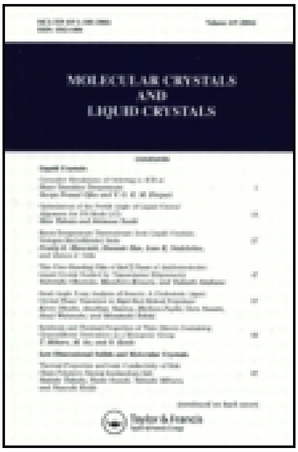

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: Min Joung Im, Ae Jin Kim, Mikyoung Yoon, Hoe Won Yoon, Jae Wook Lee, Yeong-Soon Gal, Jun Hee Lee & Sung-Ho Jin (2011): Synthesis and Photovoltaic Performance of Polythiophene Dye for Polymer-Sensitized Solar Cells, Molecular Crystals and Liquid Crystals, 538:1, 208-215

To link to this article: http://dx.doi.org/10.1080/15421406.2011.564028

Mol. Cryst. Liq. Cryst., Vol. 538: pp. 208–215, 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.564028

Synthesis and Photovoltaic Performance of Polythiophene Dye for Polymer-Sensitized Solar Cells

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Poly[(3-thiophenecarboxylic acid)-co-*(3-thienyl)-8-(4-octyloxy-4′-nitrostilbenyl) acetate]] (P3TAA*-co-*P3TDANS) has been synthesized to examined the photosensitizer property on polymer-sensitized solar cells (PSSCs). The resulting copolymer, P3TAA*-co-*P3TDANS, has good solubility and reasonable molecular weight. The weight-average molecular weight (M_w) and polydispersity of P3TAA*-co-*P3TDANS were 7.9×10^3 g/mol and 1.73, respectively. PSSCs with a configuration of SnO_2:F/TiO_2/polymer dye/electrolyte/Pt devices were fabricated by using P3TAA*-co-*P3TDANS as a photosensitizer. The maximum power conversion efficiency (PCE) of the PSSC based on liquid electrolyte is 0.01% (at 1 sun) for PSSCs.*

Keywords Photovoltaic performance; polymer-sensitized solar cell; polythiophenes

Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention as low-cost photovoltaic cells and have become a rapidly expanding field with potential applications, especially after the discovery of an efficient photovoltaic cell by O'Regan and Grätzel [1]. There are four main factors that affect the performance of the DSSCs: anode [2], cathode [3], electrolyte [4], and photosensitive dyes [5]. As a key part of DSSCs, the dyes take the function of light absorption and injection of the photoexcited

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Address correspondence to Sung-Ho Jin, Department of Chemistry Education, Interdisciplinary Program of Advanced Information and Display Materials, and Center for Plastic Information System, Pusan National University, Busan 609-735, Korea. E-mail: shjin@pusan.ac.kr; jlee@donga.ac.kr electrons to the conduction band of the TiO_2 in anode. There have been two kinds of dyes, namely, metal-organic complexes and metal-free organic dyes. Up to now, Ru complexes [6] have exhibited that the power conversion efficiencies (PCE) over 11% for solar power to electricity with a liquid electrolyte [7]. However, it remains the need for alternative photosensitizers due to the high cost of Ru complexes and the long time unavailability of these noble metal materials [8]. As an inexpensive alternative to the Ru complexes, π-conjugated polymers are attracting more and more interest because of their wide absorption coefficients leading to efficient light harvesting property [9].

Recently, polymer-sensitized solar cells (PSSCs) have been demonstrated using π-conjugated polymers as photosensitizer in the PSSCs, especially using polythiophene derivatives due to their environmental stability and tailor-made electrochemical properties [10]. For example, poly(3-thiopheneacetic acid) was used to sensitize TiO_2 in DSSCs with PCE of 1.5% [11]. In this study, we synthesized poly(3-thiophenecarboxylic acid) based on copolymer with (8-4-octyloxy-4′-nitrostilbenyl)-3-thiophene acetate and investigated as photosensitizer of nanoporous TiO_2 electrode in PSSCs. We describe its thermal, optical and photovoltaic properties.

