

Energy level alignment at organic heterojunctions: Role of the charge neutrality level

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We present a mechanism that explains the energy-level alignment at organic-organic (OO) semiconductor heterojunctions. Following our work on metal/organic interfaces, we extend the concepts of charge neutrality level (CNL) and induced density of interface states to OO interfaces, and propose that the energy-level alignment is driven by the alignment of the CNLs of the two organic semiconductors. The initial offset between the CNLs gives rise to a charge transfer across the interface, which induces an interface dipole and tends to align the CNLs. The initial CNL difference is reduced according to the screening factor S , a quantity related to the dielectric functions of the organic materials. Good quantitative agreement with experiment is found. Our model thus provides a simple and intuitive, yet general, explanation of the energy-level alignment at organic semiconductor heterojunctions.

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Organic-organic (OO) heterojunctions have become the focus of considerable attention in recent years, since these interfaces are at the heart of multilayer organic-based devices, such as organic light-emitting devices¹ and photovoltaic cells.² In these devices, electron-hole recombination or separation takes place at or near interfaces between electron and hole transport layers. A detailed understanding of the energy-level alignment at these OO heterojunctions is thus essential for the control and optimization of these organic-based devices.

The energetics of OO heterojunctions apparently exhibit contradictory behaviors. In the majority of cases, vacuum level alignment is observed within experimental error of photoemission spectroscopy (± 50 – 100 meV), the technique of choice to measure interface energetics.^{3,4} In some cases, however, a significant electrostatic dipole (up to 500 meV) is observed at the interface. Recently, a series of experiments performed on OO heterojunctions with one of the two materials doped p -type revealed the presence of a large interface dipole (0.5–0.6 eV).⁵ Up to now, no consistent explanation of these data has been put forward, and the energy-level alignment at OO interfaces remains an open problem.

The energetics of metal/organic (MO) interfaces are, too, under discussion, and have been analyzed with different models which include: (i) simple charge transfer based on the relative values of the metal work function and the organic electron affinity or ionization energy;^{6,7} (ii) chemical bonding;^{7,8} (iii) metal-molecule chemical reaction and formation of gap states;^{7,9} and (iv) compression of the metal surface electronic tail by the adsorbed molecule (the “pillow effect”).^{7,8,10} In two recent papers,^{11,12} we have shown that the energy-level alignment at MO interfaces can be explained using the concept of charge neutrality level (CNL) and the induced density of interface states (IDIS) model, used in the past for metal/inorganic semiconductor interfaces.¹³ According to this approach, the difference between the initial metal work function and the CNL of the organic semiconductor (measured with respect to a common vacuum level) determines the charge transfer between the

two materials, and thus governs the formation of the interface electronic structure. This energy difference is screened by the polarization of both materials. The screening power is measured by the parameter $S = dE_F/d\phi_M$, which describes how the position of the Fermi level at the MO interface in the organic gap depends on the metal work function. By the same token, S also gives the variation of the electron injection barrier, ϕ_{Bn} , at the interface: $S = -d\phi_{Bn}/d\phi_M$.

In the present paper, we extend these ideas and show that the OO barrier formation is controlled by charge transfer between the two organic semiconductors. The sign and magnitude of the charge transfer is determined mainly by the energy difference between the CNLs of the two materials. We discuss how an interface parameter, S , similar to the one introduced for MO interfaces, can be used to evaluate the electrostatic dipole induced at the OO heterojunction. Using these ideas, we show how the apparently contradictory behavior of the OO offsets finds a simple explanation.

It is convenient to start with a discussion of the IDIS model at MO interfaces. In Refs. 11 and 12, we studied interfaces between gold (Au) and three π -conjugated organic molecular materials: 3,4,9,10 *perylene*tetracarboxylic dianhydride (PTCDA), 3,4,9,10 *perylene*tetracarboxylic bisbenzimidazole (PTCBI), and 4,4'-*N,N'*-dicarbazolyl-biphenyl (CBP). Here, we restrict the discussion to *copper phthalocyanine* (CuPc) on Au.

The metal-induced molecular density-of states (DOS) and associated CNL is shown in Fig. 1 for a metal-molecule distance of 3.2 Å. Our calculations, detailed in Refs. 11 and 12, neglect the intermolecular interactions, which introduce only a small additional broadening of the molecular levels but do not create a DOS inside the molecular energy gap. The metal/molecule interaction, on the other hand, broadens the molecular levels, so that the initial delta-like distribution of the isolated molecule is transformed into a continuum DOS with, in particular, non-negligible density in the molecular energy gap (Fig. 1). The position of the CNL is such that the total integrated density of states up to the CNL accommodates the number of electrons in the isolated molecule.

