

Induced Density of States model for weakly-interacting organic semiconductor interfaces

H. Vázquez^a, F. Flores^{a,*}, A. Kahn^b

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

^b *Department of Electrical Engineering, Princeton University, Olden Street, Princeton, NJ 08544, USA*

Available online 14 August 2006

Abstract

The Induced Density of Interface States model is revisited and discussed for weakly-interacting organic semiconductor junctions. First, unreactive ‘ideal’ Au/organic interfaces are analyzed and described as a function of the organic Charge Neutrality Level (CNL) and the slope parameter S_{MO} specific to the case of Au: these values are similar, though not necessarily equal, to those obtained from a fit to reactive and unreactive metal/organic interfaces. Then, using the information provided by the Au/organic cases, we obtain the organic/organic screening parameters and calculate molecular level offsets without any adjustable parameter. The good agreement found between our theoretical results and experimental data for weakly-interacting metal/organic and organic/organic interfaces shows that our analysis in terms of the organic CNL and the corresponding (S_{MO} or S_{OO}) slope parameter provides a consistent and predictive description of the energy level alignment at these interfaces.

© 2006 Elsevier B.V. All rights reserved.

PACS: 73.61.Ph; 73.30.+y; 68.43.Bc

Keywords: Charge neutrality level; Interface states; Energy level alignment; Organic semiconductor; Fermi level pinning; Metal/organic interface; Organic/organic interface

1. Introduction

Research in organic electronics over the past decades has given rise to a series of new organic-based devices, such as light-emitting diodes, thin-film transistors and photovoltaic cells, many of which are based on small-molecule organic materials [1,2]. Since the performance of these devices is ultimately determined by charge injection at interfaces [3,4],

the study of metal/organic and organic/organic interfaces is the focus of considerable theoretical and experimental work.

Concerning metal/organic interfaces, the Schottky–Mott model, which consists of the simple alignment of the vacuum levels of the metal and organic material, was soon disproved [5,6], and interface dipoles and partial pinning of the Fermi level were observed. Several models have been proposed to explain this behaviour based on charge transfer between metal and molecule using the organic ionization and affinity levels [7,8], chemical

* Corresponding author.

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

reaction and formation of gap states [7–11], energetically distributed valence states and band bending [12], orientation of permanent molecular dipoles [13,14], as well as the reduction of the metal work function through the compression of the metal electron tail by the adsorbed molecules [8,15,16] (the ‘pillow’ effect).

Of these, probably the two most important and frequent mechanisms are chemical reaction at the interface and the ‘pillow’ effect. Chemically reactive interfaces are abundant and of obvious importance, and are characterized by the formation of metal–molecule bonds and the appearance of chemistry-induced gap states. While methods based on Density Functional Theory can be directly applied to these reacted interfaces, the main drawback is that the outcome of a particular reaction is unpredictable, so that each interface must be studied individually. Moreover, since the results are often very sensitive to the details of the interaction, it is difficult to extrapolate the conclusions to other cases. Thus, knowledge of reactive interfaces is hampered by its advancement in a stepwise manner.

Concerning the ‘pillow’ effect, the rearrangement of the metal electronic tail by the adsorbed molecules affects the dipole at the interface, effectively reducing the metal work function. Notice that, while the contributions from other mechanisms do not have a definite direction, the ‘pillow’ effect always tends to reduce the metal work function. This effect has been analyzed theoretically by Crispin et al. [15,17] for chemisorptive interfaces, while for physisorptive junctions, results for small organic molecules [16,18] have demonstrated this effect, though a systematic, quantitative understanding at a fundamental level is still lacking.

In a series of recent papers [19,20], we presented a model based on the Induced Density of Interface States (IDIS), in which the driving mechanism is the tendency of the Charge Neutrality Level (CNL) to align with the metal Fermi level.

While the importance of reactive or interdiffusive metal/organic interfaces is obvious and the effects of chemical reactions or defects cannot be understated, our aim is in fact to focus on the *opposite* class of interfaces: free of the complexity of chemical reactions or defects, which can obscure the understanding of the interface, the study of unreactive, ‘ideal’ interfaces can unveil the basic fundamental mechanisms governing the Schottky barrier formation. Our aim is to stress that, in the absence of chemical reaction or defects, there

is an ‘intrinsic’ mechanism operating at organic semiconductor interfaces.

