Intrinsic dielectric properties and charge transport in oligomers of organic semiconductor copper phthalocyanine

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Various contributions are distinguished in the experimentally detected dielectric response of organic semiconductor copper phthalocyanine. While a giant dielectric constant of virgin samples is shown to be due to extrinsic effects, the temperature dependence of the intrinsic dielectric constant, being of the order of 10, indicates two structural phase transitions, as well as a dielectric relaxation reflecting the charge carriers' response. Ac-conductivity data reveal not only the universal dielectric response arising from the polaron tunneling process, but also that another mechanism, which results in the superlinear power law increase in a frequency dependent conductivity, governs the charge transport at lower temperatures.

Ever since semiconductivity in metal phthalocyanines (MePcs) has been discovered,[1] these compounds are among the most interesting organic semiconductors, mainly due to their high chemical stability and various possible synthetic modifications. Not only that ferroelectriclike properties in thin films of copper phthalocyanine (CuPc) deposited on the metal surface[2] and in Langmuir-Blodgett CuPc films[3] have been reported, but MePcs have also been presented as a very promising material for a thin-film transistor[4] and light emitting diode.[5] Furthermore, CuPc oligomers have recently been used as a filler to a polymer matrix in developing an all-organic composite actuator material with a high dielectric constant.[6]

As charge transport properties in organic semiconductors are quite different from those in inorganic materials,[7] this issue has attracted a great interest also in MePcs.[8–10] In addition, the influence of different metal contacts[11,12] and oxygen[13] on the electrical and junction properties of MePcs has been studied. However, despite facts that metal electrodes alter electric properties and that dielectric properties are dependent on the sample treatment,[14] there is still a lack of experimental data which would enable the separation of extrinsic and intrinsic contributions to the dielectric response and conductivity of MePcs. It has namely been shown that extrinsic effects can induce giant values of dielectric constant in inorganic semiconductors.[15]

We have therefore conducted high-resolution dielectric measurements in CuPc oligomers and separated various contributions to the detected response. Results clearly demonstrate that extrinsic effects induce a giant dielectric constant in samples exposed to air. The intrinsic dielectric data reveal the existence of two phase transitions, as well as a dielectric relaxation reflecting the charge carriers' response. Furthermore, besides the universal dielectric response (UDR), which has already been observed in CuPc,[8,14] also a superlinear power-law increase in a frequency dependent conductivity has been detected. This effect has recently been reported to

exist in a variety of complex inorganic systems.[16] In addition, results on ac conductivity reveal that tunneling of polarons is one of the dominating charge transport mechanisms in CuPc.

Multiring CuPc oligomer samples were synthesized by the solution method as described in Ref. 6. The complex linear dielectric constant $\varepsilon^*(\nu,T)=\varepsilon'-i\varepsilon''$ was measured between 10 and 450 K in the frequency range of 0.1–3 MHz using a Novocontrol alpha high-resolution dielectric analyzer. The amplitude of the probing ac electric signal, applied to samples having thicknesses of 280 μm and being covered with sputtered gold or silver paste electrodes, was 1 V. Temperature was stabilized within ±0.1 K using an Oxford Instruments continuous flow cryostat (10–300 K) or lock-in bridge technique with a Pt100 resistor as a thermometer (100–450 K). The real part of the complex ac conductivity $\sigma^*(\nu,T)=\sigma'+i\sigma''$ was calculated via $\sigma'=2\pi\nu\varepsilon_0\varepsilon''$, with ε_0 being the permittivity of vacuum.

