



JOHANNES KEPLER
UNIVERSITÄT LINZ
Netzwerk für Forschung, Lehre und Praxis



Photoelectrochemical Cells based on Photoactive Polymers

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eingereicht von
Alexander Gusenbauer

unter der Betreuung von
o. Univ. Prof. Dr. Serdar N. Sariciftci

Co-Betreuung:
Dr. Antonio Cravino
Ass. Prof. Dr. Helmut Neugebauer

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Abstract

In plastic solar cells, electron acceptors like fullerenes are blended with the photoactive polymers to improve charge separation of excited species. Consequently, the efficiency of the cell is improved. Also in photoelectrochemical cells photoactive polymers can be used. In this work the influence of fullerenes as electron acceptors on the performance of photoelectrochemical cells based on photoactive polymers is investigated.

The main topics of this work are the preparation of suitable polymeric photoelectrodes and their characterisation in terms of absorption behaviour as well as part of photoelectrochemical cells. In-situ spectroelectrochemistry and in-situ photospectroelectrochemistry were used to support the obtained results. A part of this study has already been published¹.

Zusammenfassung

In organischen Solarzellen werden Elektronenakzeptoren wie Fullerene zum photoaktiven Polymer gemischt, um die Ladungstrennung von angeregten Spezies zu fördern; in der Folge wird die Effizienz der Zelle gesteigert. Auch in photoelektrochemischen Zellen können photoaktive Polymere eingesetzt werden. In dieser Arbeit wird nun der Einfluss von Fullerenen als Elektronenakzeptoren auf die Leistung photoelektrochemischer Zellen untersucht.

Die Schwerpunkte der Arbeit bilden die Herstellung geeigneter polymerbasierter Photoelektroden sowie deren Charakterisierung hinsichtlich ihres Absorptionsvermögens sowie als Teil einer photoelektrochemischen Zelle. Weiters wurde in-situ Spektroelektrochemie sowie in-situ Photospektroelektrochemie derartiger Materialien durchgeführt, um vorher erhaltenen Ergebnisse zu unterstützen. Ein Teil dieser Studie wurde bereits publiziert¹.

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1 Introduction

1.1 Semiconductor-electrolyte interfaces

Photoelectrochemical cells allow the conversion of light to electricity. Their main characteristic is a semiconductor-electrolyte solution interface, which was intensely studied by Gerischer^{2,3}. For an n-type semiconductor, a scheme of the energetics of the interface before and after contact is shown in Fig. 1.1.

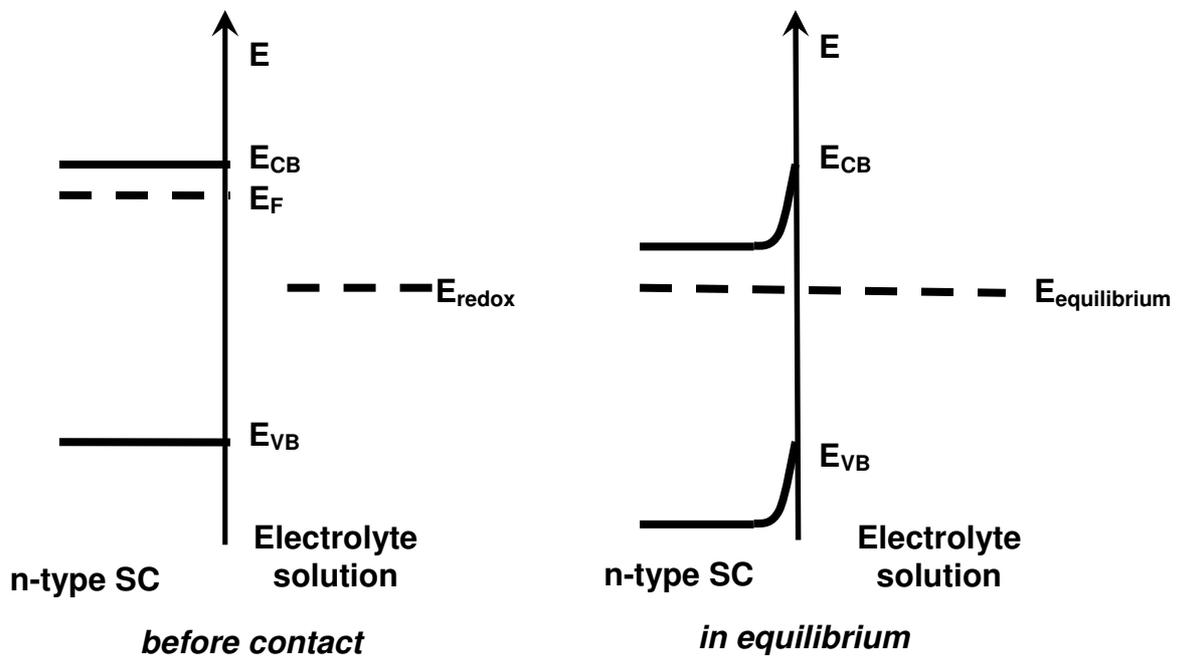


Fig. 1.1: Energetics of a n-type semiconductor-electrolyte solution interface, before contact and at equilibrium.

After contact, the former different redox potential E_{redox} of the electrolyte solution and the Fermi level E_F of the semiconductor equilibrate. As a result, the interface gets charged, which leads to a bending of the valence band (VB) and the conduction band (CB) of the semiconductor. Due to illumination of the semiconductor electrons may be excited, jumping from the valence band to the conduction band. In the space charge layer the generated charges are now separated, because the holes are attracted towards the interface and the electrons to the opposite direction. As a result, a current is observed in an outer circuit.

For a p-type semiconductor the situation is reversed. Valence and conduction bands are now bent downwards, and consequently the electrons excited by illumination are attracted by the interface, pushing the holes away. The current flowing through an outer circuit has now opposite sign. A scheme of the situation in a p-type semiconductor is shown in Fig. 1.2.

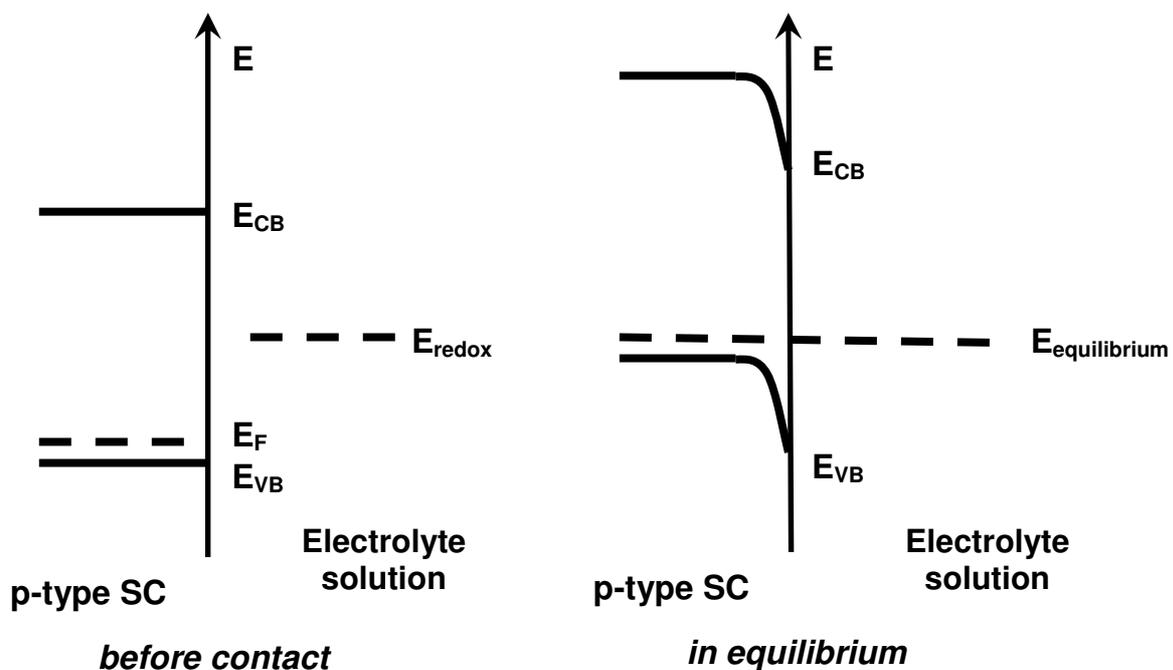


Fig. 1.2: Energetics of a p-type semiconductor-electrolyte solution interface, before contact and at equilibrium.

After the first oil crisis in 1973 alternative energy sources became of great interest, therefore a lot of research was done in the field of sunlight-to-electricity conversion. The investigated systems were mainly based on inorganic semiconductors.

When the high electrical conductivity of oxidised polyacetylene was discovered by Shirakawa, Heeger and MacDiarmid⁴⁻⁶, suddenly a new class of materials was available. Depending on their doping state, conjugated polymers offer beside insulating and metal-like conducting behaviour also semiconductor properties. Moreover, they can be processed like other polymers⁷. The application of conjugated polymers has been investigated in many fields, e.g. in batteries⁸, transistors⁹, photodiodes¹⁰, lasers¹¹, solar cells¹²⁻¹⁶ and light emitting diodes^{17,18}.

1.2 Conjugated polymers in photoelectrochemical cells

Conjugated polymers are also of interest in the studies of photoelectrochemical cells because of their semiconductor behaviour and, as a result, their photoactivity. Besides many other polymers like polyacetylenes, polyanilines (PANI) and polyphenylene-vinylenes (PPV), polythiophenes were of great interest¹⁹⁻²³. Even solid electrolytes were applied in photoelectrochemical cells²⁴, paving a way to all-solid state photoelectrochemical cells.

The working principle of such photoelectrochemical cells is shown in Fig. 1.3. For simplicity, the effects occurring at the interfaces described above (bending of conduction and valence band) are neglected in the scheme. Due to illumination electrons are excited from the valence band to the conduction band. The excited electrons are then transferred to the redox couple, i.e. reducing I_3^- to I^- . When the electrons are transferred further to the back electrode, the former reduced species is oxidised back, leaving no net chemical reaction²⁵. The hole left in the valence band is refilled from the front side by transfer of an electron from the ITO electrode to the polymer.

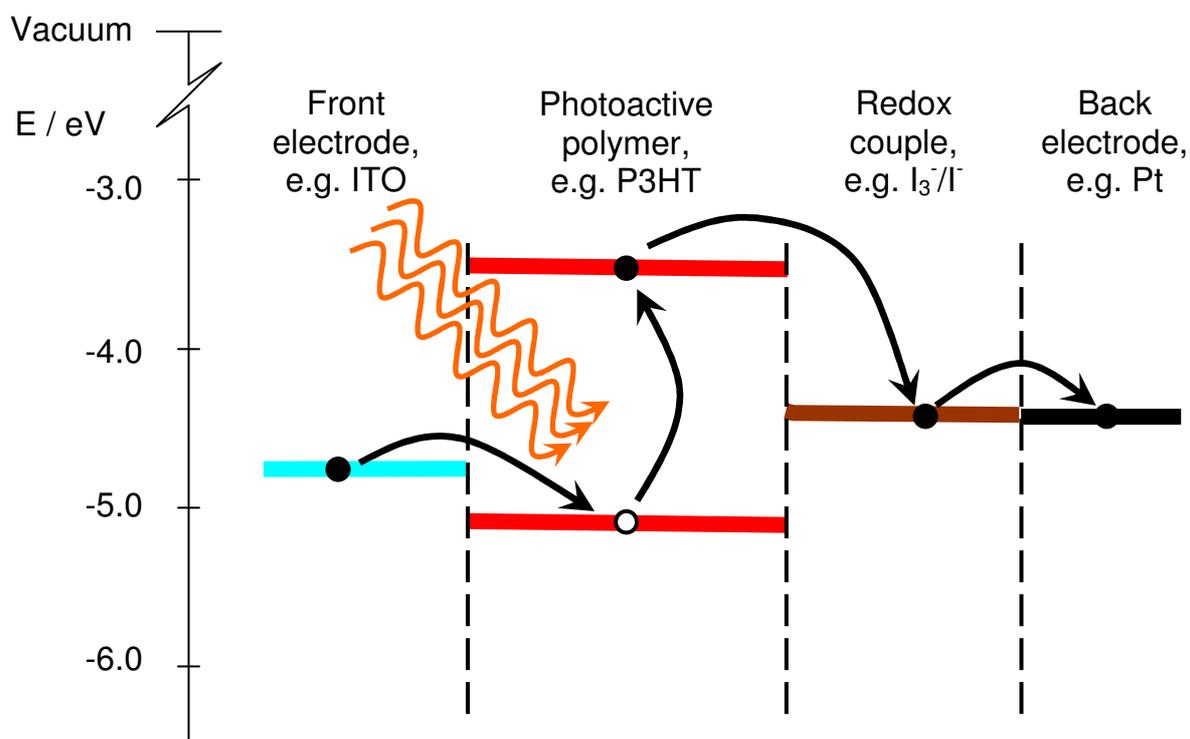


Fig. 1.3: Working principle of a photoelectrochemical cell

The properties of a photoelectrochemical cell under illumination can be investigated by applying a certain voltage and measuring the resulting current density. The current density in the situation when no voltage is applied is called short circuit current density j_{SC} , the voltage measured when no current is flowing through the cell is called open circuit voltage V_{OC} . Within these limits, at a certain point the power output, calculated as product of current density and voltage, reaches a maximum. This point is called maximum power point (mpp). Consequently, V_{mpp} and j_{mpp} are the corresponding voltage and current density values. In Fig. 1.4 an illustrating example of such a j/V characterisation is shown.

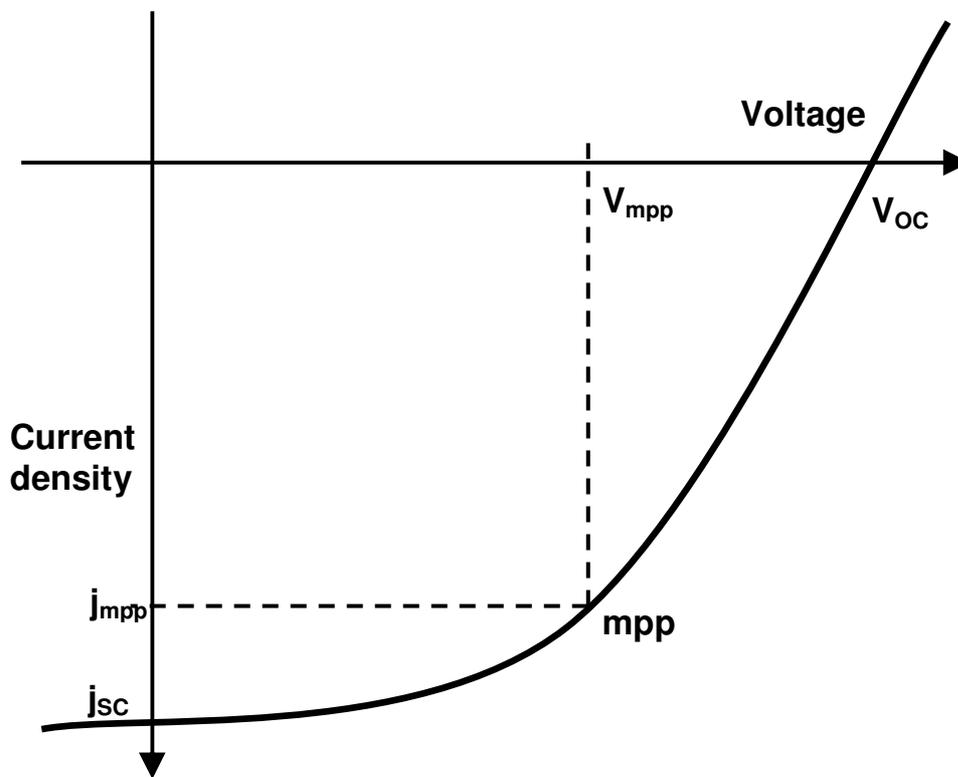


Fig. 1.4: j/V characteristics of a photoelectrochemical cell under illumination

Further important characteristics are the fill factor FF and the conversion efficiency η . They can be calculated by

$$(1) \quad FF = j_{mpp} \cdot V_{mpp} / j_{SC} \cdot V_{OC}$$

$$(2) \quad \eta = V_{OC} \cdot j_{SC} \cdot FF / P_{ill}$$

where P_{ill} as total power of light irradiating per square unit²³.

1.3 Fullerenes in photoelectrochemical cells

In typical organic polymeric solid-state solar cells the photoactive conjugated polymer is blended with electron acceptors like methanofullerenes. These materials improve the charge separation, allowing efficiencies up to 2.5%¹⁵. Therefore, regarding the ultra fast electron transfer from the polymer to the electron acceptor, they might also be useful in photoelectrochemical cells: Electron acceptor intermediate layers could improve the charge separation before the electrons would be transferred further to the redox couple. Moreover, photoelectrochemical cells using C₆₀ as photoactive material were investigated²⁶. From this point of view, conjugated polymers which have better light absorption properties could improve the cell's characteristics. In Fig. 1.5 the energetic levels of such a device is shown.

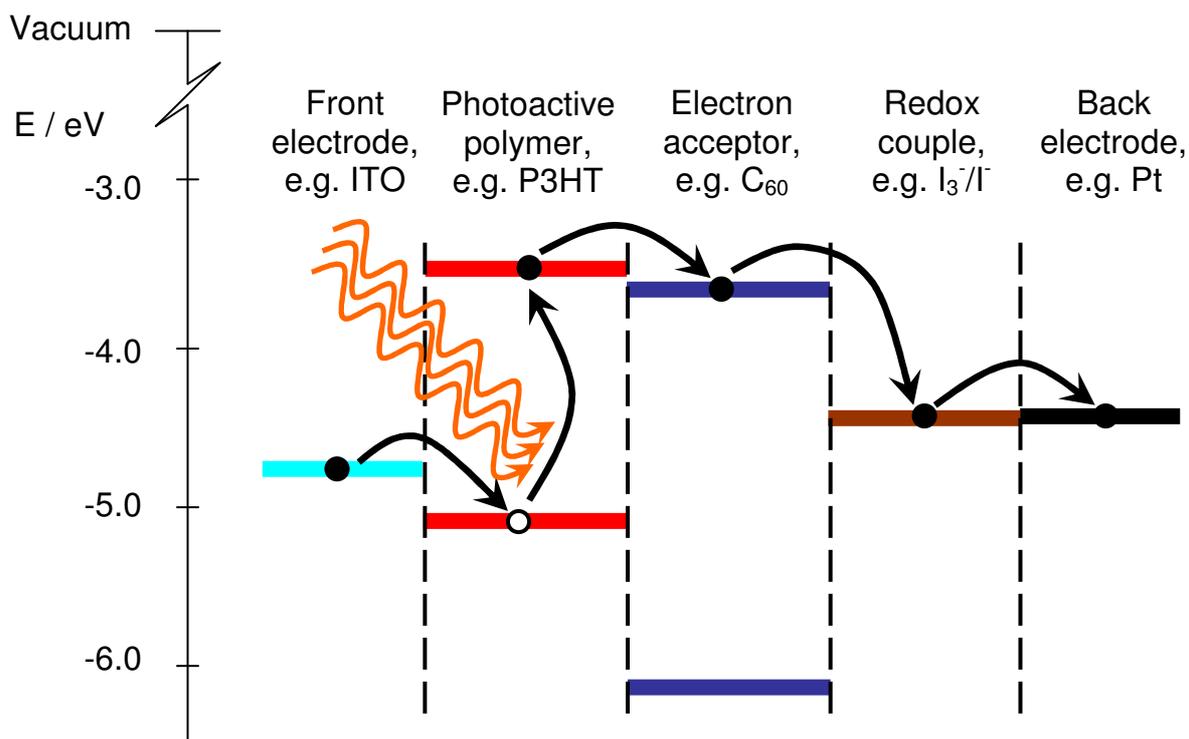


Fig. 1.5: Modification of a photoelectrochemical cell by addition of acceptor materials

The conduction band of the electron acceptor has to be lower than the photoactive polymer. So the excited electrons can be transferred from the CB of the polymer to the CB of the acceptor and further to the electrolyte.

In this study the influence of fullerenes on photoelectrochemical cells based on photoactive polymers is investigated. Various ways have been tried to incorporate electron acceptors in the polymers.

The conjugated polymers used were polythiophene derivatives, starting from soluble ones that allowed casting from solutions. Moreover, electropolymerisation was used to synthesise polymers directly on a suitable electrode. In a second step, C₆₀ was deposited on these electrodes. Finally, photoactive conjugated polymers with covalently linked acceptor units were synthesised.

UV/VIS spectroscopy of the films and j/V characterisation of the photoelectrochemical cells built from them was performed to investigate the material properties.

In addition, in-situ spectroelectrochemistry and in-situ photospectroelectrochemistry, combining electrochemistry and FTIR spectroscopy were performed to investigate the infrared spectral changes in the polymers upon oxidation and reduction as well as under illumination.

Using in-situ spectroelectrochemistry (SEC), changes in optical properties during oxidation and reduction processes can be investigated. Both electrochemistry and spectroscopy are done in the same time; therefore they are called in-situ techniques. With in-situ IR spectroscopy of conjugated polymers, polaronic transitions in the NIR/MIR can be observed^{27,28}, in addition characteristic bands, corresponding to the so-called infrared active vibration (IRAV) modes, occur below 1600 cm⁻¹ ^{29,30}.

In photospectroelectrochemistry (PSEC) the sample is additionally illuminated³¹. Using this technique, changes in the FTIR spectra caused by illumination (=photodoping) can be observed. In addition, the potential and as a result the electrochemical doping level of the photoactive polymer can be controlled and even altered during the measurement process.

2 Experimental

2.1 Sample Preparation

According to the different properties of the materials investigated in this study, the preparation of samples had to be done in various ways. For example, samples containing soluble material like poly-3-hexylthiophene (P3HT; chemical structure shown in Fig. 2.1) and 6,6-phenyl-C₆₁-butyric acid methyl ester (PCBM; Fig. 2.2) were spuncast from a solution in chlorobenzene, other materials like poly-3-methylthiophene (P3MT) were obtained by electropolymerisation.

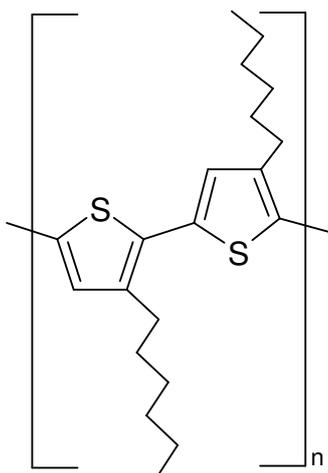


Fig. 2.1: Chemical structure of poly-3-hexylthiophene

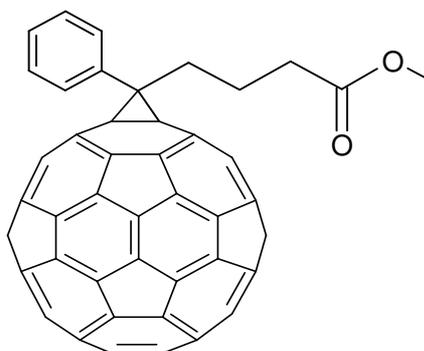


Fig. 2.2: Chemical structure of 6,6-phenyl-C₆₁-butyric acid methyl ester

2.1.1 Preparation of ITO substrates

Indium tin oxide (ITO) coated glass slides were used as substrate for all samples. They were cut into pieces of 45 x 9.5 mm, labelled and cleaned with toluene (purchased from Baker Inc.) first. Then they were rinsed with acetone (purchased from Baker Inc.) and kept in acetone on an ultrasonic bath for 10 minutes. Afterwards, the procedure was repeated using 2-propanol (purchased from Baker Inc.), and finally they were rinsed again with 2-propanol and dried in a nitrogen stream.

2.1.2 Preparation of P3HT/PCBM films

Films of pure poly-3-hexylthiophene (P3HT, purchased from Rieke Inc.) as well as blends with 6,6-phenyl-C₆₁-butyric acid methyl ester (PCBM) were processed from solution with different amounts of PCBM in 1% w/w P3HT solution in chlorobenzene (purchased from Aldrich Inc.). For comparison, a solution containing only 1% PCBM in chlorobenzene was prepared.

