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Are Electron Affinity and Ionization Potential Intrinsic Parameters to Predict the Electron or Hole Acceptor Character of Amorphous Molecular Materials?

Enrique Louis,[*,†,‡] Emilio San-Fabián,[¶,‡] María A. Díaz-García,[*,†,‡] Guillermo Chiappe,[†,‡] and José A. Vergés[§,‡]

†Departamento de Física Aplicada, Universidad de Alicante, 03080 Alicante, Spain.

‡Unidad Asociada del CSIC and Instituto Universitario de Materiales, Universidad de Alicante, 03080 Alicante, Spain.

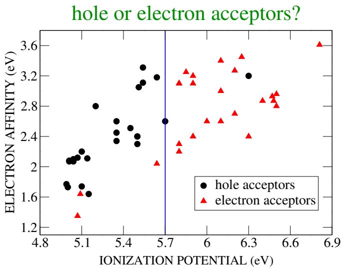
¶ Departamento de Química Física, Universidad de Alicante, 03080 Alicante, Spain.

§ Departamento de Teoría y Simulación de Materiales, Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 Madrid, Spain.

E-mail: enrique.louis@ua.es; maria.diaz@ua.es

Abstract

It seems universally accepted that amorphous molecular materials with low ionization potential (IP) and low electron affinity (EA) will function as hole-acceptor materials, while electron-acceptor materials usually have high electron affinity and high ionization potentials. Using previously published experimental data for amorphous charge-transporting molecular materials, we hereby show that actually only one of these two magnitudes matter, the ionization potential. A plot of up to 50 pairs (IP,EA) indicate that materials having IP $>$ 5.7 eV are electron-acceptors while those with IP $<$5.7 eV are hole acceptors. Only three exceptions are found for which DFT calculations of the IP, incorporating the polarized continuum model for various dielectric constants, were carried out. The resulting IP values are at variance with the experiments, but compatible with their observed character (as hole- or electron-acceptors).



Organic Light Emitting Diodes (OLED's) are current-driven devices that utilize light emission from excited states of molecules.[1] Operating OLED's involve charge injection from the anode and the cathode into the adjacent organic layers, transport of injected charge carriers through the organic layers, and exothermic recombination of holes and electrons to generate electronically excited states of molecules. Subsequent deactivation of molecules produces Electroluminescence (EL) that goes out of the device. Attaining high quantum efficiency for EL requires: i) efficient charge injection from both electrodes into the adjacent organic layers at low drive voltage, ii) charge balance, and, iii) confinement of charge carriers within the emitting layer to increase the probability of emissive recombination. The insertion of hole-acceptor and electron-acceptor layers between the electrodes and the emitting layer substantially increases efficiency. A multilayer structure of OLED's consists of the emitting layer sandwiched between hole- and electron-acceptor layers that in turn are in contact with the metallic anode and cathode, respectively. Amorphous molecular materials have been proven to show several characteristics that qualify them as excellent materials to be used in OLED's.[1] Their most remarkable feature is that, due to their homogeneous and isotropic properties, they form smooth thin films allowing uniform contact with the metallic electrodes and between organic layers. An issue concerning nomenclature is here worth of comment. As remarked above, device operation involves three main processes, namely, charge injection, charge transport and light emission. Although in this work we will only focus on the first, we shall also use the accepted terminology of hole- or electron-transporters, being aware of the fact that the correct one would be "acceptors" instead of 'transporters" (investigating their transport performance[2] would require considering also carrier mobility). Hereafter both terminologies will be used indifferently.

