A Poly(3-methylthiophene) Diode based on a p–n Homojunction prepared by Combination of Electrochemical Cation Doping and Photochemical Anion Doping

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An organic p–n homojunction diode was made using a single poly(3-methylthiophene) film electrochemically cation-doped on one side and photochemically anion-doped on the other side.

Conjugated conducting polymers have attracted special interest recently as a new class of electronic materials applicable to Schottky type and p–n junction solar cells, batteries, sensors and conducting coatings. Most conducting polymers, including polyacetylene, are sensitive to oxygen and humidity. This sensitivity causes problems in applying these polymers to various devices. Poly(thiophene) and its derivatives are conducting polymers that are fairly stable toward oxygen and moisture in their undoped and doped states.[1] They can be synthesized chemically or electrochemically. An electrochemically synthesized poly(3-methylthiophene) (P3MT) is obtained in the oxidized (anion-doped or p-doped) conducting state and can be electrochemically undoped to its insulating state. Further electrochemical reduction results in conversion to the n-type material.[2] The p-type and n-type semiconductances of the oxidized and reduced P3MT films have been confirmed by measurements of the conductivities and work functions of the films.[3] In the present work, further confirmation is obtained by the thermoelectric power measurements: the oxidized and reduced films yield positive and negative Seebeck coefficients consistent with p- and n-type conductance, respectively.

In this paper, we propose a novel technique for building an organic p–n homojunction diode based on a single P3MT film.

The electrochemical measurements were carried out using a three-electrode system. A saturated calomel electrode (SCE) and a Pt wire were used as the reference and counter electrodes, respectively. MeCN was distilled over P_2O_5 under dry and oxygen-free N_2. 3-Methylthiophene (3MT) was distilled in an N_2 flow. Tetramethylammonium hexafluorophosphate (Me_4NPF_6) was recrystallized from MeCN and then dried at 200 °C for 12 h. Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate {$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$} and ammonium peroxydisulfate {$(NH_4)_2S_2O_8$} were recrystallized from distilled water.

The p–n homojunction was made in the following way. First, a P3MT film was obtained by oxidation of the monomer (0.1 mol dm^{-3} 3MT) at 2 V *vs.* SCE on an ITO electrode immersed in MeCN containing 5×10^{-2} mol dm^{-3} Me_4NPF_6. The amount of electricity passed during the electrolysis was controlled to be 1 C cm^{-2}. The P3MT film was initially in the anion-doped state. Secondly, the resulting polymer film was transferred to a MeCN solution containing 5×10^{-2} mol dm^{-3} Me_4NPF_6 and then electrochemically undoped to the insulating state at 0 V *vs.* SCE. Subsequently, it was reduced by switching the potential from 0 to −2 V *vs.* SCE (0.4 C cm^{-2}). Under these conditions the polymer was lightly cation(n)-doped as checked by measuring the work functions and conductivities of the polymer films by employing the four-probe method and the Kelvin probe method.[3] Lastly, the cation-doped P3MT film thus prepared was rinsed with pure MeCN and contacted with a degassed mixture of MeCN–water (3 : 1) containing 5×10^{-2} mol dm^{-3} Me_4NPF_6, 1×10^{-4} mol dm^{-3} $[Ru(bpy)_3]^{2+}$ and 1×10^{-2} mol dm^{-3} $S_2O_8^{2-}$. $[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$ act as photosensitizer and sacrificial oxidant, respectively, for photochemical anion doping. The polymer surface in contact with the solution was irradiated with white light (150 mW cm^{-2}). The photoexcited species, $[Ru(bpy)_3]^{2+*}$, is quenched with $S_2O_8^{2-}$ to produce $[Ru(bpy)_3]^{3+}$, $SO_4^{\bullet-}$ and SO_4^{2-}. Since the standard redox potentials of the couples of $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ and $SO_4^{\bullet-}/SO_4^{2-}$ are 1.48 V and > 3.42 V *vs.* SCE, respectively,[4,5] $[Ru(bpy)_3]^{3+}$ and $SO_4^{\bullet-}$ have sufficient oxidizing power to undope and oxidize the n-doped P3MT. Consequently, the irradiated part of the polymer contacting the solution was oxidized to lead to the anion(p)-doped state, whereas the other side of the film remained as a cation(n)-doped state provided that the experimental conditions, *e.g.* irradiation time, are appropriate.

Fig. 1 illustrates the irradiation time dependence of the absorption spectrum of a thin P3MT film (orange–violet) prepared by electrochemical reduction at −2 V *vs.* SCE with 4×10^{-2} C cm^{-2}. This film was initially prepared by electrochemical oxidation at 2 V *vs.* SCE (0.1 C cm^{-2}) and electrochemically undoped at 0 V in advance. The shape of spectrum (*g*) was similar to that for an electrochemically anion(p)-doped film (deep blue). The peaks at 480–500 nm are attributed to the interband transition.[1] Such a change in absorption spectrum or colour was not observed in the absence of either the sensitizer or the oxidant. Hence, it can be assumed that the photochemical anion doping proceeds as shown in Scheme 1.

