Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2007) 378–382
applied surface science
www.elsevier.com/locate/apsusc

A unified model for metal/organic interfaces: IDIS, ‘pillow’ effect and molecular permanent dipoles

H. Vázquez, Y.J. Dappe, J. Ortega, F. Flores *

Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

Abstract

A unified model, embodying the induced density of interface states (IDIS) model, the reduction of the metal work function due to the adsorbed molecules (‘pillow’ effect) and molecular permanent dipoles, is presented for describing the barrier formation at metal/organic interfaces. While the IDIS model and ‘pillow’ effect have been described in previous approaches, in this paper we show how to introduce molecular permanent dipoles in the interface barrier formation. Examples for Au or Al/organic interfaces are discussed, which show the validity of our results and the generality of our formalism.

PACS : 73.30.+y; 71.20.Rv; 73.61.Ph

Keywords: Metal/organic interface; Change neutrality level; Energy level alignment; Fermi level pinning; Interface states

1. Introduction

Organic semiconductors have been attracting much attention for over a decade, partly due to their electronic structure, in between localized states of molecules and delocalized states of solids, and partly because these materials can be used in new electronic or optoelectronic devices, such as light-emitting diodes, organic solar cells or field-effect transistors [1,2].

The issue of charge injection at metal/organic interfaces has too been the subject of considerable theoretical and experimental research: since many electronic devices use metallic electrodes, the formation of metal/organic contacts and the key parameters which control charge injection have been intensively studied. The alignment of the relevant electronic levels at metal/organic interfaces has become therefore the subject of increased interest [3,4]: this alignment is interesting both from a fundamental point of view and also due to its relevance in organic-based devices. The most important parameter determining charge injection at such interfaces is the Schottky barrier. Thus, theoretical models are needed to understand the formation of the Schottky barrier and the energy level alignment at metal/organic interfaces.

When the metal and the organic material are isolated, the position of the relevant electronic levels (the metal work function and the molecular highest occupied or lowest unoccupied molecular orbitals—HOMO and LUMO, respectively) relative to the vacuum level can be measured or calculated. As the interface is formed, however, the vacuum levels of both materials do not, in general, align. This phenomenon, known as the breakdown of the vacuum alignment rule, can be caused by many factors taking place at the interface, such as defects, chemical reaction, charge transfer, the presence of molecular permanent dipoles, or the reduction of the metal work function due to the presence of adsorbed molecules. The observation that, in general, the vacuum level rule is not followed [5,6] implies the existence of interface dipoles at these junctions, which shift the electronic levels of one material relative to those of the other. Since injection barriers depend on the magnitude of these interface dipoles, the ability to model and predict the formation of these dipoles is of considerable theoretical interest. Interfaces of inorganic semiconductors offer some inspiration as to the behaviour at these junctions, though the models developed for those systems are not directly applicable.

In this paper, we present a unified model which incorporates several mechanism operating at metal/organic interfaces: the

---

* Corresponding author.
E-mail address: fernando.flores@uam.es (F. Flores).

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2007.07.047

induced density of interface states (IDIS) [7–10], the 'pillow' effect [11–15] and we describe how to include the case of molecules exhibiting molecular permanent dipoles within our formalism. We focus on 'ideal' interfaces and take gold as a prototypical unreactive metal, which forms clean and abrupt interfaces with the organic semiconductor. We have considered the following organic materials: 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI), 4,4′,N,N′-dicarbazolyl biphenyl (CBP), copper phthalocyanine (CuPc) and tris-(8-hydroxyquinoline) aluminium (Alq_3).

2. Theoretical model

In a recent paper [15], we described how the reduction of the metal work function due to the compression of the metal electronic tail by the adsorbed molecules ('pillow' effect), could be incorporated into our IDIS formalism. The main idea was to calculate the electrostatic 'pillow' dipole induced at the interface, which translates into a reduction of the metal work function, and then to include this modification in the IDIS equations. Here, we show how the same approach can be extended to include the case of molecular permanent dipoles.