At organic heterojunctions, which are weakly-interacting, the vacuum level rule is observed in a number of cases, with notable exceptions exhibiting significant (up to 0.5 eV) interface dipoles. While no consistent explanation for this behaviour had been presented, our model, based on the partial alignment of the CNLs of both organic materials, provided an intuitive, yet general and consistent, explanation for the sign and magnitude of the observed dipoles [21,22].

In this paper, we present a revision of the results of the IDIS model, which we argue is appropriate for understanding the behaviour of weakly-interacting interfaces. Concerning metal/organic junctions, Au is the prototypical case of a non-reactive metal, since its interaction with organic materials has been shown to be very weak. Although the ‘pillow’ effect is not included in the results presented here, it can be incorporated phenomenologically at this stage through a reduction of the initial metal work function, as will be discussed below.

First, we address Au/organic interfaces and discuss how to extract, using theoretical and experimental information, the CNL of the organic material and the slope parameter (S) of the interface. Here, the values of S are specific to the case of Au and are similar, though not necessarily equal, to the values obtained from several reactive and unreactive metal/organic interfaces [2]. Both the CNL and the S parameter are shown to be related to the interface dipole Δ and the hole injection barrier ϕ_{Bh} .

In addition, given their weak interaction, organic/organic interfaces are studied within our model: the added interest of Au/organic interfaces is the information they provide for understanding organic heterojunctions. A way of obtaining reliable screening parameters, S_{OO} , for the different heterojunctions is presented. It is then shown how these values, together with the CNLs of the organic materials, can be used to calculate molecular level offsets at organic/organic interfaces.

Results for interface dipoles, injection barriers and molecular level offsets are presented for 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), N,N' -diphenyl- N,N' -bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD),

bathocuproine (BCP) and tris-(8-hydroxyquinoline) aluminium (Alq_3). As good quantitative agreement with experiment is found for interface dipoles and injection barriers, our approach provides the first consistent means of understanding the energy level alignment at weakly-interacting organic semiconductor interfaces. Since some values have been slightly modified in light of new data, we consider them to be our most robust and ‘up to date’ set of results.

2. Discussion of the model

The origin of the concept of CNL can be traced back as early as Pauling and Mülliken. Even though their work focused on quantum atomic properties, such as trends in the periodic table or atom electronegativities, Mülliken proposed considering the average of the ionization (I) and affinity (A) energies an intrinsic property of atoms. Consider, for instance, two atoms having ionization and affinity levels given by I_1 , A_1 , and I_2 , A_2 (Fig. 1). If an electron is removed from 1 and placed at 2, the energy difference is $I_1 - A_2$. Charge transfer in the opposite direction gives $I_2 - A_1$. The difference between both processes yields $I_1 + A_1 - (I_2 + A_2)$, which suggests considering $\frac{I+A}{2}$ as a quantity which characterizes each atom, and whose relative values will determine the direction and magnitude of charge transfer: the atom with the higher (less negative) value of $\frac{I+A}{2}$ donates electrons to the one with the lower (more negative) value. This idea was pursued by Pauling to determine atom electronegativities [23] as a function of $\frac{I+A}{2}$.

In inorganic semiconductors, a generalization of this $\frac{I+A}{2}$ concept which consists on averaging the optical gaps in the Brillouin zone, yields the CNL of the semiconductor. It is well established that the CNL model for inorganic semiconductors can

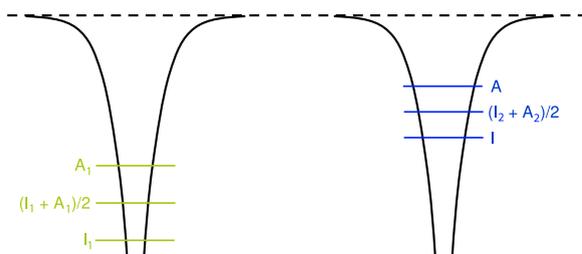


Fig. 1. Ionization (I) and affinity (A) levels for two different atoms. The average $\frac{I+A}{2}$ can be used to determine atom electronegativities.

explain the band offsets and Schottky barrier formation associated to the energy level alignment [24]. Concerning organic semiconductors, the average $\frac{I+A}{2}$ was used by Crispin et al. [15,17] to study reactive metal/organic interfaces within a chemisorption approach.

