Electronic Supplementary Material for PCCP

UV-Vis-NIR spectroelectrochemical and in-situ conductance studies of unusual stability of n and p-doped poly(dimethyldioctylquaterthiophene – alt-oxadiazole) under high cathodic and anodic polarizations

Z. Pomerantz[1], M.D.Levi[1*], G. Salitra[1], R.Demadrille[2], A. Fisyuk[2a], A. Zaban[1], D.Aurbach[1] and A.Pron[2]

[1] Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel. E-mail: levimi@mail.biu.ac.il

[2] DRFMC, UMR 5819-SPrAM (CEA-CNRS-Univ. J. Fourier-Grenoble I), Laboratoire de Physique des Métaux Synthétiques, CEA Grenoble, 17 Rue des Martyrs 38054 Grenoble Cedex 9, France

[a] *permanent address: Department of Chemistry, Omsk State University (Russia)*

Contents for Supporting Information:

1. The mode of spectroelectrochemical measurements.
2. The procedure of the in situ conductance measurements
3. Figures 1S and 2S

1. The mode of spectroelectrochemical measurements.

The electronic spectra of both conducting polymers were measured from neutral to highly doped state using a strict sequence of the preceding and following electrochemical steps: (i) the film was initially polarized at -0.5 V for half-an-hour (for n-doping the initial potential was -1.0 V); (ii) a linear voltage scan (LVS) was applied at 20 mVs^{-1} from this potential to the desired potential, let us say, X V; (iii) the film was polarized at this potential for a period of time between 50 and 150 s (shorter time was used at high polarizations); (iv) absorption spectra were measured under constant polarization at X V; (v) the LVS was performed down to -0.5V and polarized at this potential for 100 s; (vi) two consecutive CV curves were measured between the initial potential of 0 V and X V. In the following spectroelectrochemical measurement, the operations from (ii) to (vi) were repeated.

Note that probing the film with CV after constant potential polarization during the electronic spectra measurements allowed us to monitor current redox-state of the polymer film and, qualitatively, the charge carriers dynamics. If, for example, after reaching an extreme potential of the film polarization, the absorption peak of PMOThOD in the vicinity of 475 nm increases rather than decreases, this means that after the preceding neutralization step by CV the resulting neutral form of the polymer may coexist with the charged forms, because the bulk effective electronic conductance is not high enough to complete the oxidation of the neutral forms at not enough slow potential scan rates (the difference in the conduction paths will be revealed). This indicates non-uniform character of the doping process, which can be usually reduced at slower rates of cycling. Examples: the p-overdoped PMOThOD (figure 1a) shows the presence of the neutral form whereas the heavily n-doped PMOThOD (figure 1c) is a fast electronic conductor with no indication of the neutral forms at all. This effect is an early indication of the beginning of the irreversible degradation of the polymer film, resulting in a drastic decrease in the intensity of the

ω_1 and ω_2 transitions, and the characteristic blue shift in the π-π* transition. A combination of both effects with the dominance of irreversible changes under overcharges is seen for the p- and n-doed POTh (figures 1b and d, respectively).

Strictly speaking, the optical absorption spectra in our work were measured under quasi-stationary conditions, so that they should be compared with the slow scan rate CV. This may result in an unreasonably long time of the measurements, so that a compromise was to choose 20 and 40 mVs^{-1} for the POTh and PMOThOD, respectively. ITO may also induce increases Ohmic drops when using fast scan rate CV. Thus in order to check the redox-state of the PMOThOD at the extreme cathodic and anodic polarizations we used slow scan rate CV on a Pt wire covered with the polymeric film (see figure 4).

2. The procedure of the in situ conductance measurements

The interdigitated array electrode used (purchased from Abtech Scientific (VA)) had two sets of comb-type arrays: 100 Å Ti/1000 Å Pt on a borosilicate glass (totally, 50 arrays). They were 5µm wide and 3 mm long, separated by 5µm insulating gaps from its adjacent elements. The gaps between two sets of arrays were bridged by a conducting polymer film under study deposited using anodic polymerization of the related monomeric species. Simultaneous measurements of CV curves and *in situ* electronic conductance were performed using Autolab 20 supplied with a bipotentiostat module (Eco Chemie, Inc., The Netherlands). One set of Pt arrays, served as working electrode WE1, polarized with respect to the high surface area Pt CE with Ag/Ag$^+$ RE. The second set of Pt arrays was connected as the working electrode WE2 to the bipotentiostat. A small constant potential difference (5 mV) was maintained between WE1 and WE2, whereas two currents, I_1 between the WE1 and CE, and I_2 between the WE1 and WE2 were measured during potentiodynamic scans. Assuming that a small potential difference does not virtually change the redox-state of the polymeric film, the current of the related voltammetric response can be evaluated as the average of the currents I_1 and I_2 (i.e. $(I_1 + I_2)/2$) whereas the conductivity is calculated from the ohmic current flowing through the film; the current is thus equal to the half of their difference: $(I_1 – I_2)/2$). We report the absolute values (unless otherwise indicated) of the conductance of the polymeric film deposited on the interdigitated electrode obtained by dividing the ohmic current by the applied small potential difference of 5 mV.

3. Figures 1S and 2S

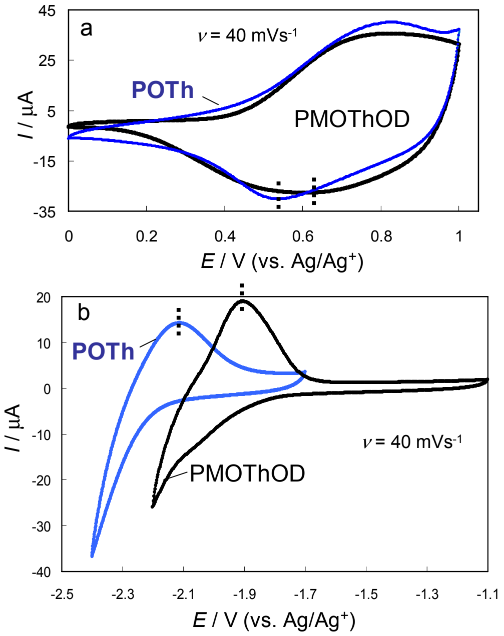

Figure 1S: Cyclic voltammograms of p-, and n-doped PMOThOD film electrode (the black curve) and POTh (the blue curve, see panels a and b, respectively) on ITO support used for an estimation of the difference in the band gaps of these polymers. The vertical dotted lines mark the peaks of the related undoping reactions.

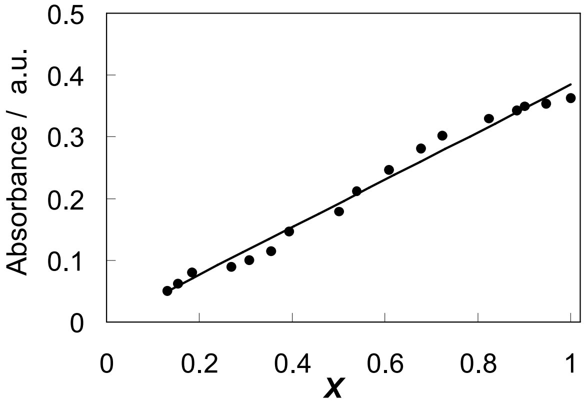

Figure 2S: The plot of the absorbance *vs*. dimensionless doping level *X* for the n-doped PMOThOD film electrode appearing at ω_3 (calculated from the data of figure 1c)