Electronic Supplementary Information

In situ monitoring of polymer redox states by Resonance microRaman spectroscopy and its applications in polymer modified microfluidic channels

Hella Logtenberg, [a] **Laurens-Jan Jellema,** [b] **Maria J. Lopez-Martinez,** [b] **Jetsuda Areephong,** [a] **Elisabeth Verpoorte,** [b] **Ben L. Feringa** [a] **and Wesley R. Browne** [*a]

Electropolymerisation on gold bead electrodes was performed to study the scan rate dependence with respect to film thickness. Different film thicknesses lead to different electrochemical scan rate dependent responses. Charge trapping is commonly observed for thicker polymer films, as described schematically in Fig S 1.

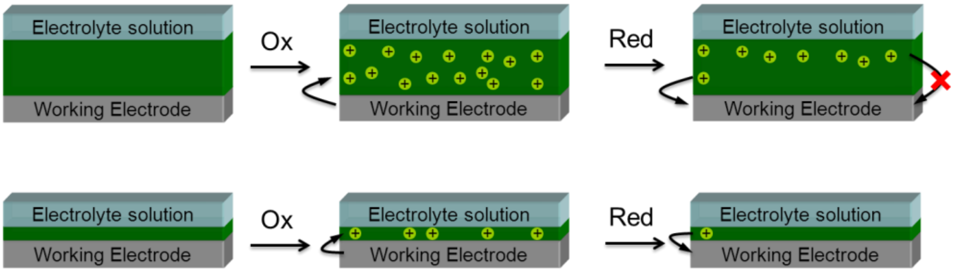

Fig S 1 Trapped charges depend on polymer film thickness.

The cyclic voltammograms from which the scan rate dependence was obtained are depicted in Fig S 2.

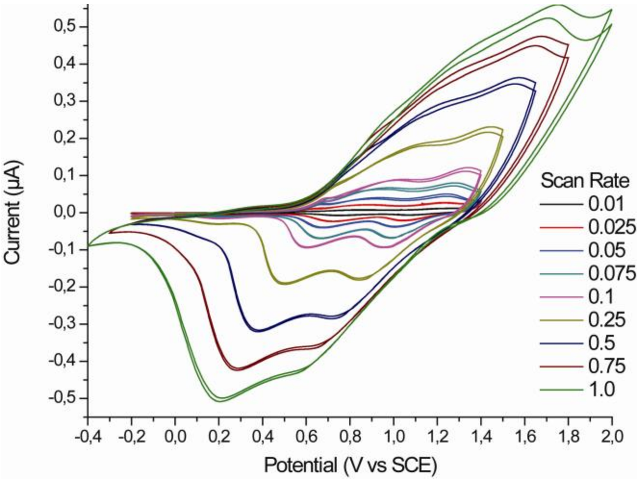

Fig S 2 Cyclic Voltammetry of a thick polymer film on a gold bead electrode (scan rate is in V s^{-1})

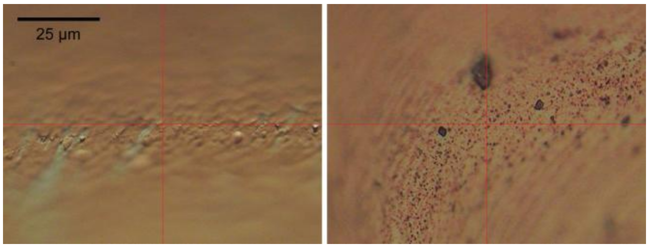

Fig S 3 Optical microscope pictures of a thin (left) and thick (right) polymer film on a gold bead electrode, 100x magnification. On the right aggregates of polymer are observed as darker spots.

A model system for this sexithiophene polymer has been reported previously, which is a phenyl capped dimer.[1] For further evidence of the monocationic species observed in Raman spectroscopy this dimer was also studied.

Fig S 4 Structure of model compound, phenyl capped dimer.

The monocation can be formed in solution by addition of TFA or Fe(III)Cl_3. The formation of the monocation is confirmed by UV/Vis spectroscopy. Resonance enhanced Raman signals are obtained corresponding to the spectrum of monopolaron of the polymer (Fig S 5).

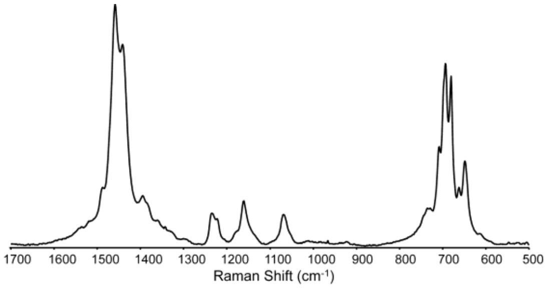

Fig S 5 Raman signals obtained by adding Fe(III)Cl_3 to a solution of the model compound **2**.