Our model for the induced DOS and CNL for weakly-interacting organic semiconductor interfaces can be regarded as a generalization of the previous cases by considering all molecular levels (rather than just the HOMO and LUMO) and their contribution to the CNL position: the simple $\frac{I+A}{2}$ argument predicts the CNL always at midgap. Instead, for several organic materials, the CNL position is located close to the LUMO [19,20], as the induced DOS is greater around the HOMO, pushing the CNL upper in the gap. Our results for Au/organic and organic/organic interfaces show that a detailed calculation, including the effect of all molecular orbitals, is necessary for a correct determination of interface properties such as induced dipoles and injection barriers.

Within our model, the resonance of molecular states with the metal continuum of states gives rise to a shift and broadening of the molecular levels (see Fig. 2). For the particular case of an energy-independent metal–organic interaction, it can be shown that, for weakly-interacting interfaces, each molecular level is broadened into a Lorentzian function $\frac{\Gamma/2}{(E-E_i)^2 + (\Gamma/2)^2}$, where Γ is the broadening of the

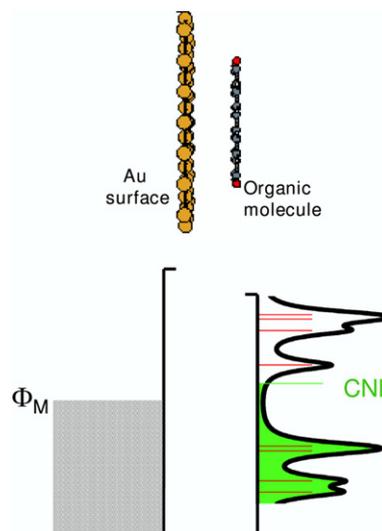


Fig. 2. At weakly-interacting metal/organic interfaces, charge transfer tends to align the organic CNL and metal work function. This gives rise to an induced dipole Δ_{MO} and the partial pinning of the Fermi level in the organic energy gap.

molecular level E_i . The sum of the contributions of the different molecular levels transforms their initial δ -like distribution into a continuum DOS with, in particular, non-negligible values in the former energy gap. By integrating this induced DOS up to the charge of the isolated molecule, the position of the CNL is determined. The relative position of the CNL and metal work function (when measured with respect to a common vacuum level) determines the size and direction of charge transfer. If the organic CNL is higher (less negative) than ϕ_M (as is the case of most organic materials on Au), electrons will be transferred from the molecule to the metal. This initial $\phi_M - \text{CNL}$ difference is reduced by the interface slope parameter S_{MO} , which determines how this initial offset is screened at the interface.

The interface Fermi level position and induced dipole can be calculated from Eqs. 1 and 2:

$$E_F - \text{CNL} = S_{\text{MO}}(\phi_M - \text{CNL}) \quad (1)$$

$$\Delta_{\text{MO}} = (1 - S_{\text{MO}})(\phi_M - \text{CNL}) \quad (2)$$

The DOS induced in the gap acts as a buffer for the transferred charge and is thus responsible for the dipole induced at the interface, the degree of Fermi level pinning at the interface and the Schottky barrier formation.

Given their weak interaction, the model was later extended to organic heterojunctions, where it was proposed [21] that the molecular level offset was determined by the relative position of the CNLs of both organic materials. A screening parameter S_{OO} , similar, but not equal to the one introduced for metal/organic interfaces, determines how this initial CNL offset will be screened when the interface is formed. In similarity to metal/organic interfaces, the initial and final CNL differences are related by (see Fig. 3)

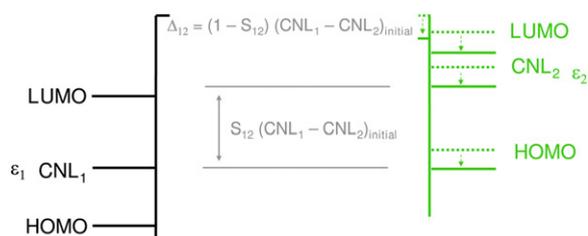


Fig. 3. Energy level alignment at organic heterojunctions: the initial CNL difference is partially screened, resulting in the formation of an interface dipole Δ_{OO} and a smaller final CNL offset.