P3HT/PCBM sample <i>molar ratio</i>	m_{P3HT} mg	m_{PCBM} mg	V_{chlorobenzene} μl	molar ratio P3HT:PCBM
P3HT only	2.0	0.0	200	-
P3HT/PCBM 4:1	2.0	2.7	200	4 : 1
P3HT/PCBM 3:1	2.0	3.6	200	3 : 1
P3HT/PCBM 2:1	2.0	5.4	200	2 : 1
P3HT/PCBM 1.5:1	2.0	8.1	200	1.5 : 1

Table 2.1: Composition of the P3HT/PCBM solutions

In Table 2.1 the amount of the dissolved compounds and the sample volume is given. The ratio between both compounds is given as molar ratio between thiophene cores and PCBM. The solutions were kept under argon atmosphere and stirred for 24

hours using a magnetic stirrer at a temperature of 50 °C. Afterwards, samples were prepared using spincoating and Doctor Blade technique, respectively.

Spincoating was done with a Spincoater[®] Model P6700 (delivered by Specialty Coating Systems, Inc). The samples were covered with 70 µl of solution heated to 50 °C. Immediately afterwards, a program was started; using 1500 rotations per minute for a period of 70 seconds, followed by another 20 seconds at 2000 rotations per minute. The samples were completely covered with the film; this latter had to be partially removed by dissolving a portion of the layer in toluene (purchased from Baker Inc.) to ensure an electrical contact to the ITO layer when placed in the device afterwards.

For the Doctor Blade technique an Erichsen Coatmaster 509 MC was used. The temperature of the plate was 60°C, the distance from the sample to the blade 600 µm. 30 µl of solution were applied on the blade, which was then driven across the sample at a speed of 25 mm·s⁻¹. The samples were completely covered except the upper area of approximately 5 mm height, which served later on as ITO contact.

After preparation, the samples were annealed, i.e. thermally treated at temperature of 70°C for 5 min, to improve the absorption behaviour of the samples. This effect of annealing will be shown in section 3.1.1.

2.1.3 Preparation of P3MT films

Poly-3-methylthiophene (P3MT, chemical structure shown in Fig. 2.3) samples were obtained using electropolymerisation.

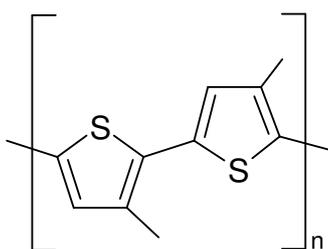


Fig. 2.3: Chemical structure of poly-3-methylthiophene

Tetrabutylammoniumhexafluorophosphate ($(C_4H_9)_4NPF_6$) (purchased from Aldrich Inc.) was dried under vacuum at a temperature of 180 °C for at least 2 hours, then it was dissolved in 50 ml acetonitrile (purchased from Merck Inc.) to obtain a 0.1 M electrolyte solution. Afterwards, 3-methyl-thiophene (purchased from Fluka Inc., distilled and stored over molecular sieve 10 Å) was added to obtain a concentration of $0.025 \text{ mol}\cdot\text{l}^{-1}$ on monomer. The solution was flushed with Argon (purchased from Linde Inc., purity 5.0) for 15 minutes.

For the electrochemical experiments, first a Jaissle 1002T NC potentiostat, a Prodis 1/4 I sweep generator and a Rikadeni RY-PIA x-y recorder were used. Later on, a computer supported system based on a Jaissle 1030 PC T potentiostat controlled by ECS WIN, developed by Ingenieurbüro Schrems, was used. The electrochemical cell consisted of an ITO/glass sample as working electrode (active area approximately 3.5 cm^2), a Pt foil as counter electrode and a silver wire coated with AgCl as quasireference electrode. The Ag/AgCl quasireference electrode was calibrated against the ferrocene/ferrocenyl redox couple (purchased from Merck Inc., $E^0 = 400 \text{ mV vs. NHE}$). A schematic picture of the setup called "standard electrochemical setup" in this thesis is shown in Fig. 2.4.

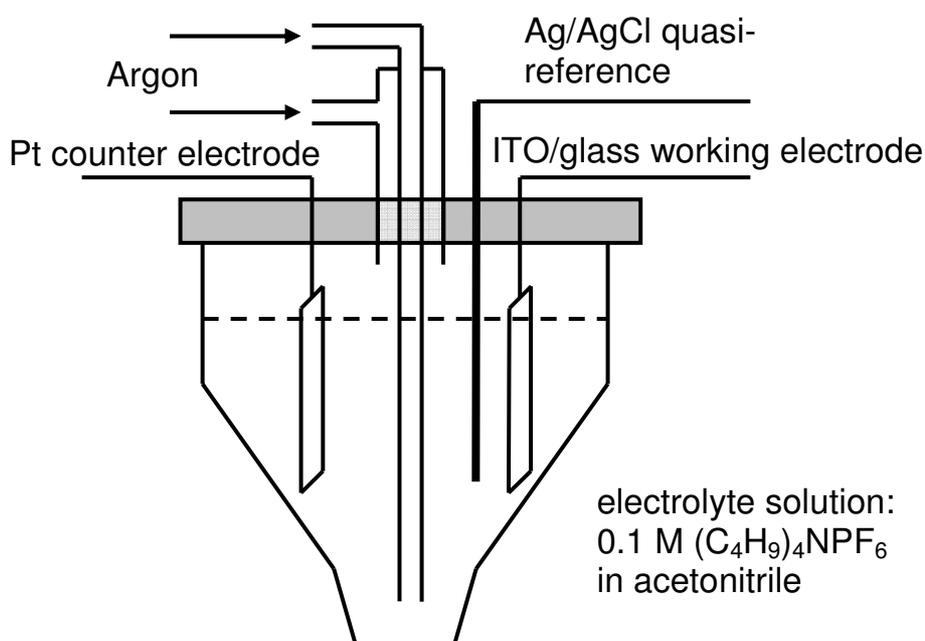


Fig. 2.4: Scheme of the standard electrochemical setup

Electropolymerisation was performed using either cyclic voltammetry (CV) or a constant potential method (CP). Cyclic voltammetry was performed between 0 and 1800 mV vs. Ag/AgCl, using a scan speed of $100 \text{ mV}\cdot\text{s}^{-1}$ and varying the number of cycles. In constant potential experiments a potential of 2000 mV vs. Ag/AgCl was applied. After preparation the polymer films were re-reduced to the neutral form by applying a potential of 0 mV vs. Ag/AgCl until the residual current dropped below $0.1 \mu\text{A}$. The samples were then rinsed with acetonitrile to remove electrolyte residues and dried under a nitrogen flow. Cyclic voltammograms of the samples were recorded using the same electrochemical measurement setup, but using monomer-free electrolyte solution ($0.1 \text{ M } (\text{C}_4\text{H}_9)_4\text{NPF}_6$ in acetonitrile).

2.1.4 Deposition of C_{60} clusters on P3MT films

Incorporation of fullerenes into electropolymerised P3MT was tried by deposition of C_{60} clusters²⁶. First, a 0.4 mM solution of C_{60} in toluene was prepared by dissolving 1.2 mg of C_{60} in 2 ml toluene (purchased from Merck Inc., stored over molecular sieve 10 \AA), storing the solution under argon and stirring it with a magnetic stirrer for 24 hours. C_{60} clusters were obtained by injecting the solution with a syringe in the threefold volume of anhydrous acetonitrile (purchased from Merck Inc., anhydrous). C_{60} is not soluble in acetonitrile; as a result C_{60} clusters with a diameter of 100 to 200 nm were formed.

A P3MT sample and a platinum electrode were assembled in a cuvette and the C_{60} suspension was transferred to the electrochemical setup by a syringe. The C_{60} clusters were electrodeposited on P3MT samples by using them as anode, the Pt foil as cathode and applying a voltage of 200 V on them by a Fluka 412 B High Voltage Power Supply. The C_{60} clusters were deposited on the anode forming a brown layer, the solution was clear within one to two minutes. To deposit less the voltage was applied for a shorter period of time. After the electrodeposition the P3MT film was partially oxidised. For reducing it to the neutral form, the sample was transferred into a 0.1 M solution of $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ in acetonitrile and used as working electrode. A potential of 0 mV vs. Ag/AgCl quasireference electrode was applied, a Pt foil served as counter electrode. Afterwards, the samples were rinsed with acetonitrile and dried under nitrogen.

2.1.5 Preparation of Poly-ITB-C₆₀ and copolymer films

Poly-ITB-C₆₀ films were prepared by electropolymerisation of ITB-C₆₀ (provided by M. Maggini, University of Bologna; chemical structure shown in Fig. 2.5). In addition, ITB-C₆₀ was copolymerised with bithiophene. The chemical structure of the obtained random copolymer is shown in Fig. 2.6.

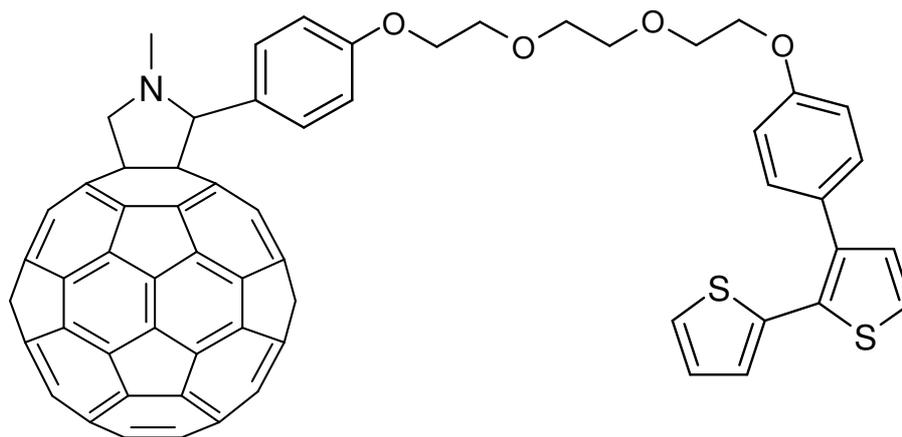


Fig. 2.5: Chemical structure of the bithiophene-fulleropyrrolidine ITB-C₆₀

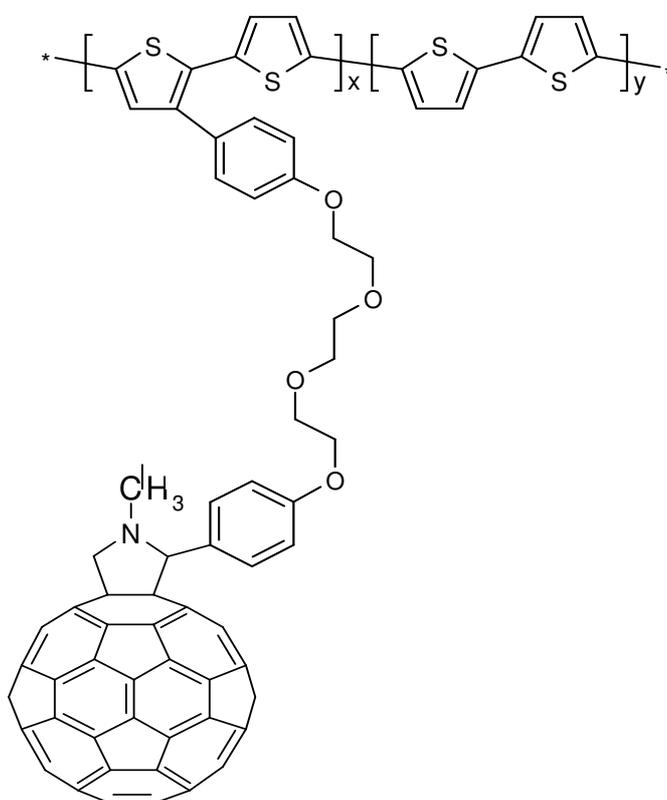


Fig. 2.6: Chemical structure of a random copolymer of ITB-C₆₀ and bithiophene

For solubility reasons acetonitrile could not be used as solvent for ITB-C₆₀, thus a 0.1 M solution of (C₄H₉)₄NPF₆ in acetonitrile/toluene (30:70, v:v) was chosen as supporting electrolyte. ITB-C₆₀ as well as bithiophene, which was copolymerised with ITB-C₆₀, were dissolved in this electrolyte solution.

The concentration of ITB-C₆₀ in the electrolyte solution was 0.3 mg·ml⁻¹ or 0.25 mM, an overview of the solutions containing both ITB-C₆₀ and bithiophene is given in Table 2.2.

ITB-C₆₀/bithiophene monomer solutions	b_{ITB-C60} mg·ml ⁻¹	b_{BiTh} mg·ml ⁻¹	C_{ITB-C60} mM	C_{BiTh} mM	b_{ITB-C60} : b_{BiTh}
ITB-C ₆₀ only	0.3	–	0.25	–	–
ITB-C ₆₀ / bithiophene	0.3	0.3	0.25	1.8	1:1
ITB-C ₆₀ / bithiophene	0.3	0.6	0.25	3.6	1:2
ITB-C ₆₀ / bithiophene	0.3	1.0	0.25	6.0	1:3

Table 2.2: Composition of the solutions used for electropolymerisation of ITB-C₆₀ as well as its copolymers

The solutions were transferred into a cuvette, serving as cell compartment. The standard electrochemical cell could not be used because it had a volume of 50 ml, which was too much when working with small quantities of substance.

ITO/glass served as working electrode, a platinum foil as counter electrode and a silver wire coated with AgCl as quasireference electrode. The reference electrode was placed inside a plastic tube to prevent any contact to the other electrodes. A schematic picture of this "mini cell" is shown in Fig. 2.7.

Argon (purchased from Linde Inc., purity 5.0) was led through the solution by a syringe needle, and the cell was placed in a plastic housing which was also flushed with Argon to prevent unwanted exposition to oxygen and moisture.

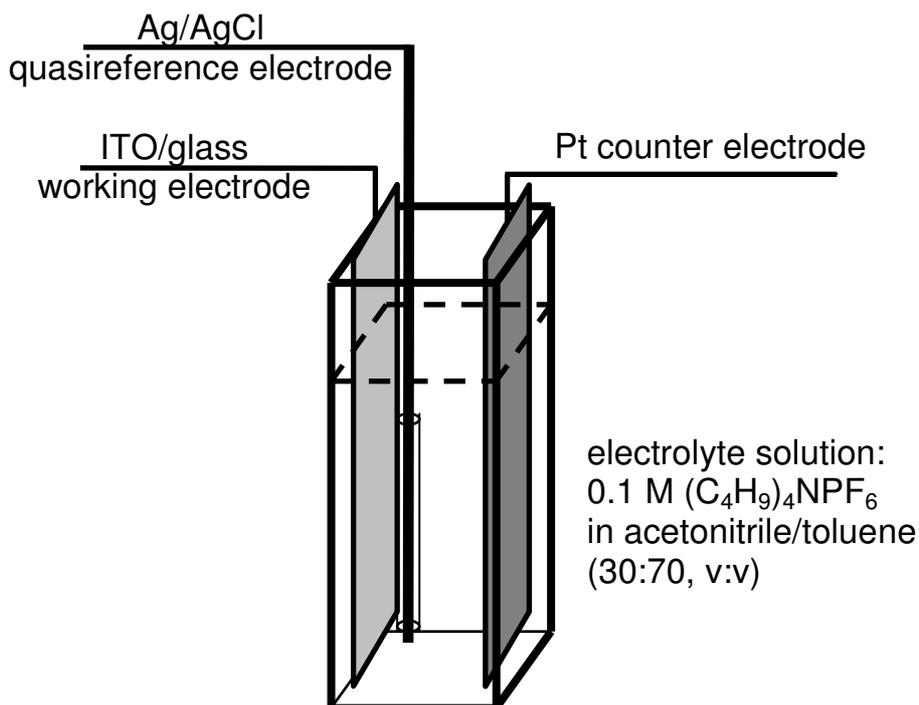


Fig. 2.7: Experimental setup for electrochemical experiments using small quantities of substance

Electropolymerisation was done using the constant potential method (CP) with a potential of 1250 mV vs. a Ag/AgCl quasireference electrode. After electropolymerisation the sample was removed from the reaction compartment still in the oxidised state, because the neutral form of the deposited polymer would have been soluble in the toluene containing electrolyte solution. Therefore, the reduction to the neutral form had to be performed in a toluene-free solution. The samples were rinsed with acetonitrile, afterwards they were reduced to the neutral form in an electrolyte solution containing 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ in acetonitrile, using the electrochemical setup described above. The samples were again rinsed with acetonitrile and dried under nitrogen.

For comparison, samples containing only polybithiophene were also produced. Electropolymerisation of bithiophene was done using the standard electrochemical setup and an electrolyte solution containing 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ in acetonitrile and 0.015 M bithiophene. A constant potential of 1250 mV vs. Ag/AgCl quasireference electrode was applied, afterwards the sample was reduced to the neutral form and characterised like the other copolymer samples.

2.1.6 Preparation of Poly-TIO-TEG-C₆₀-NCH₃ films

Like ITB-C₆₀, TIO-TEG-C₆₀ (provided by G. Possamai and M. Maggini, University of Bologna) is a fulleropyrrolidine covalently linked to a thiophene group, its chemical structure is shown in Fig. 2.8.

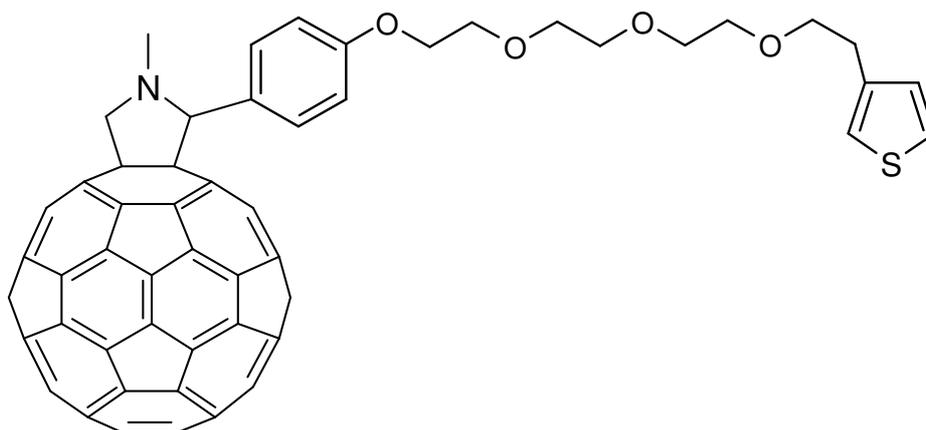


Fig. 2.8: Chemical structure of the thiophene-fulleropyrrolidine TIO-TEG-C₆₀-NCH₃

Because electropolymerisation of this monomer following the same procedure using ITB-C₆₀ (see chapter 2.1.5) was not possible, different electrolyte solutions (0.1 M (C₄H₉)₄NPF₆ in acetonitrile/toluene (30:70, v:v); 0.1 M (C₄H₉)₄NPF₆ in dichloromethane) and different working electrodes (platinum, ITO/glass) had been tried. The experiments were performed using the mini cell electrochemical setup.

Finally, it was possible to deposit a yellow material on Pt, using 0.1 M (C₄H₉)₄NPF₆ in dichloromethane as electrolyte solution, a concentration of 0.30 mg·ml⁻¹ TIO-TEG-C₆₀-NCH₃ and a constant potential of 1700 mV vs. Ag/AgCl quasireference electrode. Cyclic voltammetry of the obtained material was performed using the standard electrochemical setup and 0.1 M (C₄H₉)₄NPF₆ in acetonitrile as electrolyte solution.

2.2 Sample characterisation

2.2.1 UV/VIS absorption

UV/VIS absorption spectra were recorded using a Hewlett Packard HP 8453 Diode array spectrometer in a spectral range between 190 and 1100 nm. First, an ITO/glass slide was used as blank sample; afterwards the spectral absorption of the polymer samples was measured. The usable spectral window was 280 to 1100 nm because of the non-transparency of ITO/glass in the spectral region below 280 nm.

2.2.2 Cyclic voltammetry

For cyclic voltammetry the same setup as for the electropolymerisation was used, namely a Jaisle 1002T NC potentiostat, a Prodis 1/4 I sweep generator and a Rikadeni RY-PIA x-y recorder, later on a computer supported system controlling a Jaisle 1030 P potentiostat and the software package ECS WIN, developed by Ingenieurbüro Schrems. In all cases 0.1 M $(C_4H_9)_4NPF_6$ in acetonitrile was used as electrolyte solution, a schematic picture of the setup had already been shown in Fig. 2.4.

2.2.3 Atomic force microscopy (AFM)

To investigate the electrode surface, AFM images were taken using a Nanoscope IIIa from Digital Instruments in contact mode.

2.2.4 j/V characterisation

For j/V characterisation, photoelectrochemical cells had to be assembled. They consisted of the polymer sample, a platinum counter electrode (rolled platinum attached on a glass slide) and a spacer (Vitron, 25 μm) separating both electrodes. A sample holder was designed to hold both electrodes in place as well as to limit the photoactive area to 1 cm^2 . As redox couple the system I_3^-/I^- was used, the electrolyte solution contained 0.5 mM $(\text{C}_6\text{H}_{13})_4\text{NI}$ (purchased from Fluka Inc.) as well as 0.06 mM I_2 (purchased from Merck Inc.) in propylene carbonate (purchased from Aldrich Inc., anhydrous). A detailed scheme of the photo-electrochemical cell is shown in Fig. 2.9.

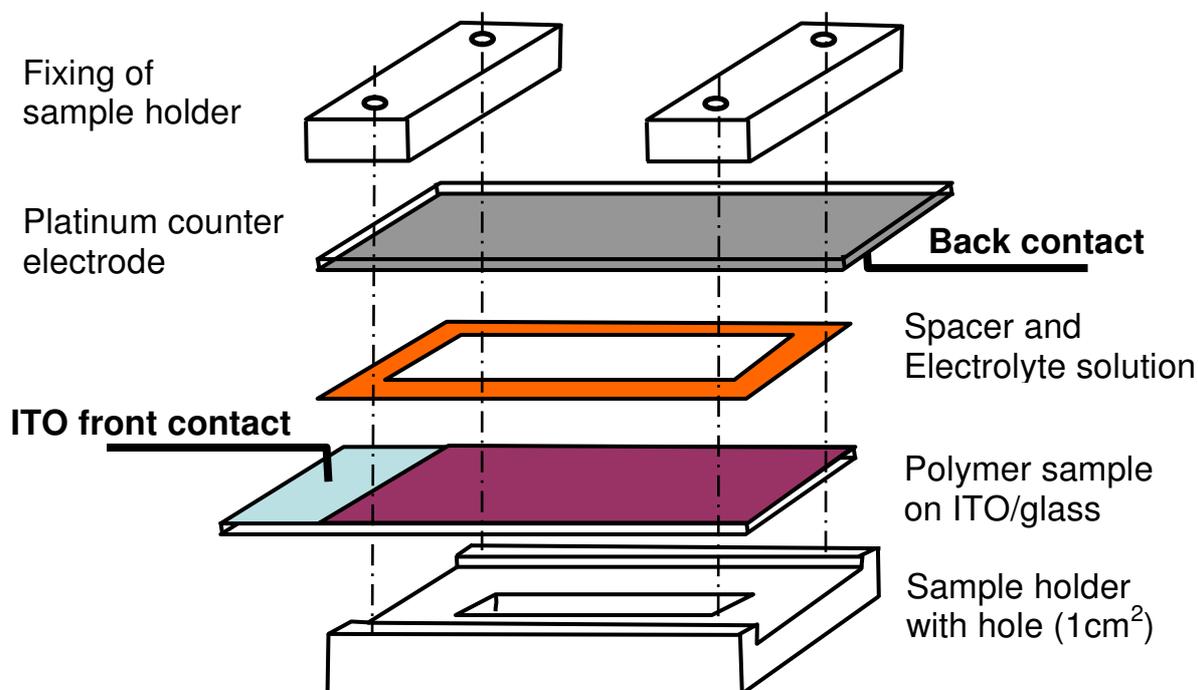


Fig. 2.9: Schematic assembling of the photoelectrochemical cells

To assemble the photoelectrochemical cell, first the sample was placed with the glass side down on the sample holder. Second, a spacer was placed on top of the sample, and some drops of electrolyte solution were put on top of the polymer surface. Afterwards the back electrode was placed on top of the spacer, leaving no air bubbles inside, and the sample was fixed with two holders. The sample could now be turned upside down and illuminated from top. Finally, two electrical contacts were connected to the front- and the back electrode.

j/V curves were recorded both in dark (photoactive area was covered with aluminum foil) and in simulated sunlight. For illumination, a Solar Constant 575 with AM 1.5 filter was used; it was calibrated to a incident light intensity of $80 \text{ mW}\cdot\text{cm}^{-2}$ using an AM 1.5 calibrated single crystal Si photodiode.

