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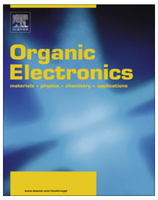

Effect of trap states on the electrical doping of organic semiconductors

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ABSTRACT

We demonstrate that direct charge transfer (CT) from trap states of host molecules to the *p*-dopant molecules raises the doping effect of organic semiconductors (OS). Electrons of the trap states in 4,4′-*N*,*N*′-dicarbazolyl-biphenyl (CBP) ($E_{HOMO} = 6.1$ eV) are directly transferred to the *p*-dopant, 2,2′-(perfluoronaphthalene-2,6-diylidene) dimalononitrile (F6-TCNNQ) ($E_{LUMO} = 5.4$ eV). This doping process enhances the conductivity of doped OS by different ways from the ordinary doping mechanism of generating free hole carriers and filling trap states of doped OS. Trap density and trap energy are analysed by impedance spectroscopy and it is shown that the direct charge transfer from deep trap states of host to dopants enhances the hole mobility of doped OS and the *I*–*V* characteristics of hole only devices.

1. Introduction

Highly efficient organic light emitting diodes (OLED) and organic photovoltaic cells (OPV) have been realized using *p*-doped/intrinsic/*n*-doped (*p*–*i*–*n*) structures [1–3]. Doping of semiconductors, which is defined as the modification of electrical properties of semiconductors by introducing impurities, provides an Ohmic contact between electrodes and semiconductor layers leading to low driving voltages and hence low power consumption. *p*-doping of organic semiconductors is explained by the “charge transfer” from host molecules to dopant molecules and the “separation” of the thereby formed charge transfer complex [4]. The generated free charges increase the conductivity of doped organic semiconductors and also change the charge injection barriers with an electrode or an adjacent organic layer [5,6].

This doping mechanism, however, does not consider trap states in the organic hosts, which can dominate the electrical properties of organic semiconductors, for instance the low mobility or trap-charge limited current (TCLC). In particular, this simple mechanism is insufficient to explain some exceptional results such as the doping effect of tetrafluoro-tetracyano-quinodimethane (F4-TCNQ) in 1,4-bis[*N*-(1-naphthyl)-*N*′-phenylamino]-4,4′-diamine (NPB) or poly(9,9-di-*n*-octylfluorene-alt-benzothiadiazole (F8BT). In these systems, doping leads to an increase in conductivity although the charge transfer should be very inefficient because the HOMO level of NPB (5.4 eV) and F8BT (5.9 eV) is lower than the LUMO level (5.2 eV) of F4-TCNQ [7–9]. The ordinary understanding of doping effect based on the filling of trap states with generated charge carrier needs to revise to include the effect of trap states on the doping mechanism [10–13].

In this paper, we demonstrate that direct charge transfer from trap states of the organic host CBP to the LUMO level of *p*-dopant can modulate the electrical properties of the host organic semiconductors. From impedance spectroscopy analysis, we find that removing electrons from

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deep trap states enhance the hole mobility of organic host molecules and also increase the conductivity of doped organic semiconductors. This new mechanism featured by direct charge transfer has to be distinguished from the ordinary doping mechanism of increased carrier density caused by the charge transfer from HOMO level of host to *p*-dopant.

2. Experimental

About 100 nm of doped organic layers were evaporated on precleaned quartz substrates and indium tin oxide (ITO) patterned glass substrates to investigate the optical absorption and the electrical characteristics of hole only devices, respectively. The current–voltage (*I*–*V*) and capacitance–frequency (*C*–*f*) characteristics of the devices consisting of ITO/MoO_3 (1 nm)/4 wt% F6-TCNNQ doped MeO-TPD, TCTA or CBP (100 nm)/MoO_3 (10 nm)/Al (100 nm) were measured by a Keithley 2400 semiconductor parameter analyser and an Autolab PG-STAT302N, respectively. The UV–vis–NIR absorption spectra of doped films were measured by the Lambda 900 spectrometer (PerkinElmer).