$$(\text{CNL}_1 - \text{CNL}_2)_{\text{final}} = S_{\text{OO}}(\text{CNL}_1 - \text{CNL}_2)_{\text{initial}}, \quad (3)$$

while the induced dipole is

$$\Delta_{\text{OO}} = (1 - S_{\text{OO}})(\text{CNL}_1 - \text{CNL}_2)_{\text{initial}} \quad (4)$$

Thus, the central quantity in our analysis is the CNL, whose relative position to the metal work function (in the case of metal/organic interfaces) or to the CNL of the other material (at organic heterojunctions) largely determines the interface properties. This initial potential offset is reduced by the S parameter of the interface, whose value reflects the ability of the materials forming the interface to screen electrostatic potential differences. S_{MO} is almost always smaller than S_{OO} because the delocalized electrons in the metal are able to screen the potential difference at the interface efficiently. The screening ability of organic materials, on the other hand, is related to their static dielectric function, as will be commented on below.

3. Au/organic interfaces

Since there is evidence that metals other than Au are reactive or interdiffusive [2], we restrict our discussion to the case of interfaces between organic materials and Au. Au is non-reactive and the junctions formed with organic semiconductors are abrupt, resulting in almost ideal interfaces [7,25–28,11,31].

The electronic structure of the interfaces between Au and PTCDA, PTCBI, CBP and CuPc has been calculated, and the molecular level positions have been appropriately corrected [19,20,29] to account for the underestimation of the gap by DFT and for the band gap reduction due to polarization effects [30]. From the calculated DOS at the interface, CNL positions and values for the S parameter are obtained, which are in good agreement with experiment (see Table 1 and Figs. 4, 5). But whereas the CNL is a robust quantity, whose position is almost independent of the details of the interface, the S parameter is more dependent on the interaction at the interface, in particular through the metal–organic distance. We have taken $S = 0.16$ for PTCDA/Au and PTCBI/Au, as result from our calculations for a metal–organic distance d of 3.2 Å. The CNL position of CBP has been recalculated and is found to be -4.05 eV. Given our previously reported value [20], we consider this figure to have an uncertainty of 0.1 eV. For CuPc/Au, our

Table 1

CNL position, HOMO center (edge) and metal work function, with respect to the vacuum level, as well as theoretical values or fits of the S_{MO} parameter used in the calculations. Comparison between theoretical and experimental interface dipoles and hole injection barriers are given. All energies are given in eV

	–CNL	–IE	– ϕ_M	S (theoretical)	Δ (theoretical)	Δ (experimental)	ϕ_{Bh} (theoretical)	ϕ_{Bh} (experimental)
PTCDA	4.8	7.3 (6.8)	5.1 [6]	0.16	0.25	0.2 [6]	2.45	2.40 [6]
PTCBI	4.4	6.7 (6.2)	5.0 [7]	0.16	0.50	0.4 [7]	2.20	2.10 [7]
CBP	4.05	6.8 (6.3)	4.9 [10]	0.50	0.43	0.5 [10]	2.33	2.40 [10]
CuPc	4.0	5.7 (5.2)	5.3 [31]	0.30	0.91	1.2 [31]	1.31	1.60 [31]
α -NPD	4.1	6.0 (5.5)	5.14 [32] 5.4 [33]	0.33	0.70 0.87	0.86 [32] 1.3 [33]	1.56 1.47	1.74 [32] 1.9 [33]
Alq ₃	3.65	6.3 (5.8)	5.2 [6]	0.58	0.65	0.65 [6]	1.75	1.75 [6]
BCP	3.65	6.9(6.4)	–	0.42	–	–	–	–