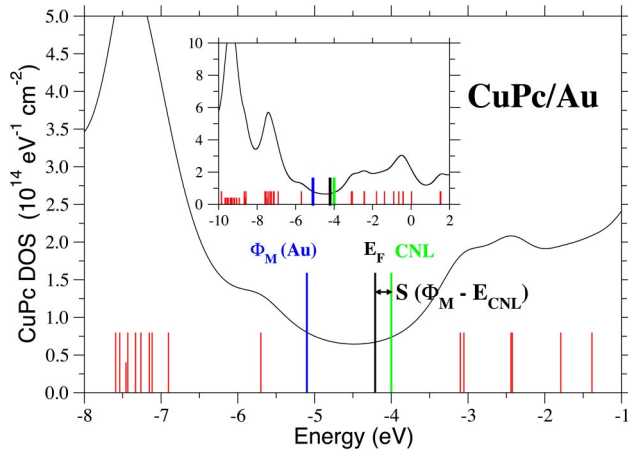


FIG. 1. (Color online) IDIS, CNL, and calculated interface E_F for CuPc/Au, for a metal-molecule distance of 3.2 Å. Long (short) bars correspond to the π (σ) states neglecting the metal-molecule interaction. The value of the initial Au work function, ϕ_M , taken to be 5.1 eV, is indicated by a vertical line. The CNL and E_F are related by Eq. (1).

An important outcome of our results is the weak sensitivity of the organic CNL to the metal/organic interaction. This has been checked by modifying the molecular level broadenings by factors of up to 2: our calculations yield the same position of the CNL irrespective of the interaction strength.¹¹ One can therefore deduce that for the deposition of the organic material on another nonreactive metal (Ag, for instance), the position of the CNL will not be significantly modified, although the interaction between them (and thus the molecular level broadenings) may be different. This is crucial for our OO heterojunctions model, as it shows that the CNL is an intrinsic property of the organic material, nearly independent of the metal on which it is deposited.

The physical meaning of this result is clear: the charge transfer at the interface is controlled by the difference between the metal Fermi level and the organic CNL. The offset between the CNL of the organic molecule and the initial metal Fermi level, or work function ϕ_M if its position is referred to the vacuum level, determines whether and in which direction charge is transferred between the metal and the organic molecule. The charge transfer induces an interface dipole which tends to align the Fermi level, E_F , and the

CNL. If, as is the case of Fig. 1, ϕ_M is below the CNL (i.e., ϕ_M is greater than the energy difference between the vacuum level and the CNL), negative charge is transferred from the molecule to the metal and a dipole is induced, which shifts the metal Fermi level upwards on the electron energy scale and reduces the initial difference between ϕ_M and E_{CNL} . A measure of this drive to align the two levels is given by S , which depends directly on the DOS around the CNL,^{11,13} and relates the initial and final energy difference by (see Fig. 1);

$$E_F - E_{\text{CNL}} = S(\phi_M - E_{\text{CNL}}). \quad (1)$$

For CuPc/Au, we obtain $S \approx 0.19$ and an interface dipole of $\Delta = 0.9$ eV, compared to the experimental value of $\Delta \approx 1.2$ eV.¹⁴ Our calculations yield $E_F = -4.2$ eV, or ~ 1.5 eV above the *center* of the highest occupied molecular orbital (HOMO) peak, in good agreement with experimental evidence.¹⁴

In summary, the energy-level alignment at MO interfaces is characterized by S , the CNL, and the work function ϕ_M of the metal: the CNL plays the role of an effective Fermi level for the organic material and S acts as a screening parameter, which determines how the initial energy difference $\phi_M - E_{\text{CNL}}$ is to be screened.

Our model for OO heterojunctions extends the previous arguments and proposes to consider the CNLs as the organic “effective” Fermi levels. This implies that the CNLs, calculated for MO interfaces, can be used to analyze OO heterojunctions. Although, strictly speaking, this should be confirmed by specific calculations of the different OO interfaces, the validity of this assumption in our model is supported by the arguments given above about the insensitivity of the CNL at MO interfaces, together with the good agreement of our results with experiment.

The initial relative position of the CNLs of the two organic materials determines how charge is transferred between them. Table I shows the calculated¹⁵ CNLs for PTCDA, PTCBI, CBP, and CuPc, as well as those deduced for α -NPD, BCP, and Alq₃. We stress that the latter three are not obtained from theoretical calculations, but are deduced from the best fit to experimental data (see below), once the calculated CNLs of PTCDA, PTCBI, CBP, and CuPc are fixed.

Table I shows the calculated (or deduced) CNL position with respect to the vacuum level and the ionization energy

TABLE I. Charge neutrality level (CNL) (with respect to the vacuum level), ionization energy (IE), and estimated static dielectric function for various organic materials. The CNLs of the bottom three compounds are deduced, as discussed in the text.

