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# Electrosynthesis of novel photochemically active inherently conducting polymers using an ionic liquid electrolyte

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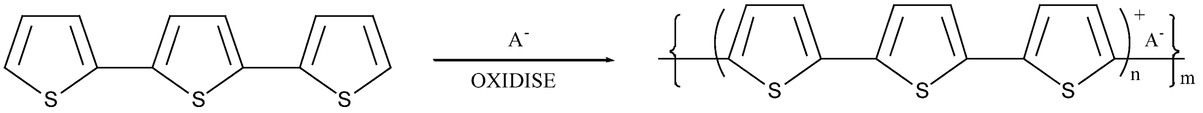
## Abstract

Use of an ionic liquid as a solvent enabled the successful preparation of films composed of polyterthiophene doped with an anionic dye. Photoelectrochemical cells constructed using these films showed significant improvements in photovoltaic properties when the films were first reduced in the presence of a cationic dye. Absorption spectroscopic studies provided evidence for retention of both dyes in the films, while photocurrent action spectra showed that the increase in photovoltaic performance was due largely to improvements in light harvesting by the polymer.

*Keywords:* Polyterthiophene; Dyes; Photovoltaics; Photoelectrochemical cells

## 1. Introduction

Conducting polymers offer exciting prospects for many applications including sensing, electrochromic displays, actuation and corrosion control [1,2]. Most of these applications require the introduction of appropriate molecular dopants ($A^-$) into the polymer structure. This is usually achieved at the time of synthesis, which is often carried out electrochemically according to Eq. (1), using the synthesis of polyterthiophene as an example, and where $A^-$ is a constituent of the electrolyte used.



(1)

A range of aqueous and organic solvents has been used to facilitate incorporation of a wide variety of anions into conducting polymers during electrosynthesis. More recently the use of ionic liquids (room temperature molten salts) with conducting polymers has been advocated. Support for this is provided by a study showing conducting polymers display greater stability when electrochemically switched in ionic liquid media compared to conventional solvents [3]. Synthesis of conducting polymers from ionic liquids has also been investigated [4–6]. A potential advantage in the use of ionic liquids during electrosynthesis is their unique solvent capabilities [7], which should allow monomer–dopant combinations not available with conventional solvents to be achieved.

There has been considerable interest in the use of conducting polymers as low-cost alternatives to silicon for the production of photovoltaic devices [8]. A variety of conducting polymers, including polyanilines and poly(*p*-phenylene vinylenes) have been used to produce photovoltaic devices that in some instances display high quantum efficiencies. Several methods have been proposed for improving the photovoltaic efficiency of devices based on conducting polymers, including enhancing structural order in the solid state, and

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increasing light harvesting by incorporating suitable chromophores, such as dyes or metal complexes as the molecular dopant [8,9]. We have been investigating the photovoltaic properties of polythiophenes [10–12], which offer a number of advantages including ease of fabrication, and the ability to readily modify chemical and physical properties through derivatisation of monomers.

Here, we report the use of an ionic liquid electrolyte to enable incorporation of anionic dyes during synthesis. Subsequent incorporation of a cationic dye during electrochemical reduction enabled a new photovoltaic material to be produced.

## 2. Experimental

### 2.1. Reagents

2,2′:5′,2″-Terthiophene (TTh, Aldrich), tetrabutylammonium percholorate (TBAP, Fluka), tetrapropylammonium iodide (Asia Pacific Specialty Chemicals (APS)), iodine (APS), propylene carbonate (Aldrich), brilliant blue R (BBr, Aldrich), erioglaucine (Erio, Aldrich), benzopurpurin 4B (BPP4B, Aldrich), brilliant green (BG, Aldrich), potassium iodide (APS), acetonitrile (APS), dichloromethane (APS), dimethylformamide (DMF, Aldrich) and isopropanol (APS) were used as received. The ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (BMI-TFSA) was obtained from Merck. Indium tin oxide (ITO) coated glass ($\leq 10\,\Omega^{-2}$) was obtained from Delta Technologies Limited (Stillwater, Minnesota, USA), and cut into 1 cm × 3 cm pieces, washed with detergent, rinsed with water then isopropanol, and then dried in air prior to use.