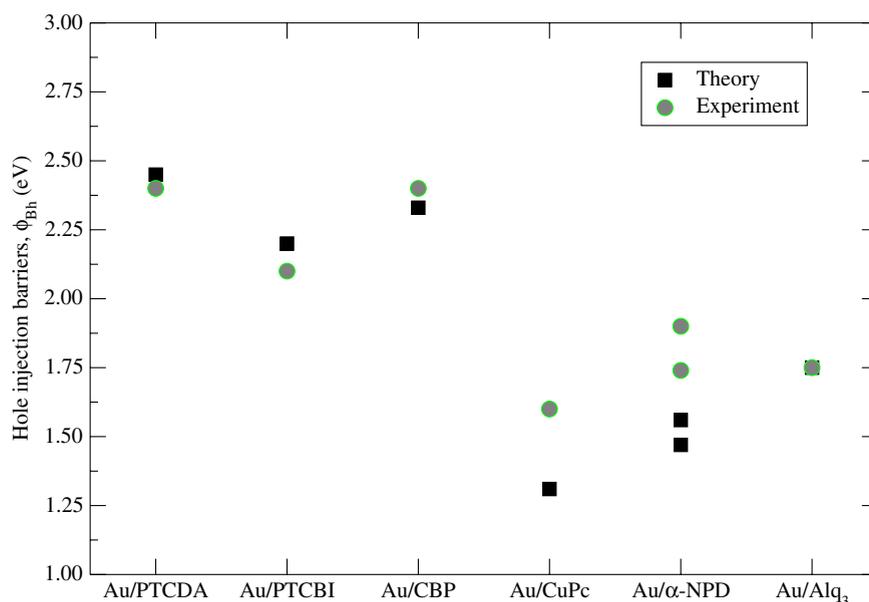


Fig. 4. Comparison of theoretical and experimental injection barriers for Au/organic interfaces, as quoted in Table 1.

choice of $S = 0.3$ ($d \sim 3.6$ Å) needs to be commented on. Experimental studies [31,39] seem to indicate that the molecular level broadening stems from intermolecular interactions, and that the interaction with the Au substrate is weaker than predicted by our model [21] (where a value $d = 3.2$ Å was taken), which would result in narrower CuPc peaks at the interface, and a larger value of S (and possibly d). Considering all this information, we have taken a larger value of S , $S = 0.3$, which is in better agreement with the reported experimental findings. For α -NPD and Alq₃, the CNL positions and the S parameters have been fitted to experimental interface dipoles and Schottky barriers, while maintaining the tendency (relative values) in S observed experimentally over a wide range of reac-

tive and non-reactive metals [2]. In particular, for α -NPD, experimental data for Au/ α -NPD interfaces [32,33] yield a low value of S , while geometrical considerations, such as its similarity in molecular structure to CBP, or having its benzene rings less tightly packed than PTCDA, PTCBI or CuPc, suggest that its value cannot be smaller than in these materials. As a compromise, we take $S = 0.3$, with an uncertainty of ± 0.1 . Interestingly, we find $S_{Au} \lesssim S_{MO}$, where the latter value is a fit over several reactive and unreactive interfaces, although the reasons for this are unclear at the moment. In the case of BCP, due to the lack of experimental information for Au/BCP interfaces, the calculation and comparison with experiment of interface dipoles and injection barriers cannot be carried out.

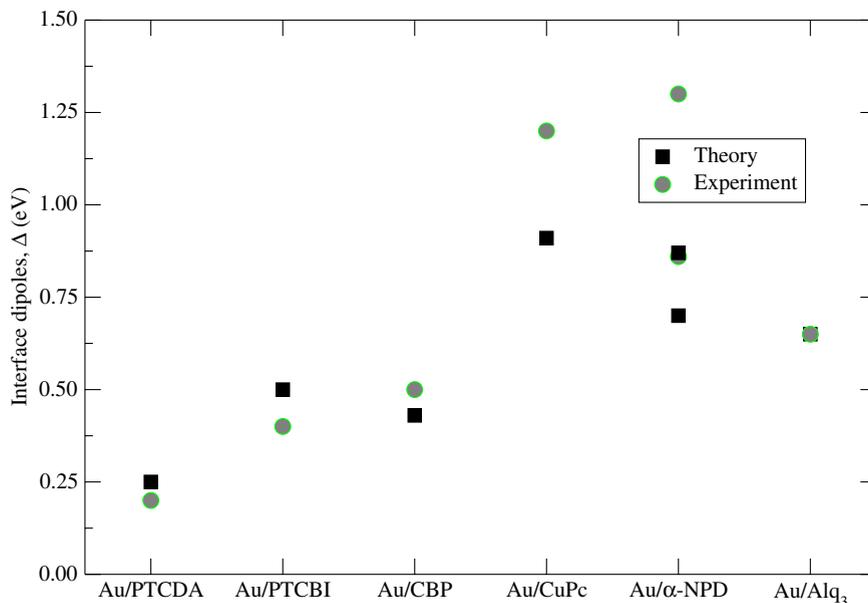


Fig. 5. Calculated and experimental interface dipoles for the Au/organic interfaces considered in this paper.

