Investigating Interfaces in Organic Photovoltaic Devices using Complex Impedance Analysis

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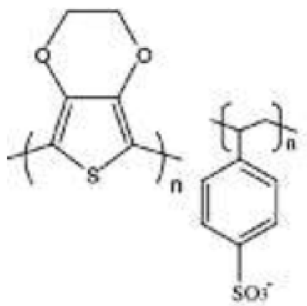
Overview

- Background of organic photovoltaics (OPVs) and their efficiency.
- Impedance spectroscopy (IS) and it's applications.
- Results and conclusions.
- Further work.

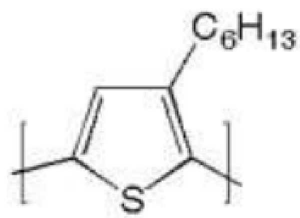
OPV Background

- Photovoltaic technology has the potential to provide a significant proportion of the worlds energy requirements.
- Solar cells based upon inorganic materials are expensive and energy intensive to manufacture.
- OPVs could potentially provide a cheap, flexible alternative.
- Maximum OPV efficiency based upon PCBM:P3HT blends so far achieved is ~6%. [1]

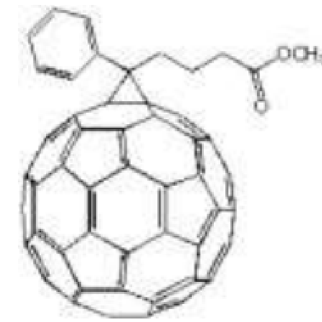
Standard OPV Structure



PEDOT:PSS – hole transport layer

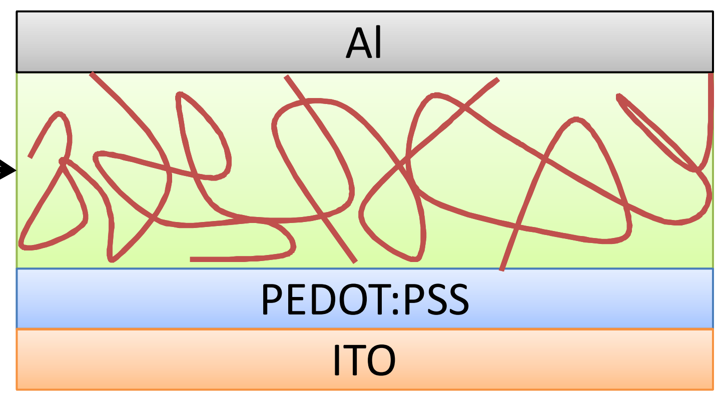


P3HT – electron donor, hole transport layer



PCBM - electron acceptor

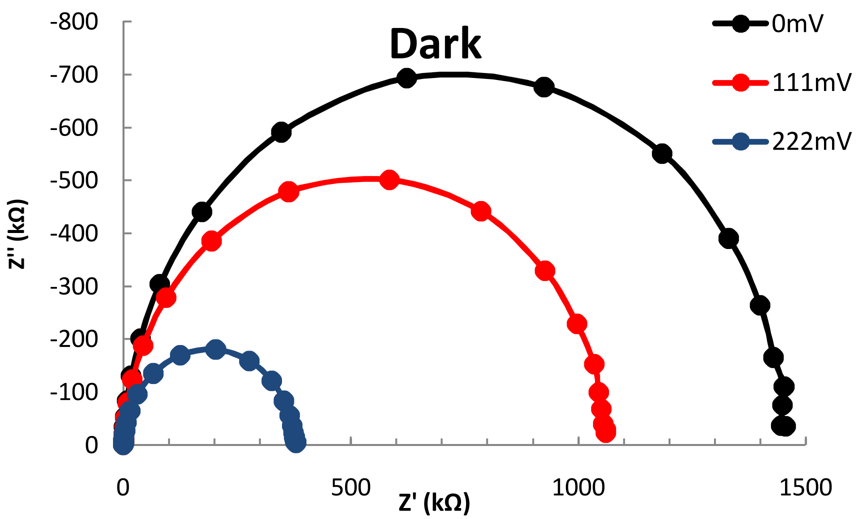
P3HT:PCBM bulk heterojunction – the two polymers phase-segregate creating pathways to electrodes



Impedance Spectroscopy

- Applies a small AC modulation to a bias voltage across a device and sweeps across a frequency range (1Mhz – 1Hz).
- Allows the determination of complex impedance, capacitance and resistance at a particular steady state.
- A small AC modulation is used to keep the linearity of the response; typically ~10-100mV.
- Beginning to allow the determination of electronic properties within the working conditions of OPV devices.[2][3]

