In-situ determination of the energy dependence of the high frequency mobility in polymers

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The high-frequency mobility ($\mu_{hf}$) in disordered systems is governed by transport properties on mesoscopic length scales, which makes it a sensitive probe for the amount of local order. Here we present a method to measure the energy dependence of $\mu_{hf}$ by combining an electrochemically gated transistor with in-situ quasi-optical measurements in the sub-terahertz domain. We apply this method to poly(2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene) (OC$_1$C$_{10}$-PPV) and find a mobility at least as high as 0.1 cm$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is limited by the weakest link in the conduction path, it usually can not provide detailed insight in the transport processes involved on mesoscopic length scales. As previously demonstrated for metal-insulator composites, chemically doped polymers and polymers in solution, measurements of $\mu$ as function of frequency are more informative for the mesoscopic structure and the conduction process. (6-7-8-9) For example, a few years ago Hoofman et al. applied their time-resolved microwave conductivity technique to investigate the charge mobility in a PPV solution. (7) In this method a high energy electron beam (3 MeV) creates doping ions, and the differences in transmission for 30 GHz radiation is translated to the mobility, which was found to be about $2 \cdot 10^{-5}$ m$^2$/Vs. Martens et al. used voltage-modulated millimeter-wave spectroscopy to determine the carrier mobility in solid state devices of OC$_1$C$_{10}$-PPV at frequencies between 10 and 200 GHz. (8) The carriers were introduced from contacts in the device by a large electric field of around hundred V/µm and the high frequency mobility $\mu_{hf}$, deduced from the attenuation of the sub-THz radiation through the device, was shown to be as high as $10^{-7}$ m$^2$/Vs. The dependence of $\mu_{hf}$ on the applied voltage over the contacts was linked to the occupation of the levels in the (almost Gaussian) density of states (DOS). (9). This finding was very recently supported by DOS data obtained with an electrochemically gated transistor (EGT). (10-11) The method was proven to be reliable for PPV and the mobility could be followed over a relatively large energy scan of more than an eV. (10-12)

In this letter we describe a method to measure the high-frequency mobility, which combines the process of electrochemical doping using an EGT with in-situ quasi-optical measurements in the sub-terahertz domain. (10-11) Knowing the amount of doping and the precise energy calibration are great advantages over the time-resolved microwave conductivity or voltage-modulated millimeter-wave spectroscopy methods. Using OC$_1$C$_{10}$-PPV as an illustration, we determine the dependence of the high-frequency mobility on the electrochemical potential.

A major problem to overcome when working with ionic solutions is that ions in the electrolyte strongly absorb at sub-THz frequencies. In earlier studies with similar electrolytes and the polymer dissolved in the solution, the absorption by the electrolyte completely dominated and prevented investigation of the properties of the polymer films. (13) To overcome this difficulty, the electrochemical cell was designed to minimize the path of the radiation in the solution. In our experiments the radiation frequencies are around 190 GHz. The cell has been made out of quartz and had a free space of 2.5 mm in the direction the radiation propagates. Still, when filled with electrolyte it absorbs more than 100 dB, which makes the measurements impossible. To minimize the absorp-

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In many materials of practical interest, like doped or amorphous semiconductors, metal-insulator composites, and doped conjugated polymers, disorder introduces charge localization, and hence charge transport is due to hopping of the carriers instead of band transport. This makes the high-frequency mobility in polymers often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5) Because $\mu_{dc}$ in a disordered system is often low. For example, in polymeric light emitting diodes the dc hole mobility ($\mu_{dc}$) for the used conjugated polymer poly([2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene]) (OC$_1$C$_{10}$-PPV) is typically of the order of $10^{-11}$ m$^2$/Vs at room temperature. (1-2-3-4-5)
In the EGT cell a counter electrode (Pt foil) and a reference electrode (Ag wire) are required, see Fig. 1 for calibrated changes in the electrochemical potential. Because PPV is air-sensitive, the cell has to be air-tight. Casting of the samples on ITO covered glass and mounting in the cell were done under nitrogen atmosphere.