3. Results and discussion

4,4′-*N*,*N*′-Dicarbazolyl-biphenyl (CBP) having a HOMO energy of 6.1 eV is used as a main host [14]. *N*,*N*,*N*′,*N*′-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) having a HOMO of 5.1 eV and 4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA) having a HOMO of 5.7 eV are selected as the second additive host to control the trap states in the CBP main host [15–17]. The organic *p*-dopant, 2,2′-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6-TCNNQ) is doped at concentrations in the range of 0–6 wt% in intrinsic, MeO-TPD or TCTA mixed CBP [18–21]. Molecular structures and energy levels of these organic molecules are summarized in Fig. 1.

Trap states of intrinsic organic semiconductors are the most important factor to understand the charge transport in organic semiconductors [10,22]. The quantitative control of trap states of organic semiconductors was investigated by von Seggern's group using thermally stimulated current (TSC) measurement [23,24]. In the case of 1-NaphDATA mixed NPB, electrons at a HOMO level of 1-NaphDATA acted as trap states in the NPB host, because 1-NaphDATA has a higher HOMO level (5.1 eV) than NPB (5.4 eV). These trap states suppressed the hole transport through the HOMO level of NPB reducing the current density of the devices [24].

Here, to control trap states in CBP, we mix additional host molecules such as MeO-TPD ($E_{HOMO} = 5.1$ eV) or TCTA ($E_{HOMO} = 5.7$ eV) having higher HOMO levels than CBP ($E_{HOMO} = 6.1$ eV). Hole transport characteristics of devices with intrinsic CBP, CBP:MeO-TPD (2 wt%) and CBP:TCTA (2 wt%) are shown in Fig. 2. Because the concentration of MeO-TPD or TCTA is small (2 wt%), these *I*–*V* characteristics are mainly influenced by hole transport across the HOMO level of CBP. When MeO-TPD or TCTA is mixed into CBP, however, the hole transport in CBP is extremely effected by the trapping–detrapping of holes in the artificial traps and the current density of devices is reduced by three or one order of magnitude for Meo-TPD or TCTA doped CBP, respectively. As expected, the devices having deeper trap states, i.e. devices mixed by MeO-TPD, have a lower current density than the devices with shallow trap states formed by TCTA molecules because the deep trap states lead to the long trapping–detrapping time.

To study the *p*-doping mechanism in CBP, we doped the *p*-dopant, F6-TCNNQ, into the MeO-TPD or TCTA mixed CBP at a doping concentration of 2–6 wt%. Based on the ordinary doping mechanism, F6-TCNNQ dopant cannot take electrons from the HOMO level of CBP and increase the number of free charge carriers in CBP because F6-TCNNQ has a higher LUMO level (5.4 eV) than the HOMO level of CBP (6.1 eV) [18]. As shown in Fig. 2a, however, the current density of the devices consisting of CBP mixed with MeO-TPD is recovered by the doping with F6-TCNNQ. This shows that the *p*-doping effect in CBP:MeO-TPD films is due to direct charge transfer from the MeO-TPD to F6-TCNNQ. Deep hole traps (electron of MeO-TPD) are eliminated, which means transferred, to the dopant F6-TCNNQ and the hole transport properties (conductivity) through the HOMO level of CBP are recovered. As the doping concentration increases, the current density of the device is

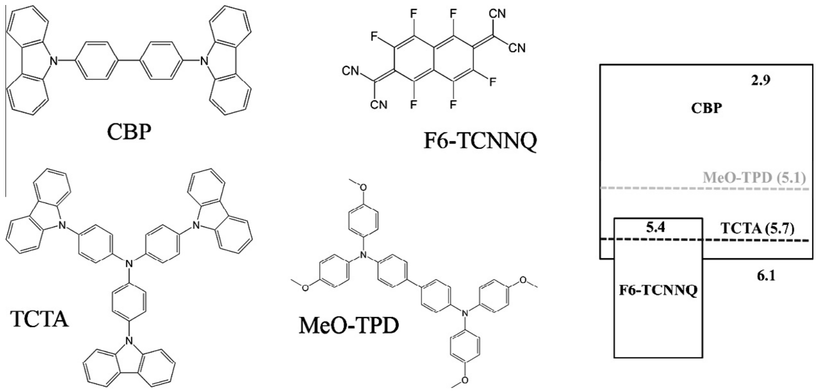

Fig. 1. Molecular structures and schematic energy diagram of CBP, MeO-TPD, TCTA and F6-TCNNQ molecules.