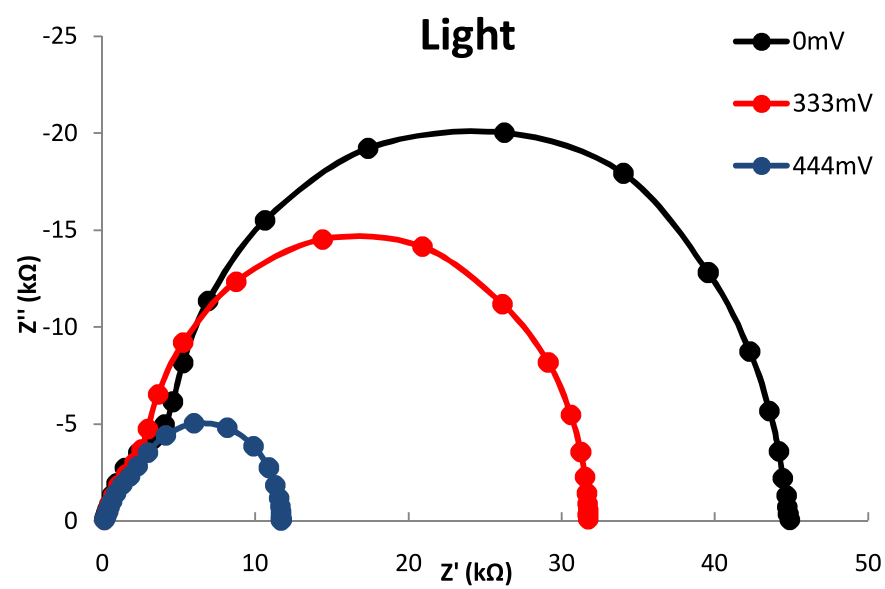
Results: Impedance Spectra



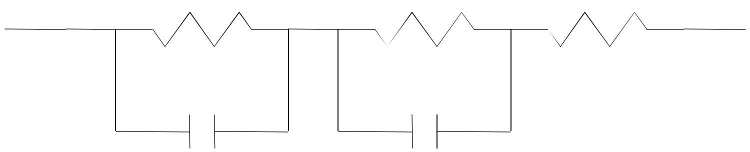
• IS in the dark is characterised by a major RC arc at low frequency and an almost straight line at high frequency.

• IS in under illumination shows a significant additional arc at high frequency as well as the features of the IS in the dark.

• The spectra seen in the dark is typical of systems in which diffusion-recombination dominates.[4]



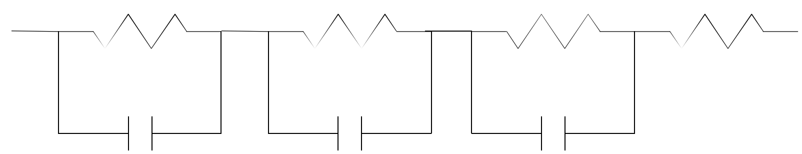
Equivalent Circuit Models



- IS in the dark was modelled based upon a double RC in series with a resistor representing contact wire effects.

- One RC pair models the low frequency (bulk) arc, the other models the high frequency (interfacial) arc.

- IS under illumination was modelled based upon a triple RC in series with a resistor.



- The third RC models the appearance of an arc at high frequency in addition to those seen in the dark.