A question of relevance concerning charge injection in amorphous organic materials is whether there is one or several *intrinsic* parameters that may be used to univocally predict its character, i.e., whether they are hole or electron acceptors. There is a widely spread agreement according to which, materials having low ionization potentials (IP) together with low electron affinities (EA) usually function as hole-transporting materials, whereas materials with high electron affinities together with high ionization potentials usually function as electron-acceptor materials.[1] Other authors prefer to adopt an obvious rule that incorporates not only intrinsic parameters of the organic material, but also external parameters related to the electrodes. In that context, a material is often referred to as a hole (electron) transporter when its ionization energy (electron affinity) closely matches the Fermi level of the electrode material.[3–5] Therefore, for cathode metals with very low work functions, the electron-injecting contact should approach ohmic behavior, something that has already been achieved for hole injection from indium-tin-oxide (ITO) into various hole acceptor materials.[1] Anyhow, it seems still worthwhile trying to find *intrinsic* parameters that could also do the job. To this end we have plotted in Fig. 1 experimental data[1] for EA versus IP for up to 50 amorphous organic materials, 25 of each group (some of the data collected in the figure correspond to different experimental results for the same molecule). Data reported in ref. 1 were obtained using ITO as anode, and Mg, Al or a MgAl alloy as cathode; in addition, IP and EA were either directly obtained by direct and inverse photoemission or derived from the oxidation potential (IP) and the forbidden gap measured by optical absorption from which the EA is derived.

At this point it is pertinent to discuss the adequacy of the methods used to measure or to calculate the ionization potential and the elecron affinity. These are the key magnitudes that allow to derive the electronic band gap $E_{BG} = IP - EA$, that coincides in solids with the transport gap.[6] The most direct experimental techniques to derive the IP and the EA are Photoemission Electron Spectroscopy (PES) and Inverse PES (or IPES) respectively. However, these techniques are not always at disposal of researchers (this is particularly severe in the case of IPES) who are then forced to seek alternative methods. If PES is available, only the EA has to be determined. A possible way is to derive the optical gap from optical absorption measurements. However, formation of electron-hole pairs (so-called excitons) implies that the optical gap is not equal to the band (transport) gap required to derive the EA. Actually the difference between the band and the optical gaps gives the exciton binding energy, which is of the order of a few meV in inorganic semiconductors, while it may be as high as several tenths of eV in organic materials.[6] As a consequence, using optical absorption to determine EA requires the knowledge of the exciton binding energy.[7] A second approach is to use easily accessible electrochemical methods.[8–10] These methods seek to correlate the IP, measured by means of PES, with the oxidation potential OP. Actually, linear relationships between these to magnitudes have been reported by several groups.[7–10] In cases where neither the IP nor the EA can be directly determined by photoemission techniques, cyclic-voltammetry can provide, besides the OP, the reduction potential from which, as discussed in Ref. 7, the EA can be derived through a linear relationship. Electrochemical techniques, however, have several shortcomings, one of them being the inaccuracy of the reference electrode potential, that limit its accuracy in optimal cases to ± 0.1 eV.[9] It should be further pointed out that due to the amorphous character of organic materials, electronic energy levels up to an energy slightly above (below) the LUMO (HOMO) are localized. These are the so-called mobility-edges[11] that due to the already localized nature of organic solids should differ only slightly from the standard LUMO and HOMO energies. In any case, the existence of the mobility edge enlarges the transport gap. As concerns calculations, the high importance of inter-molecular interactions[10] should be remarked. In our case, and due to the amorphous character of the organic materials here considered, we have approximated these interactions by a polarized continuum model (see below). To close this discussion it should be pointed out that the experimental data herewith analyzed[1] may likely need some revision in the forthcoming years.

It is readily noted in Fig. 1 that except for three molecules, all others are separated into two groups: those having an IP > 5.7 corresponding to electron acceptors, while hole acceptors are confined to the region IP < 5.7 (there is an electron acceptor molecule with IP=5.64 eV that we do not consider as 'failure" because taking into account experimental errors, it lies in the borderline). Apparently, the EA plays a minor role, if any, in defining the two groups of charge transporter amorphous organic molecules. In order to further illustrate this result, we have calculated the overall averages of IP and EA (5.7 and 2.62 eV, respectively) and depicted in the same figure the regions where hole (electron) transporters are expected to lie, i.e. low (high) IP and EA. A total of twelve failures are noted, while if only the IP is used as the relevant parameter, only three failures is observed (see below).