The measurement system consisted of a Keithley 2400 SMU source meter controlled by a LABVIEW[®] measurement program. The measurement started at a voltage of -20 mV and usually ended about 50 mV after reaching the open-circuit voltage, normally between 150 and 250 mV . The potential was stepwise increased, averaging over 10 measurement points, the average step height was chosen between 4 and 5 mV .

2.3 In-situ FTIR spectroscopy

For both spectroelectrochemistry and photospectroelectrochemistry measurements a Bruker IFS 66/S FTIR spectrometer in attenuated total reflection (ATR) geometry was used³²⁻³⁴.

The electrochemical cell consisted of a germanium reflection element which was covered with the photoactive polymer and served as working electrode, and a teflon housing that contained a platinum counter electrode, an Ag/AgCl quasireference electrode and in- and outlets for a continuous circulation of the electrolyte solution. A scheme of the setup is shown in Fig. 2.10. In addition, for photospectroelectrochemistry the tip of a laser fibre had to be inserted into the cell.

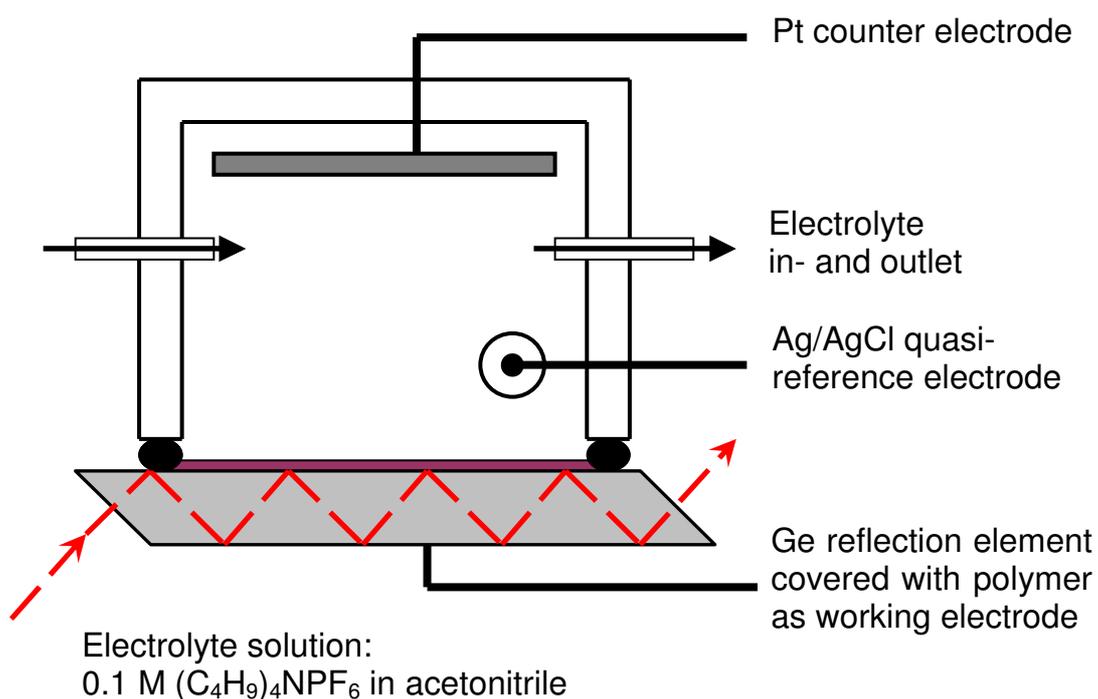


Fig. 2.10: Experimental setup for in-situ FTIR spectroelectrochemistry, performed in ATR geometry. For in-situ FTIR photospectroelectrochemistry the same setup was used, moreover the tip of a laser fibre was inserted in the cell.

The germanium reflection elements were polished using 1 μm and 0.25 μm diamond paste, afterwards they were rinsed with deionised water and distilled acetone. For improving the electrochemical behaviour of the working electrode, a thin platinum (purchased from Aldrich Inc.) layer was evaporated on the germanium element, using a Balzers MED 010 WF 302. The thickness was controlled by a comparison of a similar treated glass slide with calculated spectra.

Before measurement the spectrometer system was purged with nitrogen for at least half an hour to eliminate unwanted H_2O and CO_2 bands.

The electrodes were connected a Jaissle 1002T NC potentiostat, controlled by a Prodis 1/4 I sweep generator. Potentials and currents were recorded by a Rikadeni RY-PIA x-y recorder.

An electrolyte solution containing monomer was injected into the cell, the monomer was electropolymerised by applying a constant potential (+1800 mV vs. Ag/AgCl quasireference electrode for thiophene-based monomers, +1300 mV for bithiophene-based monomers) for about 30 seconds. Afterwards, the cell was purged with monomer-free electrolyte solution and a constant potential of 0 mV was applied to reduce the polymer to the neutral form.

2.3.1 In-situ FTIR spectroelectrochemistry

In-situ FTIR spectroelectrochemistry was performed by recording FTIR spectra simultaneously to cyclic voltammetry. Starting from 0 mV vs. Ag/AgCl quasireference electrode, the potential was increased to +1000 mV, afterwards decreased to -1500 mV and finally increased again to 0 mV. The scan rate was 5 $\text{mV}\cdot\text{s}^{-1}$. Meanwhile FTIR spectra were recorded, consecutively taking 32 scans for one spectrum.

The recorded spectra were compared to a reference spectrum of the neutral polymer by calculating $\Delta(-\log T_{\text{ATR}})$, with T_{ATR} being the transmittance in the ATR geometry.

2.3.2 In-situ FTIR photospectroelectrochemistry

For in-situ FTIR photospectroelectrochemical studies, a laser fibre was inserted in the cell. An Ar⁺ laser with a wavelength of 476 nm was used; the light intensity on the fibre tip was 30 mW. Moreover, a shutter was placed in the pathway of the laser beam, so the illumination of the cell could be easily turned on and off. A constant potential was applied and after the residual current had stabilised an alternating series of 10 times 10 spectra in dark and under illumination was recorded. During this process the current flowing through the cell was recorded.

The relative spectra were calculated by $-\Delta T/T$, that is the difference between the spectra in dark and under illumination divided by the spectrum in dark.

3 Results and Discussion

3.1 P3HT/PCBM films

In typical organic polymeric solid state devices used for light-to-current conversion photoactive polymers are blended with acceptor molecules like C_{60} or its derivatives to improve charge separation of the excited species in the polymer. Moreover, charge transport and consequently both short circuit current as well as efficiency of the cell are improved^{15,35}. As already discussed in chapter 1.3, the fast electron transfer from the photoactive polymer to the electron acceptor could be also used in photoelectrochemical cells to enhance the electron transfer to the redox couple of the photoelectrochemical cell.

Poly-3-hexylthiophene (P3HT) and 6,6-phenyl- C_{61} -butyric acid methyl ester (PCBM) have been already used to produce solid state devices³⁵, therefore these compounds have been chosen to start investigations in photoelectrochemical cells. Both P3HT and PCBM are soluble compounds; their structures have been already shown in Fig. 2.1 and Fig. 2.2. Blends of these materials can be obtained quite easily by processing solutions containing both compounds.

To investigate the influence of C_{60} on the polymer's properties in a photoelectrochemical cell, samples with varying composition were prepared. Starting with pure P3HT, the molar ratio of PCBM to thiophene cores was subsequently increased from 1:4 to 1:1.5. The compounds were dissolved in chlorobenzene, and films on an ITO/glass substrate were spincoated or prepared by Doctor Blade technique, respectively.

3.1.1 P3HT/PCBM - spincoated

After preparation, the films were annealed to improve absorption in the spectral region between 450 and 650 nm. In Fig. 3.1 UV/VIS absorption spectra of a spincoated blend of P3HT and PCBM before and after the annealing process are shown. The molar ratio of P3HT to PCBM was 3:1. It can be seen easily that the absorption of the annealed film in the spectral region mentioned above is increased significantly³⁵.

Fig. 3.2 shows UV/VIS absorption spectra of spincoated P3HT films with varying PCBM content. Starting from pure P3HT, blends with a molar ratio of 1:4, 1:3, 1:2 and 1:1.5 (PCBM to thiophene core) are shown. Higher PCBM content leads to higher adsorption in the spectral range below 450 nm, on the other hand the adsorption in the spectral region between 450 and 650 nm is decreased.

These P3HT/PCBM films on an ITO electrode were characterised in a photoelectrochemical cell (PEC), using I_3^-/I^- in propylene carbonate as electrolyte solution and a platinum counter electrode. j/V curves were measured in a voltage range between -20 and $+200$ mV, both in dark and under illumination by simulated sunlight (AM 1.5, $80 \text{ mW}\cdot\text{cm}^{-2}$). Fig. 3.3 shows the recorded j/V curves, in Table 3.1 the characteristics of these cells are given in numbers. It is shown that both V_{OC} and j_{SC} are increased dramatically by adding PCBM to the pristine material. Therefore, the efficiency of such a device could be increased by two orders of magnitude.

P3HT/PCBM sample ratio	V_{oc} mV	j_{sc} $\mu\text{A}\cdot\text{cm}^{-2}$	fill factor	η %
P3HT only	62	-10	0.22	0.0002
P3HT/PCBM 4:1	105	-171	0.18	0.0039
P3HT/PCBM 3:1	134	-258	0.20	0.0086
P3HT/PCBM 2:1	148	-373	0.19	0.0130
P3HT/PCBM 1.5:1	154	-398	0.19	0.0145

Table 3.1: Characteristics of PECs from P3HT/PCBM samples, prepared by spincoating

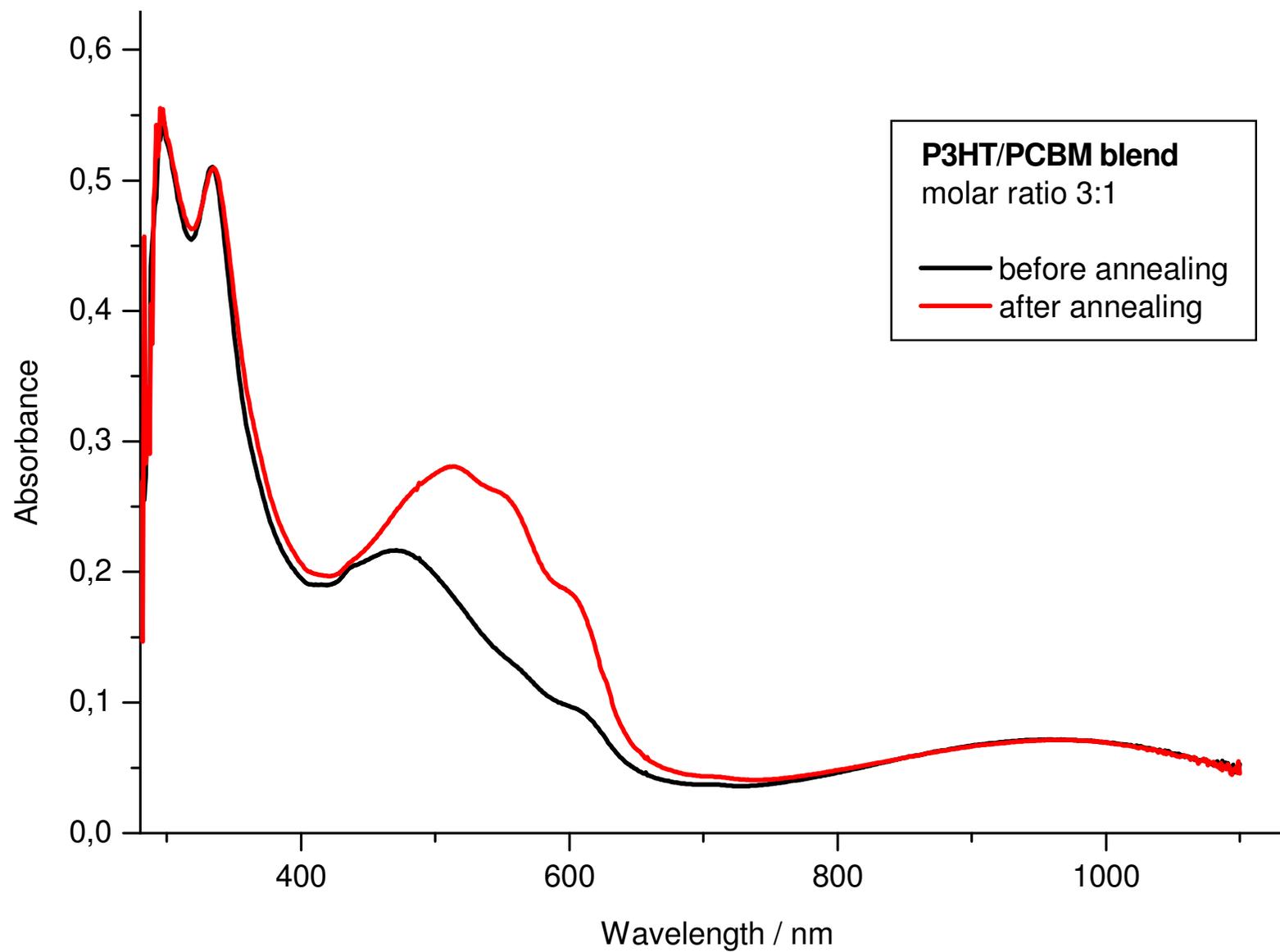


Fig. 3.1: Absorption spectra of a P3HT/PCBM blend before and after annealing

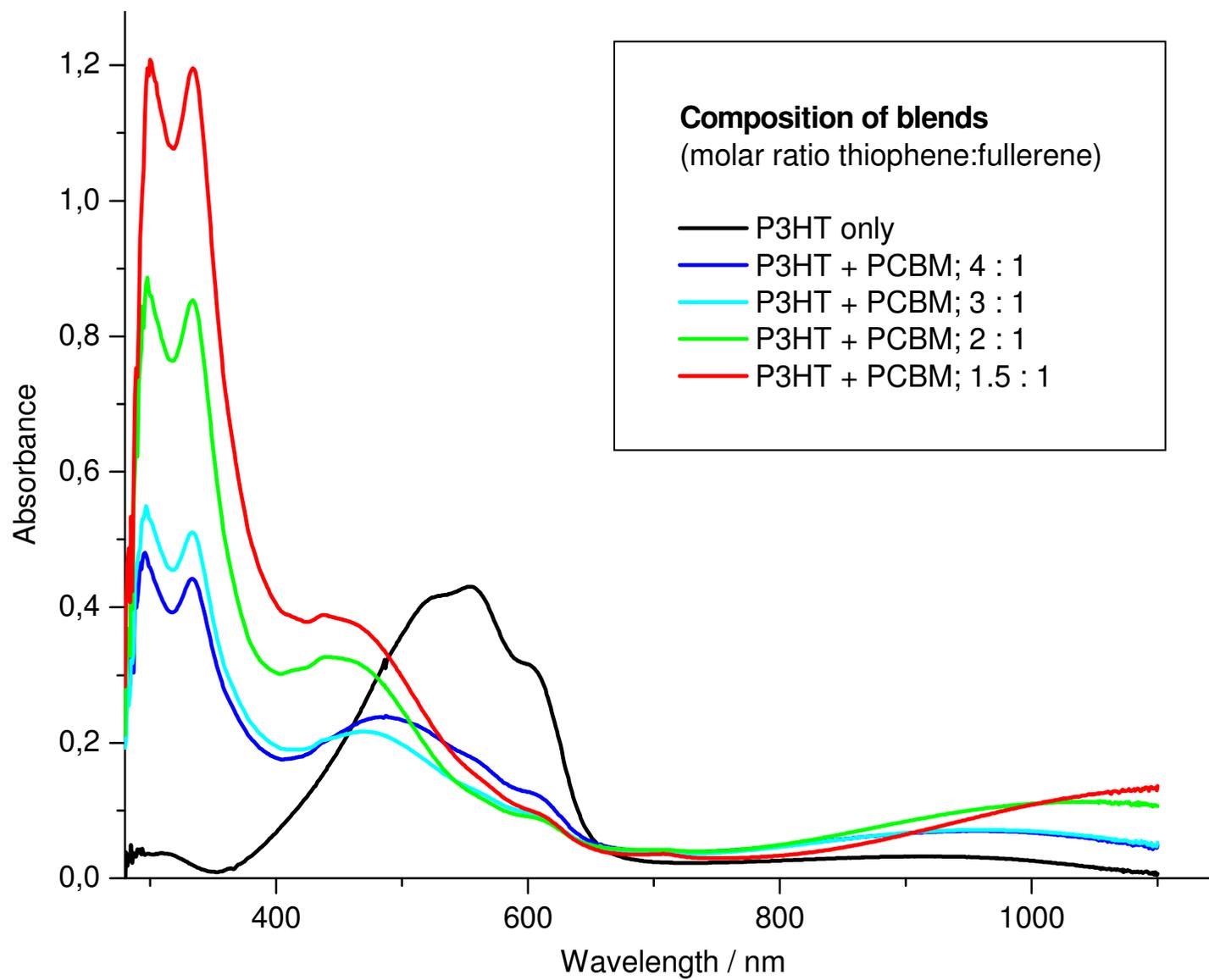


Fig. 3.2: Absorption spectra of annealed P3HT/PCBM samples

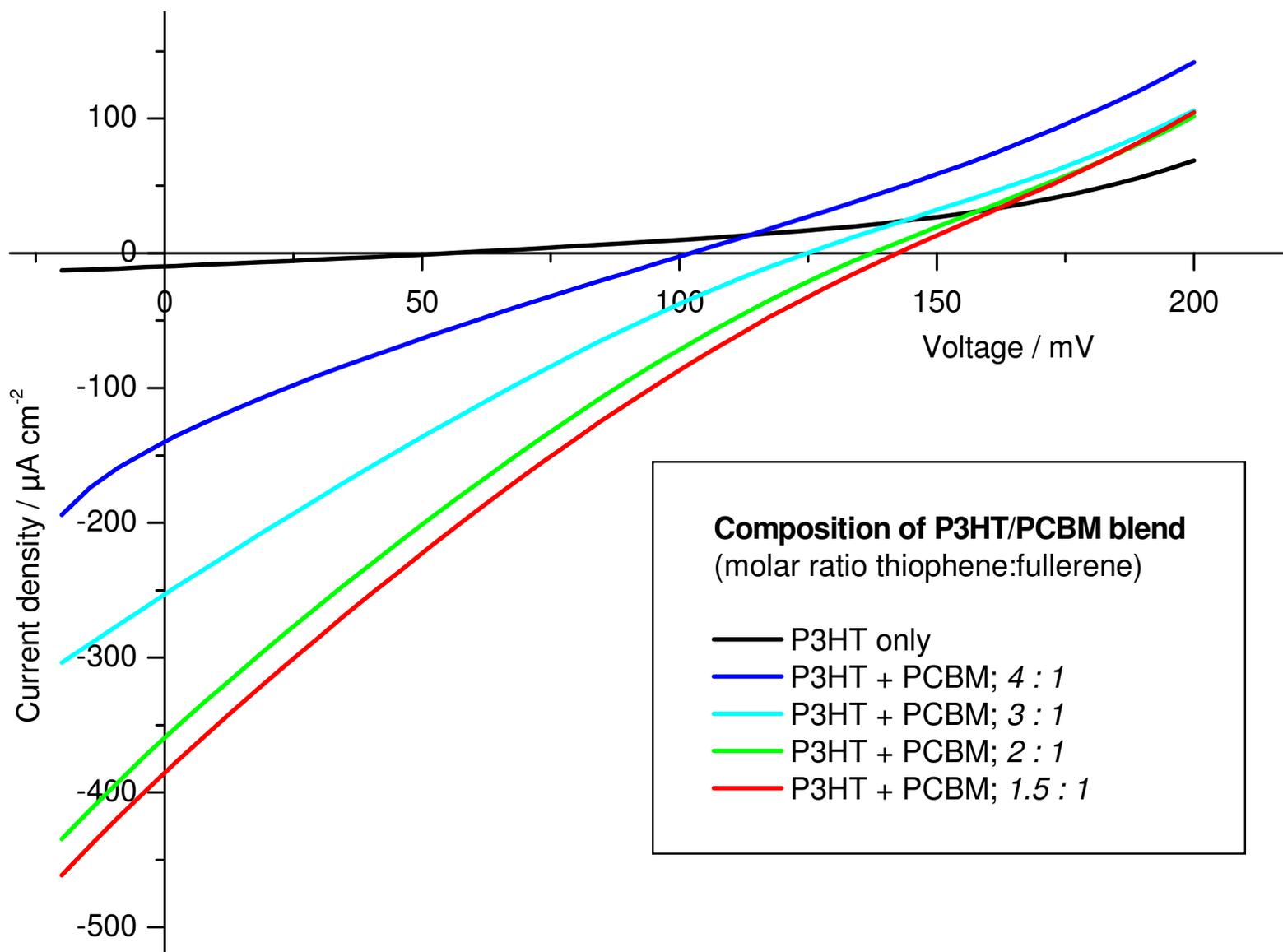


Fig. 3.3: j/V curves of PECs from spincoated P3HT/PCBM films

In addition, films containing only PCBM without any photoactive polymer were also prepared. They could not be characterised like the blends, because the PCBM layer was rapidly dissolved during the measurement.

Such a loss of PCBM was also observed during the j/V characterisation of the blends, but the changes in the cell's performance were less dramatic. These losses led to a colour change of the film towards purple, an illustrating example is shown in Fig. 3.4.

The spectral absorption below 450 nm is decreased because of the loss of PCBM, the absorption in the spectral range between 450 nm and 650 nm is slightly increased. The reason for this behaviour could be crystallisation processes, which can take place when PCBM, having caused disorder within the polymer matrix before, is removed by the solvent during the experiment.

It has to be mentioned that PCBM should not have too much solubility in polar solvents like propylene carbonate. Nevertheless, during operation a charge transfer from the excited photoactive polymer to the fullerene takes place; consequently the molecule gets charged and therefore more soluble in a polar solvent.

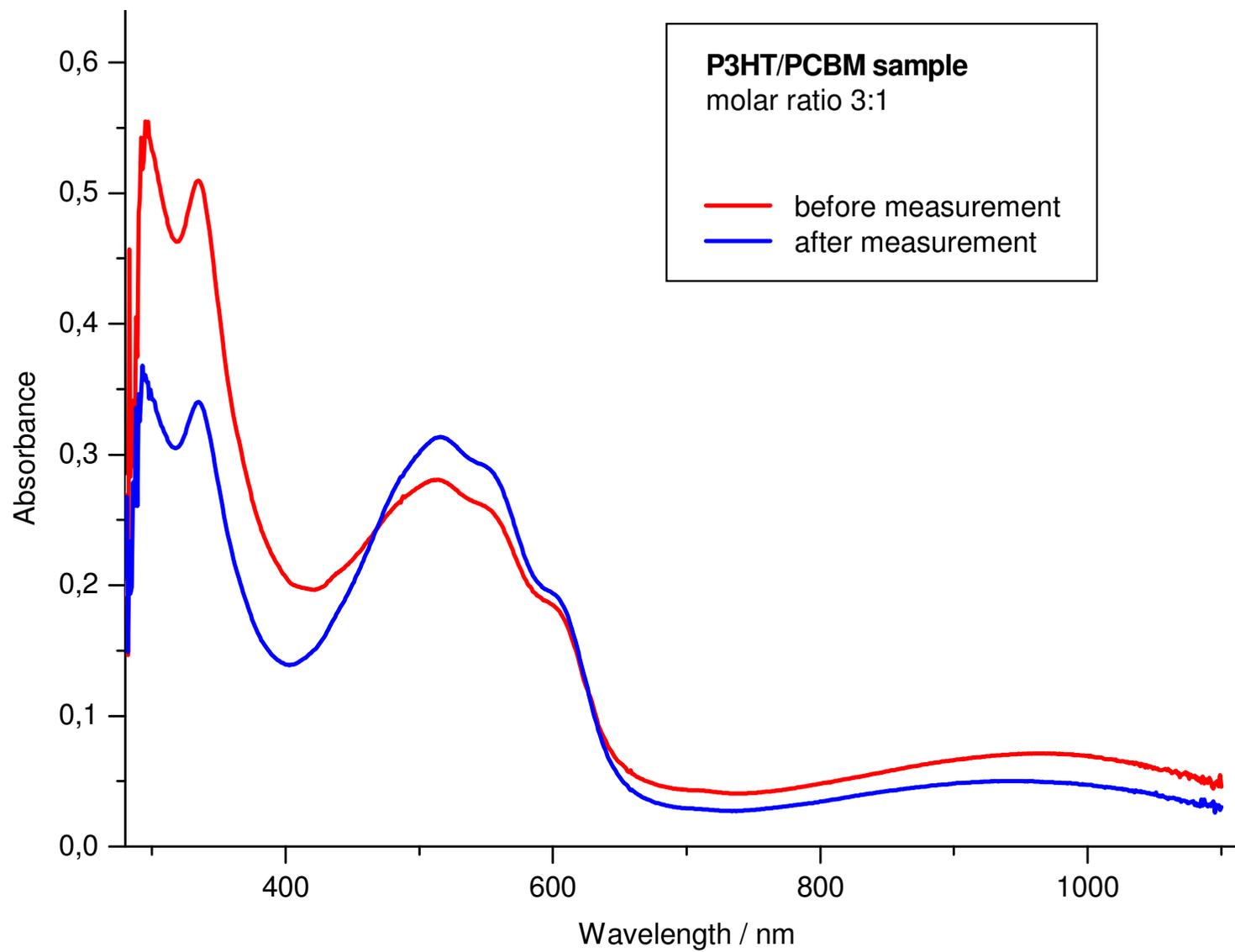


Fig. 3.4: Absorption spectra of a P3HT/PCBM sample, before and after measurement

3.1.2 P3HT/PCBM – Doctor Blade technique

Another method to cast polymer films on ITO/glass substrates is Doctor Blade technique. Using the same solutions as for spincoating, similar films were produced. The samples were also annealed and characterised in a PEC. The results which were obtained are comparable to those of the spincoated films; a detailed overview is given in Table 3.2. Again, both V_{oc} and j_{sc} are increasing with higher PCBM content.