### 2.2. Polymer growth

All polymers were prepared electrochemically in a three-electrode electrochemical cell, consisting of an indium tin oxide coated glass working electrode, $Ag/Ag^+$/0.1 M TBAP (acetonitrile) reference electrode and reticulated vitreous carbon (RVC) auxiliary electrode. Polymerisations were performed using potentiostatic, potentiodynamic and galvanostatic conditions, and solutions containing 10 mM terthiophene and different concentrations of dyes, depending on the solvent/dye combination. After growth, all films intended for photovoltaic testing were poised at −400 mV in acetonitrile solutions containing either 0.1 M TBAP or 0.1 M brilliant green to ensure the material was in the fully reduced form. The samples were then rinsed in acetonitrile to remove any loose particles and residual monomer and/or dopant.

### 2.3. Instrumentation

Absorption spectra of polymer samples grown on ITO coated glass were measured over the wavelength range 300–1100 nm using a Shimadzu UV1601 spectrophotometer. Photocurrent action spectra were obtained at the Department of Physics, University of Newcastle, Australia, by Chris McNeil.

### 2.4. Photovoltaic device fabrication and testing

The methods used for assembling polyterthiophene coated ITO coated glass slides into photoelectrochemical cells, and subsequent evaluation of photovoltaic properties, have been described in detail previously [11]. Essentially photoelectrochemical cells consisted of a liquid electrolyte containing a $I_3^-/I^-$ redox mediator sandwiched between an anode, consisting of a polymer coated ITO coated glass slide, and a counter electrode consisting of platinum sputter coated ITO coated glass. A parafilm gasket (2 mm × 2 mm testing area) was placed between the two electrodes to ensure a constant testing area and avoid short-circuiting. The entire assembly was held tightly together using alligator clips to prevent formation of air bubbles.

Photovoltaic experiments were performed immediately after device fabrication using a system comprised of a EG&G PAR model 363 potentiostat/galvanostat, MacLab/400 analog to digital converter, Macintosh computer equipped with ADInstruments software (EChem Version 1.3.2) and halogen lamp (500 $\mathrm{W\,m^{-2}}$ Solux MR-16, Wiko Ltd.) located within a blacked out box. Using a two-electrode configuration linear sweep voltammetry was performed with lower potential limit −50 mV, upper potential limit +200 mV, and scan rate 100 $\mathrm{mV\,s^{-1}}$. Photoelectrochemical devices were first scanned in the dark, after which a scan was performed under illumination to record the change in current due to absorption of light. The resulting current–voltage ($I$–$V$) curves were used to calculate the short circuit current ($I_{sc}$), open circuit voltage ($V_{oc}$), and voltage at peak power ($V_{pp}$). From these parameters, the fill factor (FF) and energy conversion efficiency (ECE) were calculated as previously described [11].

## 3. Results and discussion

Fig. 1 illustrates the structures of the dyes used in this work. The solubility of these dyes and of terthiophene was investigated in a number of organic solvents and BMI-TFSA. The results of these investigations are summarised in Table 1, and were used to select appropriate concentrations of monomer and dopants for this study.

### 3.1. Polyterthiophenes grown in organic solvents

Attempts to synthesise polyterthiophene doped with the anionic dyes shown in Fig. 1, from acetonitrile solution using potentiodynamic polymerisation were unsuccessful. When galvanostatic methods (current density = 0.5 or 1.0 $\mathrm{mA\,cm^{-2}}$) were used, polymer deposition was patchy. Chronopotentiograms recorded during polymer growth showed increasingly high and unstable potentials being