Experimental

4-Hydroxy-4′-nitrostilbene **(1)** and 4-(8-bromooctyloxy)-4′-nitrostilbene **(2)** were prepared according to the procedure published earlier [12,13]. All reagents were purchased from Aldrich or TCI, and used without further purification. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer, and chemical shifts were recorded in ppm units with chloroform as an internal standard. UV-visible spectra were recorded with a Shimadzu UV-3100 spectrophotometer with a baseline correction and normalization carried out using Microsoft Excel software. The molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) using a PLgel 5 μm MIXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and calibration with polystyrene standards. Thermal analysis was carried out on a Mettler Toledo TGA/SDTA 851 under an N_2 atmosphere at a heating rate of 10°C/min. PSSCs were fabricated using TiO_2 films made from the transparent pastes (Ti-Nanoxide HT, Solaronix SA) were spreaded on FTO glass by the doctor blade method. The paste on FTO glass was then annealed at 450°C for 30 min to produce a 13 μm thick nanocrystalline TiO_2 film. The polymer sensitizer was dissolved in chloroform in a concentration of 20 mg per 100 mL of solution. Nanoporous TiO_2 film was dipped in this solution at 50°C for 24 h. Afterwards the polymer-sensitized TiO_2 electrode was rinsed with chloroform and then used to fabricate the PSSCs, according to the procedure reported elsewhere. The liquid electrolyte and polymer gel electrolyte were consisted of 1-methyl-3-propylimidazolium iodide (MPII, 0.7 M), iodine (I_2, 0.03 M), guanidinium thiocyanate (GuSCN, 0.05 M), 4-tert-butylpyridine (TBP, 0.5 M) in acetonitrile (0.1 mL) and ethylene carbonate (0.6 g), propylene carbonate (0.2 g), I_2 (0.06 g), tetrabutylammonium iodide (TBAI, 0.18 g), MPII (0.2 g), polyacrylonitrile (PAN, 0.1 g), and acetonitrile (0.1 mL), respectively. The active areas (0.25 cm^2) of dye-coated TiO_2 films were measured by an image analysis program equipped with a digital microscope camera (Moticam 1000). After adding the hot electrolyte solution, the holes were sealed with a Surlyn sheet followed by a thin glass cover by heating. The performance of PSSCs were measured using a calibrated

AM 1.5 G solar simulator (Orel 300 W simulator, models 81150) with a light intensity of 100 mW/cm^2 adjusted using a standard PV reference cell (2 cm × 2 cm monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA) and a computer-controlled Keithley 236 source measure unit.

Synthesis of 4-hydroxy-4′-nitrostilbene (1)

A mixture of 4-hydroxybenzaldehyde (5 g, 42 mmol), 4-nitrophenylacetic acid (9.1 g, 50 mmol) and piperidine (4.3 g, 50 mmol) in DMSO (25 mL) was heated at 140°C with vigorous stirring for 24 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with diethyl ether. The extract was concentrated after dried over anhydrous $MgSO_4$. A crude product was purified by column chromatography on silica gel using dichloromethane as an eluent to give 4-hydroxy-4′-nitrostilbene (7.7 g, 76%). mp 203°C; ^{1}H NMR (300 MHz, DMSO-d$_6$, δ ppm) 6.78 (d, J = 5.24 Hz, 2H, aromatic protons), 7.13 (d, J = 16.48 Hz, 1H, =CH−), 7.39 (d, J = 16.48 Hz, 1H, −CH=), 7.48 (d, J = 8.56 Hz, 2H, aromatic protons), 7.76 (d, J = 8.56 Hz, 2H, aromatic protons), 8.16 (d, J = 8.52 Hz, 2H, aromatic protons). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 116.4, 123.7, 124.7, 127.4, 128.0, 129.5, 134.1, 145.4, 146.3, 159.0.

