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CHARGE CARRIER MOBILITY IN NON-EQUILIBRATED TRANSPORT IN MOLECULAR MATERIALS

Non-equilibrated transport of charge carriers in the molecular material depends on the structure and packing of the molecules. Explanation of the measurements of the photocurrent generated with use of UV flash light in organic layer needs to define the quantity of charge carriers mobility. Definition of this quantity in the scope of some defined transport model requires the detailed analysis of generation, recombination and charge transfer between neighbouring molecules. The problem is discuss on the basis of transport properties of two anthracene derivatives.

Keywords: charge transfer mobility, photocurrent, hopping transport, Marcus-Hush theory.

1. INTRODUCTION

Nowadays, molecular electronics requires new research aimed at development of the technology of new low-weight organic semiconducting materials. This technology allows the optimal usage of their strengths, *i.e.* low production costs, flexibility, low molecular weight, the ability to modulate their properties by changing the structure of the molecule leading to proper space charge distribution in molecule favourable for strengthening π - π interactions. Organic semiconductors can be used to produce the continuous and homogeneous layers with a large surface in terms of large scale production

technology [1]. The essential stage for research in the field of organic electronics is determining the potential of organic semiconductor material properties for their adaptation in practice [2, 3].

The mobility of charge carriers is an important parameter used to determine the potential applications of the organic semiconductor. Experimental measurement of this quantity requires the construction of a measuring cell in which metallic contacts attached to the layer of the measured organic material play an important role. Although the mobility of the charge carriers is a quantity characterizing a given material, the obtained result of mobility is always dependent on the method of performing this measurement [4,5]. Therefore, appropriate theoretical methods of description are sought. They will allow estimation of the value of charge carrier mobility, as a material constant.

Preliminary X-ray examinations can be helpful to determine the properties of the transport of charge carriers in organic material. Conventional X-ray structural analysis tries to develop the description of the ideal internal structure of crystalline bodies. The limitation of this method is the fact that it is based on the assumption that the electron density of the atom in the crystal is well described by spherical averaging of the electron density of individual atoms [6]. Diffraction methods belong to the group of indirect methods that allow obtaining structural data after appropriate mathematical processing of the recorded measurement data. This means that the diffraction pattern is obtained by averaging the electron density distribution of many atoms (at least on the order of 10^{18} atoms per diffractogram). As a result, the crystal is considered to be composed of isolated non-interacting atoms. Of course, additional X-ray analysis allows inferences about existing bonds. An additional limitation of the X-ray method is that reduction of measurement temperature is required to reduce the thermal movement of atoms for accurate analysis of diffraction data. In practice, however, organic electronics devices most often work in the range from room temperatures to about 80 °C. Therefore, it is helpful to calculate electrical properties in a theoretical way in order to determine the electrical properties of the organic material at the molecular level. Theoretical calculations using quantum-chemical calculations allow for an accurate description of the molecular orbitals of a single molecule or molecules in a unit cell at any temperature. Such calculations using GAUSSIAN 09 package software [7] were carried out by our team previously in the case of unit cells made of anthrone and anthraquinone particles [8,9]. These two anthracene derivatives can be used in the form of layers to produce organic field effect transistors (OFET) [10]. Anthrone and anthraquinone are two derivatives of anthracene similar in shape. They can be considered as a model set of two compounds crystallizing in almost identical structures and with almost identical molecules but differing in presence

of permanent dipole moment. The anthrone molecule possesses a significant natural dipole moment, and when measured in benzene is of 3.66 D ($1.22 \cdot 10^{-29}$ Cm), but anthraquinone possesses much lower value of natural dipole moment when measured in benzene of 0.6 D ($2.00 \cdot 10^{-30}$ Cm) [11]. Our previous researches were related to the evaluation of the molecule geometry change during charge carrier transport. The main result of calculations revealed that the difference between the hole mobility for both materials was due to the presence of permanent dipole moment. Permanent dipole moment in the gas phase is present only in the case of anthrone molecule. In this paper we want to check whether the direct application of the Marcus-Hush model with the two anthracene derivative compounds would allow for explanation of differences in measured mobility values.

1.1. Mobility in diabatic and adiabatic processes

The mobility of charge carriers is defined as the charge carrier velocity induced by external unit value of electric field. In solid, it is a tensor quantity, μ_{ij} , describing the relationship between vector components of averaged charge carrier velocity $\langle v \rangle_i$ and components E_j of the vector of external electric field

$$\mu_{ij} = \langle v \rangle_i / E_j . \quad (1)$$

For amorphous materials it may be assumed that macroscopic mobility is considered as a scalar quantity

$$\mu = \langle v \rangle / E \quad (2)$$

This assumption takes into account the disorder of the positions of the molecules relative to each other and energy disorder. The thermal vibrations that interfere with the transfer of charges between adjacent molecules are the source of disorder, even in crystalline materials at temperatures close to applications of organic electronics, *i.e.* at room temperatures (RT). This results in the localization of charge carriers. Such an effect destroys the translational symmetry of the system making the description of band conduction inadequate for the charge carrier transport phenomena at RT [12]. Calculation shows that the fluctuations in the amplitudes of the transfer integrals are of the same order as their average values [13].