The measuring procedure is straightforward: the electrochemical cell is placed between the source and detector horns of the sub-THz setup and by creating a potential difference (∆V) between the working electrode (ITO) and the reference electrode (Ag) doping is achieved. Results of a typical measurement, where the transmission is monitored as function of time, are shown in Fig. 2a. To get a measurable difference in transmission between the undoped and doped OC$_3$C$_{10}$-PPV sample, the thickness of the PPV layer had to be more than 10 micron. Initially ∆V is zero, that means no doping. After about 200 seconds ∆V is changed to a value of 1 V. Once the steady-state value in transmission is achieved (∼10$^3$ seconds after the potential change) ∆V is set to 0 V, corresponding again to an undoped sample. While doping, we observe that the transmission decreases by 6-7 dB and on switching back to a non-doped state (0 V) the original transmission value is recovered. Repeating this procedure several times we obtained the transmission changes corresponding to different values of the applied potential on the working electrode. From the measured transmission the conductivity $\sigma$ can be calculated via

$$|T| = \frac{A}{1 + [(d/2\varepsilon_0)\sigma(\omega)]^2},$$

with $A$ a constant that takes into account the transmission of the substrate, electrolyte, cell’s walls, etc., $d$ is the polymer film thickness, $c$ the speed of light, $\varepsilon_0$ the permittivity of free space and $\sigma(\omega)$ the film conductivity. Eqn. 1 is only valid, if the optical thickness of the film is less than the wavelength of the probing radiation, which is satisfied in our case for films with thickness less than 25 µm. The calculated conductivity as function of time is shown in Fig. 2b.

The measured conductivities for different potentials, see Fig. 3a, compare well with those of organic crystals or amorphous silicon, with typical values of the order of 300 S/m. From the conductivity, the high frequency mobility can be extracted if we know the number of participating carriers. This number depends on the density of states and the electrochemical potential. In dc-transport, which is an interchain and intrachain process, due to the Fermi-Dirac statistics especially transitions in

\[ \begin{align*}
\text{FIG. 1 Front view of the electrochemical cell used. The regions indicated by dotted lines are: 1 - sample (PPV on a glass substrate), 2 - Ag reference, 3 - Pt counter electrode, 4 - Teflon spacer positioned behind the sample, and 5 - level of the electrolyte in the cell. The cell dimensions are about 5 cm $\times$ 5 cm. A cap with a rubber O-ring seals the cell. Four feed-through connections in the cap enable electrical contact with the reference and counter electrodes and the source and drain contacts on the sample. The direction in which radiation propagates is perpendicular to the plane of the figure.}
\end{align*} \]
In conclusion, we have developed a method to measure the high frequency mobility based on an electrochemically gated transistor. The advantages over the existing methods are its ability to deal with solid state films, higher doping levels than the ones obtained in diode configurations, and the precise energy and concentration calibration. The results show that the structure at short length scales supports a mobility which comes close to those of organic crystals.

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References

[1] H. Meyer, D. Haarer, H. Naarmann, and H. H. Horhold, Phys. Rev. B 52, 2587 (1995).
[2] A. Y. Kryukov, A. C. Saidov, and A. V. Vannikov, Thin Solid Films 209, 84 (1992).
[3] M. Gailberger and H. Bässler, Phys. Rev. B 44, 8643 (1991).
[4] P. W. M. Blom, M. J. M. de Jong, and J. J. M. Vleggaar, Appl. Phys. Lett. 68, 3308 (1996).
[5] I. N. Hulea, R. F. J. van der Scheer, H. B. Brom, B. M. W. Langeveld-Voss, A. van Dijken, and K. Brunner, Appl. Phys. Lett. 83, 1246 (2003).
[6] L. J. Adriaanse, J. A. Reedijk, P. A. A. Teunissen, H. B. Brom, M. A. J. Michels, and J. C. M. Brokken-Zijp, Phys. Rev. Lett. 78, 1755 (1997).
[7] R. J. O. M. Hooftman, M. P. de Haas, L. D. A. Siebbeles, and J. M. Warman, Nature 392, 54 (1998).
[8] H. C. F. Martens, O. Hilt, H. B. Brom, P. W. M. Blom, and J. N. Huiberts, Phys. Rev. Lett 87, 086601 (2001).
[9] H. Bässler, Phys. Stat. Sol. (b) 175, 15 (1993).
[10] A. L. Roest, J. J. Kelly, D. Vannanckelbergh, and E. Meulenkamp, Phys. Rev. Lett. 89, 036801 (2002).
[11] I. N. Hulea, H. B. Brom, A. Houtepen, J. J. Kelly, D. Vannanckelbergh, and E. Meulenkamp, Phys. Rev. Lett. 93, 166601 (2004).
[12] C. Tanase, E. J. Meijer, P. W. M. Blom, and D. M. de Leeuw, Phys. Rev. Lett. 91, 216601 (2003).
[13] J. A. Reedijk, PhD. Thesis, Leiden University (1999).
[14] I. G. Romijn, H. J. Houpkens, H. C. F. Martens, H. B. Brom, A. K. Mukherjee, and R. Menon, Phys. Rev. Lett. 90, 176602 (2003).
[15] A. F. Stassen, R. W. I. de Boer, N. N. Iosad, and A. F. Morpurgo, Appl. Phys. Lett. 85, 3899 (2004).
[16] V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, and J. A. Rogers, Science 303, 1644 (2004).