Synthesis of 4-(8-bromooctyloxy)-4′-nitrostilbene (2)

A mixture of 4-hydroxy-4′-nitrostilbene (1) (2.4 g, 10 mmol), 1,8-dibromooctane (5.4 g, 20 mmol) and anhydrous potassium carbonate (2.8 g, 20 mmol) in acetonitrile (60 mL) was refluxed with stirring for 20 h. The reaction mixture was poured into water and extracted with dichloromethane. The extract was concentrated after dried over anhydrous $MgSO_4$. The product was recrystallized from ethanol by two times to 4-(8-bromooctyloxy)-4′-nitrostilbene (2.5 g, 61%). mp 86°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 1.41–1.84 (m, 12H, $-CH_2-$), 3.39 (t, J = 6.87 Hz, 2H, $-CH_2Br$), 3.96 (t, J = 6.59 Hz, 2H, $-OCH_2$-), 6.90 (d, J = 5.24 Hz, 2H, aromatic protons), 6.99 (d, J = 16.48 Hz, 1H, =CH−), 7.23 (d, J = 16.48 Hz, 1H, −CH=), 7.47 (d, J = 8.56 Hz, 2H, aromatic protons), 7.56 (d, J = 8.56 Hz 2H, aromatic protons), 8.18 (d, J = 8.52 Hz, 2H, aromatic protons). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 25.8, 32.7, 40.0, 67.9, 114.8, 123.8, 124.0, 126.4, 128.4, 128.7, 132.9, 144.3, 146.3, 159.8.

Synthesis of (8-4-octyloxy-4′-nitrostilbenyl)-3-thiophene Acetate (3)

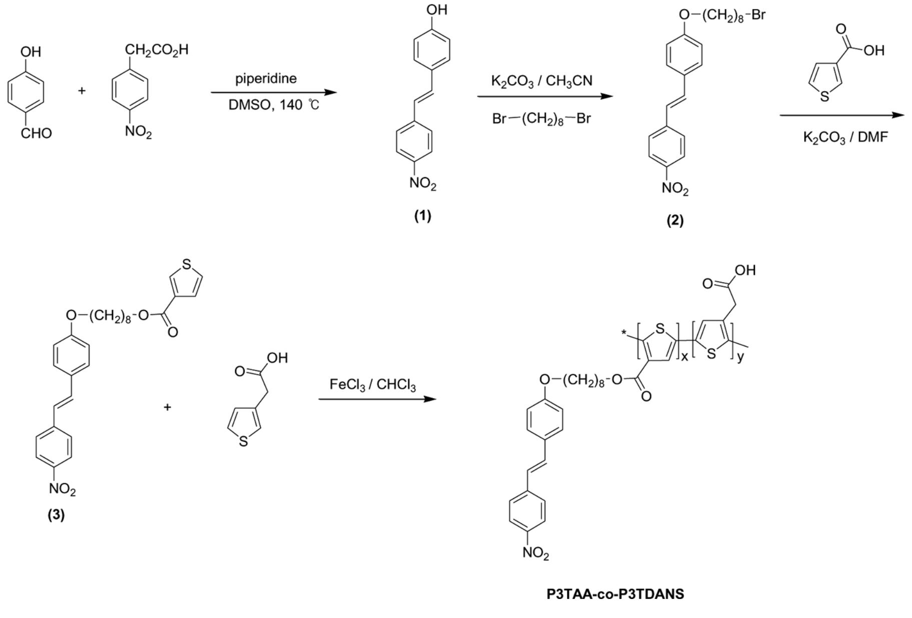
A mixture of 4-(8-bromooctyloxy)-4′-nitrostilbene (2) (1 g, 2.3 mmol), 3-thiophenecarboxylic acid (0.4 g, 3 mmol) and anhydrous K_2CO_3(0.64 g, 4.6 mmol) in DMF (50 mL) was heated at 100°C for 24 h. The reaction mixture was poured into water and extracted with dichloromethane. The extract was concentrated after dried over anhydrous $MgSO_4$. A crude product was purified by column chromatography on silica gel using dichloromethane/hexane (2:1) as an eluent. Yield: 0.9 g (85%), mp; 101°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 1.14–1.84 (m, 12H, $-CH_2-$), 4.00 (tt, J = 6.87 Hz, 2H, $-CH_2O-$), 4.28 (tt, J = 6.59 Hz, 2H, $-OCH_2-$), 6.92 (dd, J = 5.24 Hz, 2H, aromatic protons), 7.00 (dd, J = 16.48 Hz, 1H, =CH−), 7.23 (dd, J = 16.48 Hz, 1H, −CH=), 7.31 (dd, J = 2.47 Hz, 1H, thiophene proton), 7.49 (dd, J = 8.52 Hz, 2H, aromatic protons), 7.54 (dd, J = 8.79 Hz, 1H, thiophene proton), 7.60 (dd, J = 8.56 Hz, 2H, aromatic protons), 8.11 (dd, 1H, thiophene proton), 8.21 (dd, J = 8.52 Hz, 2H, aromatic protons). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 25.9, 28.69, 29.15, 29.21, 64.75, 68.04, 114.86, 123.92, 124.13, 125.92, 126.45, 127.89, 128.39, 128.74, 132.45, 132.97, 133.95, 144.33, 146.37, 159.83, 162.86.

