ($Ru[LL'(NCS)_2]$, L = 2,2′-bypyridyl-4,4′-dicarboxylic acid, L' = 2,2′-bypyridyl-4,4′-ditetrabutylammonium carboxylate) for 24 h at ambient temperature. Pt counter electrodes were prepared by thermal reduction of a thin film formed from 7 mM H_2PtCl_6 in 2-propanol at 400°C for 20 min. The dye-adsorbed nc-TiO_2 electrode and Pt counter electrode were assembled using 60 µm-thick Surlyn® (Dupont 1702). The quasi-solid-state electrolyte was composed of iodine (I_2), guanidium thiocyanate (GuSCN), 1-butyl-3-methylimidazolium iodide (BMII), 4-tert-butylpyridine, PEMPI and DMF. The quasi-solid-state electrolyte was filled between two electrodes using a vacuum pump in hotplate.

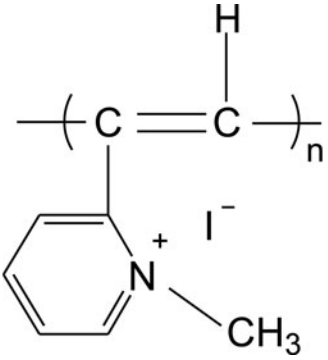

Figure 1. The chemical structure of PEMPI.

Results and discussion

Here, the monomeric 2-ethynyl-N-methylpyridinium iodides are spontaneously polymerized to form highly conjugated, charged polyacetylenes. The polymerization proceeded homogeneously to give a high yield of polymer. The polymer structure was characterized to have a conjugated polymer backbone with the designed substituents. This material is a solid state polymer with quaternary nitrogen atoms showing positive charges, anchoring on a polyacetylene pyridine backbone, and combining I anions with the quaternary nitrogen atom (PEMPI, Fig. 1). This polymer was soluble in such organic solvents as methanol, ethanol, DMF, NMP, and DMSO, and air-stable. The inherent viscosity of PEMPI was 0.14 dL/g. The optical bandgap of PEMPI was estimated from the onset absorption edge of thin film absorption spectrum and was found to be 1.92 eV. CV was employed to estimate the energy level of PEMPI. The HOMO energy level was calculated to be −4.81 eV from onset oxidation potential. LUMO energy level for PEMPI was calculated from the HOMO level attained from the CV analysis and the Egopt (ELUMO = EHOMO + Egopt). Accordingly, the LUMO level was found to be −2.88 eV.PEMPI was used as a polymer matrix to trap liquid electrolyte to form a quasi-solid-state electrolyte.

The DSSCs performance of PEMPI, the pyridine-based ionic conjugated polymer, was firstly examined in this study. The DSSCs architecture was a SnO_2:F/TiO_2/D719 dye/quasi-solid-state electrolyte/Pt device (Fig. 2).

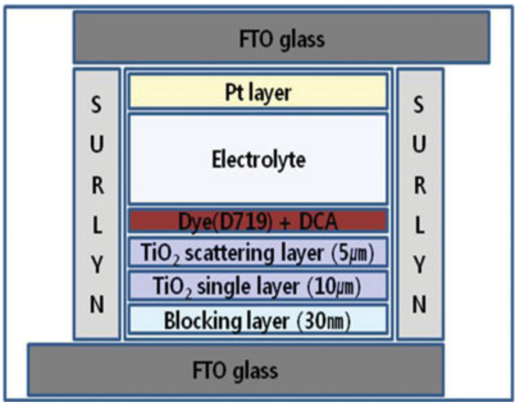

Figure 2. The device structure of DSSC.

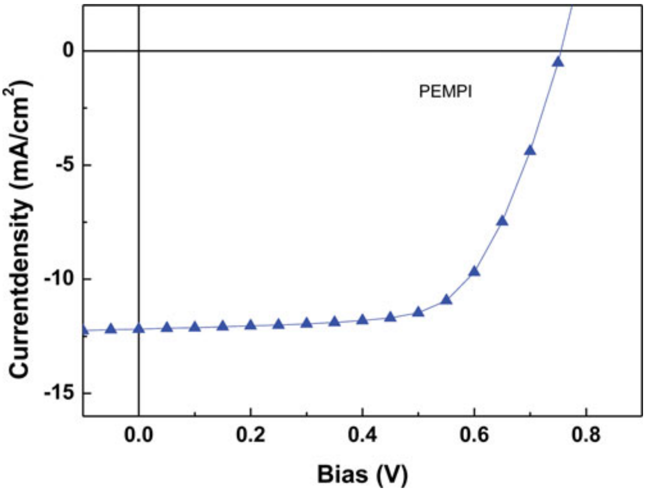

Figure 3. J-V curves under AM 1.5G 1 sun illumination (100 mW/cm^2) of quasi-solid-state DSSCs with PEMPI embedded in polymeric electrolytes. Each DSSC for J-V measurement was covered with an aperture mask to eliminate additional light.

Figure 3 shows the J-V curves of a SnO_2:F/TiO_2/N719 Dye/quasi-solid-state electrolyte/Pt device using PEMPI as the polymer matrix for the quasi-solid-state electrolyte under AM 1.5G illumination (100 mW/cm^2). The absorption characteristics and molar absorption coefficient of the dye or polymer play important roles in determining the performance of the DSSCs. Although *cis*-di(thiocyanato)-N,N'-bis(2,2′-bipyridyl-4-carboxylate-4′-tetrabutylammonium carboxylate) ruthenium(II), (N719) showed good dye coverage on TiO_2 and was also reasonably stable, still it has a drawback of low molar absorption coefficients. The quasi-solid-state DSSCs exhibited a photovoltaic performance with a PCE of 6.01% for PEMPI ($V_{oc} = 0.76$ V, $J_{sc} = 12.18$ mA/cm^2, FF = 0.65). The higher photovoltaic performance of PEMPI was due to its low molecular weight and the higher molar absorption coefficient, which allowed the quasi-solid-state electrolyte based on PEMPI to easily penetrate the dye adsorbed nanocrystalline porous TiO_2 electrode.

Conclusions

In this article, an ionic polyacetylene with pyridinium moieties was applied for DSSCs. PEMPI, which is a solid state polyelectrolyte with quaternary nitrogen atoms showing positive charges, anchoring on a polyacetylene pyridine backbone, and combining I anions with the quaternary nitrogen atom, was easily prepared via the non-catalyst polymerization of 2-ethynylpyridine using iodomethane. PEMPI embedded in polymeric electrolytes were developed for obtaining high efficiency of quasi-solid-state dye-sensitized solar cells (DSSCs). The overall PCE of the newly developed ionic polyacetylene, PEMPI embedded in polymeric electrolyte was 6.01%.

Acknowledgment

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