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Traps for Charge Carriers in Molecular Materials Formed by Dipolar Species: Towards Light-Driven Molecular Switch

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Summary: The influence of polar species on the transport and trapping of charge carriers is discussed. Calculations performed on a model molecular lattice demonstrate that polar dopants locally modify the polarization energy thus creating traps for charge carriers in the vicinity of the dipole. The presence of polar dopants in disordered solids gives rise to a broadening of the density-of-states function. A scheme of a molecular switch has been put forward, based on electrostatic interactions between photochromic moieties and charge carriers travelling on a molecular wire (conjugated polymer chain).

Keywords: charge transport; dipolar traps; molecular switch; photophysics; polarization energy

Introduction

Owing to numerous current and emerging applications of molecular materials, there has been a continued interest in studies of electrical properties of low-molecular-weight single-crystal and polycrystalline materials, molecular glasses and polymers.[1-9] Many concepts, useful in explaining electrical properties of molecular solids stem from ideas developed at early stages of investigations.[6-9] In particular, the origin of local centres capturing charge carriers (carrier traps) in molecular materials has been explained[10-12] employing the electrostatic model put forward by Lyons[6,13] almost half a century ago. The traps are formed on sites where, locally, the ionization energy is lower than that in a perfect lattice (traps for holes) or the electron affinity is higher than the respective value in the perfect crystal (traps for electrons). Local modifications of these

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parameters can be achieved in two ways: *(i)* substitution of a host molecule with a chemically different guest, or *(ii)* a suitable local change of the polarization energy.

The polarization energy *(P)* is the energy of electrostatic interactions between a charge carrier momentarily localized at a given site of the lattice with a polarizable molecular solid.[14] If the molecular crystal is built of non-polar molecules, then, within the approach put forward by Lyons, [6,13] the latter parameter can be written as a sum of terms representing electrostatic interactions of increasing order (and decreasing importance)

$$P = P_{\mathrm{id}} + P_{\mathrm{dd}} + \ldots , \tag{1}$$

where the successive terms stand for energies of interactions between the localized charge (ion) and induced dipoles, interactions between induced dipoles, etc. P_{dd} and higher-order terms usually account for ca. 20 % of the total effect[6] and may be neglected in semiquantitative (zeroth-order) calculations. In this case, only the first right-hand term is left in Eq. (1).

Important for the matter of this paper is the case when a non-polar crystal is doped with polar guest molecules. Irrespective of whether the guest molecules themselves act as chemical traps, their presence should locally modify electric field acting on neighbouring molecules. Thus one should expect local changes of the polarization energy.

Calculations on a model lattice

Details of the calculations have been described in earlier papers of the present authors.[15-17] The calculations reported in the present paper have been performed on a model 'anthracene-like' crystal: a primitive regular lattice with numerical values of appropriate parameters chosen so as to mimick properties of the anthracene crystal: the lattice constant was assumed equal to 0.62 nm (i.e., was adopted to yield the molecular volume equal to that of an anthracene molecule in a real crystal),[18] and the (isotropic) polarizability was chosen to amount to 2.78×10^{-39} $\mathrm{m^2F}$ (25×10^{-24} $\mathrm{cm^3}$).[19] The calculation of the polarization energy in the vicinity of a polar impurity requires, even within the zeroth-order approximation, that at least three terms be retained

$$P^{\mathrm{loc}} \approx P_{\mathrm{id}} + P_{\mathrm{im}} + P_{\mathrm{md}} , \tag{2}$$

with P_{id} describing energy of interactions between induced dipoles and the charge, P_{im} - between the permanent dipole(s) and the charge, and P_{md} - between the permanent and induced dipoles. Within the point-dipole approximation, these energies can be calculated from the equations[14]

$$P_{\mathrm{id}} = -\frac{\alpha}{2}\sum_{\mathrm{j}} F_{\mathrm{j}}^{2}\,, \tag{3}$$

$$P_{\mathrm{md}} = -\frac{e}{4\pi\varepsilon_{\mathrm{o}} r_{\mathrm{km}}^{3}}\,(\vec{m}\cdot\vec{r}_{\mathrm{km}})\,, \tag{4}$$

$$P_{\mathrm{im}} = \frac{\alpha}{4\pi\varepsilon_{\mathrm{o}}}\sum_{\mathrm{j}}\left[-\frac{3}{r_{\mathrm{mj}}^{5}}(\vec{m}\cdot\vec{r}_{\mathrm{mj}})(\vec{F}_{\mathrm{j}}\cdot\vec{r}_{\mathrm{mj}}) + \frac{1}{r_{\mathrm{mj}}^{3}}(\vec{m}\cdot\vec{F}_{\mathrm{j}})\right], \tag{5}$$

$$\vec{F}_{\mathrm{j}} = \frac{1}{4\pi\varepsilon_{\mathrm{o}}}\left[\frac{1}{r_{\mathrm{mj}}^{5}}\left[(\vec{m}\cdot\vec{r}_{\mathrm{mj}})\vec{r}_{\mathrm{mj}} - r_{\mathrm{mj}}^{2}\vec{m}\right] + \frac{e}{r_{\mathrm{kj}}^{3}}\vec{r}_{\mathrm{kj}}\right]. \tag{6}$$