P3HT/PCBM sample <i>ratio</i>	V_{oc} mV	j_{sc} $\mu A \cdot cm^{-2}$	fill factor	η %
P3HT only	39	-6	0.24	0.0001
P3HT/PCBM 4:1	121	-185	0.22	0.0062
P3HT/PCBM 3:1	120	-244	0.22	0.0079
P3HT/PCBM 2:1	108	-315	0.20	0.0087
P3HT/PCBM 1.5:1	135	-420	0.21	0.0153

Table 3.2: Characteristics of PECs from P3HT/PCBM samples, prepared by Doctor Blade technique

3.1.3 PEDOT/PSS - P3HT/PCBM – Doctor Blade technique

In the photoelectrochemical cell, the redox couple in the electrolyte solution is reduced by the electrons which were generated in the polymer molecules excited by illumination. The counter reaction, in this case the oxidation of the redox couple, should take place on the back electrode. Unfortunately, the reaction will take place also at the ITO front electrode if the dissolved species can penetrate the photoactive polymer layer, causing internal shorts and therefore reducing both currents and efficiencies of such devices.

An attempt to overcome this problem was the deposition of a hole conducting layer prior to the photoactive layer on the ITO substrate. A layer of poly-3,4-ethylenedioxythiophene mixed with polystyrene sulfonic acid (PEDOT:PSS, Baytron P, purchased from Bayer) was applied on the ITO/glass sample by Doctor Blade technique, afterwards P3HT/PCBM layers were cast on top using the same technique.

Unfortunately, it was not possible to improve the device using this intermediate layer, because it was dissolved by the electrolyte solution. As a result, the photoactive layer did not stick any longer to the ITO substrate and the photoelectrochemical cells did not work any more.

3.2 P3MT films

Poly-3-methylthiophene (P3MT) is another thiophene-based photoactive polymer, its chemical structure has been shown in Fig. 2.3. It can be easily produced by electrochemical oxidation of 3-methylthiophene, and photoelectrochemical cells using P3MT have been well studied in the past¹⁹⁻²¹.

First, P3MT films were prepared by electrochemical oxidation to study the properties of the pure material. Afterwards, further experiments were carried out to incorporate fullerenes as acceptor materials onto the polymer film. Again, photoelectrochemical cells using such films were assembled and their properties were investigated and compared to those of pure P3MT films.

In addition, in-situ FTIR-studies have been performed. The results of these in-situ spectroelectrochemical and in-situ photospectroelectrochemical studies are shown in section 3.4.1 and 3.4.2 respectively.

3.2.1 Pure P3MT films

3-Methylthiophene was oxidised in a solution of 0.1 M tetrabutylammonium-hexafluorophosphate in acetonitrile. The techniques which were used to deposit the polymer on a ITO/glass electrode were cyclic voltammetry (CV) as well as constant potential method (CP). After deposition, the samples were rinsed with acetonitrile, and the polymer was reduced to neutral form in a monomer-free electrolyte solution. The sample were rinsed again with acetonitrile and dried under nitrogen.

In Fig. 3.5 a cyclic voltammogram of P3MT in 0.1 M $(C_4H_9)_4NPF_6$ in acetonitrile, containing 1.5 mM 3-methylthiophene, is shown. ITO on glass was used as working, Pt as counter and Ag/AgCl as quasireference electrode. The cyclic voltammetry was performed between 0 and 1800 mV, the scan rate was $100 \text{ mV}\cdot\text{s}^{-1}$.

During the first cycle only the oxidation of 3-methyl-thiophene at about 1700 mV can be observed, later on also the oxidation of the deposited polymer at about 1000 mV can be seen. The negative peak at about 800 mV indicates the reduction of the oxidised material back to the neutral form. Both peaks are increasing in magnitude, because with every cycle more material is deposited on the ITO/glass electrode.

In addition, cyclic voltammetry was also performed after the electropolymerisation. The samples were rinsed with acetonitrile and transferred to a monomer-free solution of 0.1 M $(C_4H_9)_4NPF_6$ in acetonitrile. Fig. 3.6 shows such a cyclic voltammogram. Again, oxidation as well as reduction of the polymer can be observed at 1000 mV and 800 mV, respectively. Because of the lack of monomer the intensity of the oxidation peak at 1800 mV is much less, but now overoxidation of the polymer takes place. Consequently, the magnitude of the peaks at 1000 and 800 mV is decreasing because of degradation of the material.

Electropolymerisation of 3-Methylthiophene

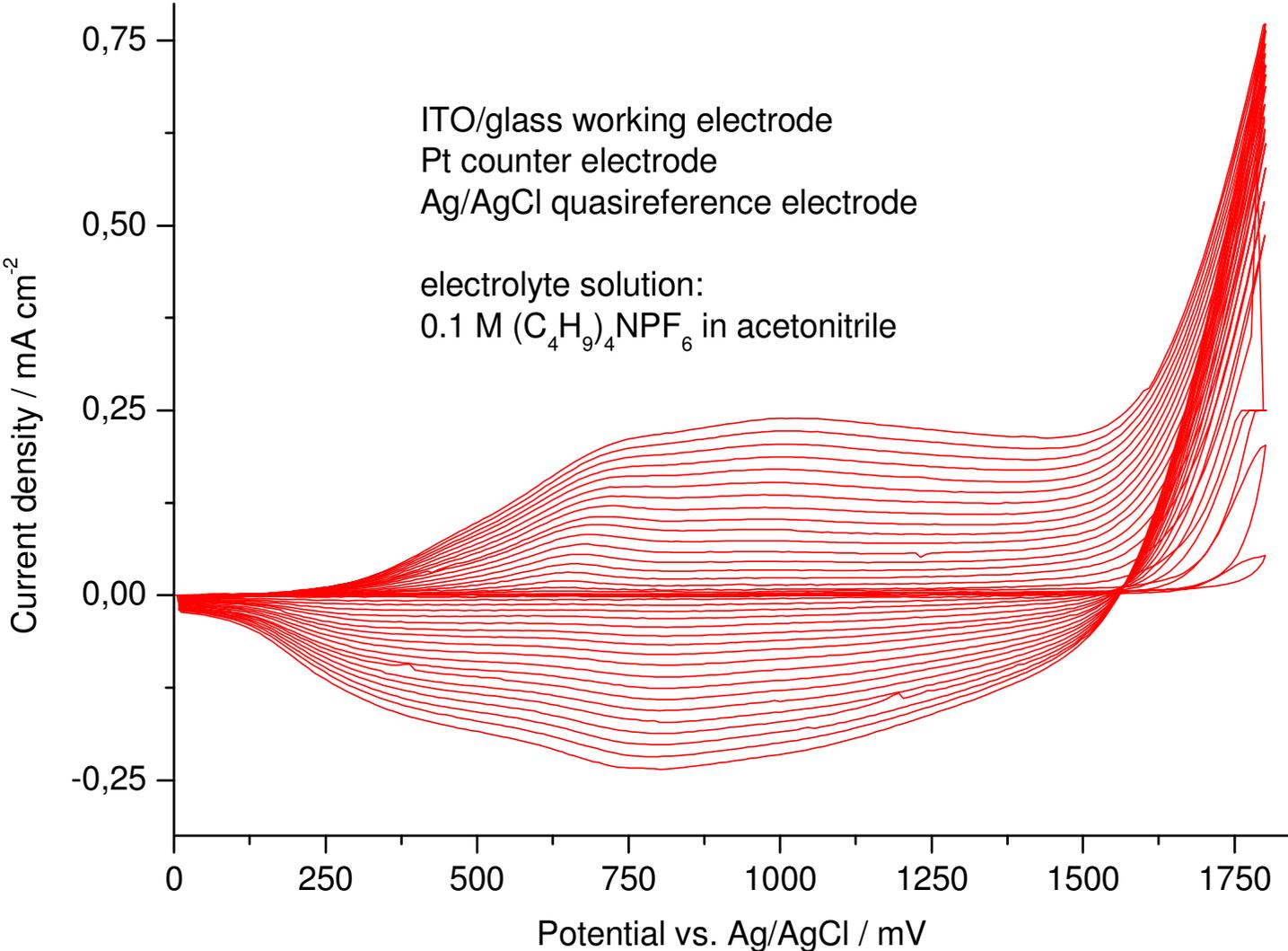


Fig. 3.5: Electropolymerisation of 3MT via cyclic voltammetry

Cyclovoltammogramm of Poly-3-Methylthiophene

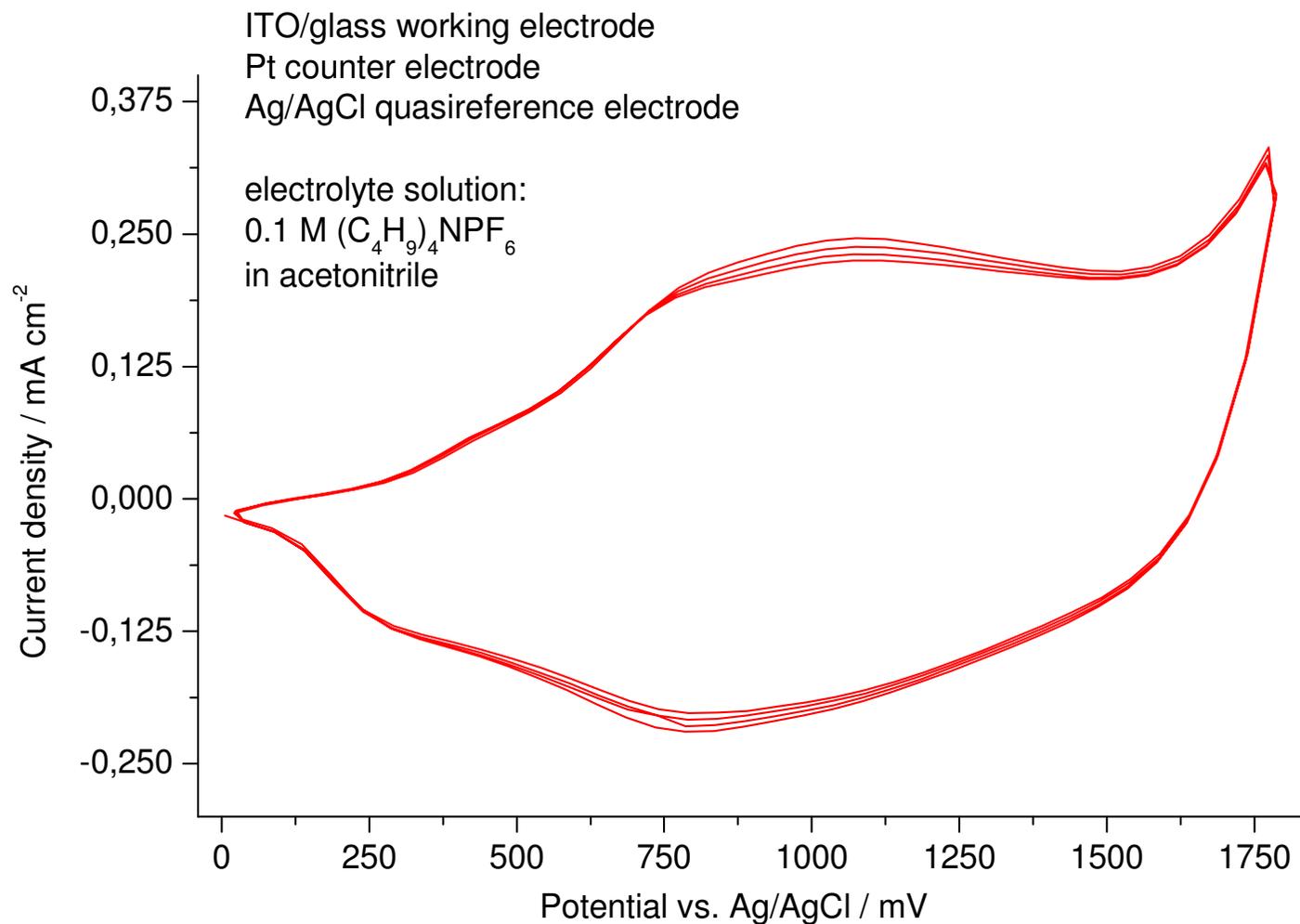


Fig. 3.6: Cyclic voltammogram of P3MT in monomer-free electrolyte solution

After electrosynthesis, UV/VIS absorption spectra were recorded. Fig. 3.7 shows spectra of P3MT samples, prepared by CP at 2000 mV vs. Ag/AgCl quasireference electrode. The material's spectra show an absorption peak in the spectral range between 350 and 650 nm and a shoulder at about 600 nm. The absorption is mainly caused by the polythiophene chain, therefore they compare favourably to those of poly-3-hexylthiophene (P3HT), shown in Fig. 3.1.

The main difference is a shift in the baseline, which does not occur with P3HT films. The reason for this behaviour is scattering on P3MT particles, which is caused by the film's rough morphology.

With these samples photoelectrochemical cells were prepared, using I_3^-/I^- in propylene carbonate as electrolyte solution and a platinum counter electrode. The j/V curves corresponding to the spectra shown in Fig. 3.7 were recorded in a voltage range between -20 and $+200$ mV, both in dark and under illumination by simulated sunlight (AM 1.5, $80 \text{ mW}\cdot\text{cm}^{-2}$). The results of the j/V characterisation are shown in Fig. 3.8 as well as in Table 3.3.

P3MT sample <i>polymerisation time</i>	V_{oc} mV	j_{sc} $\mu\text{A}\cdot\text{cm}^{-2}$	fill factor	η %
CP 2000 mV, 15 s	130	-192	0.26	0.0081
CP 2000 mV, 30 s	122	-403	0.23	0.0144
CP 2000 mV, 60 s	107	-262	0.26	0.0092
CP 2000 mV, 120 s	74	-169	0.30	0.0047

Table 3.3: Characteristics of PECs from P3MT samples

As can be seen above, the polymerisation time and therefore the thickness has an important impact on the PEC's performance. The best results were obtained by a polymerisation time of 30 seconds. The sample with a polymerisation time of only 15 seconds shows less spectral absorption and therefore less short circuit current, samples with a polymerisation time over 30 s are probably too thick, therefore charge transfer from the polymer to the redox couple might be hindered.

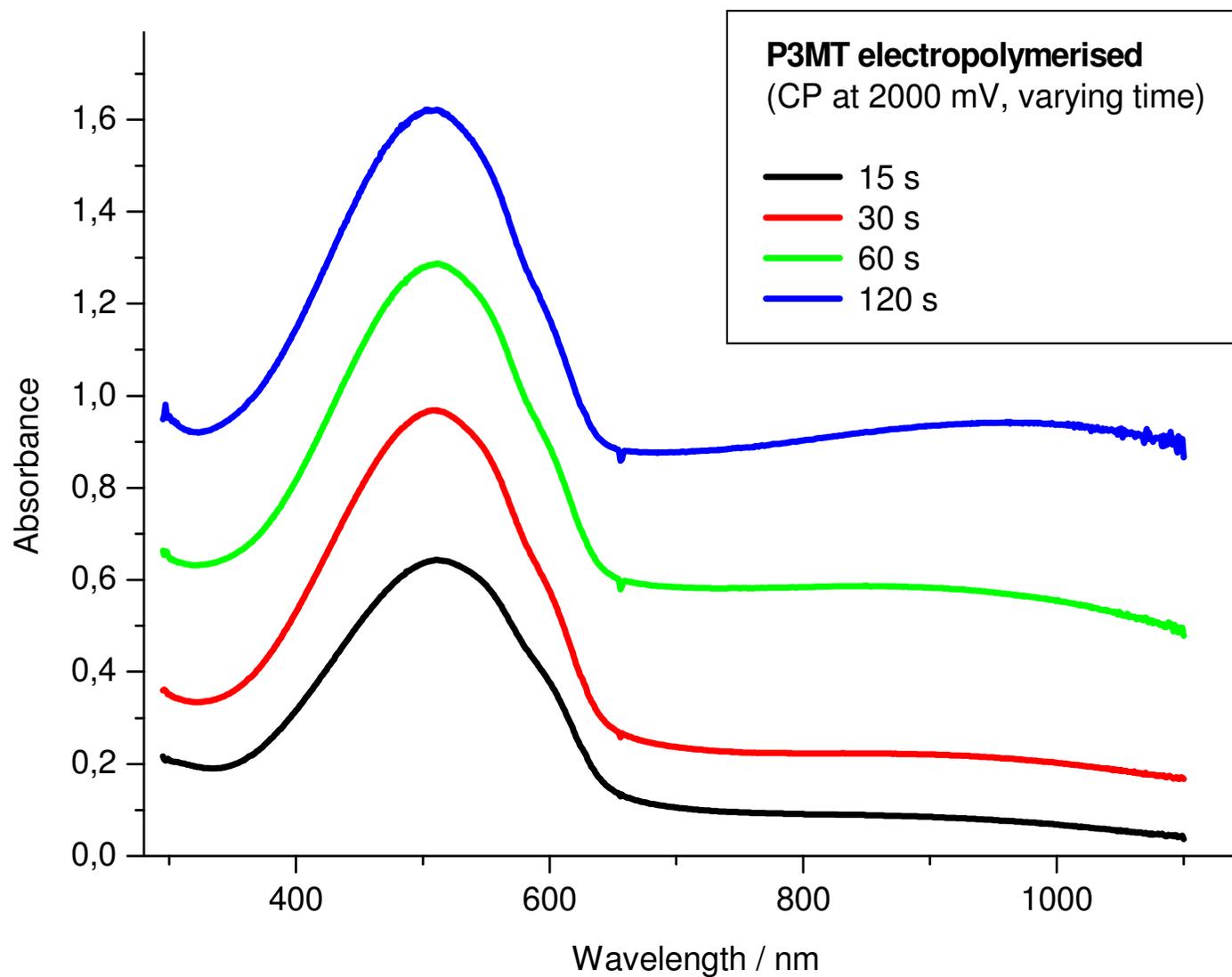


Fig. 3.7: UV/VIS absorption spectra of P3MT, prepared by electropolymerisation

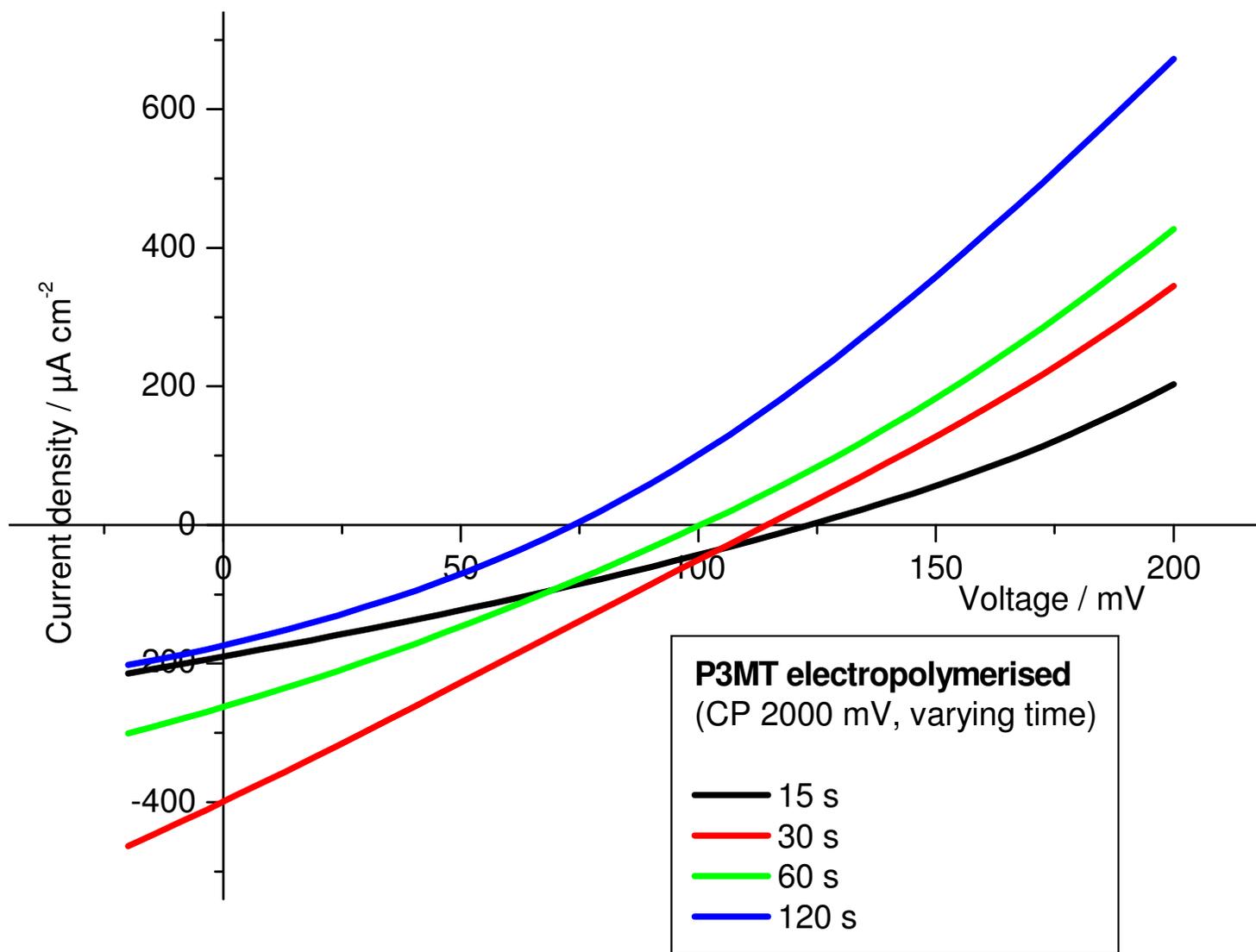


Fig. 3.8: j/V curves of P3MT samples

3.2.2 Deposition of C₆₀ clusters on P3MT films

To improve the charge separation and as a result short circuit current density as well as efficiency of photoelectrochemical cells, the influence of attached acceptor molecules like fullerenes was studied. As acceptors, C₆₀ clusters were deposited on the P3MT films.

To investigate the surface morphology, AFM images were taken. In Fig. 3.9 the surface morphology of the C₆₀/P3MT/ITO/glass electrode which was obtained after the C₆₀ cluster deposition is shown. The film has a rough structure, therefore the quality of the AFM image is rather poor. Nevertheless, spheric particles with a diameter of about 150 nm can be seen, which compares favourably with literature values²⁶.