2.1. 'Pillow' effect

The reduction of the metal work function due to the orthogonalization of the metal and organic wavefunctions (the 'pillow' effect) is a mechanism operating at metal/organic interfaces [14]. A theoretical analysis of this effect and its inclusion within our formalism was recently carried out [15]. This was done by analyzing the modification of the many-body interactions due to the overlap between the metal and adsorbate wavefunctions, expanding these interactions in powers of the overlap up to second order. Then, an expression for the electrostatic dipole at the interface was derived, which reflects the repulsion and subsequent rearrangement of metal and organic charge densities at the interface. In our analysis, we obtain the electrostatic dipole coming from the 'pillow' effect D^{pillow} as the sum over all metal-organic orbital pairs:

$$\vec{D}^{\text{pillow}} = \sum_{\mu\mu'\sigma} \vec{D}^{\text{pillow}}_{\mu\mu'\sigma}, \tag{1}$$

where the expression for a pair of orbitals across the interface (μ labelling a metal orbital and μ' one from the organic molecule) is

$$\vec{D}^{\text{pillow}}_{\mu\mu'\sigma} = -(n_{\mu\sigma} + n_{\mu'\sigma}) S_{\mu\mu'} \int \vec{\Delta} r' \phi_{\mu'} \phi_{\mu} + (n_{\mu\sigma} - n_{\mu'\sigma}) S_{\mu\mu'} \frac{\vec{d}}{4}. \tag{2}$$

Here, $S_{\mu\mu'}$ is the overlap between orbitals μ and μ' across the interface and $\vec{d}$ connects the origins of these orbitals. The electrostatic dipole (1) has the effect of giving rise to a potential discontinuity at the interface according to

$$\Delta\phi = \frac{4\pi D}{A}, \tag{3}$$

where D is the corresponding dipole $\vec{D}^{\text{pillow}}$ (Eq. (1)) projected in the direction perpendicular to the interface and A is the area associated with each organic molecule.

2.2. Permanent molecular dipoles

Molecular permanent dipoles can cause interface dipoles [16,17] and should therefore be taken into account. Our way of dealing the effect of permanent molecular dipoles D^{mol} is the same than in the case of the 'pillow' dipole: the molecular dipole gives rise to a potential drop at the interface, according to Eq. (3), so that the existence of D^{mol} translates into a potential drop Δ^{mol} and the metal work function is reduced by this amount.

In our previous works [7–10], since we did not consider the effect of molecular dipoles, whenever we considered the energy level alignment for molecules exhibiting a permanent dipole (such as Alq_3, which will be discussed below), it was assumed that the molecules were deposited in such a way that the total dipole of the molecular film was zero. In this way, the molecular dipoles would cancel each other out and would have no effect on the position of the Fermi level. Here, we show how the inclusion of the molecular dipoles can be easily included in our formalism.

2.3. IDIS model

The 'bare' IDIS model, originally developed for inorganic semiconductor interfaces [18,19], describes the molecular level alignment in terms of the tendency of the metal work function and the charge neutrality level (CNL) of the organic material to align.

When the organic material is deposited on the metal surface, the tails of the metal wavefunctions tunnel into the gap of the organic material. This interaction has the effect of broadening the molecular levels, so that the initial discrete distribution is transformed into a continuum DOS with, in particular, a non-negligible DOS in the energy gap. This DOS (the IDIS, which gives name to the model) acts as a buffer for charge transfer and pins the Fermi level. The CNL position is such that the integral of the induced DOS up to the CNL yields the charge of the isolated molecule.

The CNL acts as an electronegativity for the organic material, and its position relative to the metal work function ϕ_M determines the direction and magnitude of charge transfer: if the CNL is closer to (further from) the vacuum level than the metal work function with respect to a common vacuum level, it will act as an electron donor (acceptor). The magnitude of the transferred charge is determined from the initial potential offset between ϕ_M and the CNL, as well as by the screening parameter $S = dE_F/d\phi_M$. This parameter $(0 < S < 1)$ describes the dependence of the interface Fermi level on the metal work function and thus the degree of anchoring or pinning of the Fermi level at the interface.

This screening parameter can be calculated theoretically from the DOS induced at the interface (the IDIS), d is the metal-organic distance and area A associated with each molecule through

$$S = \frac{1}{1 + (4\pi e^2 D(E_F) d/A)} \tag{4}$$

From the calculated values of the CNL and S, and the value of ϕ_M determined experimentally in each case, the Fermi level position E_F and dipole induced at the interface Δ can be calculated:

$$E_F - \text{CNL} = S(\phi_M - \text{CNL}) \tag{5}$$

$$\Delta^{\text{IDIS}} = (1 - S)(\phi_M - \text{CNL}) \tag{6}$$

In some recent papers [7,8,10], we showed how the energy level alignment at Au/organic interfaces could be predicted and understood using the ideas described above.