Instead, the CNL of BCP has been fitted to data from organic heterojunctions (see below).

Table 1 shows CNLs and S parameters for the organic materials considered, and compares the theoretical and experimental values of the interface dipole Δ and hole injection barrier ϕ_{Bh} . Notice that not only the fitted values, as expected, yield good agreement with experiment but so do the theoretical ones, calculated with no aid from external parameters. The agreement in Δ and ϕ_{Bh} is in most cases within 0.1 eV, and the calculated and fitted S values are not necessarily equal though certainly compatible with experimental values derived from a range of several reactive and non-reactive interfaces.

Notice that the ‘pillow’ effect, not considered in our approach, depends on the S_{MO} parameter, since this reduction of the metal work function is, too, screened by the interface charge. Thus, it can be expected to have a greater impact on those interfaces having larger values of S . Although we are currently working on a proper description of the ‘pillow’ effect within our formalism, it can nevertheless be immediately incorporated phenomenologically through a modification of the initial work function. As an additional contribution to the interface dipole, which shifts the organic electronic spectrum, it increases the values of Δ and ϕ_{Bh} given in Tables 1, but its effect in Δ (Eq. 1) is proportional to $(1 - S_{\text{MO}})$, and can thus be expected to be negli-

gible for interfaces having $S \sim 0$ (as with PTCDA or PTCBI in Table 1), and have a non-negligible impact on those interfaces exhibiting a smaller interface screening (Au/Alq₃ is an example). For these systems, we estimate the changes in Δ and ϕ_{Bh} to be no larger than 0.2 eV.

4. Organic/organic interfaces

Since there is evidence that organic/organic interfaces interact only weakly [2], our model for non-reactive Au/organic interfaces can be extended to organic heterojunctions. The calculation of molecular level offsets, as described previously, requires the knowledge of the screening parameter at the heterojunction, S_{OO} . Following Tersoff’s proposal for inorganic semiconductors [34], if the potential drop is equally shared by the two organic materials, the screening parameter is given by

$$S_{12} = \frac{1}{2} \left(\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} \right) \quad (5)$$

However, the static dielectric function in the direction perpendicular to the interface ϵ_{\perp} has, to our knowledge, only been measured for PTCDA ($\epsilon_{\perp} = 1.9$ [35,36]). Using this value as a reference, we propose to make an ‘educated guess’ of the values of the dielectric function for the other organic materials using Mönch’s approximation [37]

$$\left(\frac{1}{S_{\text{Au}}} - 1\right) \sim (\epsilon_{\perp} - 1)^2, \quad (6)$$

where S_{Au} is the metal/organic slope parameter of the corresponding organic material with Au. The results for ϵ_{\perp} using this approximation are shown in Table 2. It must be mentioned that they are slightly different from our previously reported values [21,22], especially in the case of CuPc. As was noted before, the case of CuPc is puzzling since experimental results suggest a weak Au–organic interaction and a large value of S_{Au} , while our theoretical calculations (which depend on the Au–CuPc distance d , introduced as an external parameter) point to somewhat smaller values of S_{Au} . We have taken $S_{\text{Au}} = 0.3$, corresponding to $d \sim 3.6$ Å, which we believe is a ‘middle point’ or compromise, compatible with both sets of results. As noted previously [21], different values of ϵ_{\perp} introduce small changes in S_{OO} but the main results and trends are not altered, showing the robustness of the results, which depend predominantly on the CNLs.

The values of ϵ_{\perp} given in Table 2 enable the calculation of the screening parameters S_{OO} , for organic/organic interfaces. With these, the interface

Table 2
Values for the Au/organic slope parameter S_{MO} and static dielectric function, obtained using Eq. 6

	S_{Au}	ϵ_{\perp}
PTCDA	0.16	1.9 [35,36]
PTCBI	0.16	1.90
CBP	0.50	1.39
CuPc	0.30	1.60
α -NPD	0.33	1.56
BCP	0.42	1.46
Alq ₃	0.58	1.33

Table 3
Initial CNL difference, screening parameter S_{OO} and calculated and experimental dipoles (in eV) for different organic heterojunctions