Mobility can be determined experimentally by time of flight (TOF) measurements. Measurement using the apparatus applied in this method allows for direct measurement of time of flight in the case of weak dispersion [14]. Therefore, no relationship between the transit time of the charge carriers through the layer and the applied external electric field is observed in the case of strong

dispersion. In the latter case, the observed transit time of the carriers is interpreted as a life-time of the carriers [15, 16]. Therefore, either the drift mobility value or the mobility value determined by the Einstein equation after determining the diffusion constant value can be obtained as a result of such measurement.

The drift mobility in TOF experiment with the weak dispersion is defined as

$$\mu_{TOF} = L/(Et_{tr}). \quad (3)$$

Here, t_{tr} is the time of flight, determined experimentally from observed shape of transit currents for the organic layer with thickness L .

In turn, the value of the observed lifetime allows determination of the diffusion constant D of charge carriers [15,16]. Value of this constant allows to calculate the Einstein mobility based on Einstein's dependence

$$\mu = (e/k_B T)D, \quad (4)$$

where e is a charge of the charge carrier, k_B is the Boltzmann constant and T is the absolute temperature. Calculation of the mobility of charge carriers in high-resistance organic material is difficult because the influence of an external electric field and the thermal interaction of molecules modify electronic states. Even for a qualitative description, a number of simplifications are required. Conduction in organic material occurs through a spatially extended molecule and then as a result of diffusion of the charge carrier between adjacent molecules. In the case of organic material, the theoretical description of charge carrier transport is facilitated because the weak intermolecular interactions (of the order of 0.4-0.8 eV/molecule) which allows to consider the interactions important for conductivity as interactions between pairs of neighbouring molecules. This fact allows to omit the crystal structure of the tested material in theoretical calculations [17].

Theoretical estimation of mobility in the absence of an electric field is possible on the basis of Marcus-Hush theory [17]. This theory allows the calculation of parameters associated with the change of spatial distribution of the electron density of a molecule when transfer of charge carrier occurs. The energy factor associated with the deformation of a molecule during charge transfer is called reorganization energy and the factor associated with the transfer of charge carriers is the transfer integral. Marcus-Hush theory uses a diabatic description of charge transfer. The diabatic description assumes that changes in the state extracted from the environment of the thermodynamic system may occur in the path of the exchange of energy with the environment under the conditions of infinitesimally small energy difference between them.

In turn, the competitive adiabatic process progresses as a result of thermodynamic changes which are associated with relaxation of the disturbed system to a state of equilibrium without heat exchange with the environment. The rate of hole transfer between two adjacent molecules, k_e , during the charge carrier transport can be defined on the basis of Marcus – Hush theory [12,18] as:

$$k_e = \left(4\pi^2/h\right) \left(J^2 \exp(-E_r/(4k_B T)) / \sqrt{4\pi \cdot E_r k_B T}\right), \quad (5)$$

where h is Planck constant, E_r is the reorganization energy and J is the charge transfer integral.

2. CALCULATIONS AND DISCUSSION

The quantum-chemical calculations were carried out with use of density functional theory (DFT) with GAUSSIAN09 program [7]. The structures of anthraquinone and anthrone were optimized at B3LYP (Becke three parameter (exchange), Lee Yang, and Parr) method using 6-311+g(d,p) basis set. Based on the optimized geometric structure, the energy of high occupied molecular orbital (HOMO), and energy of low unoccupied molecular orbital (LUMO) and band gap calculations were performed with the same level of theory at the ground state and cation and anion state for the molecules being in the gas. We calculated reorganization energy E_r and charge transfer integral J in the manner similar to shown in [19]. The results of calculations are presented in the Table 1. For comparison, apart from anthrone and anthraquinone, the calculation results for anthracene are shown.

Table 1
Calculated reorganization energy E_r , charge transfer integral J and rate of charge transfer k_e for anthrone, anthraquinone and for anthracene

		Anthrone	Anthraquinone	Anthracene
E_r , holes	[eV]	0.174	0.135	0.139
E_r , electrons	[eV]	0.371	0.354	0.198
J , holes	[eV]	0.111	0.092	0.611
J , electrons	[eV]	0.600	0.564	0.337
k_e , holes	[Hz]	$9.29 \cdot 10^{13}$	$1.02 \cdot 10^{14}$	$4.35 \cdot 10^{15}$
k_e , electrons	[Hz]	$2.73 \cdot 10^{14}$	$2.92 \cdot 10^{14}$	$6.28 \cdot 10^{14}$

To describe the diffusion process, it is necessary to estimate the diffusion constant D of charge carriers [17,19]. If the charge carrier transfer rate between two molecules obtained on the basis of the Marcus-Hush formula is k_e , then the

estimation of the diffusion constant for the conductivity of holes requires the use of the expression similar as in [20,21] when taking into account the amorphous structure of the layer:

$$D = (1/(2nM))(L^2 k_e / L_k), \quad (6)$$

where n is the dimensionality of the transport process (we assume here that $n = 3$), L_k is the number of possible charge carrier transfers to neighbouring molecules, M is a number of independent molecules in the unit cell, k_e is the rate of charge transfer equation (5), L is the effective distance between centroids (center of mass) of neighbouring molecules.