3. Unified IDIS-pillow-permanent-dipoles model

The unified model which incorporates the IDIS, 'pillow' and molecular dipole effects is a straightforward extension of that presented in ref. [15].

The 'bare' IDIS mechanism (as discussed in Section 2.3) shows how the organic CNL tends to align with the work function of the metal, where the degree of (mis)alignment depends on the initial potential offset and on the screening at the interface S. The effect of the 'pillow' mechanism and of molecular dipoles can be straightforwardly included as a modification in the value of ϕ_M.

In a first step, we take into account the effects of the orthogonalization of the metal and organic wavefunctions and the subsequent reduction of the work function of the metal. This reduction is reflected in our analysis by replacing the original work function ϕ_M with ϕ'_M.

We now consider molecular permanent dipoles: as discussed above, these would have the effect of reducing the metal work function (equivalently, they could be thought of as changing the CNL position but for simplicity we will adopt the former convention). Thus, the effect of molecular permanent dipoles on alignment is to change the metal work function from ϕ'_M to ϕ''_M. The 'pillow' and permanent dipoles, therefore, change the value of the metal work function from ϕ_M to ϕ''_M (Fig. 1 a).

The Fermi level position results from the application of the IDIS equations (Eqs. (5) and (6)) using the corrected value of the work function; i.e. after the 'pillow' and molecular dipole effects have been taken into account. This is illustrated in Fig. 1.

Thus, the potential drop at the interface resulting from the IDIS ($\Delta^{\text{IDIS}''}$) and 'pillow' (Δ^{p}) effects, as well as from molecular dipoles (Δ^{mol}) is given by

$$\begin{aligned}\Delta^{\text{IDIS-p-mol}} &= \Delta^{\text{p}} + \Delta^{\text{mol}} + \Delta^{\text{IDIS}''} = \Delta^{\text{p}} + \Delta^{\text{mol}} \\ &\quad + (1 - S)(\phi_M - \Delta^{\text{p}} - \Delta^{\text{mol}} - \text{CNL}) \\ &= (1 - S)(\phi_M - \text{CNL}) + S(\Delta^{\text{p}} + \Delta^{\text{mol}})\end{aligned} \tag{7}$$

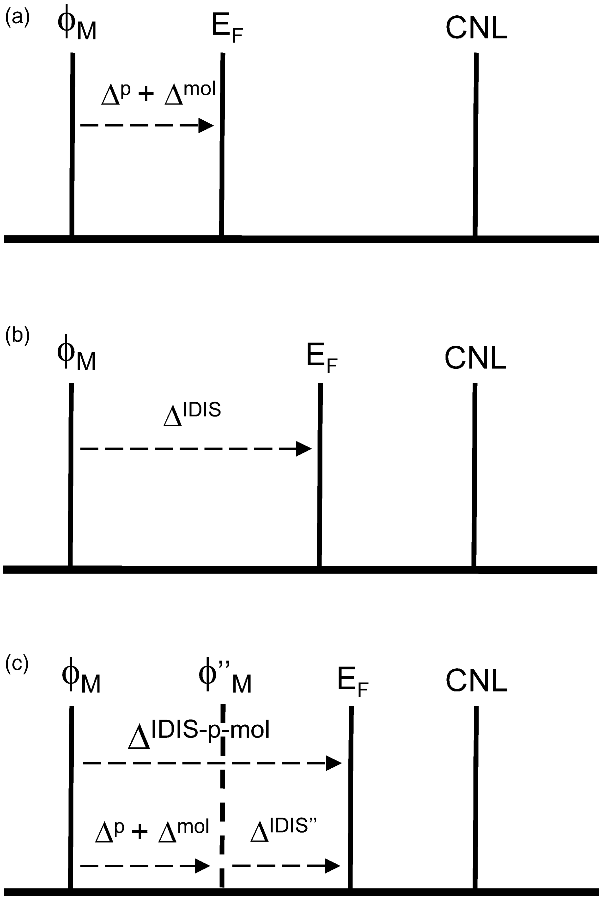

Fig. 1. (a) The 'pillow' effect and molecular permanent dipoles reduce the value of the metal work function; (b) the 'bare' IDIS mechanism results in an interface dipole Δ^{IDIS}; (c) combined IDIS-pillow-permanent dipoles model, whereby the effects described in (a) reduce ϕ_M to ϕ''_M, and the subsequent IDIS alignment is calculated using this corrected work function, as described in the text.