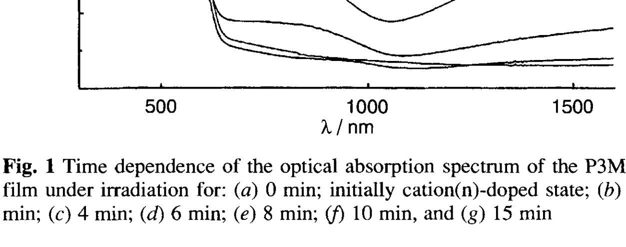
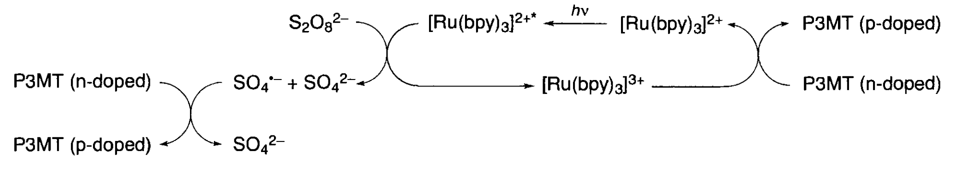


Fig. 1 Time dependence of the optical absorption spectrum of the P3MT film under irradiation for: (*a*) 0 min; initially cation(n)-doped state; (*b*) 2 min; (*c*) 4 min; (*d*) 6 min; (*e*) 8 min; (*f*) 10 min, and (*g*) 15 min



Scheme 1 Representation of photochemical anion(p)-doping

When more concentrated $[Ru(bpy)_3]^{2+}$ (2×10^{-3} mol dm^{-3}) solution was used, irradiation for 1 min was sufficient to cause a colour change from orange–violet to deep blue in the front, irradiated part of the P3MT film (5 μm in thickness), while no colour change was observed on the reverse part. This shows the formation of a p–n homojunction in the P3MT film.

Fig. 2 shows the current–voltage (*J–V*) curves of the sandwich-type cell consisting of Al (50 nm thickness) | (n-doped : p-doped) P3MT (5 μm) | Au (20 nm), where the contacts of P3MT with Al and Au were made by the physical vapour deposition method. The rectifying *J–V* characteristics are attributable to the p–n junction formed in the polymer film as the cells of Al | n-doped P3MT | Al and Au | p-doped P3MT | Au exhibited ohmic behaviour. This was inferred from the work function values of 4.4, 5.1, 3.9 and 5.1 eV obtained for the electrochemically n-doped P3MT, photochemically p-doped P3MT, Al and Au films, respectively. The forward bias direction is consistent with the character of the p–n junction. A diode quality factor (q) of 21 was estimated from the linear region of the $\ln J$ *vs.* V curve at the forward bias, which deviated greatly from ideality ($q = 1$). Under irradiation with white light at 38 mW cm^{-2}, a short circuit photocurrent of 0.16 μA cm^{-2}, an open circuit photovoltage of 0.23 V and a fill factor of 0.30 were obtained. As shown in the inset of Fig. 2, the photoresponse is fairly fast and the reproducibility is very good. These results show that a p–n homojunction has been successfully fabricated using a single P3MT film electrochemically cation-doped on one side and photochemically anion-doped on the other side. This combination electrochemical–photochemical doping technique might be applicable widely to other semiconducting polymers, *e.g.* poly(3-phenylthiophene), switchable between p- and n-doped states.[6]

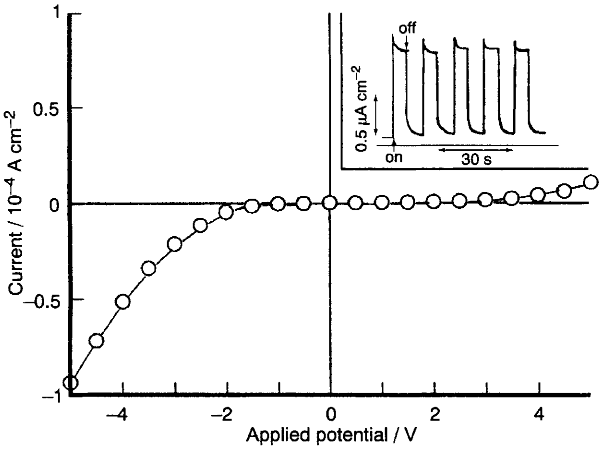


Fig. 2 Darkcurrent–voltage characteristics of the Al | (n-doped : p-doped)P3MT | Au cell. The inset depicts the time profile of the photocurrent at the reverse bias voltage 1.0 V applied to the Al electrode. The irradiation was carried out through the Au film.

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