Using equation (6), assuming that the parameter $L \approx 4 \text{ \AA}$ [17], and using the calculated values of carrier transfer rate k_e for anthrone and anthraquinone, $9.29 \cdot 10^{13} \text{ Hz}$ and $1.02 \cdot 10^{14} \text{ Hz}$, respectively, we obtain, based on formula (4), the mobility of the holes which is about $1.7 \cdot 10^{-2} \text{ cm}^2/\text{Vs}$ for both materials. Mobility of the electrons for both materials calculated in the same manner is equal to $4.7 \cdot 10^{-2} \text{ cm}^2/\text{Vs}$.

Table 2
Experimental hole [14] and electron [22] mobility for anthrone and anthraquinone for amorphous layers and calculated for the values from Table 1 with use Eqs. (4) and (6)

Compound	Type of charge carrier	Structure	Experimental μ, [cm^2/Vs]	Calculated, μ, [cm^2/Vs]
anthraquinone	hole	amorphous	$(0.9-6.0) \cdot 10^{-4}$	$1.7 \cdot 10^{-2}$
anthrone	hole	amorphous	$(0.6-4.0) \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$
anthraquinone	electron	amorphous		$4.7 \cdot 10^{-2}$
anthrone	electron	amorphous	$(0.6-3.0) \cdot 10^{-3}$	$4.7 \cdot 10^{-2}$

Table 2 compares the experimental mobility values for the amorphous layers of anthrone and anthraquinone with the mobility values calculated using data from Table 1 with use of formulas (4) and (6). Both the experimental and calculated mobility values for both compounds are at least two orders of magnitude smaller than the value of $1 \text{ cm}^2/\text{Vs}$, which is the limit value above which the transport of charge carriers is a band transport. Therefore, the calculated mobility values allow us to assume that for both compounds we are dealing with hopping transport. This assumption is valid for both holes and electrons.

3. CONCLUSIONS

Mobility values calculated using Marcus-Hush theory for both materials with similar molecules and almost identical crystal packing are almost identical. However, the empirical mobilities for both compounds are different almost by an order of magnitude. We think that the reason for this difference in the mobilities determined experimentally for both compounds is the presence of a permanent dipole moment in the anthron molecule and its absence in the anthraquinone molecule. To ensure better correlation of the calculations with the experimental results, it is necessary to consider factors that may influence on the value of the estimated diffusion constant of charge carriers and may influence on the value of the calculated transfer integral. More accurate calculations must take into account the presence of a constant dipole moment in the anthrone molecule because the presence of this moment creates an additional interaction between the anthrone molecules comparable with the energy of van der Waals interactions.

Despite the simplicity of theoretical considerations applied in this paper, the obtained calculation results give a qualitatively correct picture of transport. For both materials, *i.e.* anthrone and anthraquinone, the mobility values obtained from Marcus-Hush theory for both hole transport and electron transport are in the range of hopping transport.

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RUCHLIWOŚĆ NOŚNIKÓW ŁADUNKU W PRZEWODNICTWIE NIERÓWNOWAGOWYM MATERIAŁÓW MOLEKULARNYCH

Streszczenie

Opis nierównowagowego transportu nośników ładunku w warunkach fotoprädu wzbudzanego impulsem światła wymaga zdefiniowania ruchliwości nośników ładunku. Definicja tej wielkości w odniesieniu do określonego modelu transportu wymaga wnikliwej analizy procesów generacji, rekombinacji i transferu ładunku pomiędzy sąsiadującymi cząsteczkami. W tej pracy do opisu transportu nośników ładunku w antronie i antrachinonie wykorzystano teorię Marcusa–Husha, która dotyczy transportu hoppingowego. Uzyskano prawie identyczne wartości ruchliwości dziur w obu materiałach, tj. $1,7 \cdot 10^{-2} \text{ cm}^2/\text{Vs}$ oraz identyczne wartości ruchliwości elektronów $4,7 \cdot 10^{-2} \text{ cm}^2/\text{Vs}$. Pomimo prostoty rozważań teoretycznych uzyskane wyniki

obliczeń dają jakościowo poprawny obraz transportu, zgodny z wynikami doświadczalnymi. Dla obu związków wartości ruchliwości obliczone za pomocą teorii Marcusa-Husha zarówno dla transportu dziur jak i dla transportu elektronów są w zakresie transportu hoppingowego.