During the cluster deposition it turned out that also the polymer film was partially oxidised, a colour change from red to blue was noticed. When the voltage was applied for too long, even all the polymer was removed, probably by oxidative decomposition. Therefore the voltage was applied only for 30 seconds, leaving some C₆₀ clusters in the solution. Afterwards, the polymer film was reduced back to the neutral form in an electrolyte solution containing 0.1 M (C₄H₉)₄NPF₆ in acetonitrile.

Again, photoelectrochemical cells were assembled, using I₃⁻/I⁻ in propylene carbonate as electrolyte solution and a platinum counter electrode. Unfortunately, the results from the measurements were worse compared to those of the pure polymer. An overview of the obtained characteristics as well as the corresponding data of the P3MT samples without C₆₀ is given in Table 3.4.

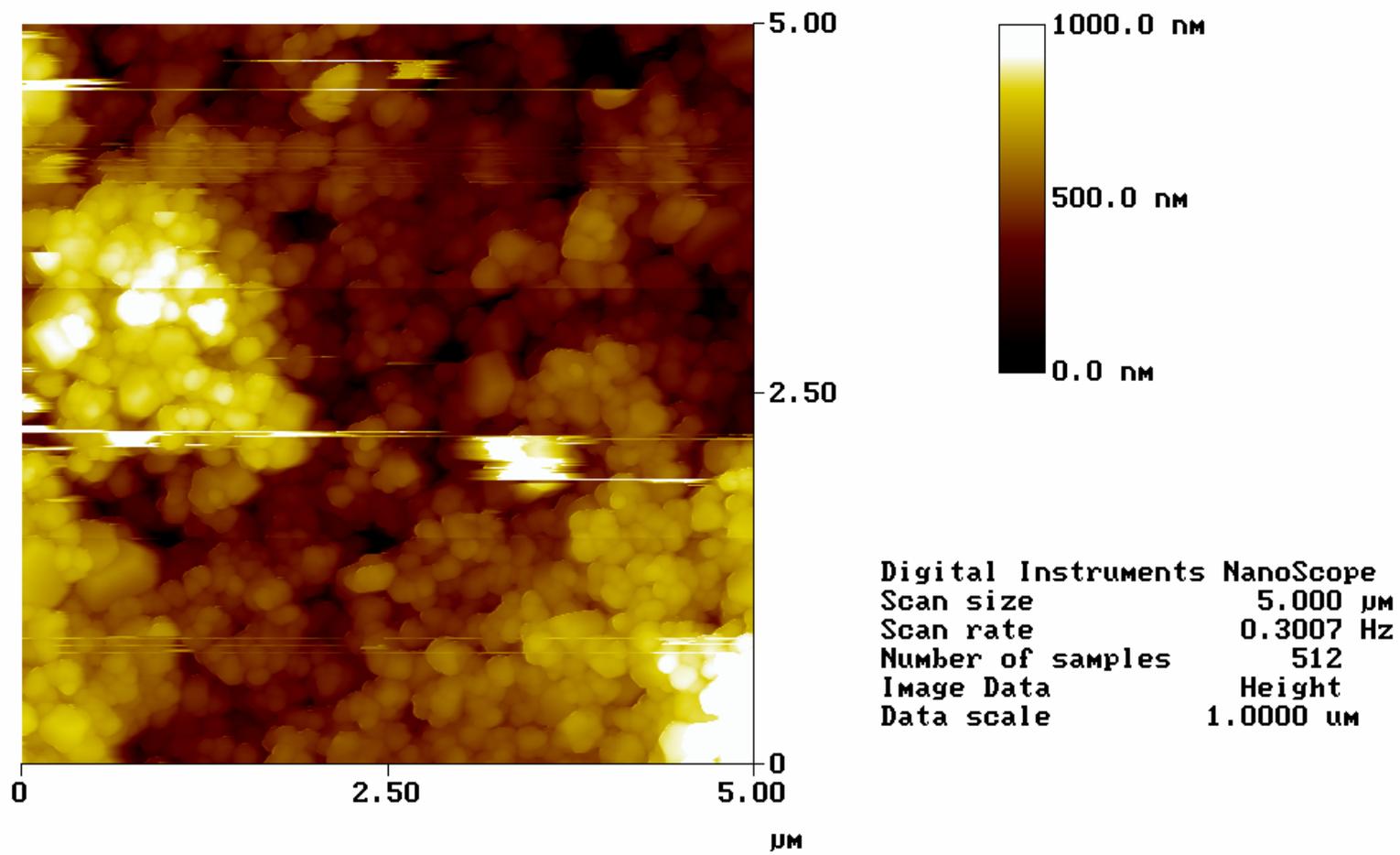


Fig. 3.9: AFM picture of C_{60} clusters deposited on a P3MT/ITO/glass electrode

P3MT sample <i>polymerisation time</i>	V_{oc} mV	j_{sc} $\mu\text{A}\cdot\text{cm}^{-2}$	fill factor	η %
CP 2000 mV, 15 s, +C ₆₀	75	-105	0.29	0.0028
CP 2000 mV, 30 s, +C ₆₀	72	-87	0.29	0.0023
CP 2000 mV, 15 s	130	-192	0.26	0.0081
CP 2000 mV, 30 s	122	-403	0.23	0.0144

Table 3.4: Comparison of the characteristics of PECs from C₆₀/P3MT/ITO samples as well as pure P3MT samples

The reason for the worse behaviour could be partial degradation of the polymer during the cluster deposition process. Indications are the partial oxidation of the polymer during the experiment and its complete removal, when the deposition voltage was applied too long.

3.3 Polymers with covalently linked acceptors

From the studies on P3HT/PCBM films (see chapter 3.1), it is clearly shown that acceptor molecules like PCBM may improve the performance of photoelectrochemical cells based on photoactive polymers. Obviously, the main problem was the photoinduced solubility of the acceptor molecules in the solvent.

A possibility to overcome this drawback is the usage of acceptors that are covalently bound to the photoactive polymer chain, so-called doublecables. Various doublecables have already been synthesised³⁶⁻³⁸.

These polymers were synthesised using electropolymerisation, starting from monomers which consisted of fulleropyrrolidines covalently linked to thiophene or bithiophene. Two such materials were studied; one of them was ITB-C₆₀³⁶, a bithiophene-fulleropyrrolidine, the other TIO-TEG-C₆₀-NCH₃, a thiophene-fulleropyrrolidine. Both molecules had been synthesised by the group of M. Maggini, University of Bologna, Italy. Their chemical structures have been shown in Fig. 2.5 and Fig. 2.8, respectively.

3.3.1 Poly-ITB-C₆₀ films

It was not possible to electropolymerise the monomer ITB-C₆₀ by cyclic voltammetry (CV), therefore the constant potential method (CP) had been chosen. The reason is that in cyclic voltammetry the deposited material is reduced to neutral form before another cycle is started. It turned out that the neutral form of the formed polymer was soluble in the electrolyte solution; therefore no defined layers could be obtained. Using the constant potential method, a potential of 1250 mV vs. Ag/AgCl quasireference electrode was applied, afterwards the potentiostat was switched to the open-circuit condition. Thus, a non-soluble oxidised film of Poly-ITB-C₆₀ was obtained.

The sample was rinsed with acetonitrile and reduced to neutral form in an electrolyte solution containing only acetonitrile, where also the neutral form is insoluble. Again, the sample was rinsed with acetonitrile and dried under nitrogen.

UV/VIS spectra of the deposited films are shown in Fig. 3.10. The high fullerene content of the compound leads to an intense absorption band in the spectral range below 400 nm, the absorption in the spectral range between 400 and 650 nm caused by the polythiophene chain is relatively less intense.

Photoelectrochemical cells were assembled, using I_3^-/I^- in propylene carbonate as electrolyte solution and a platinum counter electrode. The corresponding j/V curves were recorded in a voltage range between -20 and $+250$ mV, both in dark and under illumination by simulated sunlight (AM 1.5, $80 \text{ mW}\cdot\text{cm}^{-2}$). The results of the j/V characterisation are shown in Fig. 3.11 as well as in Table 3.5.

Poly-ITB-C₆₀ sample <i>polymerisation time</i>	V_{oc} mV	j_{sc} $\mu\text{A}\cdot\text{cm}^{-2}$	fill factor	η %
CP 1250 mV, 10 min	234	-49	0.26	0.0037
CP 1250 mV, 20 min	202	-40	0.32	0.0031

Table 3.5: Characteristics from PECs from Poly-ITB-C₆₀, prepared by CP electro-polymerisation

As can be seen, photoelectrochemical cells using poly-ITB-C₆₀ show higher open-circuit voltages than those using P3HT/PCBM or P3MT. Nevertheless, the cell's efficiency is poor because of low short-circuit currents.

One reason for the low current may be the poor absorption in the spectral region between 450 and 650 nm. Therefore the cell's performance might be improved by increasing the absorption in this spectral range. By decreasing the acceptor content of the polymer, e.g. by copolymerisation with other heteroaromatic compounds, both an increased absorption as well as the acceptor properties of the doublecable's fullerene moieties may be obtained.

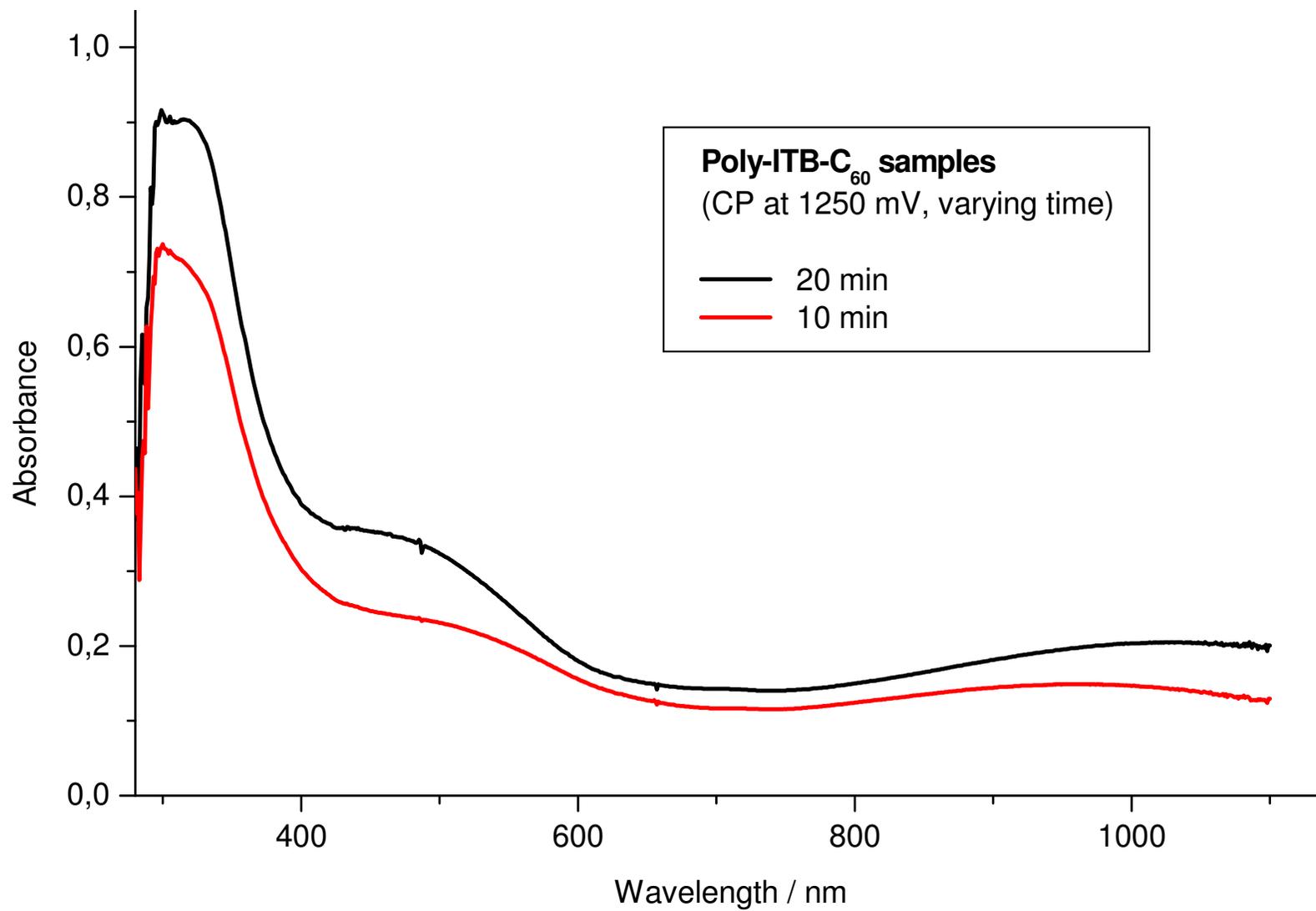


Fig. 3.10: UV/VIS absorption spectra of Poly-ITB-C₆₀, prepared by CP electro-polymerisation

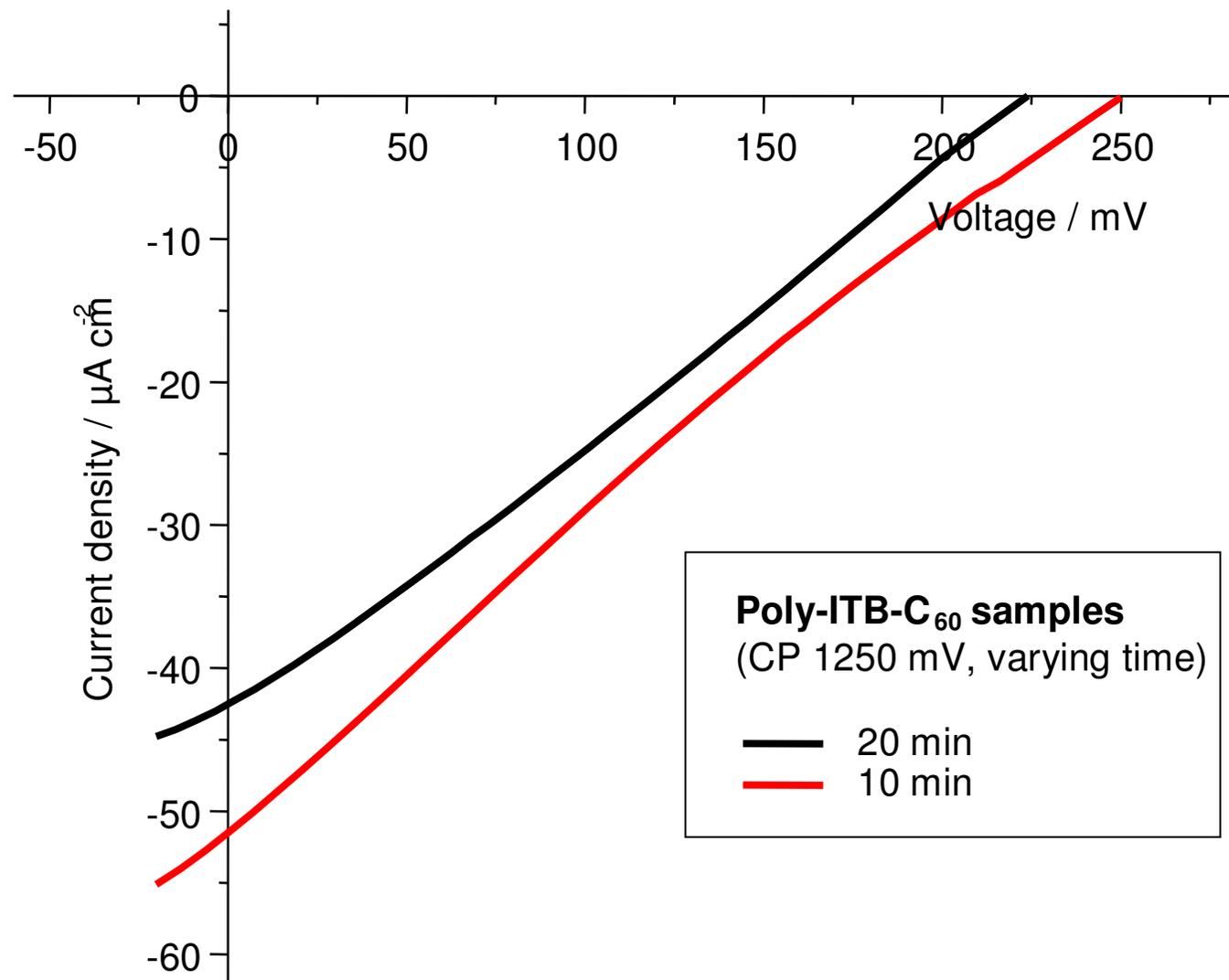


Fig. 3.11: j/V curves from poly-ITB-C₆₀ samples

3.3.2 Poly-ITB-C₆₀ copolymer films

Copolymerisation of ITB-C₆₀ with another photoactive polymer is a way for increasing the absorption in the spectral range between 450 and 650 nm compared with pure poly-ITB-C₆₀. As suitable partner for random copolymerisation bithiophene had been chosen, because also ITB-C₆₀ is a derivative of this compound, and the oxidation potentials of both compounds are similar. The chemical structure of such a copolymer is shown in Fig. 2.6.

Monomer solutions containing both compounds have been prepared, using 0.1 M (C₄H₉)₄NPF₆ in acetonitrile/toluene (30:70, v:v) as electrolyte solution. In addition to solutions containing only one of the monomers, mixtures with a mass concentration ratio BiTh:ITB-C₆₀ of 1:1, 2:1 and 3:1 were prepared. Again electropolymerisation was done using the constant potential method (CP) because cyclic voltammetry (CV) was not suitable for solubility reasons, which were already discussed in section 3.3.1.

After film preparation and their reduction to the neutral form, UV/VIS absorption spectra were taken which are shown in Fig. 3.12. While poly-ITB-C₆₀ shows an intense absorption below 400 nm and lower absorption at longer wavelengths, pure polybithiophene has its main absorption in the spectral range between 350 and 650 nm. The copolymer films show absorption characteristics of both compounds, the ratio between the backbone's absorption peak and the acceptor's absorption peak is increasing with increasing concentration of bithiophene in the monomer solution.

After assembling photoelectrochemical cells using I₃⁻/I⁻ in propylene carbonate as electrolyte solution and a platinum counter electrode, j/V characterisation was performed. The corresponding j/V curves were recorded in a voltage range from – 20 to a maximum between + 150 and +250 mV, both in dark and under illumination by simulated sunlight (AM 1.5, 80 mW·cm⁻²). The results of the j/V characterisation are shown in Fig. 3.13 as well as in Table 3.6.

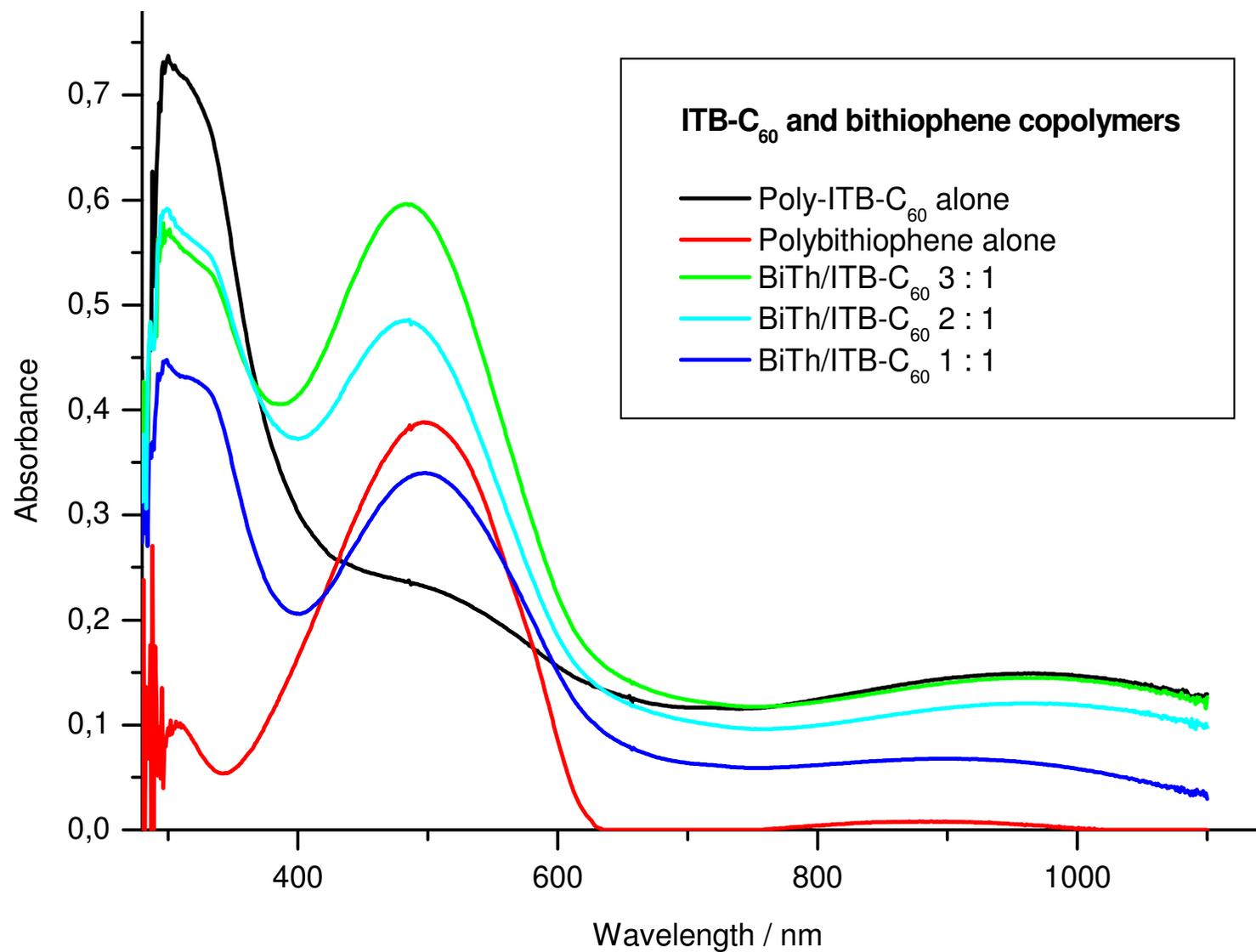


Fig. 3.12: UV/VIS absorption spectra of electropolymerised ITB-C₆₀ and bithiophene copolymers

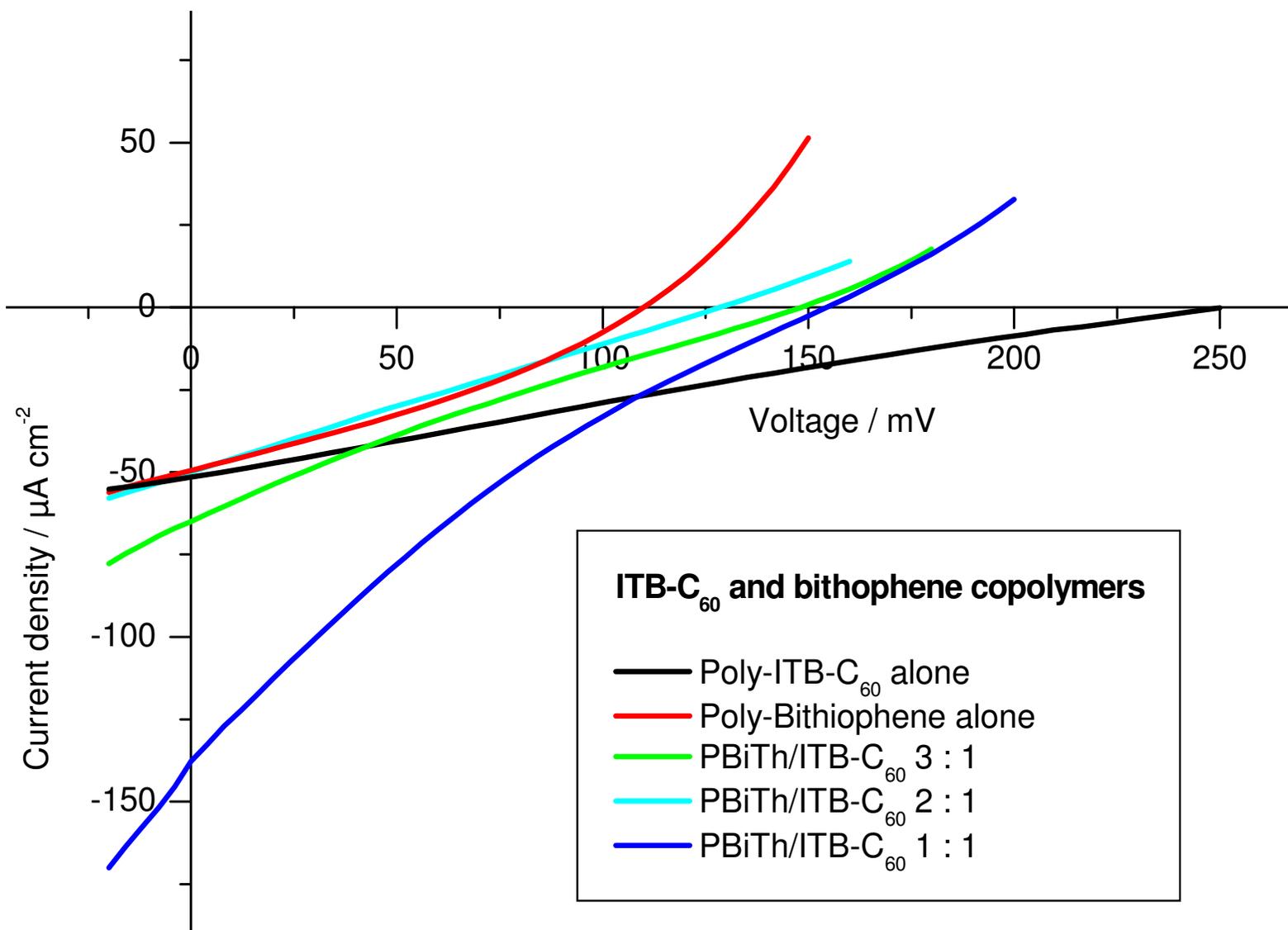


Fig. 3.13: j/V curves from ITB-C₆₀ and bithiophene copolymers

Copolymer sample <i>concentration ratio</i>	V_{oc} mV	j_{sc} $\mu\text{A}\cdot\text{cm}^{-2}$	fill factor	η %
Polybithiophene	110	-50	0.30	0.0022
P-BiTh/P-ITB-C ₆₀ , 3:1	148	-65	0.22	0.0026
P-BiTh/P-ITB-C ₆₀ , 2:1	129	-49	0.25	0.0020
P-BiTh/P-ITB-C ₆₀ , 1:1	155	-138	0.19	0.0051
Poly-ITB-C ₆₀	250	-51	0.23	0.0037

Table 3.6: Characteristics of PECs from ITB-C₆₀ and bithiophene copolymers, prepared by electropolymerisation

Although the open-circuit voltage is decreasing with increasing amount of bithiophene backbone, the copolymer sample obtained from a monomer solution with a mass concentration ratio bithiophene:ITB-C₆₀ of 1:1 shows the highest short-circuit current density as well as the highest efficiency in this sequence. Indeed, with copolymerisation the absorption was increased in the spectral range between 450 and 650 nm without disturbing the charge transfer to the covalently bound fullerene moieties, leading to a higher absorption of photons and therefore to higher currents.