In Eq. (7), notice how, in a similar way as that described in ref. [15], the effects of the 'pillow' mechanism and permanent dipoles is first included, and then the IDIS formalism is applied using the resulting work function. This is equivalent to the usual IDIS equation, plus a screened term for the 'pillow' and permanent dipole terms.

Thus, our approach enables the easy inclusion of the effects of the 'pillow' mechanism and molecular permanent dipoles into our IDIS formalism.

4. Results and discussion

The unified model presented above allows the study of interface properties by looking at the sign and magnitude of the potential drop Δ induced at the metal/organic interface. Since most organic solids are composed of molecules which do not exhibit a permanent dipole, molecular permanent dipoles are not responsible for the energy level alignment taking place at most metal/organic interfaces. We have analyzed interfaces of two types, corresponding to organic molecules lacking or exhibiting permanent molecular dipoles.

Table 1
CNL positions, as well as interface dipoles and injection barriers with Au resulting from the combined IDIS-pillow model, as well as experimental [6,20–22] results

	PTCDA	PTCBI	CBP	CuPc
CNL (eV)	−4.8	−4.4	−4.05	−3.8
Δ^{IDIS} (eV)	0.25	0.50	0.43	1.05
$\Delta^{\mathrm{IDIS-p}}$ (eV)	0.39	0.67	0.64	1.27
Δ^{exp} (eV)	~0.25	0.4	0.5	~1.2
$\phi_{\mathrm{Bh}}^{\mathrm{IDIS}}$ (eV)	2.45	2.20	2.33	1.25
$\phi_{\mathrm{Bh}}^{\mathrm{IDIS-p}}$ (eV)	2.59	2.37	2.54	1.47
$\phi_{\mathrm{Bh}}^{\mathrm{exp}}$ (eV)	2.4	2.1	2.4	1.4

Below we quote our results for several interfaces calculated using Au as the metal, in which the organic material does not present a permanent dipole, and we later discuss the case of $\mathrm{Alq_3}$, where the effect of its permanent molecular dipole is analyzed.

Table 1 shows the results for several organic materials deposited on the Au substrate. The results obtained correspond to taking the IDIS and 'pillow' mechanism into account [15]. The results of Table 1 show good agreement with experiment (where 0.5 eV has been added to the experimental values of $\phi_{\mathrm{Bh}}^{\mathrm{exp}}$ to refer them to molecular level centers, rather than edges, as is done experimentally). As can be seen, the IDIS and combined IDIS-pillow results are very similar, and while the 'pillow' corrections are important, they do not alter the results given by the IDIS mechanism alone (recall the last term of Eq. (7), which shows that the 'pillow' term is screened). Thus, while the unified IDIS-pillow approach is more complete, the IDIS model alone already provides a good description of the trends observed at the interface and a good approximation to the interface dipole. Notice that in the Au/PTCDA and Au/PTCBI cases the values of Δ and ϕ_{Bh} are slightly overestimated, but in all cases the calculated values are within 0.1–0.2 eV of the experimental results, close to the experimental resolution.