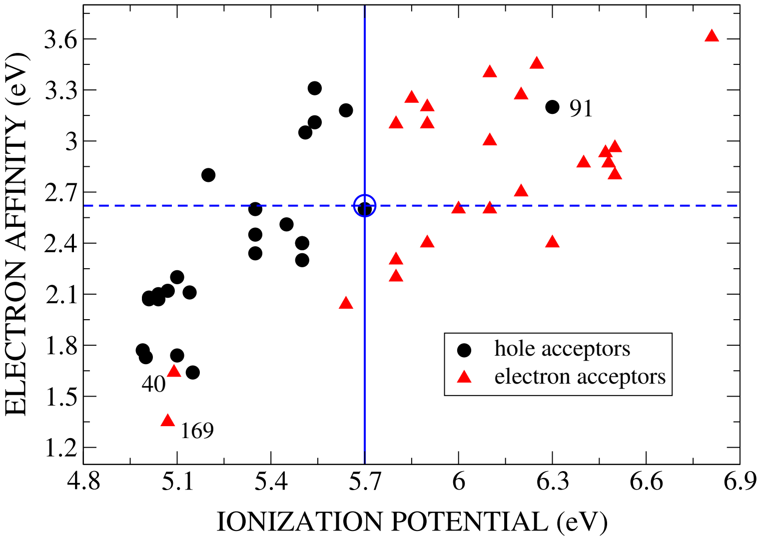


Figure 1: (Color online) Electron affinity vs. ionization potential of 50 organic amorphous materials (25 hole- and 25 electron-acceptors) as reported in Tables 2 and 3, respectively, of ref. 1. The large blue open circle corresponds to the average IP and EA, 5.7 and 2.62 eV, respectively. IP=5.7 eV seems to be the frontier between hole and electron acceptor molecules. Only three molecules clearly fail in following this criterion. These are numbered as in ref. 1, namely 40 (1,3,5-tris(phenyl-2-pyridylamino)benzene), 169 (2,4,6-tris[di(2-pyridyl)amino]-1,3,5-triazine) and 91(4,4'-di(N-carbazolyl)biphenyl, CBP).

Then, we turn our attention to the eventual role of the electrodes that inject holes or electrons into the device. In almost all devices ITO is used as anode. Its work function has been measured by many groups and is known to lie within the narrow range of 4.4-4.5 eV.[12] As concerns the cathode, many metals have been tried (some of them needing a protective layer of a noble metal, Ag in most cases). One of the most detailed studies of the effects of varying the metallic cathode and, thus, its work function, on the performance of a multilayer OLED device, has been reported in Ref.[3] The device consisted of an ITO anode a layer of a hole-transporter molecule (N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine, TPD), a layer of Alq3 that acted both as electron-transporter and emitter, a layer of the metal acting as cathode, and, finally a protective layer of Ag. According to the data gathered in ref. 1, Alq3 has an average IP (EA) of 5.9 eV (3.2 eV). The authors tried up to eight metals with work functions varying from 2.63 eV (Yb) up to 4.7 eV (Cu). They found that Mg cathodes (work function of 3.7 eV) produced much better luminiscence and efficiency than any other metal. More specifically, metals having work functions lower than Mg varying in the range 2.63-3.0 eV had luminiscences in the range 0.7-0.8 relative to that of Mg, while those having work functions in the range 4.3-4.7 eV had relative luminiscences in the range 0.08-0.47. Thus, they concluded that Mg provided by far the best performance to the OLED's under study.[12]

It is further noted that the ideal electrode,[4,13] is that which poses no barrier height for one type of charge carrier (ohmic contact) and a high barrier height for the other carrier (blocking contact). Fig. 2 shows hole versus electron barrier heights in junctions of organic molecules (hole or electron transporters) with the conducting materials most widely used in contact with either hole (ITO) or electron (Mg) transporters. Large blue symbols are the respective average values. It is appealing that average values indicate that in "wrong" junctions (hole transporters/Mg and electron transporters/ITO) the two barrier heights are very similar, thus both electrodes could be actually acting as ambipolar transporters. On the other hand, the lowest barrier heights for either holes or electrons correspond to the "right" junctions, whereas the barrier height for the other ('wrong") carrier is rather large. This qualifies ITO and Mg as excellent anode and cathode, respectively. If Mg is replaced by Al, the barrier heights for electron and holes become significantly more similar and, moreover, the difference in performance when Al is used as anode or as cathode is not as high as that found in Mg. This illustrates its poorer performance as compared to Mg.

