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Wide Energy-Window View on the Density of States and Hole Mobility in Poly(p-Phenylene Vinylene)

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Using an electrochemically gated transistor, we achieved controlled and reversible doping of poly(p-phenylene vinylene) in a large concentration range. Our data open a wide energy-window view on the density of states (DOS) and show, for the first time, that the core of the DOS function is Gaussian, while the low-energy tail has a more complex structure. The hole mobility increases by more than 4 orders of magnitude when the electrochemical potential is scanned through the DOS.

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Charge transport in disordered conjugated polymers like poly(p-phenylene vinylene) (or PPV), polypyrrole and polythiophene [1], and disordered systems in general [2–6] usually proceeds via thermally activated hopping allowing the charge carriers to move from one site to the next. In this process, the energy-dependent density of states (DOS) and the charge mobility (μ) [or the diffusion constant (D)] are two key parameters. The energy distribution of the DOS is often assumed to be Gaussian [3,7,8] (for dipolar interaction [9] the width will be proportional to the strength of the dipoles [2,4,10]) or exponential [11] and both shapes have been applied with success to explain transport properties under different conditions [12–15]. In devices such as polymeric light emitting diodes (LEDs), where the carrier concentration is low, only the tail of the DOS is directly involved in the charge injection. In field-effect transistors (FETs) the carrier concentration c is orders of magnitude larger and the DOS further towards the center of the level distribution is important. These examples show that, for a proper understanding of the electronic properties of such materials, a direct experimental determination of the shape of the DOS function over a large range of energy (or charge concentration) is essential. Until now, only a few measurements have been reported. One attempt to determine the DOS (from now on only valence states are considered) in OC_1C_{10}-PPV, the workhorse in light emitting diodes, has used the temperature and concentration dependence of the hopping conductivity with $FeCl_3$ as a dopant [16]. In another approach it is assumed that the DOS is Gaussian shaped. It then follows [3,8,9,17,18] that the carrier mobility μ depends on temperature via $\ln\mu \propto -(\sigma_d/k_BT)^2$. From the experimental determination of the mobility as a function of temperature the width σ_d of the distribution was determined[17,18] (for a discussion of some of the simplifying assumptions see [8,19]). Recently, concentration dependent DOS and μ data were obtained in a FET and a LED configuration [18]. All of the above mentioned experiments showed the mobility to be strongly concentration dependent. In the charge carrier concentration range covered by chemical doping with $FeCl_3$ the DOS increased linearly with c [16], while for the analysis of the FET and LED experiments [17,18] an exponential and Gaussian DOS were assumed, respectively. It can be concluded that there is still no consensus on the DOS of PPV in a broad energy range.

This letter reports on the DOS and conductivity of thin spin-coated PPV films in a wide, well defined energy range. The data are obtained using an Electrochemically Gated Transistor (EGT), which was recently developed . Using the impressive energy range of the EGT, we are able to confirm the previous data and to show for the first time that the core of the DOS function is Gaussian, while the flank has an exponential energy dependence. The low-energy tail has a more complex structure. Conductance measurements were performed over a wide carrier concentration range and show that the hole mobility is strongly energy-dependent, as also seen in results obtained with a classical FET [18]. The maximum value of the mobility exceeds previously reported values by a factor of 40. The mobility is found to vary over more than 4 orders of magnitude when the Fermi-level is scanned over less than half an eV. In addition, our measurements allow an energy calibration of the DOS and the mobility.

The electrochemically gated transistor offers a unique possibility of studying the transport properties of polymers as a function of doping in a reversible way. The operating principle is based on changing the electrochemical potential $\tilde{\mu}_e$ of the sample (OC_1C_{10}-PPV) with respect to a Ag pseudoreference electrode (RE) by means of a potentiostat, see Fig. 1. The PPV layer is in electrochemical equilibrium with the Au source-drain electrodes. Any change in potential with respect to the Ag

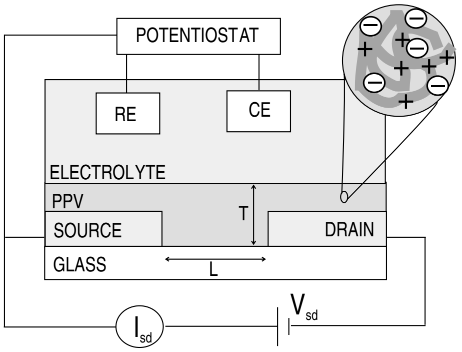

FIG. 1. Schematic picture of the electrochemically gated transistor or EGT. The sample (PPV) is placed in an electrolyte solution. The electrochemical potential of the sample is controlled with respect to a reference electrode using a potentiostat. The conductivity was measured by applying a small dc bias between source and drain. The enlargement shows schematically how the holes on the polymer chain are compensated by the anions in the film.

