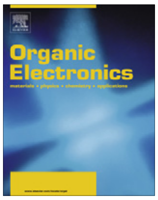
Organic Electronics 12 (2011) 589–594

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Mechanism of enhanced mobility and conductivity at donor–acceptor organic interfaces

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ARTICLE INFO

Article history:
Received 20 September 2010
Received in revised form 18 December 2010
Accepted 17 January 2011
Available online 1 February 2011

Keywords:
Organic semiconductors
Donor–acceptor interface
Integer charge transfer
Energy level alignment
Charge delocalization
Charge carrier transport

ABSTRACT

The model of metallic type or enhanced hopping conductivity with reduced activation energy at the donor–acceptor interface formed by organic dielectrics is suggested. High density of electrons and holes at the interface arises due to the integer charge transfer from donor to acceptor molecules. Significant part of charge carriers can avoid thermal activation and tunneling in course of their transport if the interfacial energy barrier is low enough. The critical value of an interfacial energy barrier, density of free electrons, the values of two-dimensional mobility and conductivity of charge carriers are estimated by numerical modeling and compared with experimental data.

1. Introduction

Electric conduction along organic interfaces attracts much attention since electronic processes at organic–organic and organic–metal interfaces can differ from those in the bulk of organic layers, and interfacial properties have a profound impact on device performance [1–4]. High conductivity is required to maintain superior device characteristics. Electronic transport at organic interfaces, as well as in organic layers, is known to be restricted typically by localization and low concentration of mobile charge carriers [5]. Typically, improvement results from electrochemical doping [6,7] and field effect [7–9]. The latter increases concentration of carriers and their mobility within a thin ($\cong 1$ nm) layer at the polymer–gate interface due to filling of deep fraction of localized states.

High mobility and conductivity in organic structures involving interface of electron donor (D) and acceptor (A) materials has been recently reported (see, for examples, [10–13]). In original materials, conductivity was found to be lower by several orders of magnitude than that in the interface structure. An important result of Ref. [11] was the saturation of conductivity with thickness of the top A-layer as soon as its thickness exceeded ca. 2 nm in the course of formation of D–A interface. The Hall mobility of both electrons and holes above 1 $cm^2\ V^{-1}s^{-1}$ was measured, suggesting the sheet density of *delocalized* charge carriers up to $5 \times 10^{10}\ cm^{-2}$ at the copper phthalocyanine (CuPc)/copper hexadecafluoro phthalocyanine ($F_{16}CuPc$) interface. In those experiments [13], the conductivity was trap-controlled hence thermoactivated one. In [10], two-dimensional (2D) conductivity above the minimal metallic level, e^2/h, characterized by metallic temperature dependence, along the interface formed by two organic crystals of tetrathiofulvalene (TTF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been demonstrated and attributed to the formation of 2D electronic gas, resulting from electron transfer from TTF to TCNQ. The question about the occurrence of *complete* (integer) or *partial* charge transfer at the concrete donor–acceptor organic interface is under debate. The complete electron transfer at the interface between two dielectrics, including organic ones, is known for a rather long time; in particular, this effect

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doi:10.1016/j.orgel.2011.01.017

is responsible for the charging of dye particles in a mixture of powders used in xerography [14]. Recent work on modeling of organic–metal and organic–organic interfaces has been summarized in the review [15]. Obviously, none of the existing models describe the whole variety of organic–organic interfaces. However, strong arguments has been reported, that integer electron transfer from donor to acceptor molecule occurs at the organic–organic interface, if (i) chemical interaction of these molecules is rather weak in order to prevent considerable hybridization of electronic molecular orbitals and (ii) this transfer is profitable energetically, i.e. the energy of highest occupied molecular orbital (HOMO) of a donor lies high enough relative to the position of lowest unoccupied molecular orbital (LUMO) of an acceptor. In particular, integer charge transfer in the structure involving TTF and TCNQ has been approved. On the other hand, many experimental and theoretical works have pointed to partial charge transfer at organic–organic interfaces, including TTF–TCNQ interface (see, for example, [16]). Perhaps, the reason of this uncertainty is the dependence of the relative energetic positions of electrons and holes at the interface on the choice of the conductive substrate (electrode) [15]. In this work, we assume that an integer charge transfer is the case for the analyzed interface, because this case (weak chemical intermolecular interaction), which is typical for organics, seems to be most questionable in view of 2D-electronic gas formation.