	$-E_{\text{CNL}}(\text{eV})$	$-\text{IE}(\text{eV})$	$E_{\text{CNL}}-\text{IE}(\text{eV})$	ϵ
PTCDA	4.8	7.3	2.5	1.9 (Ref. 18)
PTCBI	4.4	6.7	2.3	2.0
CBP	4.2	6.8	2.6	1.5
CuPc	4.0	5.7	1.7	2.5
α -NPD	4.2	6.0	1.8	1.5
BCP	3.8	6.9	3.1	1.4
Alq ₃	3.8	6.3	2.5	1.6

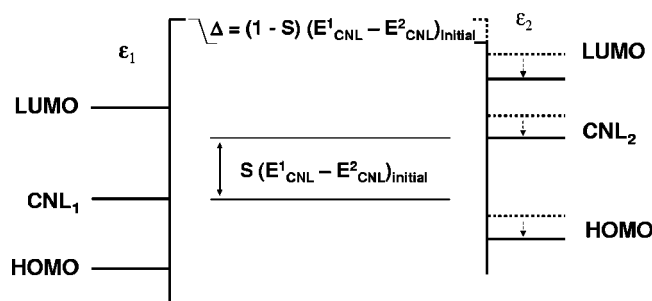


FIG. 2. CNL alignment in organic heterojunctions: an interface dipole $\Delta = (1-S)(E_{\text{CNL}}^1 - E_{\text{CNL}}^2)_{\text{initial}}$ is induced, lowering the initial levels of organic₂ (dotted lines) and reducing $(E_{\text{CNL}}^1 - E_{\text{CNL}}^2)_{\text{initial}}$ by a factor S .

(IE) of several organic materials. IE is measured on molecular films by photoemission spectroscopy⁴ and is defined in Table I as the difference between the vacuum level and the center of the HOMO peak.

Consider, for instance, the CuPc/PTCDA interface. The values of Table I suggest that negative charge is transferred from CuPc to PTCDA and that the electrostatic dipole induced between the two materials shifts the PTCDA energy levels upwards and reduces the initial energy difference between the CNLs. This is in qualitative agreement with experiment, which shows a 0.40 eV dipole in the same direction at this interface.¹⁶

The quantitative evaluation of the interface dipole is achieved by introducing the interface screening parameter, S . In accordance with the model developed for MO interfaces, the final (mis)alignment between the CNLs of the two materials is given by (Fig. 2)

$$(E_{\text{CNL}}^1 - E_{\text{CNL}}^2)_{\text{final}} = S(E_{\text{CNL}}^1 - E_{\text{CNL}}^2)_{\text{initial}}, \quad (2)$$

and the induced dipole is

$$\Delta = (1-S)(E_{\text{CNL}}^1 - E_{\text{CNL}}^2)_{\text{initial}}. \quad (3)$$

We estimate S by considering how a given external potential offset is screened by the organic materials. In principle, this can be calculated by means of the static dielectric function, ϵ , in the direction perpendicular to the interface. For MO interfaces, S varies between 0 and $1/\epsilon$, where the lower and upper bounds depend on whether the screening takes place in the metal ($\epsilon_{\text{metal}} \rightarrow \infty$, $S \approx 0$), or in the semiconductor ($S \approx 1/\epsilon$).¹⁷ For OO heterojunctions, a simple electrostatic argument, assuming that the potential offset is equally screened by each organic material, yields¹⁷

$$S = \frac{1}{2} \left(\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} \right). \quad (4)$$

The problem with the application of Eq. (4) is the lack of experimental data for ϵ_i . We know, however, that $\epsilon(\text{PTCDA}) \approx 1.9$ (Refs. 18 and 19), and that $(\epsilon-1)$ is inversely proportional to the square of the energy gap of the material. This suggests using the approximate values of ϵ_i given in Table I, estimated using the optical gaps of the organic materials.²⁰ With these, the calculated values of S for the interfaces of Table II vary between 0.41 and 0.70.

TABLE II. Calculated and experimental Ref. 16 interface dipoles (in eV) for different OO heterojunctions.

	$\Delta(\text{theory})$	$\Delta(\text{exp.})$
CuPc/PTCDA	0.43	0.4
CuPc/PTCBI	0.22	0.1
CuPc/CBP	0.09	0.0
CuPc/ α -NPC	0.09	0.0
PTCDA/Alq ₃	-0.42	-0.5
PTCDA/ α -NPD	-0.24	-0.1
BCP/Alq ₃	0.00	0.0
BCP/CBP	0.12	0.0
BCP/PTCBI	0.24	0.4
BCP/ α -NPD	0.12	0.0
Alq ₃ / α -NPD	0.14	0.25
Alq ₃ /CBP	0.14	0.1

The quality of our model can be judged by comparing the calculated and experimental interface dipoles (see Table II). The signs of calculated and experimental dipoles always agree. Moreover, the agreement between the absolute values is reasonable, the largest difference being 0.16 eV for BCP/PTCBI, which is close to the 0.1 eV experimental error.