electrode is followed by charge transfer from the Au electrodes to the PPV or vice versa and current flow to the Pt counter electrode (CE). When the potential is increased holes are injected into the PPV [23]. The hole charge is counterbalanced by anions (ClO_4^- or PF_6^-) from the electrolyte solution (0.1 M TBAP (tetrabutylammonium perchlorate), $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) or $LiClO_4$ in acetonitrile) [24] which permeates the PPV. The number of holes stored in the PPV film is determined by monitoring the differential capacitance. Important advantages of electrochemical gating over the conventional field-effect transistor are the uniform charging[22] of the PPV film together with a wider doping range. At a given doping level the conductance is measured with a very small source-drain bias (10 mV, $I_{SD} \propto V_{SD}$) supplied by a Keithley 2400 source meter. Another advantage of the EGT is that the electrochemical potential can be correlated with the vacuum level. To achieve this the potential of the Ag RE was measured with respect to the electrochemical potential of the ferrocenium/ferrocene redox reaction (0.68 V). From the literature value of the latter[25] with respect to vacuum (5.14 V), the Ag RE was calculated to be at 4.47 V below the vacuum level.

The PPV samples with a typical thickness T of 180 nm were spin-coated on glass substrates with Au electrodes separated by a gap L of 1.25 up to 10 μm and with an effective transistor length of 1 up to 50 cm (interdigitated electrodes). The electrochemical potential was controlled with a Princeton Applied Research Potentiostat/Galvanostat 273A and all experiments were carried out under Ar atmosphere. The volume V_P of the various polymer films was between 0.03mm^3 to 0.1mm^3 (accuracy 5%). From the specific weight of the PPV one can determine the density N of PPV monomers [26]. The density of states $g(\tilde{\mu}_e)$, was obtained from the charge ΔQ stored in the PPV film per $\Delta\tilde{\mu}_e = 10$ meV increase of $\tilde{\mu}_e$, i.e.

$$g(\tilde{\mu}_e) = \frac{\Delta Q}{e\Delta\tilde{\mu}_e N V_P} \tag{1}$$

with e the elementary charge [see Fig. 2(a)]. The DOS is therefore determined directly; no assumptions are required. From 0 to 0.6 eV the amount of injected charge is small. After this point a strong increase is observed. At around 0.8 eV a shoulder is visible and above 1.1 eV, $\Delta Q(\tilde{\mu}_e)$ starts to decrease. With decreasing $\tilde{\mu}_e$ the maximum and the shoulder are well reproduced. Measurements on different samples, with different potential steps and other ions in solution gave very similar results. The number of holes per monomer $c(\tilde{\mu}_e)$ at a given electrochemical potential is obtained by integration of $g(E)$: $c(\tilde{\mu}_e) = \int_0^{\tilde{\mu}_e} g(E)dE$ [see Fig. 2(b)]. It can be seen that the doping level can be varied by electrochemical gating in a controlled and reversible manner between 10^{-5} and 0.4 holes per monomer.

The density of states g(E) is plotted in Fig. 3, where the energy on the vertical axis is given with respect to the vacuum level. The values for $g(E)$ on the horizontal axis range from 10^{-4} to one states/monomer eV. At $E = -5.55 \pm 0.02$ eV, g has a maximum. This shows that due to disorder and dispersion the highest occupied molecular orbital (HOMO) levels are spread in energy and we are able to access the center of the distribution. The shoulder at about -5.3 eV reveals some additional structure in the measured DOS. By fitting the data to a