We now turn our attention to the more general case of an organic material where molecular dipoles are important. Such a situation takes place with $\mathrm{Alq_3}$. Since the issue of how the $\mathrm{Alq_3}$ molecules are deposited on the metal substrate and in particular the orientation of the molecular dipole (pointing towards or away from the metal) has not been resolved experimentally, we compare with DFT calculations carried out for the weakly-interacting Al(1 1 1)/$\mathrm{Alq_3}$ interface [23,24]. From the results of Yanagisawa and Morikawa [23], we estimate that the initial reported molecular dipole (6.52 D) would result (using Eq. (3) and $A \simeq 117$ Å^2) in a potential drop of −2.1 eV, reducing the work function by this amount. At the same time, the 'rounded' shape of the molecule, in which only a few atoms are in close proximity to the metal substrate, allows us to neglect the 'pillow' effect in this case. The $\mathrm{Alq_3}$ dipole therefore reduces the initial value of $\phi_{\mathrm{M}} = -4.0$ eV [Morikawa2] to $\phi'_{\mathrm{M}} = -1.9$ eV. The offset between this (corrected) metal work function and the CNL position of $\mathrm{Alq_3}$ (which we place at −3.65 eV [10]), together with the screening parameter of $\mathrm{S} \simeq 0.58$ [10], result in an IDIS dipole density of $\Delta^{\mathrm{IDIS}''} = +0.74$ eV. The total potential drop is the sum of the contributions coming from the $\mathrm{Alq_3}$permanent dipole (−2.1 eV) and the IDIS mechanism (+0.74 eV), resulting in a final interface dipole of $\Delta^{\mathrm{IDIS}''} = -1.36$ eV, in excellent agreement with the reported value of −1.47 eV calculated by Yanagisawa et al. [23]. The energy level diagram for this interface is shown in Fig. 2.

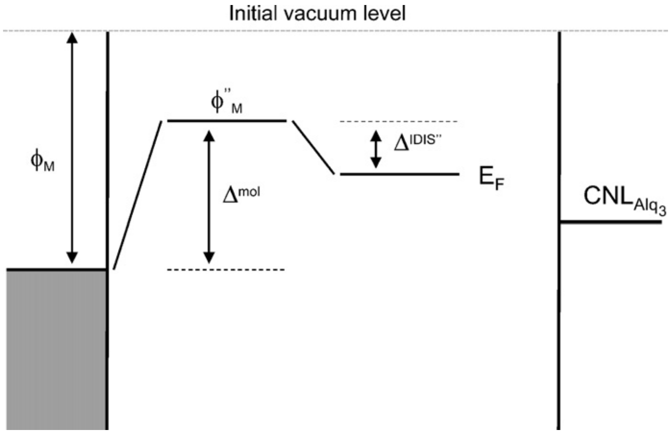

Fig. 2. Energy level alignment diagram for the Al/$\mathrm{Alq_3}$interface, showing the reduction of the metal work function due to the $\mathrm{Alq_3}$permanent dipole and the subsequent charge transfer and IDIS alignment. The calculated interface dipole is in excellent agreement with other DFT calculations.

Thus, in the absence of molecular permanent dipoles our unified formalism allows for the correct description of the interface properties, in agreement with experimental observations, while in cases where molecular permanent dipoles are significant, as is the case of $\mathrm{Alq_3}$, our results corroborate our theoretical approach.

5. Conclusions

We have presented a unified model which incorporates three important mechanisms taking place at metal/organic interfaces. The compression of the metal electronic wavefunction due to the orthogonalization with that of the adsorbed organic molecule leads to a reduction of the metal work function. Using the same formalism, molecular permanent dipoles (if present) are taken into account, which give rise to a variation of the metal work function. Finally, using this value of ϕ_{M} corrected by the previous mechanisms, the molecular level alignment is analyzed by means of the IDIS model, in which the CNL tends to align with the metal work function: charge transfer takes place between metal and molecule, the sign and magnitude of which is determined by the relative positions of the organic CNL and the (corrected) work function of the metal. The Fermi level position and final molecular level arrangement are determined by the initial offset as well as by the screening at the interface.

While the IDIS and 'pillow' effects are intrinsic to metal/organic interfaces and are thus present (to a stronger or lesser degree) at these junctions, permanent molecular dipoles cannot be regarded as a general mechanism, since relatively few organic molecules exhibit a permanent dipole in the direction perpendicular to the interface. However, when the adsorbed molecules do exhibit permanent dipoles, its effect on the interfacial level alignment is very important [16,17].

Results for interfaces between Au or Al and organic materials both showing and lacking permanent molecular dipoles are presented. The results are found to be in good agreement with experiment and other theoretical work, indicating the validity of our results and the generality of our formalism.

The strength of our approach lies in its intuitive and general formalism, which allows for the easy incorporation of several mechanisms taking place at metal/organic interfaces. We therefore believe our model, which combines important mechanisms operating at interfaces, to be of importance when analyzing the molecular level alignment at metal/organic interfaces.

