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Fabrication of Dye-sensitized Solar Cells and Fluorescence Quenching Study Using Thiophene Based Copolymers

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Photovoltaic performance of dye sensitized solar cells fabricated with a commercially available thiophene based copolymer was investigated. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(bithiophene)], a highly soluble polythiophene, was used as a sensitizer. An open-circuit voltage of 0.64 V and a short-circuit current density of 0.36 mA/cm^2 were measured. The incident photon to current conversion efficiency for the polymer was measured. Fluorescence from the other polythiophene, poly(3,3′-didodecyl quarter thiophene) was found to be quenched when blended with phenyl C_{61} butyric acid methyl ester (PCBM) (1:1 wt ratio), indicating the charge transfer from the conjugated polymer to PCBM.

Keywords: Thiophene copolymers, fluorescence quenching, solar cells, IPCE

1 Introduction

Organic solar cells have recently elicited considerable research interest as they offer several unique advantages such as flexibility, being lightweight and amenable to easy processing in large scale which can potentially result in high throughput low-cost devices (1–3). Both dye sensitized solar cells (DSSCs) and bulk heterojunction solar cells have attracted great attention over the past decade. DSSCs using organometallic dyes as sensitizers and nanoporous semiconducting films can yield power conversion efficiency as high as 10% with liquid electrolytes (4, 5). TiO_2 nanoparticles and ruthenium based organic dyes are routinely utilized. Recently, a significant amount of research has been devoted for the development of the conjugated polymer based DSSCs (6–8). Since their electronic and optical properties can be easily tailored by extending the conjugation lengths and changing side groups, the conjugated polymers have been used either as sensitizers or as charge transporters to replace the expensive ruthenium based organic dyes and the corrosive electrolytes respectively. In the bulk heterojunction solar cells, the spontaneous phase separation between a conjugated polymer (as donor) and the fullerene molecule (as acceptor) lead to a self-assembly of nanoscale heterojunction throughout the bulk of the film (9–12). The photovoltaic performance of the solar cells highly depends on the morphology of the composite film and the efficacy of the photo-induced charge separation. Furthermore, the exciton dissociation and open circuit voltage depend on the suitable energy level matching between polymer donor and fullerene derivatives.

Polythiophenes, a class of conjugated polymer have been extensively used both in dye sensitized solar cells and bulk-heterojunction solar cells (7–9). The carboxyl groups attached to the polythiophene can be easily anchored on the surfaces of TiO_2 nanoparticles leading to efficient dye absorption (8). In this study, DSSCs were fabricated with a commercially available thiophene copolymer. A highly soluble thiophene polymer was used as the sensitizer in DSSCs. Fluorescence quenching was studied with another commercial available regioregular polythiophene.

2 Experimental

2.1 Materials and Characterization

The thiophene copolymers, poly[(9,9-diocylfluorenyl-2-7-diyl)-co-(bithiophene)] (ADS2008P) and poly(3,3′-didodecyl quarter thiophene (ADS12PQT) were purchased from American Dye Source, Inc. The chemical structures of ADS2008P and ADS12PQT are shown in Figure 1.

Dedicated to the memory of Professor Sukant K. Tripathy

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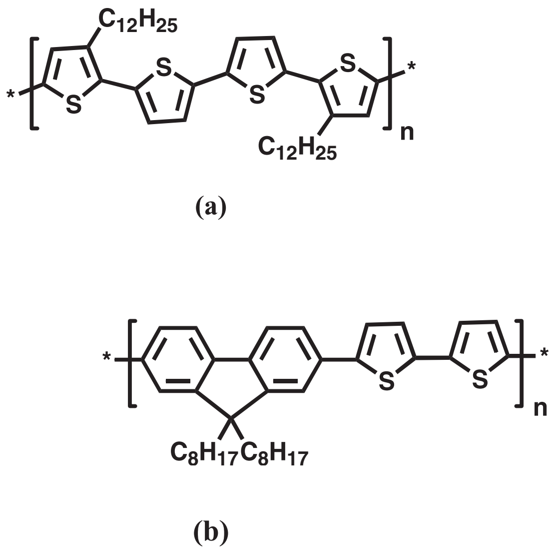


(a)

(b)

Fig. 1. Chemical structures of ADS2008P (a) and ADS12PQT (b).