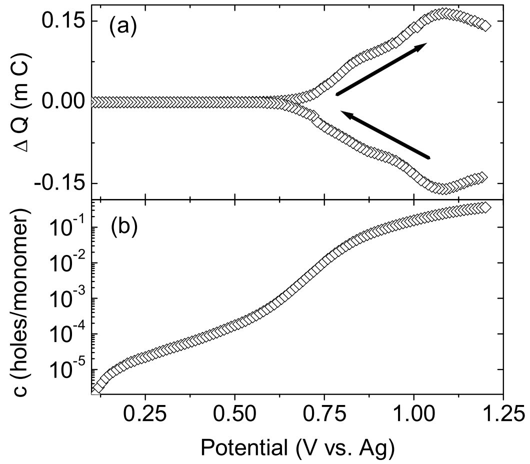

FIG. 2. Electrochemical injection of holes into the PPV film. (a) The differential charge $\Delta Q(\tilde{\mu}_e)$ stored in PPV when successive 10 mV steps are applied. The potential is defined with respect to the Ag pseudoreference. The arrows show the two scanning directions: doping and dedoping while changing $\tilde{\mu}_e$. (b) Doping per monomer $c(\tilde{\mu}_e)$ calculated from the data in (a). The reversible doping range extends over 4 orders of magnitude.

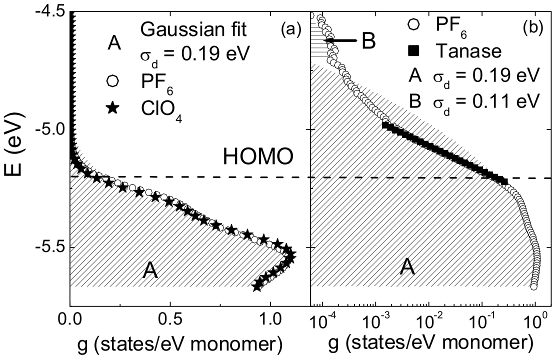

FIG. 3. The E dependence of the experimentally determined DOS ($g(E)$) where E is with respect to the vacuum level. The horizontal dashed line marks the HOMO position found from cyclic voltammetry [28,29]. (a) E vs $g(E)$ using PF_6^- and ClO_4^- as anions. A Gaussian function with $\sigma = 0.19$ eV (area A) fits the data well. (b) E vs $g(E)$ for PF_6^- on a linear-log scale. Below $g = 0.1$states/(eVmonomer) deviations from the Gaussian fit are visible. The filled squares are the PPV FET-data by Tanase *et al.* [18], which are well described by an exponential function. At the lowest values of $g(E)$ additional structure appears, which in a limited energy range would allow a description with a Gaussian with a width of 0.11 eV (area B) as used for PPV LEDs by Martens *et al.* [9] and Tanase *et al.* [18].

Gaussian distribution

$$g(E) = \frac{N_m}{\sqrt{2\pi}\sigma_d}\exp\left[-\left(\frac{E - E_{ct}}{\sqrt{2}\sigma_d}\right)^2\right], \qquad (2)$$

we find a width $\sigma_d = 0.19 \pm 0.01$ eV, centered at $E_{\mathrm{ct}} = -5.55 \pm 0.02$ eV (diagonally shaded area A in Fig. 3). The number of states per monomer $N_m = \int g(E)dE$ has a value of 0.52 ± 0.01 when we integrate over the whole Gaussian [27]. The measured DOS validates the assumption of a Gaussian distribution [3] in the core [$g > 10^{-1}$ states/(eV monomer)]. For g between 10^{-3} and 10^{-1} states/(eV monomer) the data follow an exponential dependence, see the logarithmic-linear plot of Fig. 3(b). The DOS in this range measured by Tanase *et al.* in a solid-state FET configuration [18] (solid squares in Fig. 3(b)] is in very good agreement with our data.

In general ions in the dielectric will influence the energy landscape and broaden the DOS [14]. The data presented here compare well with those of Tanase *et al.* [18], where no ions are present in the film. Hence, the intrinsic level distribution of the investigated OC_1C_{10}-PPV must be sufficiently broad, such that an extra contribution by the ions is not observable in our experiments. There is no guarantee that this also holds for the data at higher doping; the intrinsic width of PPV might therefore be lower than 0.19 eV. At very low doping the influence of the ions is expected to be small. Here, around $g \sim 10^{-4}$states/(eVmonomer), the data allow for fitting to a Gaussian with $\sigma_{\mathrm{d}} = 0.11$ eV (horizontally shaded area B in Fig. 3(b)], as reported in Refs. [17,18]. Note, see Fig. 3(b), that the Gaussian distribution in this doping regime is a tail effect, which is not representative for the main distribution.