	$(\text{CNL}_1 - \text{CNL}_2)_{\text{initial}}$	S_{12}	Δ (theory)	Δ (experimental)
CuPc/PTCDA	0.80	0.58	0.34	0.4
CuPc/PTCBI	0.40	0.58	0.17	0.1
CuPc/CBP	0.05	0.67	0.02	0.0
CuPc/ α -NPD	0.10	0.63	0.04	0.0
PTCDA/Alq ₃	−1.15	0.64	−0.42	−0.5
PTCDA/ α -NPD	−0.70	0.58	−0.29	−0.1
BCP/Alq ₃	0.00	0.72	0.00	0.0
BCP/CBP	0.40	0.70	0.12	0.0
BCP/PTCBI	0.75	0.61	0.30	0.4
BCP/ α -NPD	0.45	0.66	0.15	0.0
Alq ₃ / α -NPD	0.45	0.70	0.14	0.25
Alq ₃ /CBP	0.40	0.73	0.11	0.1

dipoles at the different heterojunctions can be evaluated by inserting S_{OO} into Eq. 4. Table 3 shows the quantitative evaluation and comparison with experimental results for the different interface dipoles for several organic heterojunctions. The sign of the calculated dipoles always agree with the measured values, and the agreement in magnitude is good, in most cases under 0.15 eV.

Recently, a study of the molecular level realignment of organic heterojunctions when one of the materials is p-doped was carried out [38]. The results, analyzed in terms of a doping-induced shift of the CNL of the doped material, show the success of the CNL interpretation of these interfaces and indicate that our set of CNLs is consistent too with the observed behaviour at these doped organic heterojunctions.

5. Conclusions

In summary, we have presented a model for weakly-interacting interfaces based on the partial alignment of CNLs. An interface parameter, S_{MO} or S_{OO} , plays an important role in determining how efficiently the potential difference at the interface is screened. At weakly-interacting Au/organic interfaces, these values have been calculated for several organic materials (PTCDA, PTCBI, CBP and CuPc), while for others (α -NPD, BCP and Alq₃) they have been fitted to experimental dipoles and injection barriers. This evidence is then used to analyze organic heterojunctions by calculating the corresponding S_{OO} parameters.

The use of either calculated or fitted values of the CNLs and S_{Au} or S_{OO} yields good agreement with experiment in interface dipoles and injection

barriers for different organic interfaces. Moreover, this agreement over a range of different weakly-interacting (Au/organic, organic/organic) interfaces suggests that the values presented here, which have been slightly modified in light of new data [33,31,39], are the most robust and ‘up to date’, since they compare well over a range of interfaces of different nature.

Our results unambiguously show that the induced DOS and CNL are important quantities, governing the energy level alignment at weakly-interacting organic semiconductor interfaces. Other mechanisms discussed previously, such as chemical reaction and the ‘pillow’ effect, are presumably small at these weakly-interacting interfaces but could, in any case, be incorporated into our formalism. Moreover, we would like to stress that this is, to our knowledge, the first consistent and *predictive* analysis of this set of interfaces.

Our model has so far been only applied to weakly-interacting interfaces, while reactive or interdiffusive cases are more specific and unpredictable, and need to be studied individually. But since the formulation of our model is general and can include these cases, strongly-interacting or chemisorptive interfaces will be the focus of future work.

Acknowledgments

We gratefully acknowledge financial support by the Consejería de Educación de la Comunidad de Madrid, the Universidad Autónoma de Madrid and the Spanish CICYT under projects MAT 2001-0665, MAT 2004-01271 and NAN-2004-09183-C10-07. Support of this work by the National Science Foundation (DMR-0408589) and the New Jersey Center for Organic Optoelectronics (A.K.) is also acknowledged.