I^-/I_3^- based redox liquid electrolyte was prepared by dissolving 0.0254 g I_2 and 0.1358 g LiI in 2 mL acetonitrile and 0.3 mL 4-tert-butylpyridine. Fluorine-doped tin oxide (FTO, TEC15) glasses were acquired from Hartford Glass Company, Hartford City, Indiana. The polymer solutions for optical studies were prepared by dissolving the thiophene copolymers (ADS2008P, 5 mg/mL and ADS12PTQ, 5 mg/mL) in chlorobenzene. Thin films for fluorescence quenching study were prepared by spin-coating from the dilute solution of ADS12PQT (2 mg/mL) and mixture of ADS12PQT:PCBM (2 mg/mL:1 mg/mL) in chlorobenzene on glass slides. UV-Visible absorption spectra were recorded using a Perkin-Elmer Lambda 9 UV-Vis-NIR spectrophotometer. Fluorescence measurements were performed with a Perkin-Elmer luminescence spectrometer.

2.2 Fabrication of Dye-sensitized Solar Cells

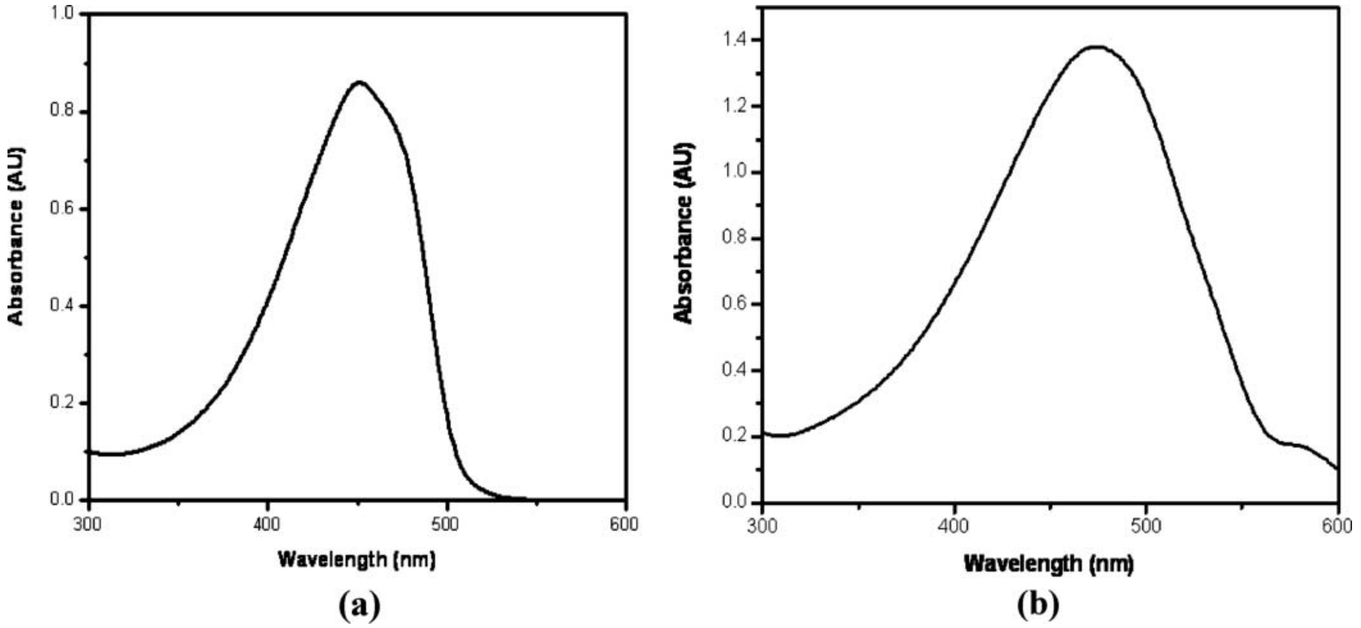
FTO glasses were cleaned with deionized water, ethanol and acetone. TiO_2 films were prepared using TiO_2 nanoparticles (Degussa, P25) by spin-coating onto the cleaned FTO glass substrates. TiO_2 films were sintered at 500°C for 1 h. The TiO_2 films were dipped in the polymer solution of ADS2008P in chlorobenzene (5 mg in 1 mL) overnight. Thick platinum (100 nm) coated FTO glasses were used as the counter electrodes. The I^-/I_3^- electrolyte was then added to the cells.

2.3 Incident Photon to Current Conversion Efficiency Measurement of DSSC

The incident photon to current conversion efficiency (IPCE) is commonly defined as:

$$\text{IPCE}\% = 1240J_{sc}/(\lambda P_i) \times 100\%$$

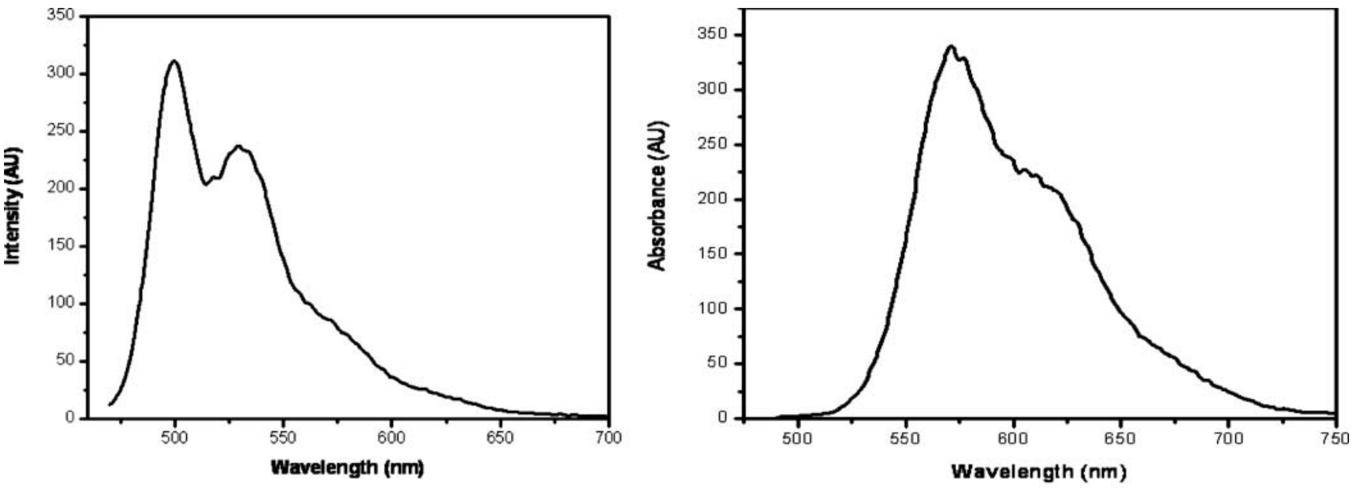
where J_{sc} is the short-circuit current density, λ is the excitation wavelength and P_i is the intensity of the incident light, respectively. The IPCE spectrum for the ADS2008P sensitized DSSC was obtained with a CVI Digikrom 240 monochromator in conjunction with a water-cooled 150W Xe lamp (Photon Technology Int. A-1010B). Intensity of the incident illuminations was measured with a Newport 835 optical power meter. The photocurrent was collected by a Keithley Model 197 multimeter.



(a)

(b)

Fig. 2. Absorption spectra of ADS2008P (a) and ADS12PQT (b).



(a) **(b)**

Fig. 3. Fluorescence spectra of ADS2008P (a) and ADS12PQT (b).

2.4 Power Conversion Efficiency Measurements

The photovoltaic performance of the solar cells was evaluated under simulated AM1.5 illumination (100 mW/cm^2) in conjunction with a Keithley SMU2400 source meter. A personal computer was used for data acquisition. The active area of the DSSCs was controlled to be 0.25 cm^2 with a mask.

3 Results and Discussion

3.1 Absorption and Fluorescence Spectra of the Thiophene Copolymers

The absorption spectra of ADS2008P and ADS12PQT in chlorobenzene are shown in Figure 2. The ADS2008P and ADS12PQT solutions show an absorption maximum around 460 nm and 480 nm, respectively. Figure 3 shows the fluorescence spectra of the two copolymers. When excited at the corresponding absorption maxima, the solutions of ADS2008P and ADS12PQT emit around 540 nm and 570 nm, respectively.

3.2 Photovoltaic Performance of DSSCs

The current-voltage (I-V) curve of the ADS2008P sensitized DSSC is shown in Figure 4. The solar cell yielded a short-circuit current of 0.36 mA/cm^2 and an open-circuit voltage of 0.64 V. Figure 5 represents the photoaction spectrum of the DSSC. The maximum IPCE was found to be 4.4%. The IPCE spectrum is similar to the UV absorption

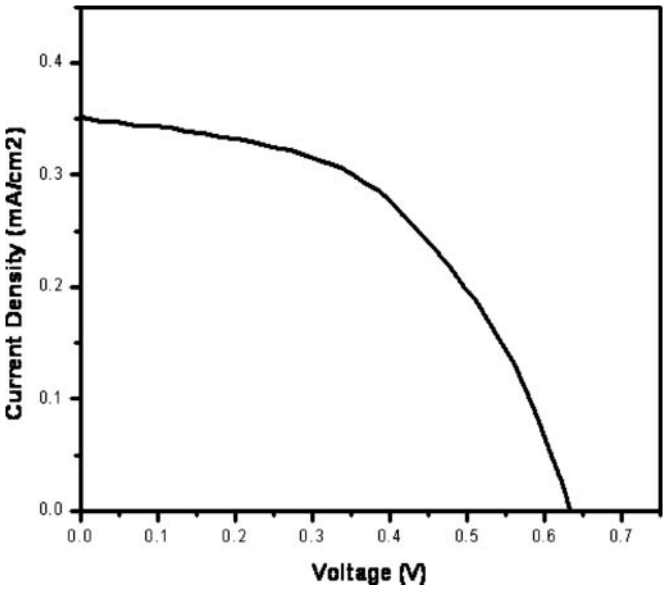


Fig. 4. I-V characteristics of the ADS2008P sensitized DSSC.