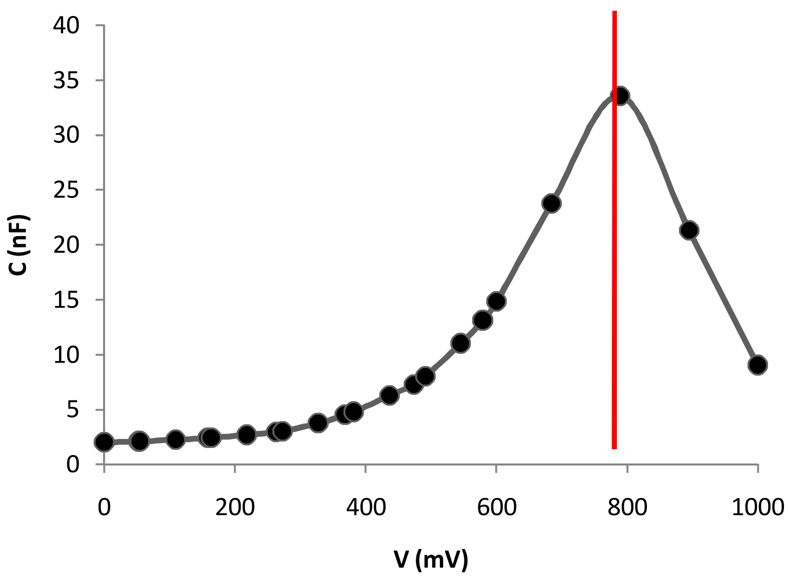
Schottky Junction

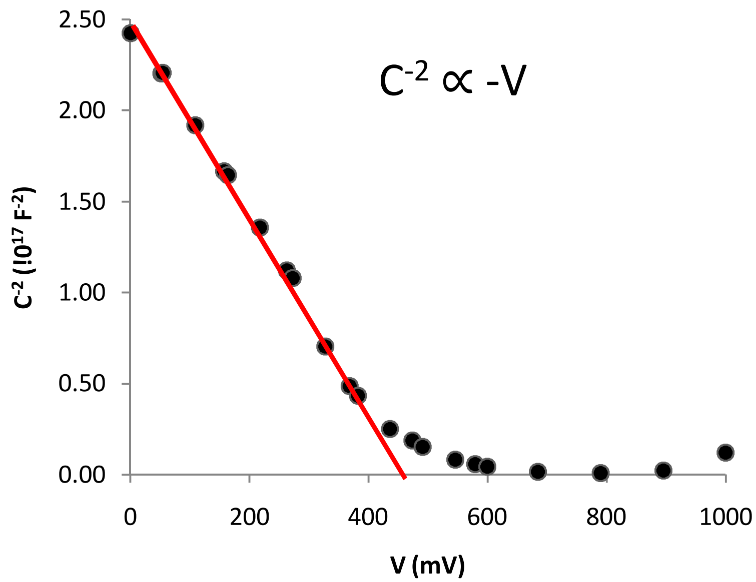
- Significant in OPVs as P3HT when exposed to oxygen and/or moisture is known to become p-doped.[5]
- Similar to a p-n junction but occurs when a p-doped material has an interface with a metal.
- Leads to the creation of a depletion layer in the p-doped material adjacent to the interface.
- By applying a voltage across the junction the width of the depletion zone can be varied, which directly affects the capacitance within the region.

$$C^{-2} = \frac{2(V_{bi} - V)}{A^2 e \varepsilon \varepsilon_0 N_A}$$

- This relationship produces a linear result with increasing bias.