In addition, in-situ FTIR studies on polybithiophene and ITB-C₆₀/bithiophene copolymers have been performed to investigate the spectral changes during oxidation and reduction of the polymers. The results of the in-situ spectroelectrochemical and the in-situ photospectroelectro-chemical studies are shown in section 3.4.3 and 3.4.4 respectively.

Electropolymerised doublecables like poly-ITB-C₆₀ have a relatively small number of repeat units³⁶. The copolymerisation with bithiophene probably leads to longer polymer chains, improving the charge transport within the chain. Indications are shown in chapter 3.4.3, where the results of spectroelectrochemical measurements of polybithiophene and a bithiophene/ITB-C₆₀ copolymer are compared with those of poly-ITB-C₆₀³⁶.

3.3.3 Poly-TIO-TEG-C₆₀-NCH₃ films

Like ITB-C₆₀, TIO-TEG-C₆₀-NCH₃ is a monomer for obtaining polymers with covalently bound acceptor moieties, consisting of fulleropyrrolidine covalently linked to thiophene. It was not possible to electropolymerise the monomer in the same way it had been done with ITB-C₆₀, therefore different electrolyte solutions (0.1 M (C₄H₉)₄NPF₆ in acetonitrile/toluene (30:70, v:v); 0.1 M (C₄H₉)₄NPF₆ in dichloromethane) and different working electrodes (ITO/glass; Pt) had been tried.

A yellowish film could be deposited on a platinum electrode from the dichloromethane electrolyte solution by applying a constant potential of 1.7 V vs. Ag/AgCl quasireference electrode for 3 minutes. Afterwards, the sample was rinsed with acetonitrile and cyclic voltammetry was performed within the potential range of + 1100 and – 1000 mV, the scan rate was 100 mV·s⁻¹. The cyclic voltammogram is shown in Fig. 3.14.

As can be seen, the cyclic voltammogram shows an oxidation peak around + 800 mV vs. Ag/AgCl, indicating the oxidation of the polythiophene chain. At negative potentials undefined reduction peaks can be identified, which could be caused by the fullerene covalently linked to the polymer.

It was also tried to electropolymerise TIO-TEG-C₆₀-NCH₃ on ITO substrates, but it was not possible to deposit any film. The only electrochemical reaction was an oxidation peak around 1700 mV, indicating oxidation of the thiophene moiety, but no film deposition could be observed.

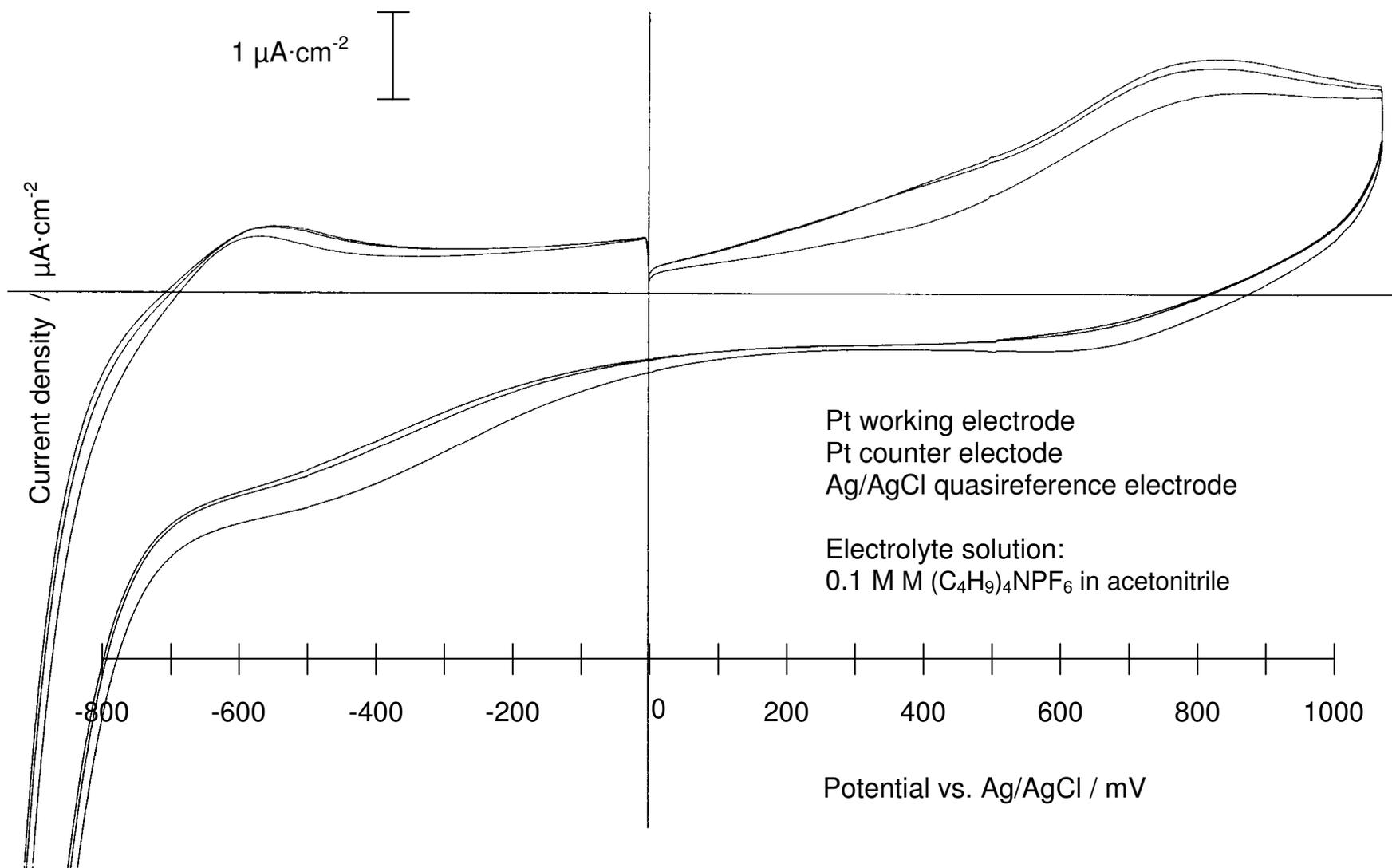


Fig. 3.14: Cyclic voltammogram of Poly-TIO-TEG- C_{60} - NCH_3

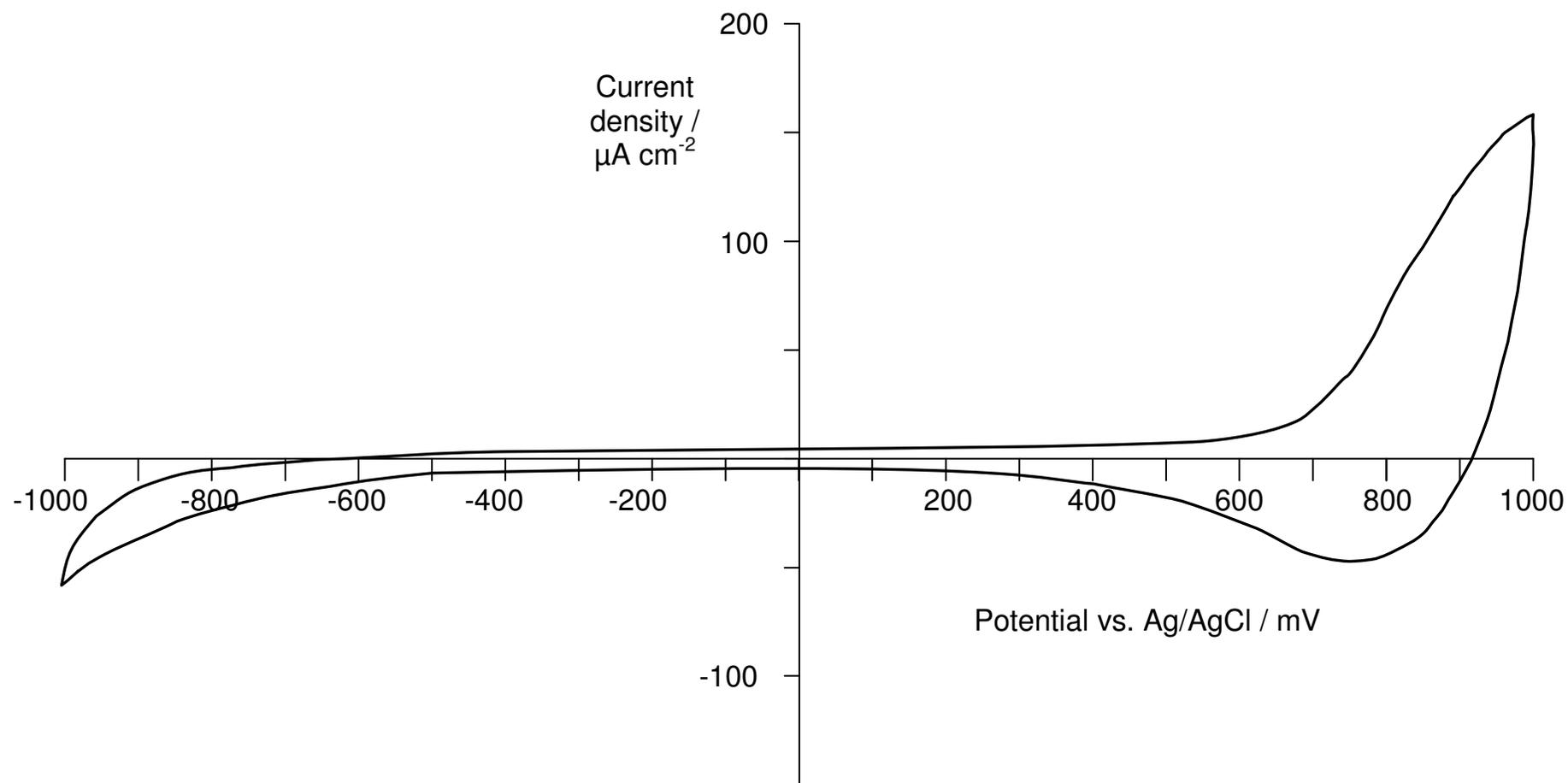


Fig. 3.15: Cyclic voltammogram of a film electropolymerised from a 3-methyl-thiophene / TIO-TEG-C₆₀-NCH₃ solution

Moreover, 3-methylthiophene was added to the electrolyte solution to investigate if a copolymerisation of TIO-TEG-C₆₀-NCH₃ and 3-methylthiophene was possible. Again, only 3-methylthiophene was deposited on the ITO electrode, the doublecable monomer was not precipitated. In Fig. 3.15 the cyclic voltammogram of the precipitated polymer is shown.

The oxidation of the polythiophene chain can be observed at a positive potential at + 1000 mV vs. Ag/AgCl quasireference electrode, at negative potentials there is no indication for the reduction of fullerenes. As a result, it can be excluded that any polymer containing TIO-TEG-C₆₀-NCH₃ has been precipitated.

3.4 In-situ FTIR spectroscopy

3.4.1 In-situ FTIR spectroelectrochemistry of P3MT

The IR spectral behaviour of poly-3-methylthiophene (P3MT) during cyclic voltammetry had been already studied well³⁹. Nevertheless, it was useful to repeat these studies to compare the results with those of in-situ photospectroelectrochemistry of P3MT.

Fig. 3.16 shows the obtained difference spectra of P3MT during oxidation. Starting from 0 mV vs. Ag/AgCl quasireference, the potential permanently increased, the higher the potential, the bigger the intensity of the signal. Between 5000 and 1500 cm^{-1} the polaronic absorption can be seen, at wavenumbers below 1500 cm^{-1} the characteristic IRAV modes occur. In Fig. 3.17 these IRAV modes can be seen in detail.

The IRAV modes represent a fingerprint of the polymer. While the peaks at 1300 cm^{-1} and 1150 cm^{-1} are characteristic for polythiophenes, the peak occurring at 840 cm^{-1} is characteristic for PF_6^- , which is absorbed in the polymer to compensate the positive charges in the oxidised material. The results compare favourably to those published by Neugebauer et al³⁹.

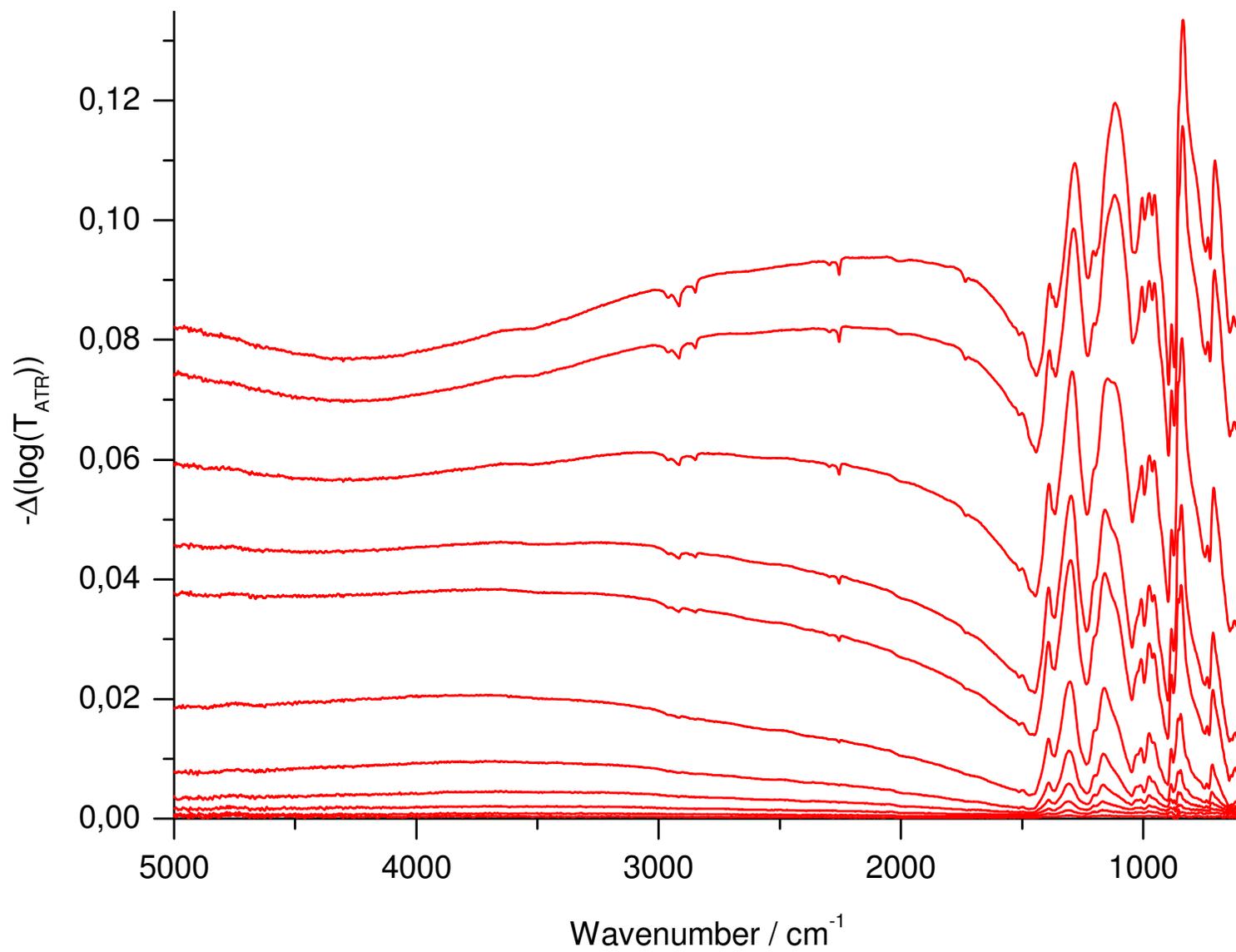


Fig. 3.16: IR difference spectra of P3MT during p-doping. Sequence: bottom to top

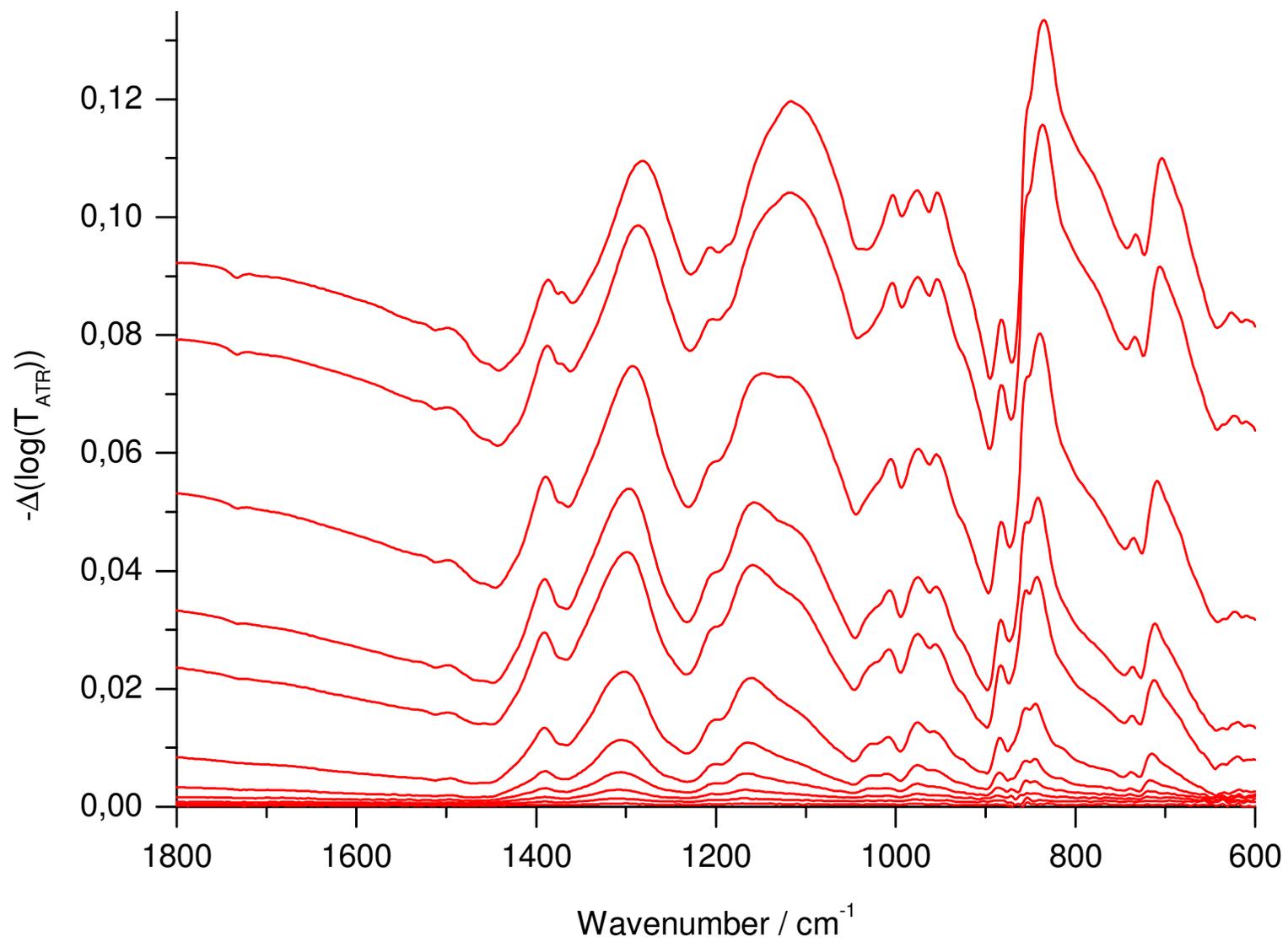


Fig. 3.17: IR difference spectra of P3MT during p-doping, IRAV range. Sequence: bottom to top

3.4.2 In-situ FTIR photospectroelectrochemistry of P3MT

Photospectroelectrochemical studies of P3MT have been performed at various potentials. Starting from -400 mV vs. Ag/AgCl quasireference electrode, the potential was increased to -200 mV, 0 mV, $+300$ mV and finally $+500$ mV. The corresponding difference spectra are shown in Fig. 3.18; the IRAV modes are shown in more detail in Fig. 3.19. Two corresponding current vs. time plots which were recorded during the experiment are shown in Fig. 3.20 and Fig. 3.21.

As can be seen, the spectral response to illumination in the experiment with a potential of -400 mV is the smallest. There is almost no difference in the spectra recorded in the potential range between -200 and $+300$ mV. The highest intensities were observed when a potential of $+500$ mV was applied. At negative potentials, the polarons generated by illumination are immediately reduced back to neutral form, resulting in a high photocurrent, but in low spectral response. At positive potentials, this reduction does not occur, resulting in a lower photocurrent, but also in a higher spectral response.

Opposite results were obtained by Neugebauer et al³¹ when investigating the properties of poly-3,4-ethylenedioxythiophene (PEDOT) by photospectroelectrochemistry. Obviously, the systems cannot be compared easily because of differences in their absorption behaviour, their oxidation potentials and their local conductivity.