Our model can be used to analyze the validity of the transitivity rule in OO heterojunctions: this rule states that the molecular level offset between two organic semiconductors can be obtained by aligning each one of them with a third organic material. It is easy to see that if the screening parameters $S_{i,j}$ were the same for the three interfaces, $S_{1,2} = S_{2,3} = S_{1,3}$, the transitivity rule would be satisfied within our model: in all three cases, the same factor is screening the difference between the CNLs.

Small differences among $S_{i,j}$ introduce some inaccuracies in the transitivity rule. Figure 3 shows the experimental results for PTCDA/ α -NPD/Alq₃/PTCDA,²¹ where the

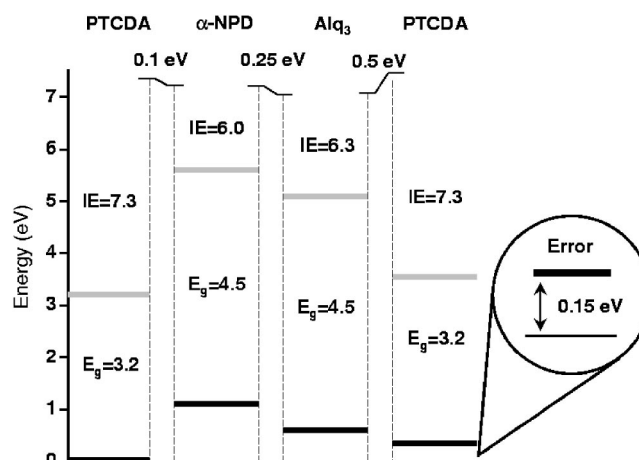


FIG. 3. Transitivity in OO heterojunctions: experimental results for PTCDA/ α -NPD/Alq₃/PTCDA (adapted from Ref. 21). The HOMO and LUMO are represented by black and gray bars, respectively. Interface dipoles, ionization energies, and peak-to-peak transport gaps are shown.

transitivity rule would imply that the PTCDA levels in the initial and final deposition are aligned, and that the sum of the interface dipoles is zero. From the theoretical values given in Table II, we find the following interface dipoles: $\Delta(\text{PTCDA}/\alpha\text{-NPD}) \approx -0.24$ eV, $\Delta(\alpha\text{-NPD}/\text{Alq}_3) \approx -0.14$ eV, and $\Delta(\text{Alq}_3/\text{PTCDA}) \approx 0.42$ eV. The sum of these values shows that the transitivity rule for these organic materials is satisfied within our model with an accuracy of ~ 0.05 eV, due to the slightly different values of S at the different interfaces. This is in good agreement with the experimental data, shown in Fig. 3.

Finally, we note that this model provides a natural, if qualitative for the time being, explanation for the introduction of a dipole at some OO heterojunctions with one of the two materials p doped (as mentioned previously). Doping introduces a density of carriers (of the order of 10^{18} cm $^{-3}$ holes in the present case), which increases considerably the dielectric constant of the organic material. As a consequence, S in Eq. (4) decreases by as much as a factor of 2, leading to an increase in Δ , according to Eq. (3). Furthermore, it is likely that the introduction of a large concentration of dopants with associated states and shift of the Fermi level towards the HOMO modifies the position of the CNL at these interfaces. The latter point remains to be investigated.

In conclusion, we have shown how the induced density of interface states model adapted to OO heterojunctions pro-

vides a good description of the energy-level alignment at these interfaces. An important difference appears with the case of inorganic semiconductors, for which screening is strong and the parameter S is close to zero.²² In the OO interfaces considered in this paper, S is larger, typically ~ 0.6 . Small differences with our calculated values of S will be found if the dielectric constants of the materials, ϵ_i , are different from our estimated values, but this will not alter the trends in the interface dipoles, which depend predominantly on the CNLs. Notice that all CNLs for the organic materials of Table I are within 4.0 ± 0.2 eV, except for PTCDA and PTCBI. This implies that large interface dipoles will be observed only at interfaces with these two materials. The other cases correspond to small interface dipoles, close to the experimental resolution of photoemission spectroscopy. This is an important effect that has obscured the physics behind the behavior of these interfaces, suggesting (wrongly) that the vacuum level alignment rule would be an appropriate way of determining all organic-organic band offsets.

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²⁰We have taken the following peak-to-peak optical gaps (eV): 2.6 (PTCDA), 2.5 (PTCBI), 3.5 (CBP), 2.0 (CuPc), 3.5 (α -NPD), 3.9 (BCP), and 3.1(Alq₃), following Ref. 16.

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