

Counterion effects in thin cationic dye films and photovoltaic devices

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Even though the redox levels of organic conjugated molecules can be conveniently measured in solution, their exact position in the solid state and in particular at a heterogeneous interface is difficult to predict. Impressive potential shifts at electrodes and organic interfaces have been reported[1-5]. Monolayers consisting of dipolar molecules of a few Debye and with a surface density of 10^{18} m^{-2} easily induce interfacial potential shifts of the order of 1V[6-8]. This was used to enhance or impede charge injection into organic materials. Mobile ions have similar effects at interfaces and are a central issue in all electrochemical processes[9]. Potential shifts induced by ions have also been used in optoelectronic devices. Light-emitting electrochemical cells provide Ohmic electrode - polymer contacts when using a polymer blend made of the electroactive conjugated polymer and a polymer electrolyte. Poly(ethylene-oxide) with dissolved lithium triflate proved to readily produce mobile positive and negative ions that accumulate at the electrode surface and facilitate charge injection.[10,11] Heterojunctions built from cationic and anionic molecules show the diffusion of negative and positive counterions across the interface. Electroluminescence and photovoltaic response in such devices brought evidence that ionic junctions are indeed built by the thermodynamically driven displacement of mobile ionic charges[12].

In this work cationic cyanine dyes with different counterions were used to fabricate heterojunction bilayer photovoltaic devices using a prototypic acceptor (C_{60}) and donor (MEH-PPV) material, respectively. We demonstrate that the mobile counterions can be easily displaced by applying an external electric field. Furthermore, the performance of photovoltaic devices can be altered tremendously by deploying ionic space charge across the organic interface (Figure 1). The cyanine model compounds allow rationalizing the conspicuous counterion effect on the spectral response and efficiency of organic bilayer photovoltaic devices [13]. Numerical modelling is carried out to explain the experimental observations.

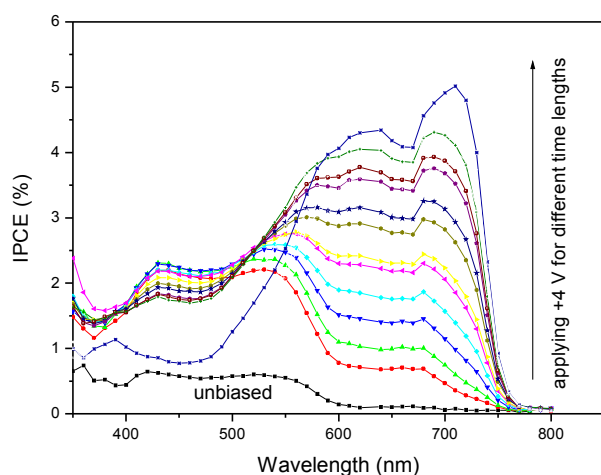


Figure 1 Photocurrent action spectrum (IPCE) of the ITO/PEDOT:PSS/MEH-PPV/cyanine dye/Al device and after biasing at + 4 V for different time lengths. The IPCE characteristic after a long relaxation time following the biasing is also indicated.

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