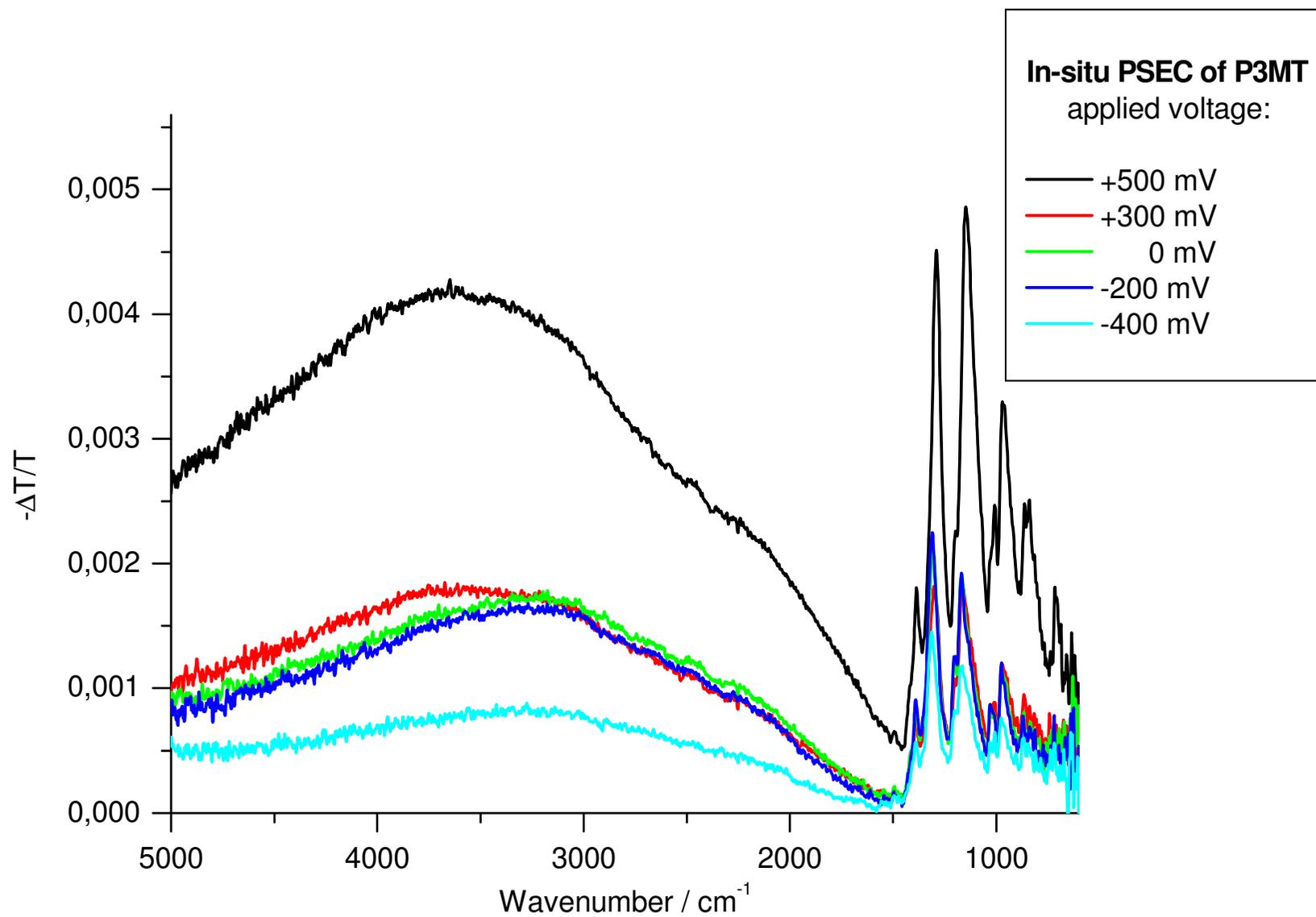


Fig. 3.18: Relative IR spectra of P3MT during photospectroelectrochemistry at different potentials

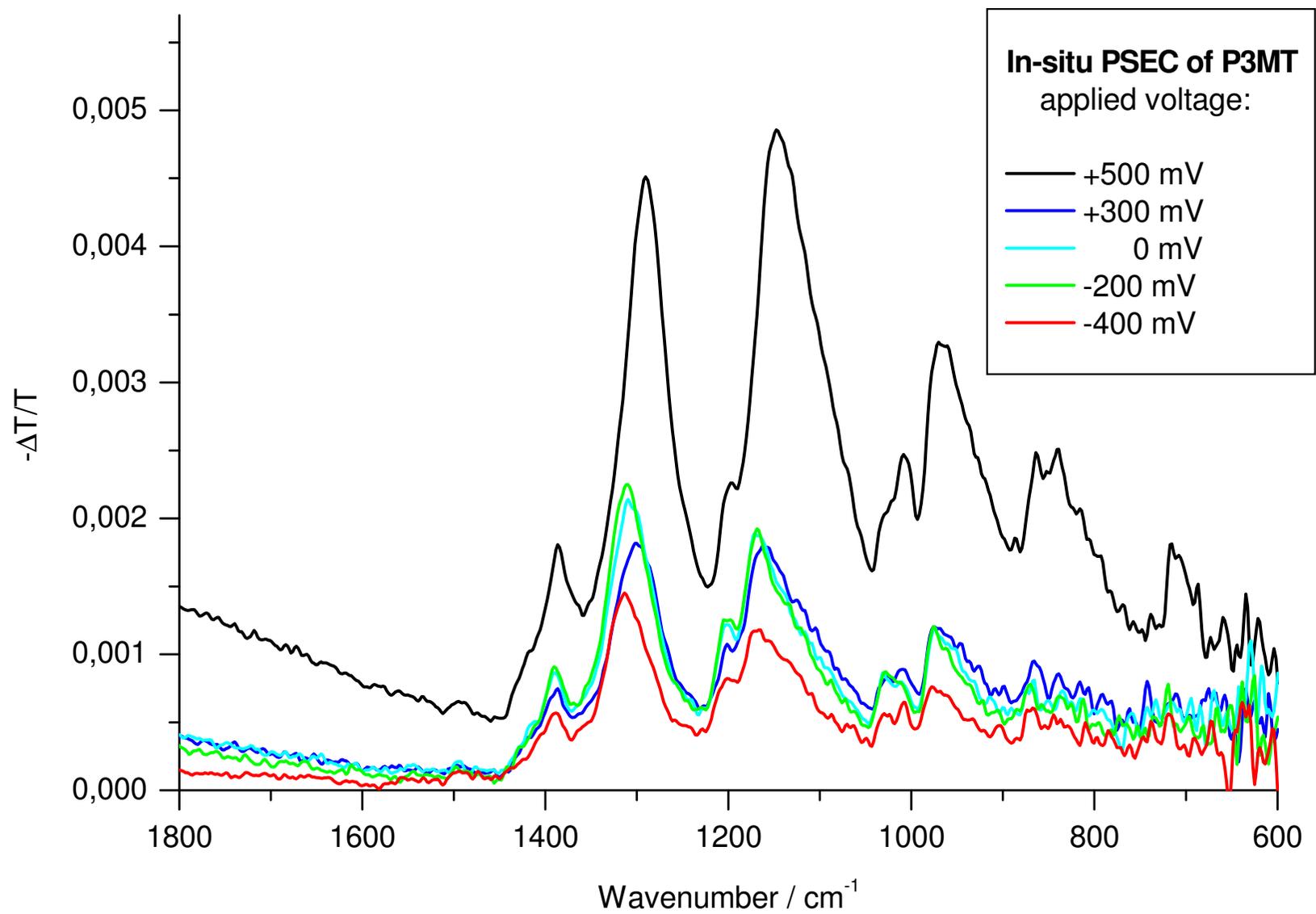


Fig. 3.19: Relative IR spectra of P3MT during photospectroelectrochemistry at different potentials, IRAV range

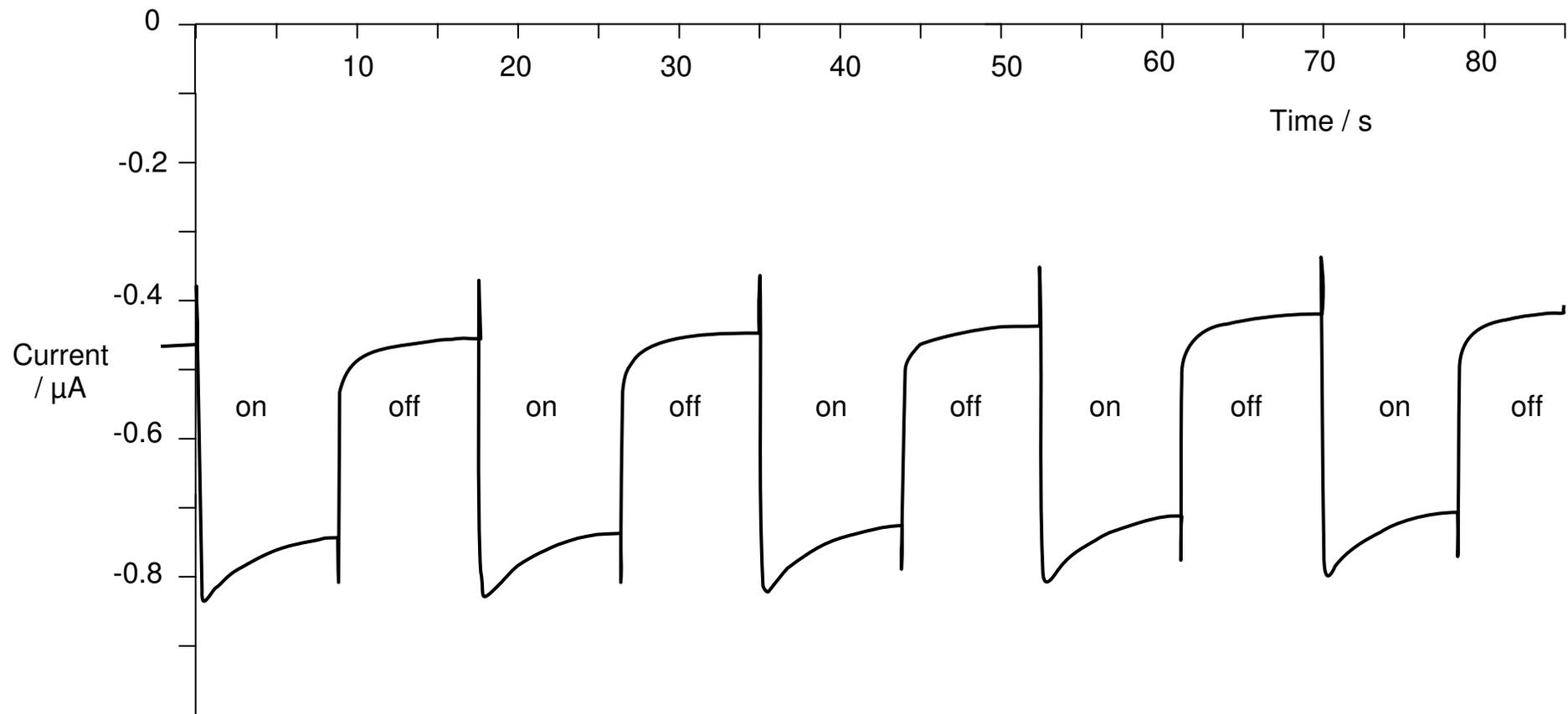


Fig. 3.20: Current vs. time plot recorded during photospectroelectrochemistry of P3MT at a potential of -400 mV vs. Ag/AgCl quasireference electrode

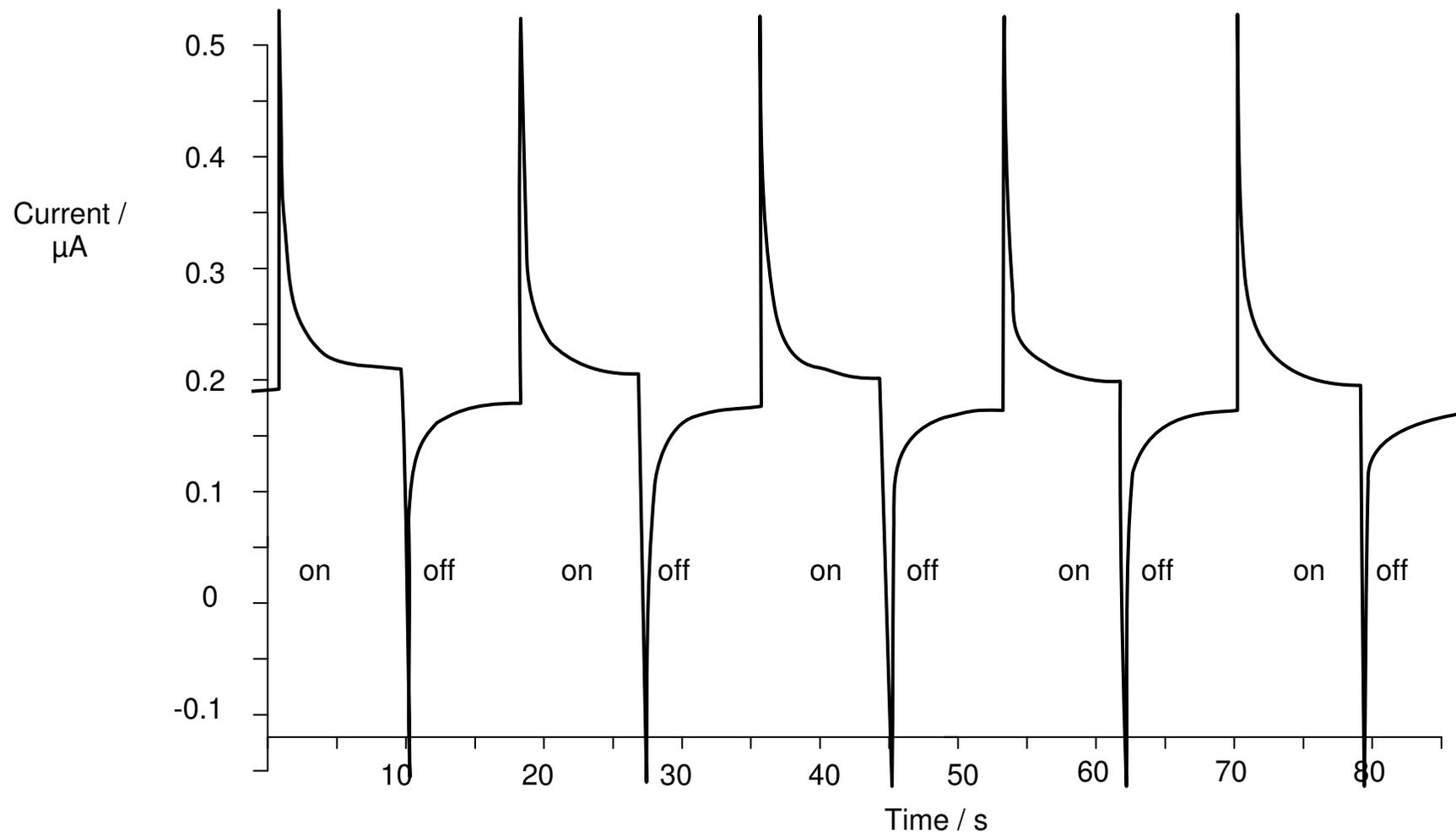


Fig. 3.21: Current vs. time plot recorded during photospectroelectrochemistry of P3MT at a potential of + 300 mV vs. Ag/AgCl quasireference electrode

From the current vs. time plots it can be seen that the photocurrents have a different sign. At a potential of -400 mV vs. Ag/AgCl quasireference electrode illumination leads to a negative photocurrent, whereas at a potential of $+300$ mV a positive photocurrent can be observed. In addition, the sign of the baseline current in dark also changes. At a potential of -200 mV it is negative, whereas at a potential of $+300$ mV it is positive.

These changes are caused by the difference of the j/V plots in dark and under illumination. At a given point, the current densities in dark and under illumination are equal. To more negative potentials, the observed currents under illumination are more negative than those in dark; consequently, a negative current pulse can be observed under illumination. A similar situation occurs at more positive potentials, where the currents under illumination are higher than those in dark, resulting in a positive current peak. The same situation was also observed by Neugebauer et al³¹ when working on photospectroelectrochemical studies of PEDOT.

Finally it can be seen that the IRAV structures of P3MT during spectroelectrochemistry and photospectroelectrochemistry are similar, this is an indication that in both processes the same IR active species are formed.

During these experiments, no n-doping was observed. One possible explanation may be that visible species with IRAV bands are generated independently from mobile charge carriers; consequently, the spectra are independent from the sign of the current. Nevertheless, the amount of photoinduced species with IRAV bands is obviously dependent on the doping level.

3.4.3 In-situ FTIR SEC of PBiTh and a BiTh/ITB-C₆₀ copolymer

Similar experiments have been performed using polybithiophene (PBiTh) and a copolymer from bithiophene and ITB-C₆₀. Again, the samples were prepared by electro(co)polymerisation of a proper monomer solution.

For polybithiophene difference spectra from 0 to + 1000 mV are shown in Fig. 3.22, the corresponding IRAV range is presented in detail Fig. 3.23. Analogously, in Fig. 3.24 the difference spectra of the bithiophene/ITB-C₆₀ copolymer between 0 and + 800 mV are shown, the detailed IRAV range can be found in Fig. 3.25.

The IRAV patterns of bithiophene and the copolymer look almost the same (apart from the peak at 840 cm⁻¹ caused by the PF₆⁻ counter ion), they also compare to the spectra of poly-ITB-C₆₀, which were published by Cravino et al³⁶.

Only two peaks occurring at 1600 and 1480 cm⁻¹ which were reported in the investigation of poly-ITB-C₆₀ and assigned to end-ring vibrations are missing. These peaks would indicate a short chain length of the polymer, which is not valid any more for the copolymer. Obviously, the spectral behaviour of the BiTh/ITB-C₆₀ copolymer as well as Poly-ITB-C₆₀ is little influenced by the fullerene moieties upon oxidation.

3.4.4 In-situ FTIR photospectroelectrochemistry of PBiTh

Like with P3MT also with polybithiophene (PBiTh) photospectroelectrochemical studies have been performed. The polymer film was electropolymerised the same way as for spectroelectrochemistry, and after applying a constant potential ATR FTIR spectra were recorded both in dark and under illumination. The potentials which were applied were 0 mV, + 200 mV, + 400 mV and + 600 mV vs. Ag/AgCl quasireference electrode.

The obtained relative spectra are shown in Fig. 3.26 (full spectrum) and Fig. 3.27 (IRAV range). Unlike P3MT, which showed clear peaks even at negative potentials, the spectra of polybithiophene in the potential range between 0 and + 400 mV vs. Ag/AgCl quasireference electrode are very noisy and not defined at all. Only when a potential of + 600 mV was applied, single peaks could be identified. Again the IRAV patterns of spectroelectrochemical and photospectroelectrochemical experiments look similar; thus in both processes the same IR active species are formed.

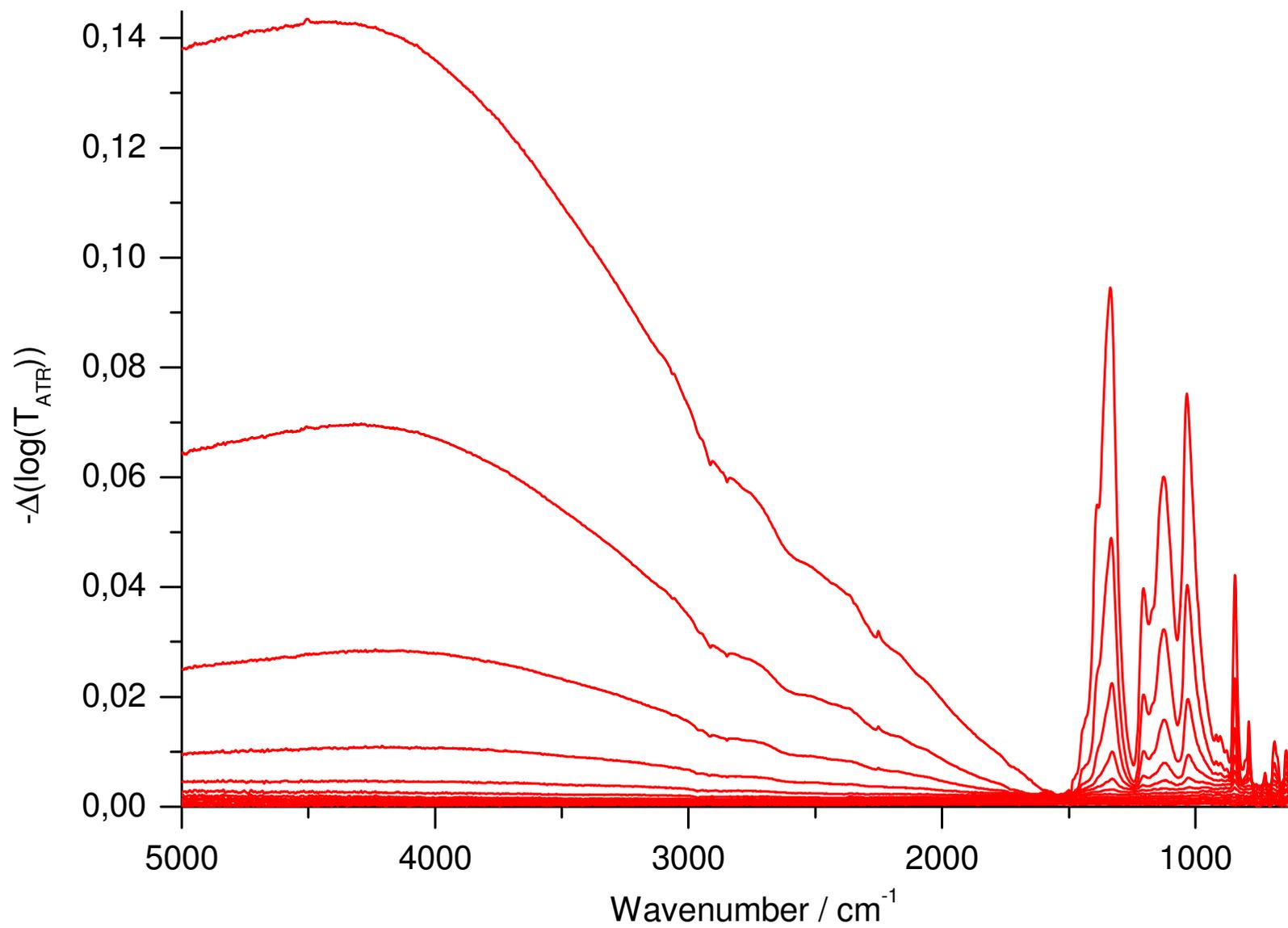


Fig. 3.22: IR difference spectra of PBiTh during p-doping. Sequence: bottom to top

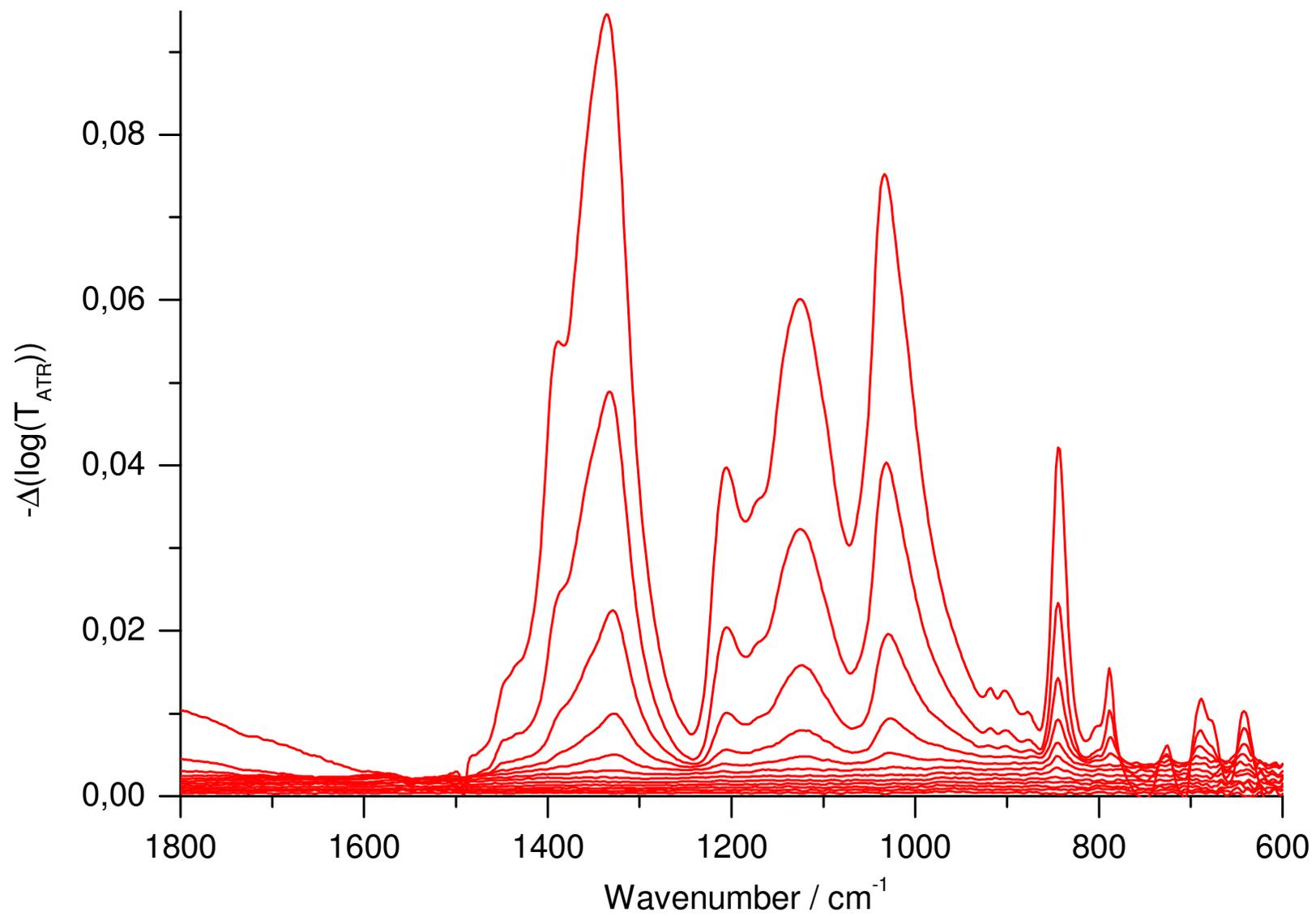


Fig. 3.23: IR difference spectra of PBIth during p-doping, IRAV range. Sequence: bottom to top