On inspection of the DOS it is clear that the assignment of the HOMO level at -5.2 eV [28,29] (horizontal dashed line in Fig. 3), as determined by cyclic voltammetry (location at 10% of the peak value), is relatively arbitrary. The value of -5.2 eV corresponds to the point at which a strong increase in DOS is observed. However, many states are already available for values of E up to -4.5 eV. This means that in LED applications a deviation of the "HOMO level" of 0.7 eV from the cyclic voltammetric value is possible. This has to be included in quantitative descriptions of charge injection and carrier mobility in devices [14].

When a small voltage difference is applied between the source-drain contacts, the conductivity σ of the PPV layer can be measured as a function of doping regulated by $\tilde{\mu}_e$, see Fig. 4. The conductivity, which was checked to be ohmic up to the highest field of 10^4V/m, increases by 5 orders of magnitude, as the doping is increased from about 0.02 to 0.30 holes per monomer. A similar strong increase was previously reported for $FeCl_3$ doped PPV [16]. The values of σ are calculated with a constant thickness of PPV, not taking into account effects of swelling. Because the measurements had to be performed in a two-point contact configuration, the flattening of σ at high c might be caused by contact resistances, which means that actual values of σ or μ might be even higher. From the measured conductivity the hole mobility (μ) can be determined via the relation: $\sigma = Np_te\mu$ with p_t

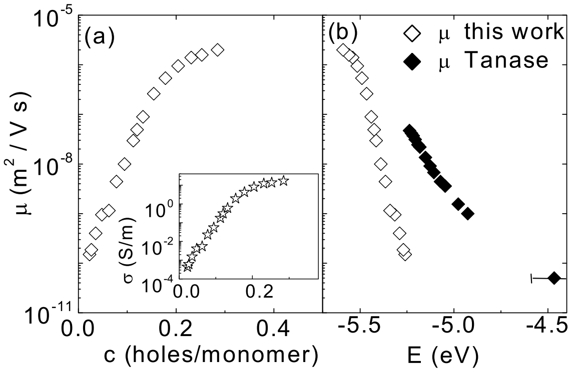

FIG. 4. (a) The hole mobility (μ) calculated from the conductivity (σ- the inset) as function of doping. Because the measurements had to be performed in a two-point contact configuration, the flattening of σ at high c might be caused by contact resistances. Hence, actual values of σ or μ might be even higher. (b) The dependence of hole mobility on energy or electrochemical potential $\tilde{\mu}_e$. At lower doping, corresponding to energies $E > -5.2$ eV, we have included μ (closed symbols) determined in a solid-state FET and LED by Tanase *et al.* [18]. The deviations are discussed in the text. Both plots are on a logarithmic-linear scale.

the number of holes per monomer participating in transport and e the elementary charge. The states involved in hopping are those within k_BT of the chemical potential [30], $p_t(\tilde{\mu}_e) \sim \int_{\tilde{\mu}_e - k_BT/2}^{\tilde{\mu}_e + k_BT/2} g(E)dE$. The results, presented in Fig. 4, confirm that the mobility is concentration, or better, energy-dependent [16,18]. For a doping level of 0.3 a mobility of 2×10^{-6} m^2/Vs is obtained, more than a factor of 10 higher than the highest value found by Tanase *et al.* [18] for comparable field values, but at 0.02 holes per monomer. The lower mobilities obtained in the EGT compared to the solid-state FET at the same doping levels are likely due to the presence of the anions that tend to localize the mobile holes. In addition, in the solid-state FET transport takes place primarily in the first PPV layers close to the interface, where a possible higher structural order will have a favorable effect on the mobility.

In conclusion, by using an EGT the DOS of a polymer can be determined over more than 1 eV or a doping range extending over 4 orders of magnitude. A comparison with the DOS obtained with a solid-state FET [18] reveals that data below 0.1 states/(eV monomer) (doping levels below 10^{-2} holes per monomer) are representative for the intrinsic level distribution of OC_1C_{10}-PPV. The shape of the DOS function is complex. While the core is well described by a Gaussian function (its width of 0.19 eV has to be considered an upper boundary for the intrinsic width), the flank decays exponentially and the tail at very low densities allows a description with another Gaussian. The hole mobility is found to vary from 10^{-10}m^2/Vs to 10^{-6}m^2/Vs, as the chemical potential changes from -5.3 eV to -5.6 eV. We have shown that PPV can be electrochemically doped with a high degree of control and reversibility. The accessible energy window is much larger than that of previously used methods. Thus electrochemical gating appears to be a powerful method for studying charging and transport properties of conducting polymers.

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