Schottky Junction



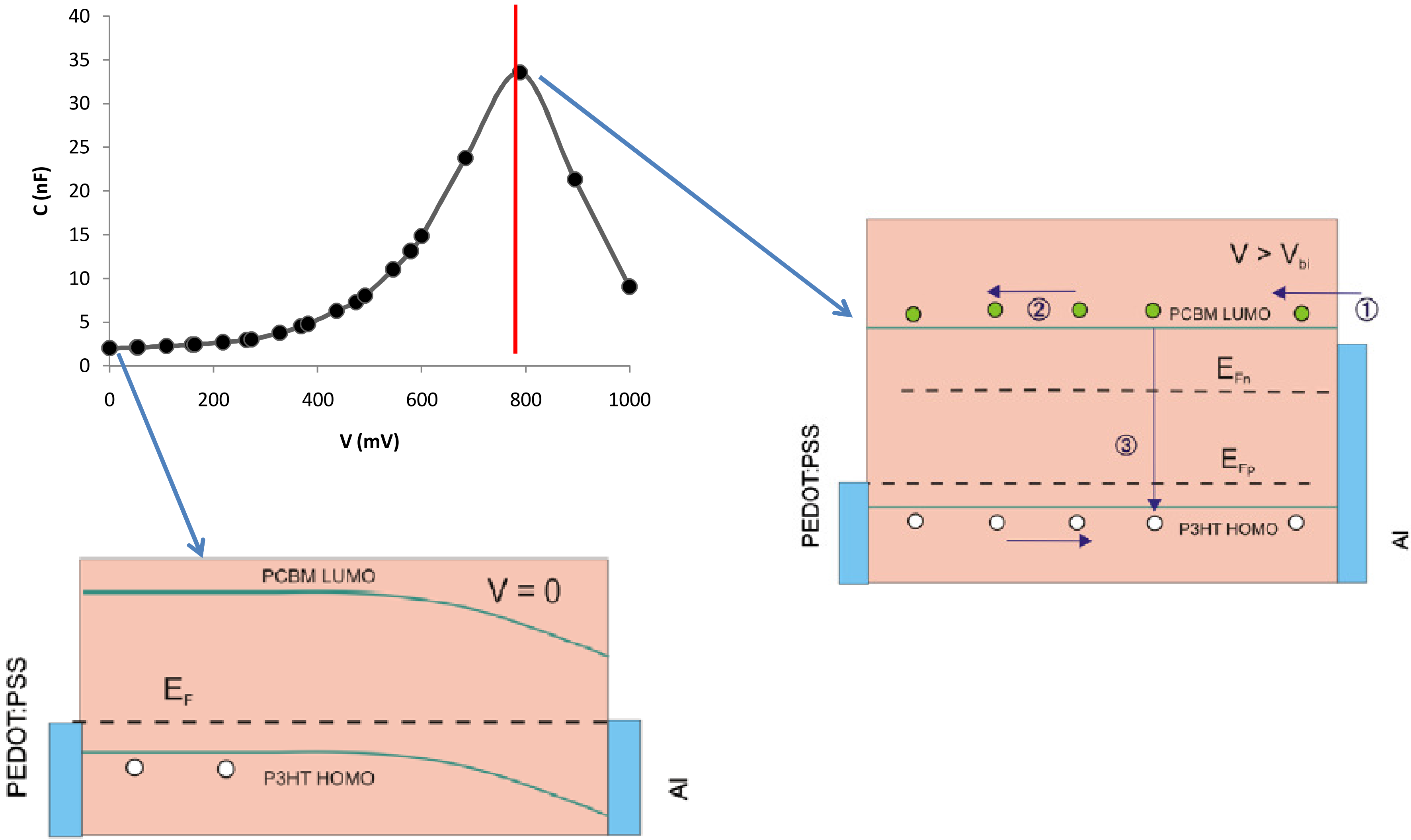


• At low forward bias the capacitance levels off at the geometric value of ~ 1.75nF.

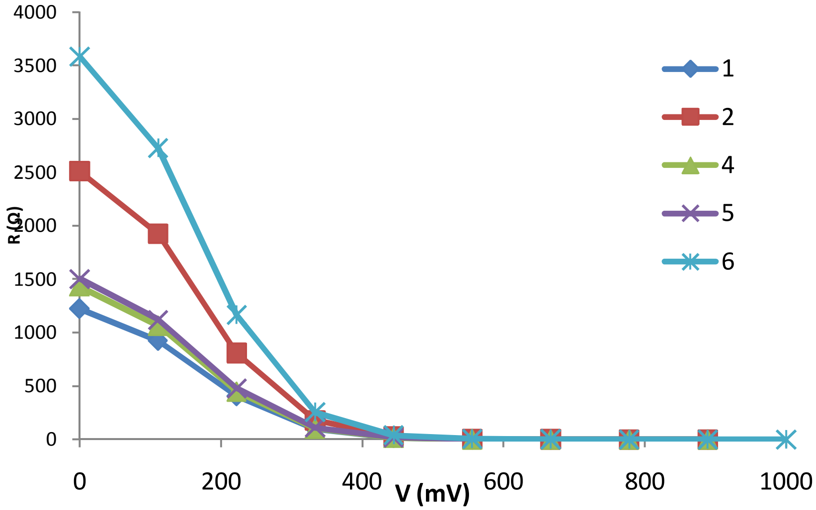
• The capacitance increases with increasing forward bias due to a modulation in the width of the depletion zone.