Acknowledgements

We gratefully acknowledge financial support by the Universidad Autónoma de Madrid, the Juan de la Cierva project and the Spanish CICYT under projects MAT 2001-0665, MAT 2004-01271 and NAN-2004-09183-C10-07.

References

[1] S.R. Forrest, Nature 428 (2006) 911.
[2] W.R. Salaneck, K. Seki, A. Kahn, J.J. Pireaux (Eds.), Conjugated Polymer and Molecular Interfaces, Marcel Dekker, New York, 2001.
[3] C. Shen, A. Kahn, I.G. Hill, in: W.R. Salaneck, K. Seki, A. Kahn, J.J. Pireaux (Eds.), Conjugated Polymer and Molecular Interfaces, Marcel Dekker, New York, 2001, pp. 351–400.
[4] H. Ishii, K. Seki, in: W.R. Salaneck, K. Seki, A. Kahn, J.J. Pireaux (Eds.), Conjugated Polymer and Molecular Interfaces, Marcel Dekker, New York, 2001, pp. 293–350.
[5] S. Narioka, H. Ishii, D. Yoshimura, M. Sei, Y. Ouchi, K. Seki, S. Hasegawa, T. Miyazaki, Y. Harima, K. Yamashita, Appl. Phys. Lett. 67 (1995) 1899.
[6] I.G. Hill, A. Rajagopal, A. Kahn, Y. Hu, Appl. Phys. Lett. 73 (1998) 662.
[7] H. Vázquez, R. Oszwaldowski, P. Pou, J. Ortega, R. Pérez, F. Flores, A. Kahn, Europhys. Lett. 65 (2004) 802.
[8] H. Vázquez, F. Flores, R. Oszwaldowski, J. Ortega, R. Pérez, A. Kahn, Appl. Surf. Sci. 234 (2004) 108.
[9] H. Vázquez, Ph.D. thesis, Universidad Autónoma de Madrid, Madrid, Spain, 2006.
[10] H. Vázquez, F. Flores, A. Kahn, Org. Electron.,in press.
[11] H. Ishii, K. Sugiyama, E. Ito, K. Seki, Adv. Mater. (Weinheim. Ger.) 11 (1999) 605.
[12] P.S. Bagus, V. Staemmler, C. Wöll, Phys. Rev. Lett. 89 (2002) 096104.
[13] X. Crispin, V. Geskin, A. Crispin, J. Cornil, R. Lazzaroni, W.R. Salaneck, J.L. Brédas, J. Am. Chem. Soc. 124 (2002) 8131.
[14] N. Koch, A. Kahn, J. Ghijsen, J.-J. Pireaux, J. Schwartz, R.L. Johnson, A. Elschner, Appl. Phys. Lett. 82 (2003) 70.
[15] H. Vázquez, Y.J. Dappe, J. Ortega, F. Flores, J. Chem. Phys., submitted for publication.
[16] S. Kera, Y. Yabuuchi, H. Yamane, H. Setoyama, K.K. Okudaira, A. Kahn, N. Ueno, Phys. Rev. B 70 (2004) 085304.
[17] M. Knupfer, G. Paasch, J. Vac. Sci. Tech. A 23 (2005) 1072.
[18] C. Tejedor, F. Flores, E. Louis, J. Phys. C: Solid State Phys. 10 (1977) 2163.
[19] F. Flores, C. Tejedor, J. Phys. C 20 (1987) 145.
[20] I.G. Hill, J. Schwartz, A. Kahn, Org. Electron. 1 (2000) 5.
[21] I.G. Hill, A. Rajagopal, A. Kahn, J. Appl. Phys. 84 (1998) 3236.
[22] H. Peisert, M. Knupfer, T. Schwieger, J.M. Auerhammer, M.S. Golden, J. Fink, J. Appl. Phys. 91 (2002) 4872.
[23] S. Yanagisawa, Y. Morikawa, Chem. Phys. Lett. 420 (2006) 523.
[24] S. Yanagisawa, Y. Morikawa, Proc. Int. Symp. Super-Functionality Organic Devices IPAP Conf. Series 6 (2006) 11.