Synthesis of Copolymer with 3-Thiophenecarboxylic Acid and (8-4-Octyloxy-4′-nitrostilbenyl)-3-thiophene Acetate (P3TAA-co-*P3TDANS)*

Dry $FeCl_3$ (0.47 g, 3 mmol) was suspended in 5 mL of dry $CHCl_3$ and stirred for 15 min. The flask was equipped with a stirring bar and a N_2 inlet. After stirring for 1 h at room temperature, 3-thiophenecarboxylic acid (0.18 mg, 0.13 mmol) and (8-4-octyloxy-4′-nitrostilbenyl) 3-thiophene acetate **(3)** (0.3 g, 0.6 mmol) were dissolved in $CHCl_3$ (5 mL), which was added via a syringe to the suspension. The reaction mixture was heated at 60°C for 5 h under a flow of N_2. The reaction mixture was poured into a large quantity of methanol and the dark yellow precipitate was collected by filtration. The resulting material was washed with methanoic hydrochloric acid (1 M). It was collected and purified by Soxhlet extraction with methanol, ether and chloroform in turn and then dried in high vacuum to give P3TAA-*co*-P3TDANS (0.13 g, 40%).

Results and Discussion

The synthetic routes for the chromophore, monomer and polymer are outlined in Scheme 1. The monomer, (8-4-octyloxy-4′-nitrostilbenyl)-3-thiophene acetate (3) was synthesized by the reaction of 4-(8-bromooctyloxy)-4′-nitrostilbene (2) and 3-thiophenecarboxylic acid using the potassium carbonate in DMF. The copolymer, P3TAA-*co*-P3TDANS, as a photosensitizer was first prepared via chemical oxidation of monomers, (8-4-octyloxy-4′-nitrostilbenyl)-3-thiophene acetate (3) and 3-thiophenecarboxylic acid in the presence of $FeCl_3$ in chloroform solution at



Scheme 1. Synthetic routes for monomer and polymer.

60°C for 5 h. These methods are advantageous because unstable intermediates or multistep reaction processes are not required. To improve photovoltaic performance, P3TAA-*co*-P3TDANS was purified by using Soxhlet extraction with different solvents, including methanol, ether and finally chloroform, in order to remove the unreacted monomers and impurities. P3TAA-*co*-P3TDANS was soluble in organic solvents such as chloroform, THF and dichloromethane etc. The weight-average molecular weight (M_w) and polydispersity of the P3TAA-*co*-P3TDANS were 7.9×10^3 g/mol and 1.73, respectively. The TGA thermogram of P3TAA-*co*-P3TDANS revealed a 5% weight loss at 318°C under a N_2 atmosphere. High thermal stability of P3TAA-*co*-P3TDANS prevents degradation of the active layer during the operation of polymer-sensitizer solar cells (PSSCs). The structures of the intermediates, monomer and P3TAA-*co*-P3TDANS were confirmed by ^{1}H-, ^{13}C-NMR, and FT-IR spectroscopies.

IR spectroscopy has been shown to be a powerful tool to exact structural information about P3TAA-*co*-P3TDANS. Figure 1 shows the typical IR spectrum of P3TAA-*co*-P3TDANS powders using FT-IR in the 3600-500 cm^{-1} range. P3TAA-*co*-P3TDANS showed a weak and broad band at 3390 cm^{-1} and 1712 cm^{-1} due to carboxylic acid and carbonyl groups. The bands of nitro group were shown at 1514 cm^{-1}(strong asymmetry stretching frequency) and 1342 cm^{-1} (strong symmetry stretching frequency).