In the above equations, $\vec{m}$ is the permanent dipole moment of the polar dopant (a guest molecule situated at an m-th site), $\vec{F}_{\mathrm{j}}$ is the effective field acting on a j-th molecule, and r's are the distances between the charge situated on a k-th molecule, the permanent dipole, and a neutral polarizable j-th molecule, the subscripts indexing the appropriate distances.

The calculations of local values of the polarization energy in the model crystal containing polar impurities, reported in this paper, were carried out for several tens of thousands of molecules adjacent to the polar dopant: in the case of an isolated dopant molecule, the values of P^{loc} were calculated for 3374 molecules (i.e., for all molecules located within the ±7 lattice constants from the dipole), with the summation going over 6858 induced dipoles adjacent to the charge localized successively on each molecule. Several values of the electrical moment of the permanent dipole (up to 10 D, i.e. 3.33×10^{-29} Cm) were employed in the calculations. Typical results are shown in Fig. 1.

The main results can be summarized as follows: *(i)* the presence of a polar impurity results in local perturbations of the polarization energies on adjacent molecules, the number of affected molecules depending on the dipole moment of the guest; *(ii)* the depth of traps E_{t} formed on molecules adjacent to the dopant is a nearly linear function of its dipole moment (cf. Fig. 2); *(iii)* the density-of-states (DOS) function is broadened, the broadening parameter increasing with increasing dipole moment (cf. Fig. 1).

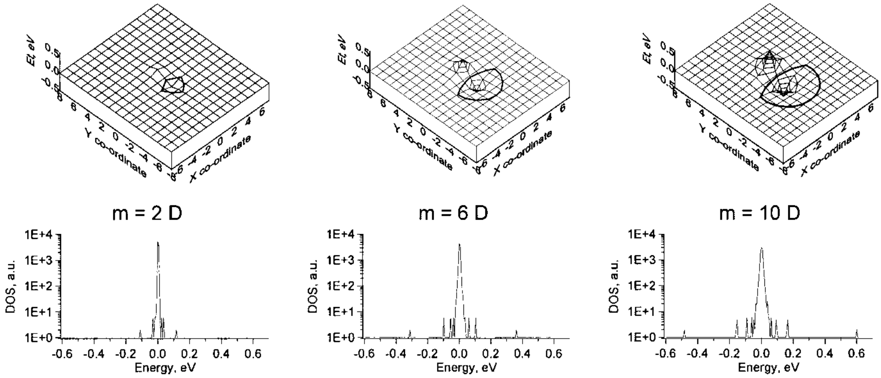

Figure 1. Upper row: Traps for holes created in a regular lattice in the vicinity of polar centres of various polarities. The dipoles are located at the origins, their positive poles pointing in the positive directions of the y axes. The nodes of the grids represent molecules, the figures showing two-dimensional cross-sections through three-dimensional lattices taken at $z = 0$ (trap depth axis). The thick contours mark the extent of the perturbation $\Delta P = E_t = -0.025$ eV. Lower row: Densities of local states associated with the presence of isolated dipoles. DOS in a perfect crystal is a δ function centred at zero.

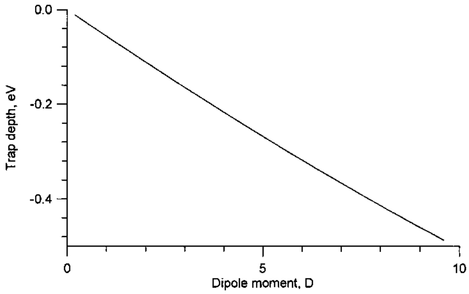

Figure 2. Depths of traps associated with the presence of a polar impurity, as function of its dipole moment. The line is a result of calculations performed on the model molecular lattice described in the text.

Due to severe simplifications introduced in the calculation procedure, the results obtained should be treated as semiquantitatve indications of trends. Nevertheless, they demonstrate that the presence of polar dopants results in creation of traps for both electrons and holes even though the dopant molecules themselves do not act as chemical traps.