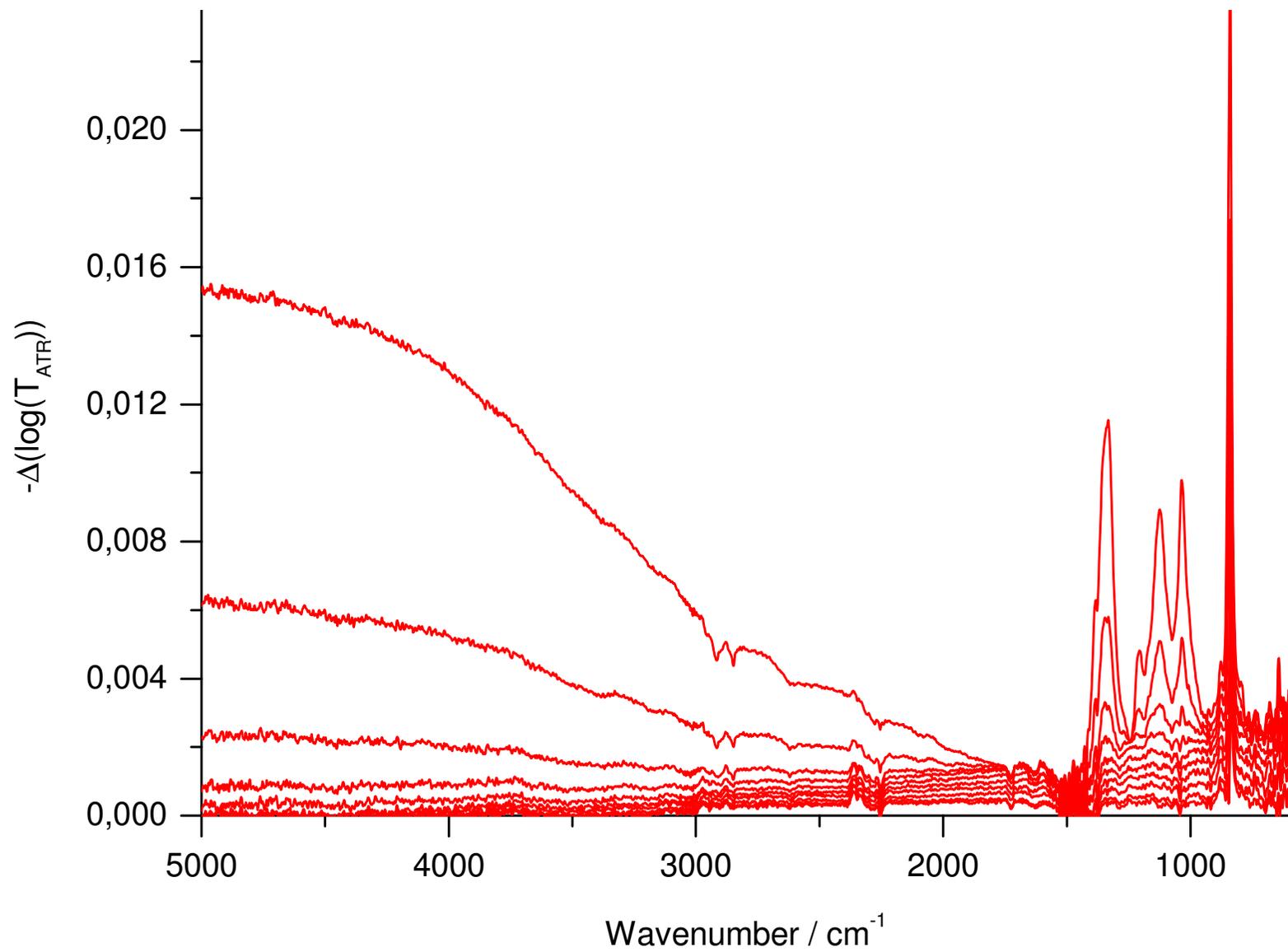


Fig. 3.24: IR difference spectra of BiTh/ITB-C₆₀ copolymer during p-doping. Sequence: bottom to top

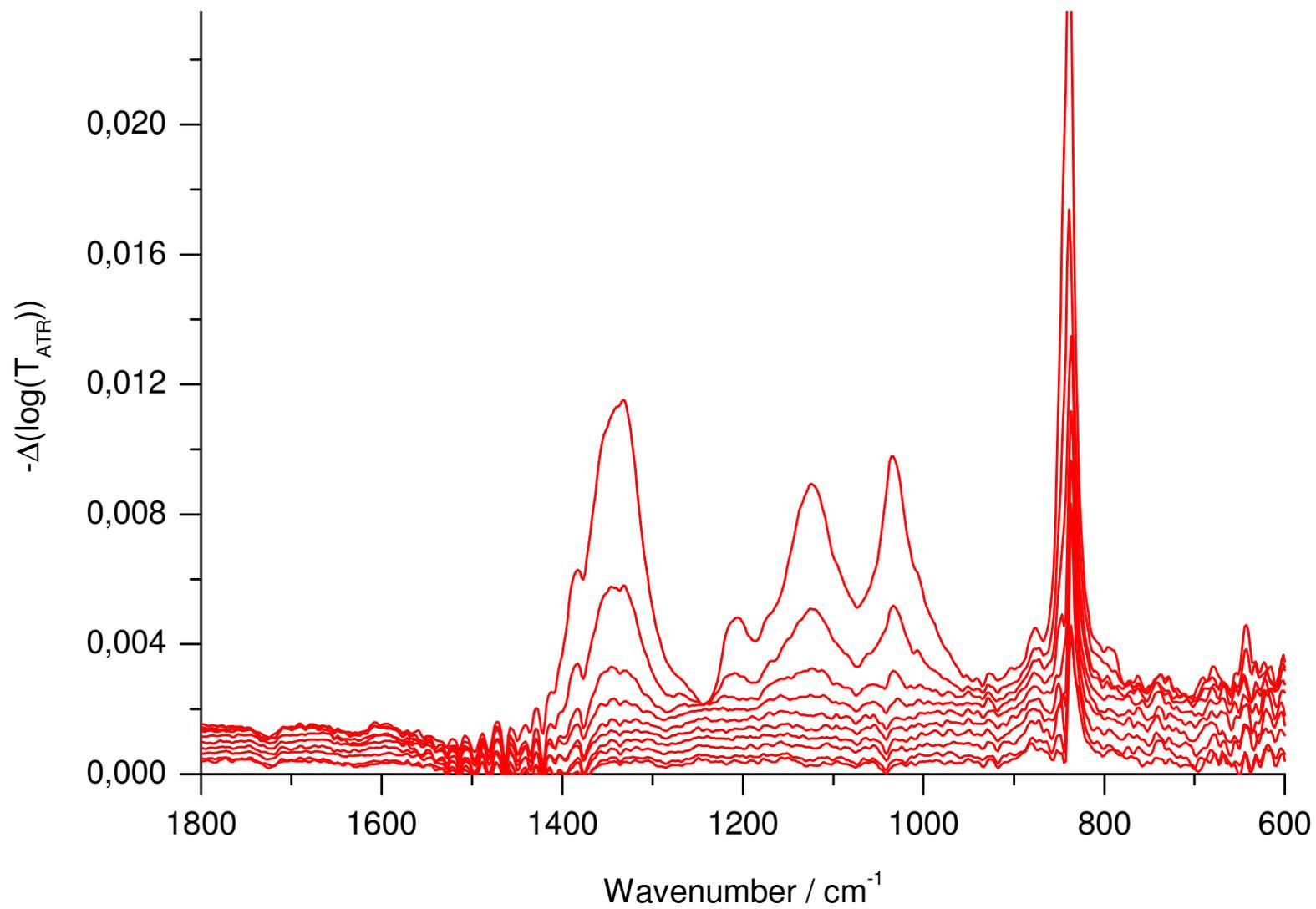


Fig. 3.25: IR difference spectra of BiTh/ITB-C₆₀ copolymer during p-doping, IRAV range.
Sequence: bottom to top

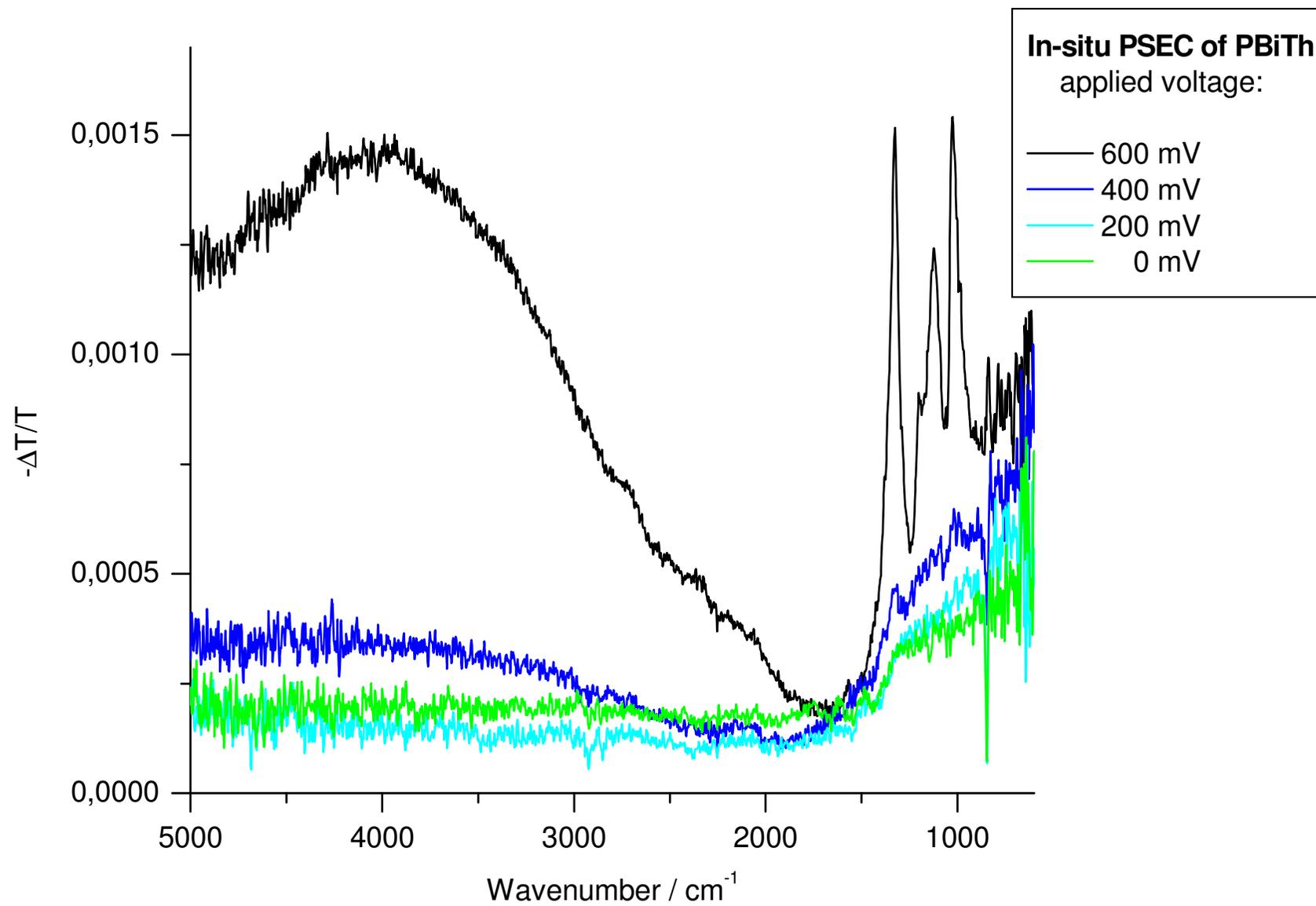


Fig. 3.26: Relative IR spectra of PBiTh during photospectroelectrochemistry at different potentials

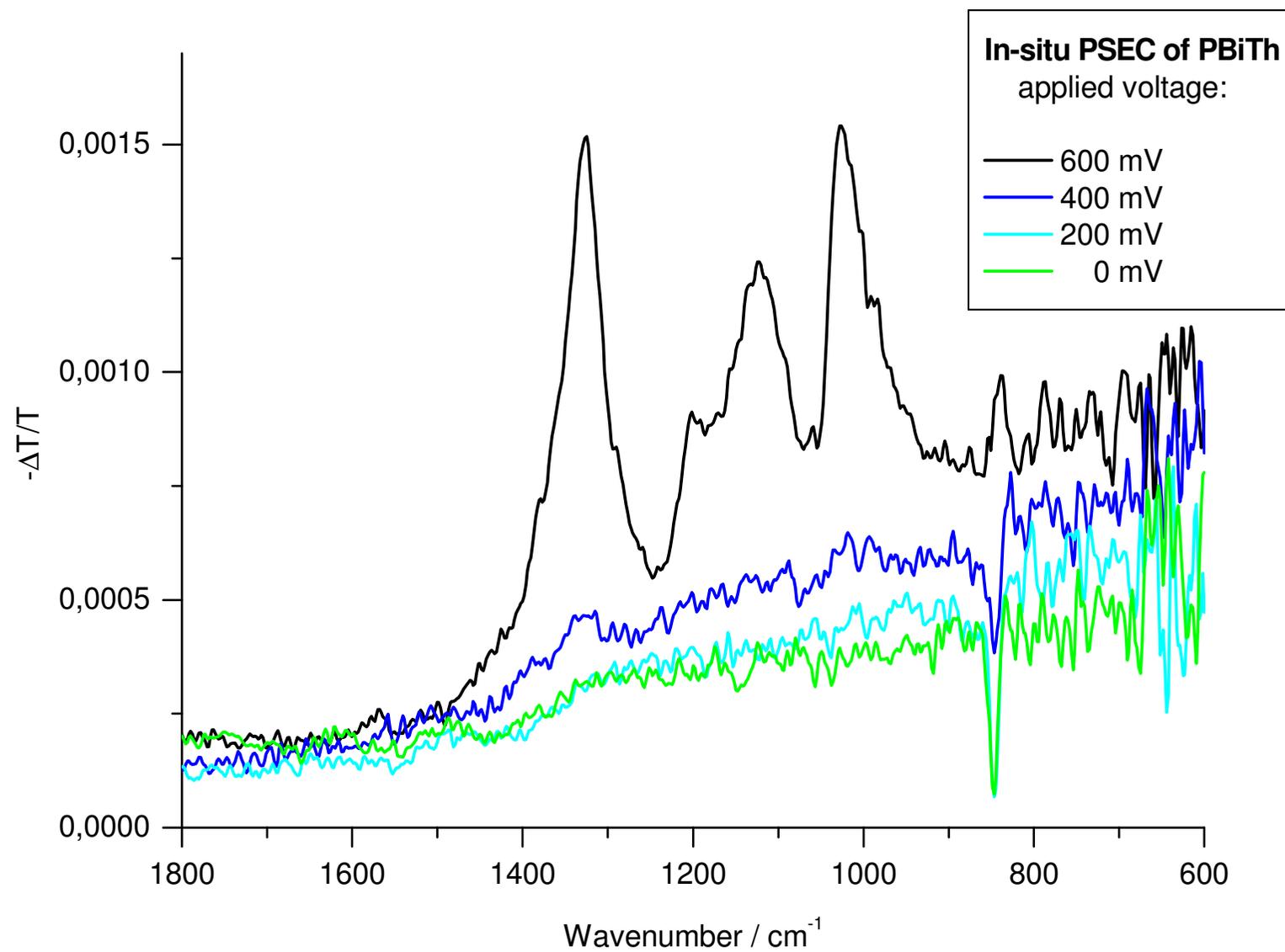


Fig. 3.27: Relative IR spectra of PBiTh during photospectroelectrochemistry at different potentials, IRAV range

4 Summary and Conclusion

Various techniques and materials have been used to investigate the influence of fullerenes on the characteristics of photoelectrochemical cells based on photoactive polymers.

In a first step, soluble P3HT was used as photoactive material; electrodes were prepared by spincoating a solution of this substance on ITO substrates. Afterwards increasing amounts of PCBM were added to the polymer solutions, thus both the polymer and the fullerene were deposited on the substrate. The influence of PCBM on the characteristics of the photoelectrochemical cells which were prepared from this sample was significant. Detailed data is given in Table 4.1. A similar study was performed by using Doctor Blade technique instead of spincoating, giving comparable results. The main problem of these cells is their poor long-term stability, because PCBM is gradually dissolved by the electrolyte solution.

P3HT/PCBM sample ratio	V_{oc} mV	j_{sc} μA·cm⁻²	fill factor	η %
P3HT only	62	-10	0.22	0.0002
P3HT/PCBM 4:1	105	-171	0.18	0.0039
P3HT/PCBM 3:1	134	-258	0.20	0.0086
P3HT/PCBM 2:1	148	-373	0.19	0.0130
P3HT/PCBM 1.5:1	154	-398	0.19	0.0145

Table 4.1: Characteristics of PECs from P3HT/PCBM electrode samples, prepared by spincoating

As a second polymeric system, P3MT was deposited on ITO substrates by electropolymerisation. The results obtained from these samples were quite promising, showing a performance comparable with the best P3HT/PCBM sample. Consequently, it was attempted to further improve the P3MT cells by depositing C₆₀ clusters on top of the polymer.

However, no improvement was obtained because of degradation of P3MT during the deposition process. An overview of the obtained results is given in Table 4.2.

P3MT sample <i>polymerisation time</i>	V_{oc} mV	j_{sc} $\mu\text{A}\cdot\text{cm}^{-2}$	fill factor	η %
CP 2000 mV, 15 s, +C ₆₀	75	-105	0.29	0.0028
CP 2000 mV, 30 s, +C ₆₀	72	-87	0.29	0.0023
CP 2000 mV, 15 s	130	-192	0.26	0.0081
CP 2000 mV, 30 s	122	-403	0.23	0.0144

Table 4.2: Comparison of the characteristics of PECs from C₆₀/P3MT/ITO samples as well as pure P3MT samples, prepared by electropolymerisation

Finally, materials containing covalently bound fullerenes were investigated. These compounds consist of polymer chains with fullerene moieties covalently attached to them. TIO-TEG-C₆₀-NCH₃ and ITB-C₆₀ are monomers containing both the fullerene and a chain fragment, by electropolymerisation polymers should be formed. Unfortunately, it was not possible to produce suitable electrodes from TIO-TEG-C₆₀-NCH₃. However, it was possible to polymerise ITB-C₆₀ on an ITO substrate, allowing the characterisation of such photoelectrochemical cells.

Pure poly-ITB-C₆₀ has a relatively weak absorption in the spectral range between 450 and 650 nm as well as a short chain length, limiting the mobility of the photogenerated charges. A copolymer of ITB-C₆₀ with bithiophene shows both the acceptor properties of the fullerene moiety as well as the increased absorption in the spectral range mentioned. In addition, the chain length is obviously increased. In Table 4.3 the results of this comparison is shown. As can be seen, the best copolymer sample shows higher short circuit current density and also efficiency than the pristine materials alone.

Copolymer sample <i>concentration ratio</i>	V_{oc} mV	j_{sc} $\mu\text{A}\cdot\text{cm}^{-2}$	fill factor	η %
Polybithiophene	110	-50	0.30	0.0022
P-BiTh/P-ITB-C ₆₀ , 3:1	148	-65	0.22	0.0026
P-BiTh/P-ITB-C ₆₀ , 2:1	129	-49	0.25	0.0020
P-BiTh/P-ITB-C ₆₀ , 1:1	155	-138	0.19	0.0051
Poly-ITB-C ₆₀	250	-51	0.23	0.0037

Table 4.3: Characteristics of PECs from ITB-C₆₀ and bithiophene copolymers, prepared by CP electropolymerisation

Finally, using both spectroelectrochemistry and photospectroelectrochemistry techniques, the existence of charged polarous species by light and by electrochemical doping was successfully investigated. Moreover, the obtained spectral information supports the assumptions concerning the chain length of the polymers when the bithiophene – ITB-C₆₀ system was investigated. The obtained results may be a hint for further studies on the nature of photogenerated charge carriers.

In conclusion, it has been shown that fullerenes can contribute to improve the performance of photoelectrochemical cells based on photoactive materials. From all the investigated strategies, simple spin coated electrodes of Poly-3-hexylthiophene with PCBM acceptors added into the polymer matrix show the most promising results. All other approaches could not be successfully implemented due to reasons like instability of the material upon oxidation and incapability of film formation.

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Curriculum vitae

Name: Alexander Gusenbauer
Date of birth: 21st January, 1979
Place of birth: Steyr, Austria
Nationality: Austrian
Marital Status: unmarried

Education

10/1998 – 11/2006 Johannes Kepler Universtiy, Linz, Austria:
Economical Engineering of Technical Chemistry
03/2002 – 10/2006 Johannes Kepler University, Linz, Austria:
Economics
09/2004 – 05/2005 Université Robert Schuman, Strasbourg, France:
University diploma “French and European management”
09/1993 – 06/1998 Grammar school, Wels, Austria
09-1985 – 07/1993 Primary and secondary school, Tragwein, Austria

Related Experience

04/2003 – 03/2004 Diploma Thesis for economical engineering of technical
chemistry at the institute for physical chemistry,
Prof. S. N. Sariciftci
01/2003 – 02/2003 Project collaborator at the institute for physical chemistry

Additional Experience

07/2005 – 12/2005 Diploma Thesis for economics at the institute for production
and logistics management, Prof. G. Zäpfel, in collaboration
with Serafin Campestrini Inc., Ottensheim, Austria:
“Transportalternativen für ein Holzgroßhandelsunternehmen”
10/2004 – 11/2004 Film project in collaboration with Pimkie, Willstätt, Germany
04/2004 – 06/2004 Logistics project in collaboration with the Austrian Post AG,
Vienna, Austria
02/2004 – 08/2004 Responsibility for father’s farm after work accident

07/2002 – 08/2002 French course, Chambéry, France

National Service

02/2000 – 01/2001 Landesfeuerwehrverband Oberösterreich, Linz, Austria

Additional Qualification

Languages	German (mother tongue) English (good working knowledge) French (good working knowledge) Italian (basic knowledge)
IT	MS Office, Origin, HTML, PHP, JavaScript
Social engagement	Active Membership of fire brigade Hinterberg, Austria, responsibility for basic training of new members
Driver's licence	A and B (since 1997)

Hobbies

Literature, languages, cinema, travelling

Eidesstattliche Erklärung

Ich erkläre an Eides statt, dass ich die vorliegende Diplomarbeit selbstständig und ohne fremde Hilfe verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt bzw. die wörtlich oder sinngemäß entnommenen Stellen als solche kenntlich gemacht habe.

Linz, den _____

(Alexander Gusenbauer)