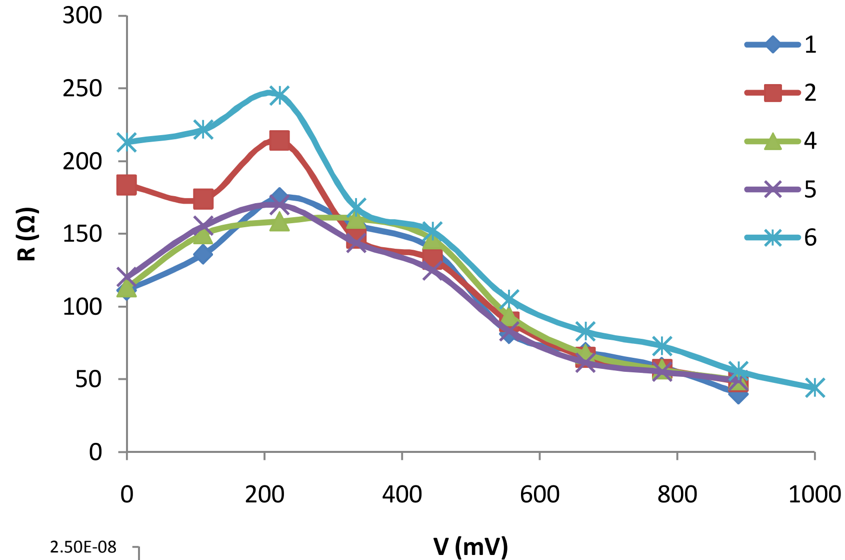
• At V_{OC} ~ 800mV the capacitance peaks and at $V > V_{OC}$ the neutral doped region extends along the bulk layer. The capacitance then decreases due to the limitation of the concentration of minority carriers in the neutral region of the device.