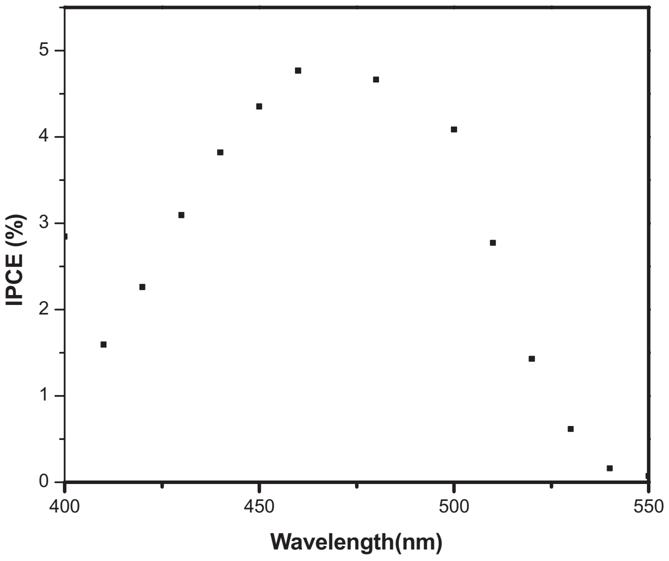


Fig. 5. IPCE of an ADS2008P sensitized DSSC.

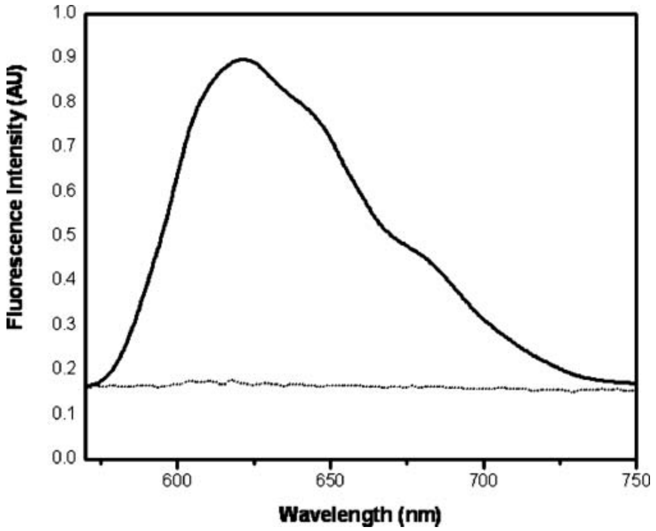


Fig. 6. Fluorescence spectra of an ADS12PQT film (solid line) and a film of ADS12PQT:PCBM (1:1) blend (dotted line).

spectrum of the ADS2008P polymer solution, indicating that the polymer indeed contributes to the short-circuit current. The low power conversion efficiency (0.12%) of the ADS2008P sensitized DSSCs could be attributed to insufficient penetration of the polymer inside the TiO_2 nanopores due to large size of the polymer. It is anticipated that higher polymer incorporation inside the TiO_2 films can be achieved by using bigger TiO_2 particles. This could lead to better photovoltaic performance.

3.3 Fluorescence Quenching of ADS12PQT/PCBM Film

The absorption maximum of the ADS12PQT film is red-shifted. When excited at its absorption maximum (527 nm), the ADS12PQT film emits around 621 nm. Figure 6 shows the fluorescence spectra of the ADS12PQT and ADS12PQT/PCBM films. It is clearly observed that the fluorescence from ADS12PQT is quenched when blended with PCBM. This provides evidence of the charge transfer from the conjugated polymer to PCBM.

Apart from charge transfer mechanism, the energy level matching is also essential in determining the photovoltaic performance of the bulk heterojunction solar cells. ADS12PQT possesses a LUMO of −2.67 eV and an HOMO of −5.13 eV (13), whereas PCBM exhibits a LUMO of −4.2 eV and an HOMO of -6.0 eV (14). The energy level matching between ADS12PQT and PCBM indicates that this regioregular polymer could be potentially used in bulk heterojunction solar cells.

4 Conclusions

In summary, we have studied photovoltaic performance of the DSSCs employing a commercial thiophene copolymer (ADS2008P) as sensitizer. The IPCE study clearly showed that the short-circuit current is from ADS2008P. The fluorescence quenching of the copolymer ADS12PQT blended with PCBM proves the charge transfer from the ADS2PQT polymer to PCBM. This unveils the possibility of using this polymer as a donor molecule in bulk heterojunction solar cells.

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