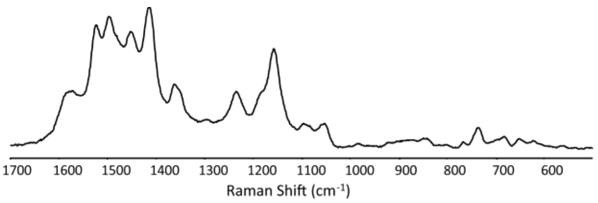

Fig S 6 Raman spectrum of polymer on ITO electrode at λ_{exc} 633 nm.

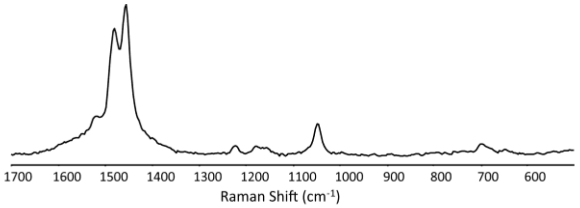

Fig S 7 Raman spectrum of thin polymer film on a gold bead electrode at λ_{exc} 532 nm

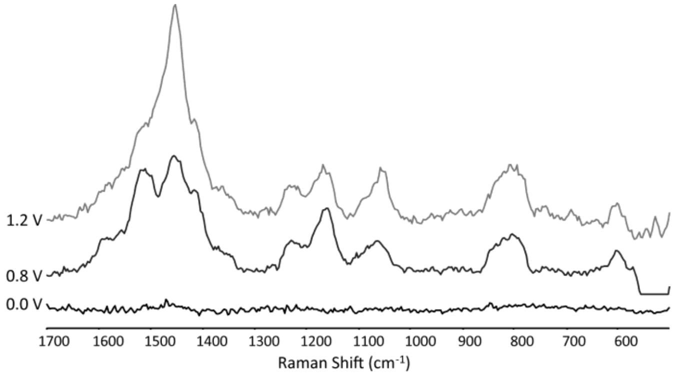

Fig S 8 Raman spectroelectrochemistry on a thin polymer film on a gold bead electrode recorded at λ_{exc} 532 nm.

An overview of the set-up used for electrochemistry in the microchannel is depicted in Fig S 9.

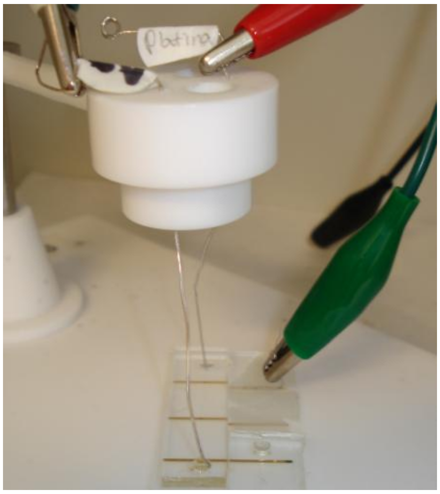

Fig S 9 Microfluidic channel used for polymerisation.

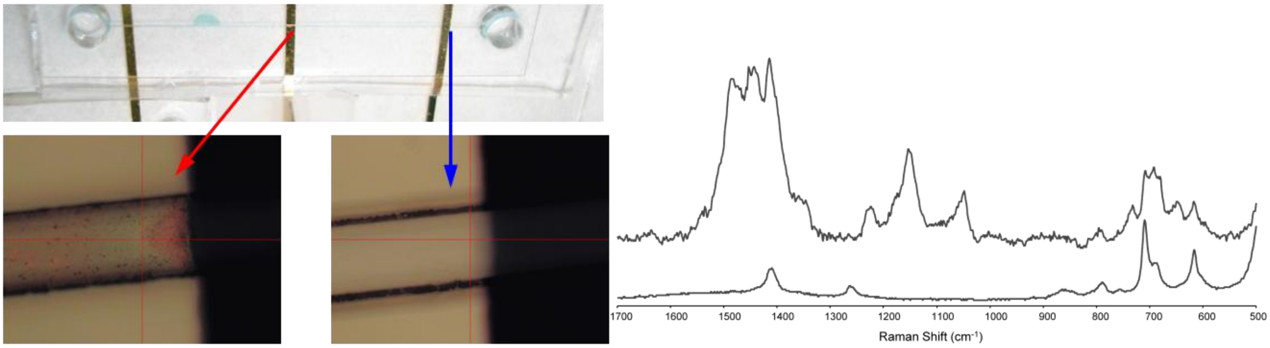

Fig S 10 Polymer was only observed on the gold-electrode connected to the potentiostat as working electrode, which was confirmed by Raman spectroscopy (λ_{exc} 785 nm), upper = left electrode, modified with polymer, lower = right electrode, not modified, Raman signals of PDMS observed.

---

[1] J. Areephong, J. H. Hurenkamp, M. T. W. Milder, A. Meetsma, J. L. Herek, W. R. Browne and B. L. Feringa, *Org. Lett.*, 2009, **11**, 721; M. T. W. Milder, J. L. Herek, J. Areephong, B. L. Feringa and W. R. Browne, *Chem. Phys.Lett.*, 2009, **479**, 137