As regards the already mentioned failures, we have carried out DFT calculations of the IP

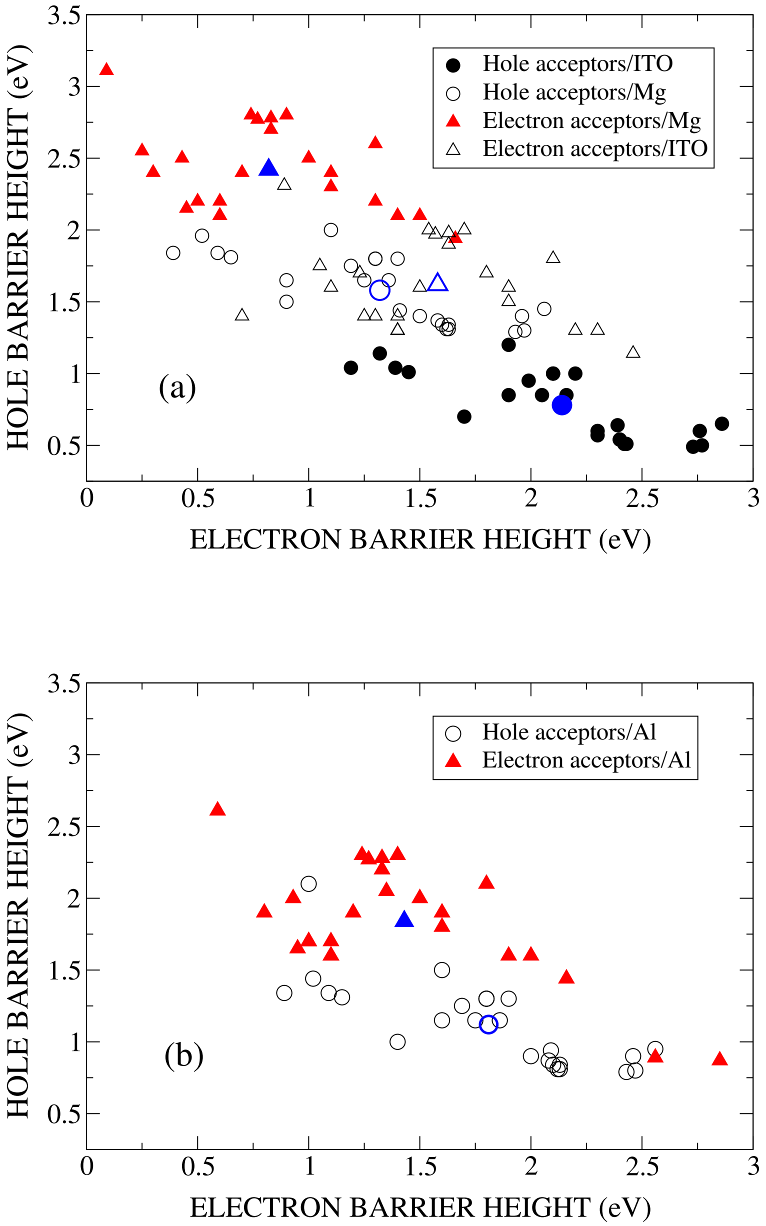


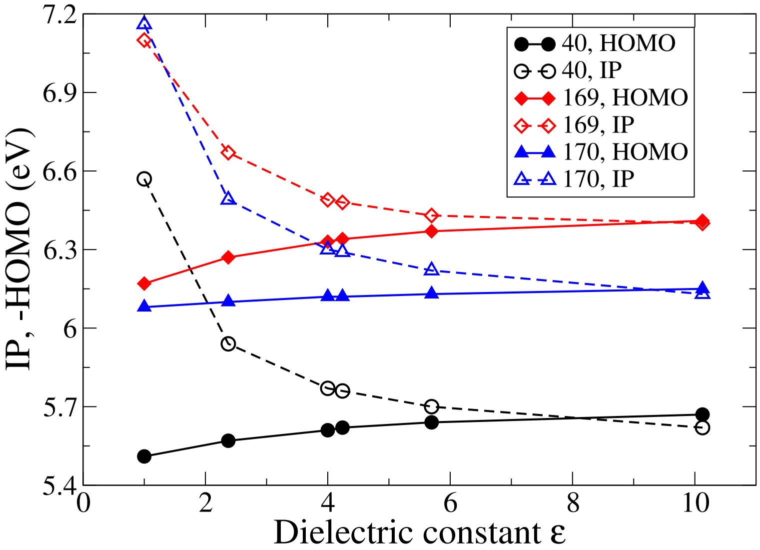
Figure 2: (Color online) a) Hole versus electron barrier heights in junctions of organic molecules (hole or electron acceptors) with the conducting materials most widely used in contact with either hole ITO (a) or electron Mg (a) and Al (b) acceptors. Large blue symbols are the respective average values: i) filled and empty triangles $(x, y) =$ (0.82, 2.42) eV and (1.58, 1.62) eV, respectively, and ii) filled and empty circles (2.14, 0.68) eV and (1.32, 1.58) eV, respectively. Note that in“wrong” junctions (hole transporters/Mg and electron transporters/ITO) the two barrier heights are very similar, whereas the lowest barrier heights for either holes or electrons correspond to the “right” junctions. Replacing Mg by Al leads to the following average values: filled blue triangle $(x, y) =$ (1.43, 1.84) and empty blue circle (1.83, 1.12) eV, respectively.