References

- [1] C.W. Tang, S.A. van Slyke, *Appl. Phys. Lett.* 51 (1987) 913.
- [2] 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.
- [3] J. Campbell Scott, *J. Vac. Sci. Technol. A* 21 (2003) 521.
- [4] Y. Shen, A.R. Hosseini, M.H. Wong, G. George Malliaras, *Chem. Phys. Chem.* 5 (2004) 16.
- [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] I.G. Hill, J. Schwartz, A. Kahn, *Org. Electron.* 1 (2000) 5.
- [8] H. Ishii, K. Sugiyama, E. Ito, K. Seki, *Adv. Mater. (Weinheim, Ger.)* 11 (1999) 605.
- [9] C. Shen, A. Kahn, *Org. Electron.* 2 (2001) 89.
- [10] I.G. Hill, A. Rajagopal, A. Kahn, *J. Appl. Phys.* 84 (1998) 3236.
- [11] M. Eremtchenko, D. Bauer, J.A. Schaefer, F.S. Tautz, *New J. Phys.* 6 (2004) 4.
- [12] G. Paasch, H. Peisert, M. Knupfer, J. Fink, S. Scheinert, *J. Appl. Phys.* 93 (2003) 6084.
- [13] S. Kera, Y. Yabuuchi, H. Yamane, H. Setoyama, K.K. Okudaira, A. Kahn, N. Ueno, *Phys. Rev. B* 70 (2004) 085304.
- [14] M. Knupfer, G. Paasch, *J. Vac. Sci. Technol. A* 23 (2005) 1072.
- [15] X. Crispin, V. Geskin, A. Crispin, J. Cornil, R. Lazzaroni, W.R. Salaneck, J.L. Brédas, *J. Am. Chem. Soc.* 124 (2002) 8131.
- [16] P.S. Bagus, V. Staemmler, C. Wöll, *Phys. Rev. Lett.* 89 (2002) 096104.
- [17] X. Crispin, *Solar Energy Mater. Solar Cells* 83 (2004) 147.
- [18] Y. Morikawa, H. Ishii, K. Seki, *Phys. Rev. B* 69 (2004) 041403(R).
- [19] H. Vázquez, R. Oszwaldowski, P. Pou, J. Ortega, R. Pérez, F. Flores, A. Kahn, *Europhys. Lett.* 65 (2004) 802.
- [20] H. Vázquez, F. Flores, R. Oszwaldowski, J. Ortega, R. Pérez, A. Kahn, *Appl. Surf. Sci.* 234 (2004) 108.
- [21] H. Vázquez, W. Gao, F. Flores, A. Kahn, *Phys. Rev. B* 71 (2005) 041306(R).
- [22] H. Vázquez, F. Flores, A. Kahn, *Proc. Int. Symp. Super-Funct. Org. Dev. IPAP Conf. Ser.* 6 (2005) 1.
- [23] L. Pauling, *The Nature of the Chemical Bond*, third ed., Cornell University Press, 1960 (Chapters 3–8).
- [24] F. Flores, C. Tejedor, *J. Phys. C* 20 (1987) 145.
- [25] T.S. Ellis, K.T. Parka, S.L. Hulbert, M.D. Ulrich, J.E. Rowe, *J. Appl. Phys.* 95 (2004) 982.
- [26] P. Fenter, P.E. Burrows, P. Eisenberger, S.R. Forrest, *J. Cryst. Growth* 152 (1995) 65.
- [27] T. Schmitz-Hübsch, T. Fritz, F. Sellam, R. Staub, K. Leo, *Phys. Rev. B* 55 (1996) 7972.
- [28] P. Fenter, F. Schreiber, L. Zhou, P. Eisenberger, S.R. Forrest, *Phys. Rev. B* 56 (1997) 3046.
- [29] R. Oszwaldowski, H. Vázquez, P. Pou, J. Ortega, R. Pérez, F. Flores, *J. Phys.: Condens. Matter* 15 (2003) S2665.
- [30] E.V. Tsiper, Z.G. Soos, W. Gao, A. Kahn, *Chem. Phys. Lett.* 360 (2002) 47.
- [31] H. Peisert, M. Knupfer, T. Schwieger, J.M. Auerhammer, M.S. Golden, J. Fink, *J. Appl. Phys.* 91 (2002) 4872.
- [32] W. Gao, A. Kahn, *J. Appl. Phys.* 94 (2003) 359.
- [33] A. Wan, J. Hwang, F. Amy, A. Kahn, *Org. Electron.* 6 (2005) 47.
- [34] J. Tersoff, *Phys. Rev. B* 32 (1985) R6968.
- [35] Z. Shen, S.R. Forrest, *Phys. Rev. B* 55 (1997) 10578.
- [36] S.R. Forrest, *Chem. Rev. (Washington, D.C.)* 98 (1997) 1793.
- [37] W. Mönch, *Appl. Surf. Sci.* 92 (1996) 367.
- [38] A. Kahn, W. Zhao, W. Gao, H. Vázquez, F. Flores, *Chem. Phys.* 325 (2006) 129.
- [39] M. Knupfer, private communication.