Figure 1 shows the frequency dependence of ε', measured at room temperature. Giant values, detected at lower frequencies in the virgin sample, strongly decrease in low pressure conditions and are further suppressed after annealing the sample under vacuum at 400 K, however, they are restored if the sample is exposed to air. These values are therefore induced by the formation of thin surface oxide layers. It is namely known that O_2 acts as a dopant of the MePcs (Refs. 11 and 13) and that thin surface layers of different conductivity than that of the bulk strongly increase the measured dielectric constant of a semiconductor.[15] Furthermore, a similar mechanism most probably governs the low-frequency dielectric response in porous silicates, where a strong decrease of the dielectric constant under vacuum and its restoration in the air has also been observed.[17] However, while in CuPc oxygen is the source of the thin surface layers which induce a giant dielectric constant, in porous silicates air humidity governs the response—water molecules namely form thin conductive layers over the surface of the grains. It
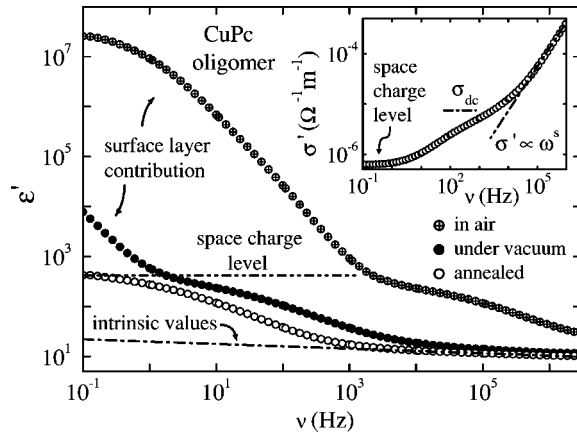
FIG. 1. The frequency dependence of the real part of the complex dielectric constant, ε', measured at room temperature after three different treatment procedures of the CuPc sample. The inset shows the frequency dependence of the real part of the complex ac-conductivity, σ', after annealing. Various contributions to the dielectric response are distinguished.

should also be stressed that giant ε' values in CuPc oligomers are correlated with the work function of the electrode. On the other hand, larger values at lower frequencies in the annealed sample are not dependent on the electrode type and are therefore the result of the space charge, i.e., interface polarization, which usually alters the response in polycrystalline samples at lower frequencies. The inset to Fig. 1 shows the frequency dependence of σ' in the annealed CuPc sample, where again the space-charge contribution can clearly be distinguished. σ_{dc} is also indicated, while at higher frequencies σ' follows UDR $\sigma' = \sigma_0 \nu^s$ ($s<1$). Concomitantly, ε' follows $2\pi\varepsilon_0\varepsilon' = \tan(s\pi/2)\sigma_0\nu^{s-1}$,[18] as indicated by the dot-dashed line in the main frame. UDR has already been observed in MePcs,[8,14] and it should be noted that there are several theoretical approaches which deduce such a behavior from the microscopic transport properties, including tunneling of the charge carriers between different localized states.[19]

In order to obtain information on intrinsic CuPc properties it is therefore essential to measure the response of the annealed sample in a low-pressure condition. Figure 2 thus shows temperature dependences of the complex dielectric constant and ac conductivity, measured in the annealed CuPc sample. Two distinctive features, a change of slope at ≈ 340 K and a step at ≈ 410 K, can be resolved. The latter has already been reported and has been, via pyroelectric current measurements, associated with the appearance of the spontaneous polarization.[14] However, the pyroelectric current has not reversed in polarity on heating/cooling[14] as is typical for the ferroelectric transition. We have therefore additionally checked the nature of this transition by performing the hysteresis loop and switching current measurements, but we have not found any confirmation for the existence of the spontaneous polarization. Furthermore, the dielectric data around 410 K in Fig. 2 are not typical for a ferroelectric transition, therefore we assume that both dielectric anomalies, at ≈ 340 K and at ≈ 410 K, are due to structural changes in CuPc. As the dielectric response at lower frequencies is
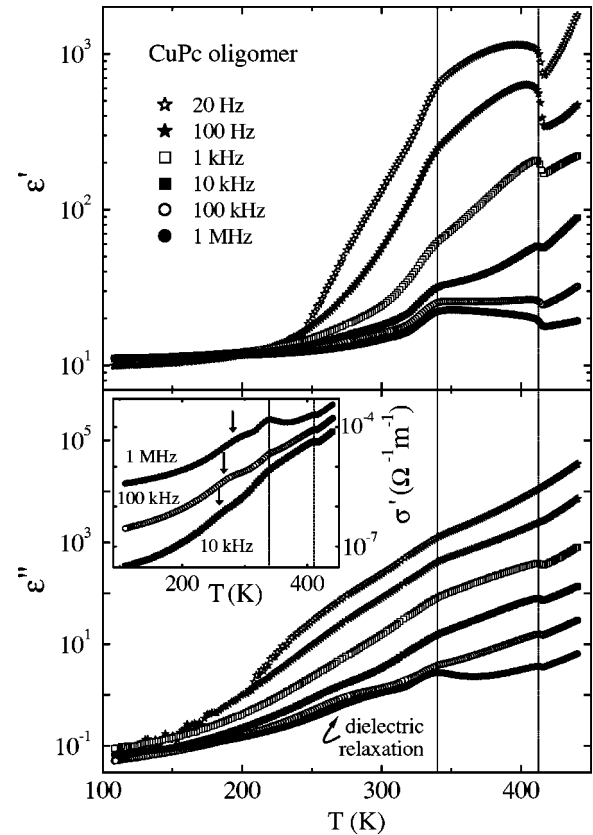