The primary step in this case is the formation of an electron–hole (e–h) pair in which the charges are separated by the distance ca. 1 nm and localized by mutual Coulomb interaction. Formation of 2D e-gas needs in rather high area density of pairs, in order to delocalize charge carriers by means of interaction with charges from adjacent pairs. However, the microscopic nature of the huge enhancement of conductivity along the D–A interface with respect to the bulk conductivity of the materials remains unclear. One has to clarify the mechanism of 2D e-gas formation at such an interface and quantify the critical parameters of the interface. The mechanism of conductivity exploited for the interfaces of perovskite transition metal oxides ABO_3 [17] seems to be not appropriate for the organic structures, in which sequential polar layers are absent.

The concept of sequence of charge carrier transfers from charge-transfer states (CTSs) to the neighboring unpaired charge (“Coulomb hole”) was suggested earlier to explain the sharp increase in the bulk conductivity of electrochemically doped polymers [18] and the electronic switching in polymers [19]. In the present paper, we show that the concept provides a mechanism describing both enhanced hopping conductivity with reduced activation energy and metallic conductivity along the D–A interface. We quantify the conditions of 2D e-gas formation as well.

2. Model

The integer charge transfer of an electron from donor to acceptor molecule produces a pair of positive (donor) and negative (acceptor) CTSs, having energies E^{+}_{ICT} and E^{-}_{ICT}, respectively. The energy $E^{+}_{ICT}(E^{-}_{ICT})$ is defined as the energy required to withdraw an electron (respectively, the energy gained when an electron is added to the molecule) producing a fully relaxed state, i.e. both electronic and geometrical relaxation and interaction of charges are taken into consideration. These energies differ from respective energies of neutral HOMO and LUMO states [15]. The electron donated at the interface is transferred to the nearby molecule of an acceptor enabling significant Coulomb interaction with the energy $U_a = e^2/4\pi\varepsilon\varepsilon_0 a$, where e is the elementary charge, ε is an effective permittivity, ε_0 is the electric constant and a is the mutual electron–hole distance. Thus, the recombination of an (isolated) electron–hole pair at the interface is suppressed by the energy barrier $\Delta E = U_a + E^{don} - E^{acc}$, where E^{don} and E^{acc} are the energies of an electron, being located at donor and acceptor molecules, respectively (see Fig. 1). Charge transfer can be energetically beneficial, i.e. $\Delta E > 0$, even if $E^{don} < E^{acc}$, due to Coulomb interaction of the pair. An electron (e) and a hole (h) in an isolated pair should be localized by this interaction.

Yet, an e–h pair is not isolated at interface. If the distance between the neighboring pairs is comparable with the spacing of charges inside the pair, it is necessary to take into account the interaction of charges with the environment consisting of dipoles (e–h pairs), “vacancies” (pairs of neutral molecules) formed due to the recombination of a fraction of e–h pairs, and unpaired charges of both signs (i.e. dissociated pairs). The random arrangement of e–h pairs, vacancies and unpaired charges produces the potential fluctuations around each e–h pair. In average, the energy barrier ΔE is compensated by the drop of the electrostatic energy ΔU in equilibrium state, hence the energy level alignment of integer CTSs, E^{+}_{ICT} and E^{-}_{ICT}, is established at the interface [15] (see Fig. 1).

One has to note that organic–organic interface is a complex of interacting molecules of both materials. Hence, the morphology of the interface can differ from the morphology in the bulk of both materials. We perform model calculations under the simplifying assumption that the pairs of molecules of both materials at the interface form a square lattice with the parameter $b \geqslant a$, and all pairs of molecules

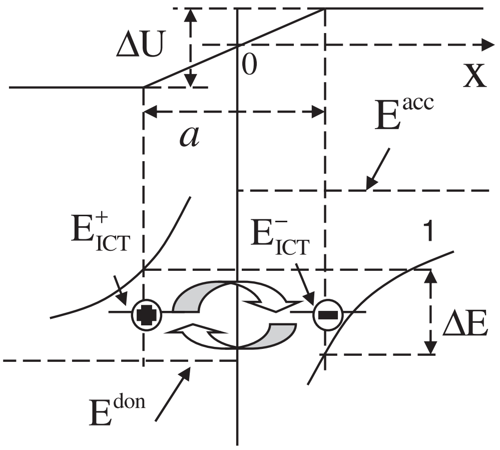

Fig. 1. Energy diagram of the interface between two organic materials. Curve 1 shows the function $E^{acc} - e^2/4\pi\varepsilon\varepsilon_0 x$.