Similar calculations have been performed for arrays of dipolar molecules,[17,20] mimicking the situation in polymers containing polar side groups. The results obtained demonstrate that, for moderately high dipole moments of guest molecules, the dipoles can be treated as isolated (non-interacting) ones if the distance between them exceeds ca. 5-6 lattice constants, i.e., if their concentration does not exceed ca. 0.1 %. Thus the effect of the dipole-dipole interaction on the charge transport cannot be neglected in molecular glasses or polymers in which the concentrations of polar species often exceed 1 %, being usually of the order of 10 %.[2]

Charge carrier mobilities influenced by polar guest molecules

As has been shown in the preceding section, the presence of dipolar species results in creation of traps, their depths and cross-sections depending on the dipole moment of the dopant. Simultaneously, high densities of spatially connected shallow local states are created which may act as transport states. It would be instructive to assess the effect of traps associated with the presence of polar impurities. In nearly-perfect solids, the trap-controlled mobilities follow the equation[21]

$$\mu = \mu_0 \left[1 + x_{\mathrm{dip}} \exp\left(\frac{-E_{\mathrm{t}}}{kT} \right) \right]^{-1} \tag{7}$$

where μ_0 is the drift mobility of the carriers in a perfect solid, x_{dip} is the mole fraction of the polar species, and E_{t} is the depth of trap created due to the presence of the dopant ($E_{\mathrm{t}} < 0$). As follows from the results shown in Fig. 3, even for moderate dipole moments of the impurity, one should expect a significant decrease in mobility.

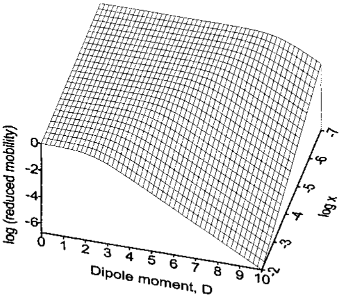

Figure 3. The reduced mobility (μ/μ_0) at 300 K, expressed in function of the mole fraction of dipolar dopants and their dipole moment. The relation between the dipole moment and the trap depth has been taken from the curve shown in Figure 2.

In disordered solids, the changes of the photochemically controlled mobilities are more difficult to assess since, apart from modification of the trap depths (cf., e.g., Ref. [22]), one should also expect a modification of the shape of the density-of-states functions. The importance of the latter effect can be estimated employing the model put forward by Bässler.[23,24] According to the model, DOS in disordered solids may be approximated by a Gaussian function

$$N(E)=\frac{N_{\mathrm{tot}}}{(2\pi\sigma^2)^{1/2}}\exp\left(-\frac{(E-E_{\mathrm{m}})^2}{2\sigma^2}\right), \tag{8}$$

N_{tot} standing for the total density of states, E_{m} for the energy of the distribution maximum, and the variance σ being a measure of the disorder; typically, $\sigma \leq 0.1$ eV. At sufficiently high voltages, the mobility is field-dependent

$$\mu(\sigma,T,F)=\mu_{\mathrm{o}}(\sigma,T)\exp\left(\vartheta F^{1/2}\right), \tag{9}$$

where ϑ is a field-independent coefficient and μ_{o} stands for the zero-field mobility. The latter parameter follows a non-Arrhenius temperature dependence

$$\mu_{\mathrm{o}}(\sigma,T)=\mu_{\mathrm{o,o}}\exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right], \tag{10}$$

$\mu_{\mathrm{o,o}}$ being usually identified with the mobility in a parent perfect material (on-chain mobility in the case of polymers). The effect of dipolar species has been rationalized invoking a dipolar contribution in the DOS function: the width of DOS is a superposition of van der Waals and dipolar components (σ_{vdW} and σ_{dip}, respectively)

$$\sigma^2=\sigma^2_{\mathrm{vdW}}+\sigma^2_{\mathrm{dip}} \ , \tag{11}$$

with the latter component related to the permanent dipole moment of the polar species and its mole fraction[25-27]

$$\sigma_{\mathrm{dip}}=\frac{\kappa x^{\mathrm{b}}_{\mathrm{dip}}m}{\varepsilon a^2_{\mathrm{o}}} \ . \tag{12}$$

Here, κ and b are constants, ε is the relative electric permittivity of the medium, and a_{o} is the intersite distance. A combination of Eqs. (10-12) yields

$$\frac{\mu_0(\sigma,T)}{\mu_0(\sigma_{\mathrm{vdW}},T)} = \exp\left[-\theta\left(\frac{x_{\mathrm{dip}}^{\mathrm{b}}m}{T}\right)^2\right], \tag{13}$$

where θ is a constant. Thus the contribution of the dipolar term manifests itself in the modification of the mobility: the mobility should decrease with increasing dipole moment of the dopant and with its concentration.