The UV-visible absorption spectra of P3TAA-*co*-P3TDANS are also shown for comparison in Figure 2. To obtain more improved photovoltaic performance in polymer-sensitized solar cells (PSSCs), one of the most important strategies is developing of the effective polymer sensitizer, which can absorb the larger visible spectral range. Transparent and uniform film was prepared on FTO glass of TiO_2 layer adsorbed P3TAA-*co*-P3TDANS in chloroform solution at room temperature. The maximum absorption spectrum of P3TAA-*co*-P3TDANS exhibited at 305 nm in chloroform solution and at 478 nm in thin film. As shown in Figure 2, absorption peak of P3TAA-*co*-P3TDANS was red-shifted by 173 nm on nanoporous TiO_2 layer. The red shift of absorption peak implies that the carboxylic group in the side chain of the polythiophene backbone and TiO_2 interacts with each other, shifting energy levels of the P3TAA-*co*-P3TDANS. This interaction can expedite photoinduced charge transfer from P3TAA-*co*-P3TDANS to TiO_2 [14,15].

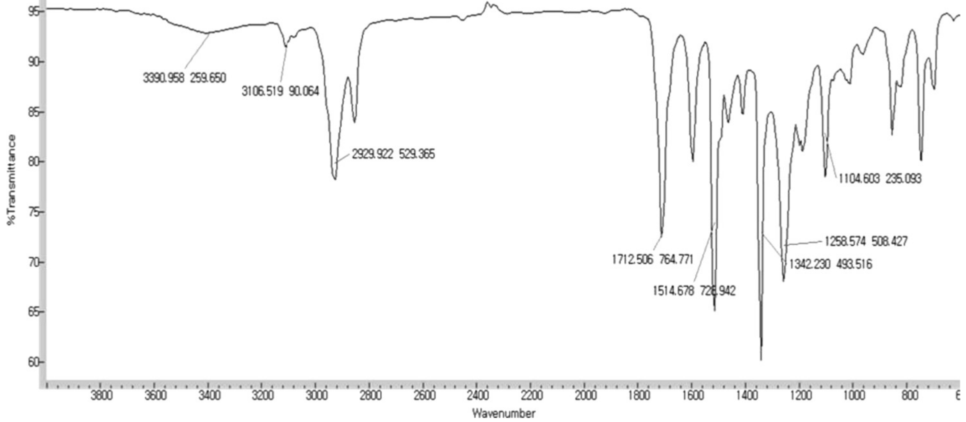


Figure 1. IR spectrum of P3TAA-*co*-P3TDANS.

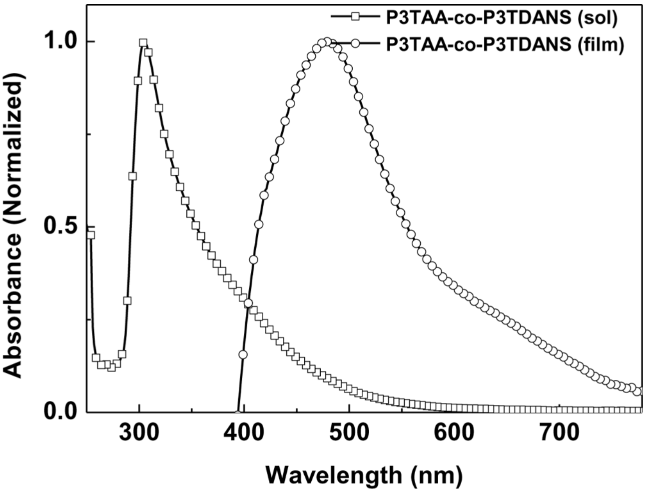


Figure 2. UV-visible absorption spectra of P3TAA-*co*-P3TDANS in chloroform and absorbed on the TiO_2 coated glass.