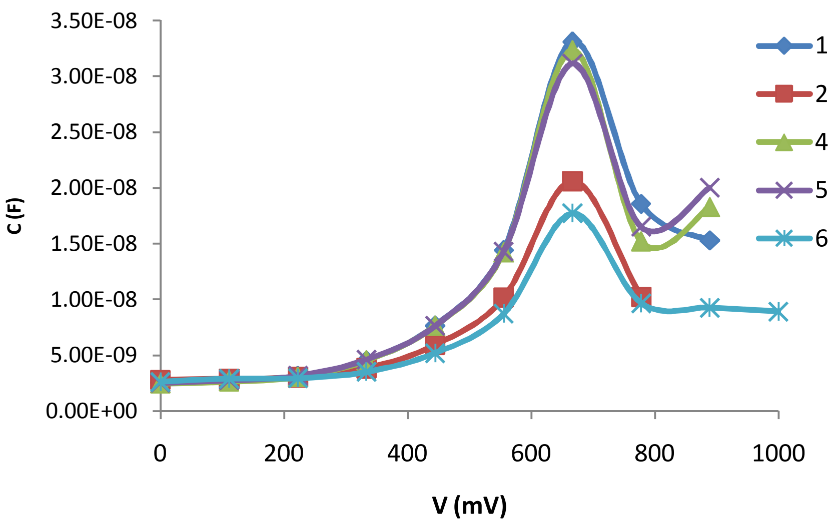
Schottky Junction

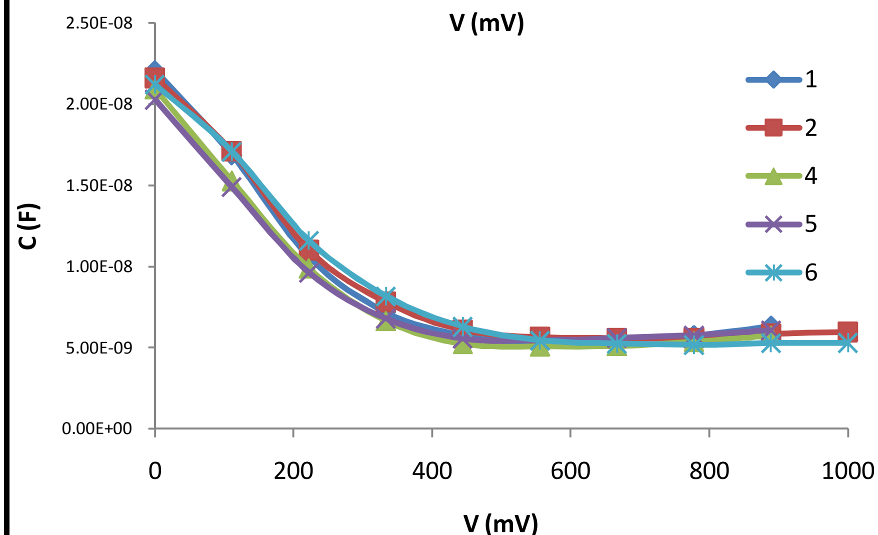


Full Equivalent Circuit Fits - Dark





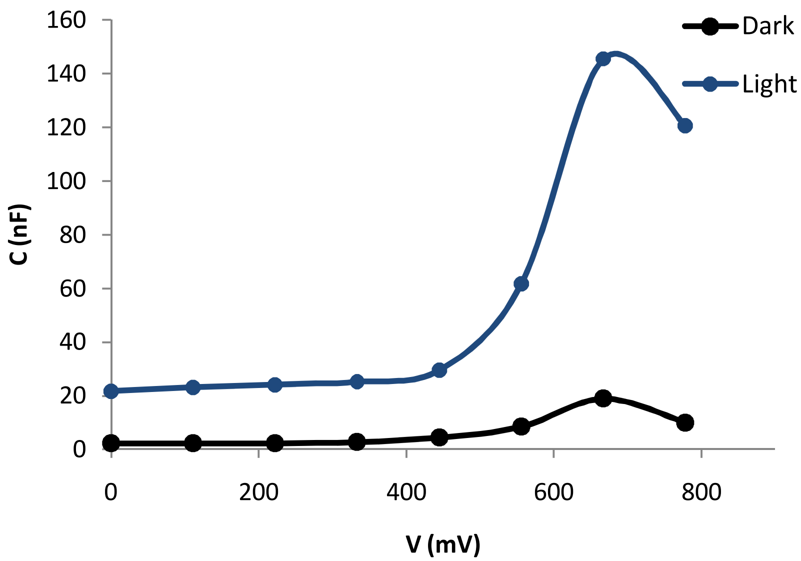


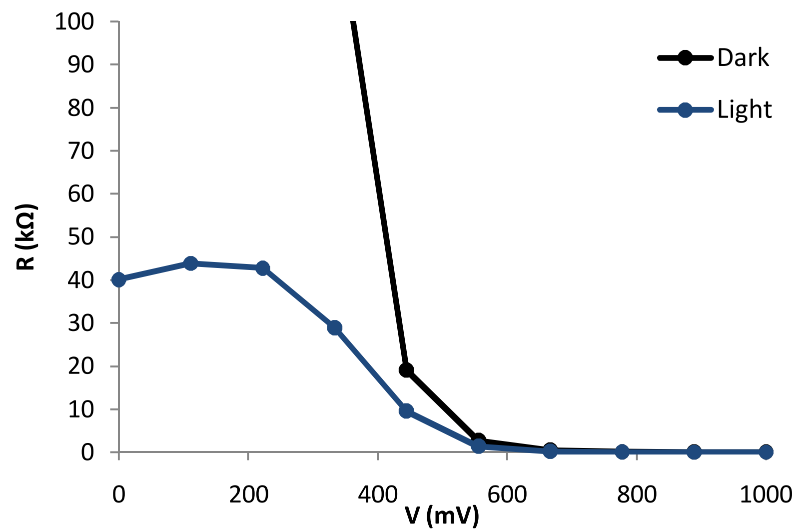


Low frequency

high frequency arc

Light/Dark Comparison





• Under illumination there is a significant increase (a factor of magnitude) in the capacitance values.

• As expected the resistance under illumination drastically reduces as current is carried by both injected charge carriers as well as generated in the active layer.

• The extremely high resistance at low bias voltages is attributed to a shunt resistances that allows current to flow between electrodes.

Summary

- IS is a powerful technique that allows the characterisation of electronic parameters in the working conditions of the device.
- The fitted capacitance of the low frequency arc revealed the formation of a Schottky junction and an associated depletion region adjacent to the P3HT-Al interface.
- Further investigation into the role of different cathode materials is required to gain a deeper insight into the appearance of a high frequency arc under illumination.

Further Work

- Impedance analysis of devices with different cathode material (Ca-Al, Ag, Ca-Ag) to provide a deeper insight into the high frequency arc.

- The role of degradation in OPV devices, in particular the formation of metal oxides (Al_2O_3) at the cathode interface, and the light-induced breakdown of polymers in the blend (IS low frequency arc) could be easily investigate using this technique.

References

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- [2] G. Garcia-Belmonte, A. Munar, E.M. Barea, J. Bisquert, I. Ugarte, R. Pacios, (2008), 'Charge carrier mobility and lifetime of organic bulk heterojunctions analyzed by impedance spectrscopy', Organic Electronics, 9:847-851
- [3] G. Garcia-Belmote, P.P. Boix, J. Bisquert, M. Sessolo, H.J. Bolink, (2009), 'Simultaneous deterimination of carrier lifetime and electron density-of-states in P3HT:PCBM organic solar cells under illumination by impedance spectroscopy', Solar Energy Materials & Solar Cells, 94:366375
- [4] J. Bisquert, (2002), Physical Chemistry B, 106:325-333
- [5] M.S.A. Abdou, F.P. Orfino, Y. Son. S. Holdcroft, (1997) American Chemistry Society 119:5088