The model calculations described in the preceding section do not allow to extract any quantitative data concerning the broadening of the DOS function, hence no quantitative results can be obtained directly from the model. Qualitatively, however, the trend is correct: the presence of polar species results in broadening od DOS (cf. Fig. 1), hence one should expect a decrease in the carrier mobility as has indeed been found in earlier experiments[28,29] performed on polysilanes. Taking the values reported in Ref. [29], one may approximate the concentration dependence of the dispersion parameter in dilute systems (x_{dip}<0.02) by the following equation

$$\sigma^2 = 8.65\times10^{-3} + 0.23m^2x_{\mathrm{dip}}^2 , \tag{14}$$

(σ in eV, m in D). Thus the carrier mobility measured in polysilane containing 2 mol % of polar additives (or polar side groups) with the permanent dipole moment equal to ca. 10 D should be almost three orders of magnitude lower than the respective value in the neat polymer.

The estimates presented above demonstrate that in all cases the presence of polar species should result in a decrease in the charge carrier mobility in macroscopic molecular samples though the magnitude of the effect may vary depending on the degree of perfection of the systems.

Modification of charge carrier mobilities by reversible photochemical reactions

The dependence of the depths and cross-sections of dipolar traps on the dipole moment of the polar dopants makes it possible to design a photoactive molecular system in which carrier mobilities are controlled by reversible changes of the dipole moment of a dopant. Suitably chosen photochromic systems come as an obvious choice: several molecular photochromic systems have been known to be weakly polar in their stable forms and zwitterionic (i.e., highly polar) in their metastable forms. For example, the dipole moments of certain spiropyrans and spirooxazines amount to ca. 1-2 D and over 10 D in their stable and metastable forms, respectively.

Taking the results obtained from the calculations carried out on the model lattice (presented in the preceding section – cf. Fig. 2) as a 'calibration curve', one can estimate depths of dipolar traps associated with the presence of photoactive dopants in the model molecular system. Assuming the dipole moments of the stable and metastable forms being respectively equal to 2 D and 10 D, one may estimate the depths of the traps to amount to ca. 0.1 eV and 0.5 eV, respectively. Photochemically driven reactions in the photochromic system should, in principle, allow for switching in a controlled way between these two states. It would be instructive to assess the effect of the switching between the 'low-moment' and the 'high-moment' states on the drift mobility. Making use of Eq. (7) and assuming $x_{\text{dip}} \approx 10^{-3}$ (corresponding to an average distance between the dipolar traps equal to 10 lattice constants), one arrives at $\mu^{(\text{high m})}/\mu^{(\text{low m})} \approx 4 \times 10^{-6}$ at ambient temperature. Similarly, the modulation of carrier mobilities in a highly disordered molecular system can be estimated taking the values obtained for polysilane[28,29] and using Eqs. (13) and (14). Taking $x_{\text{dip}} \approx 0.02$ and assuming the 'low' and 'high' dipole moments equal to 2 and 10 D, respectively, one obtains $\mu^{(\text{high m})}/\mu^{(\text{low m})} \approx 3 \times 10^{-3}$ at ambient temperature.

Towards a molecular switch

The estimates given in the preceding section point to the possibility of a controlled modulation of charge carrier mobilities in ordered and disordered molecular materials, by a light-induced reversible photochemical reaction. Moreover, one may envisage the construction of a molecular-scale switch acting on the same principle. The idea has been put forward in earlier papers of the

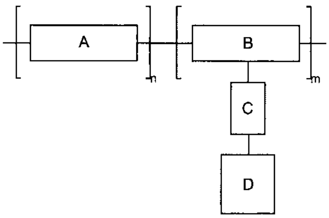

Figure 4. A scheme of a molecular switch based on the principle discussed in the paper. A, B – segments of a conjugated polymer chain; C – spacer; D – photochromic group.

present authors.[30,31] The switch, schematically depicted in Fig. 4, would consist of a molecular wire (a π- or σ-conjugated polymer chain) with suitable photochromic moieties, either placed in its vicinity or chemically attached as side groups, embedded in a neutral (electrically inactive) dielectric medium. In the vicinity of the polar centres formed on the photochromic units, new local electron states arise as a consequence of the electrostatic interaction of the charge carrier on the polymer wire with the dipoles of the side groups. Thus the electrons travel through the polymer wire in the system of potential wells whose parameters can be controlled by light. This feature leads to a modulation of the on-chain charge carrier mobility.

Discussing the architecture of the molecular switch, one should consider the role of the spacer. In particular, two limiting cases are possible: (*i*) a neutral spacer fixing the geometry of the photoactive side group and its distance from the main chain, and (*ii*) a spacer electronically connecting the side group with the main chain, i.e., allowing for the trapping of a charge carrier on the side group. In the former case, one deals with a dipolar trap created *on the chain* due to electrostatic interactions of the carrier with the dipole of the side group, whereas the latter case is equivalent to creation of a chemical trap *on the side group*, whose behaviour cannot be described within the electrostatic model employed throughout this work.

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