To investigate the charge carrier injection properties of the P3TAA-*co*-P3TDANS and evaluate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, we carried out redox measurement using cyclic voltammetry. The HOMO binding energy for the standard ferrocene/ferrocenium (−4.8 eV) was −5.40 eV. The band gap of P3TAA-*co*-P3TDANS obtained from the onsets of the absorption spectrum was 2.20 eV. The LUMO energy level was calculated from the value of the band gap and HOMO energy and determined to be −3.2 eV.

Figure 3 shows the current density-voltage (J-V) curves with PSSC configuration of a SnO_2:F/TiO_2/P3TAA-*co*-P3TDANS dye/electrolyte/Pt devices under AM

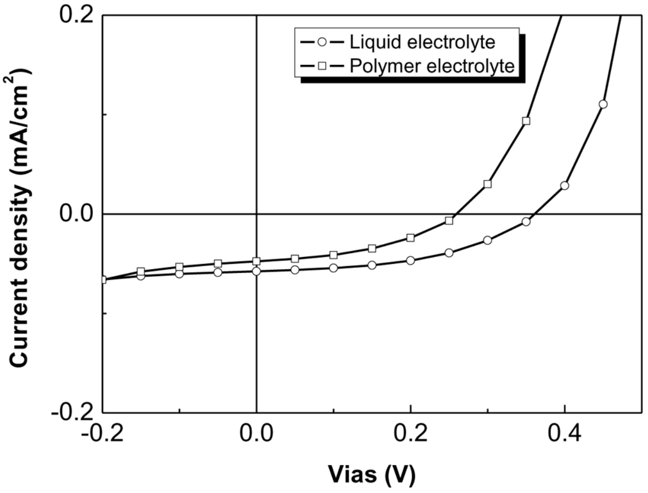


Figure 3. Current density-voltage characteristics of PSSCs using by liquid electrolyte and polymer electrolyte (AM 1.5 conditions).

Table 1. Photovoltaic properties of the PSSCs comprised of liquid electrolyte and PAN-based polymer electrolyte with P3TAA-*co*-P3TDANS dye

Electrolyte	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
Polymer	0.26	0.05	43	0.005
Liquid	0.36	0.06	46	0.010

1.5 G (100 mW/cm^2) by using the P3TAA-*co*-P3TDANS as a photosensitizer instead of Ru complexes and PAN-based polymer electrolyte and/or a liquid electrolyte. The corresponding photovoltaic parameters of the PSSCs are listed in Table 1. The respective short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and PCE are 0.06 mA/cm^2, 0.36 V, 0.46, and 0.01% for the PSSC made from the conventional liquid electrolyte. In contrast, the PSSC with a PAN-based polymer electrolyte displays smaller J_{sc} (0.05 mA/cm^2), V_{oc} (0.26 V) and FF (0.43) values that result in a PCE of 0.005%. The PCE of polymer sensitizer is low compared to the Ru complexes, but there is a possibility of improving the PCE by modification of polymer sensitizers. This work is expected to explore new avenues for the application of π-conjugated polymers in PSSCs, which will facilitate the generation of new functional novel materials in the future.

Conclusions

We have fabricated the PSSCs using polythiophene-based photosensitzer, P3TAA-*co*-P3TDANS containing nonlinear optical chromophore as a pendant group. TGA analysis revealed that the P3TAA-*co*-P3TDANS showed good thermal stability, as the value of a 5% weight losses was 318°C. The maximum PCE of the PSSCs using P3TAA-*co*-P3TDANS dye probed was found to be 0.01% in the system using an liquid electrolyte component with the configuration of SnO_2:F/TiO_2/polymer dye/electrolyte/Pt. Further studies aimed at the development of new polymer dyes to enhance PSSC performance are currently underway.

Acknowledgment

This work was supported by the New & Renewable Energy program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (No. 20103020010050) funded by the Ministry of Knowledge Economy, Republic of Korea, and the Converging Research Center Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0082141), and the Korean Center for Artificial Photosyntheis (KCAP) located in Sogang University funded by the Ministry of Education, Science, and Technology (MEST) through the National Research Foundation of Korea (NRF-2009-C1AAA001-2009-0093879).

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