FIG. 2. The temperature dependences of ε' and ε'', measured at several frequencies in the annealed CuPc sample. Detected phase transitions are indicated by vertical dotted lines, while the observed dielectric relaxation is marked by arrows in the $\varepsilon''(T)$ dependence and in the inset, which shows the temperature dependence of σ' at higher frequencies.

clearly altered by the space-charge effect (large ε' and ε'' values), $\sigma'(T)$ is in the inset to Fig. 2 shown only at frequencies above 10 kHz. Arrows mark a dielectric relaxation, which appears in the same temperature and frequency range as in the CuPc–P(VDF-TrFE-CFE)-terpolymer composite,[20] where it was ascribed to the nomadic polarization phenomenon[21]—completely delocalized π electrons act very much like dipoles. This effect is here, in comparison to a CuPc molecule, strongly enhanced, as delocalized electrons can move over the relatively large distance of several molecules forming the oligomer.

The frequency dependence of σ', measured at several temperatures in the annealed CuPc sample, is shown in Fig. 3. While at higher temperatures the space-charge effect, σ_{dc}, and UDR contributions can be identified (cf. the inset to Fig. 1), at lower temperatures data at higher frequencies tend towards the superlinear power law $\sigma' \propto \nu^n (n>1)$. Unfortunately, due to extremely high values of a typical sample's resistance, which at lower temperatures almost exceed the experimental range limit, as can be seen in the inset to Fig. 3, ac conductivity at lower frequencies cannot be determined accurately. However, $\sigma'(\nu)$ data, detected at 10 K, clearly indicate the superlinear power-law dependence. Such a behavior (UDR followed by a superlinear power law) has re-
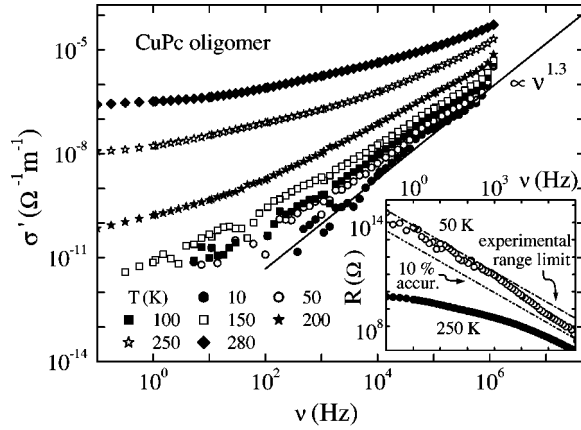
FIG. 3. The frequency dependence of σ', measured at several temperatures in the annealed CuPc sample. The solid line demonstrates that at lower temperatures σ' follows the superlinear power law. Due to extremely high values of a typical sample's resistance, which at lower temperatures almost exceed the experimental range limit (the inset), ac conductivity at low frequencies cannot be determined accurately.

FIG. 4. The temperature dependence of the UDR parameter s, determined in the annealed CuPc sample in the frequency interval shown in the upper inset, compared to data obtained in the CuPc–P(VDF-TrFE-CFE)-terpolymer composite (Ref. 19). Solid lines denote the fit (CuPc-terpolymer) and the calculation (CuPc oligomer) using the model for polaron tunneling [Eq. (1)].

cently been reported to exist in a variety of complex inorganic systems[16] and indicates that, besides a process which results in UDR, another mechanism governs the charge transport in CuPc oligomers.

A detailed analysis of UDR is shown in Fig. 4. The frequency interval, where UDR in CuPc can clearly be distinguished, is shown in the upper inset, while the main frame presents the temperature dependence of the UDR parameter s, compared to data obtained in the CuPc–P(VDF–TrFE–CFE) composite.[20] Data obtained in the composite were fitted[20] to the model for polaron tunneling which yields the temperature dependence of s as[19]

$$s = 1 - \frac{4 + 6W_\infty r_0'/kTR'^2(W_\infty, r_0', \tau_0)}{R'(W_\infty, r_0', \tau_0)[1 + W_\infty r_0'/kTR'^2(W_\infty, r_0', \tau_0)]^2}. \quad (1)$$

W_∞ and r_0' denote the energy barrier and reduced polaron radius, respectively, while R' is the reduced tunneling distance, also being a function of W_∞ and r_0' and additionally, of the inverse attempt frequency τ_0.[19] The solid line through the CuPc data in Fig. 4 is calculated from the Eq. (1) using values of $W_\infty = 0.79$ eV, $\tau_0 = 10^{-13}$ s, and $r_0' = 1.6$. These values slightly differ from those determined in the CuPc-terpolymer composite ($W_\infty = 0.59$ eV, $\tau_0 = 10^{-13}$ s, $r_0' = 2.43$). We are aware that the model predicts a frequency dependence of s and that the frequency interval where UDR can clearly be resolved in CuPc oligomer differs from that in the CuPc-terpolymer composite (compare insets to Fig. 4).
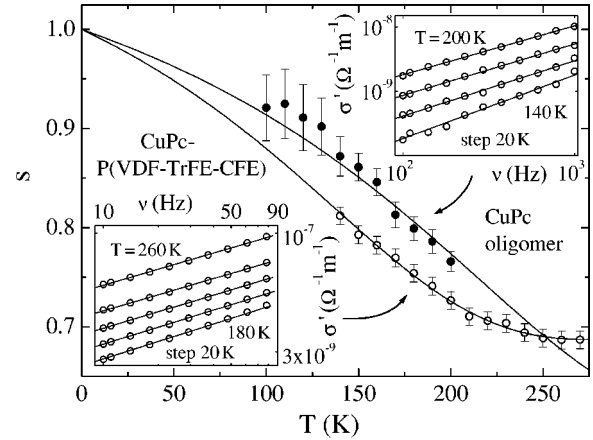
However, it can be assumed that the rather weak $\ln(\nu)$ dependence of the reduced tunneling distance[19] leads to only small deviations in s in these relatively narrow frequency ranges. Thus, differences in W_∞, τ_0, and r_0, determined in CuPc oligomer and in the CuPc-terpolymer composite, are in fact due to different tunneling properties in both systems. It should also be stressed that in the composite the distinctive dielectric relaxation disabled the determination of s at lower temperatures,[20] while in the CuPc oligomer s cannot be accurately determined at lower temperatures due to the high sample's resistance values (cf. inset to Fig. 3), which prevent accurate ac-conductivity measurements. Nevertheless, data in Fig. 4 demonstrate that tunneling of polarons is one of the dominating charge transport mechanisms in CuPc oligomers.

In summary, by separating various contributions to the dielectric response of CuPc oligomers we have shown that the giant dielectric constant in samples exposed to air is due to extrinsic effects. The intrinsic dielectric data revealed the existence of two, most probably structural phase transitions, as well as a dielectric relaxation reflecting the charge carriers' response. The temperature dependence of the UDR parameter s demonstrates that tunneling of polarons is one of the dominating charge transport mechanisms. In addition, a superlinear power-law increase detected in a frequency dependent conductivity indicates another process driving the charge transport in CuPc at lower temperatures.

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