Table 1: HOMO, LUMO, ionization potential (IP) and electron affinity (EA) calculated with B3LYP/Def2TZVPP method using a polarized continuum model (PCM)[14] with several solvents of dielectric constant ϵ in the range 1-78.36. The results correspond to three Electron Acceptor (EAC) and two Hole Acceptor (HAC) molecules for which experimental data are collected in Ref. 1 (numbers correspond to those assigned in Ref. 1 to each molecule). All energies in eV.

EAC, no. Ref. 1 (IP, EA)	solvent ϵ	HOMO	LUMO	IP	EA
40 (5.09, 1.64)	vacuum, 1	-5.51	-1.24	6.57	0.14
	Toluene, 2.37	-5.57	-1.29	5.94	0.93
	ε =4.0	-5.61	-1.33	5.77	1.19
	DEE, 4.24	-5.62	-1.33	5.76	1.21
	CB, 5.70	-5.64	-1.35	5.70	1.30
	DCE, 10.13	-5.67	-1.37	5.62	1.43
	ACN, 35.69	-5.71	-1.40	5.56	1.56
	Water, 78.36	-5.72	-1.41	5.54	1.59
169 (5.07, 1.35)	vacuum, 1	-6.17	-1.13	7.10	0.08
	Toluene, 2.37	-6.27	-1.24	6.67	0.88
	ε =4.0	-6.33	-1.30	6.49	1.13
	DEE, 4.24	-6.34	-1.31	6.48	1.18
	CB, 5.70	-6.37	-1.34	6.43	1.27
	DCE, 10.13	-6.41	-1.39	6.40	1.44
	ACN, 35.69	-6.46	-1.45	6.35	1.60
	Water, 78.36	-6.48	-1.46	6.34	1.64
170 (6.0, 2.60)	vacuum, 1	-6.08	-1.73	7.16	0.60
	Toluene, 2.37	-6.10	-1.74	6.49	1.33
	ε =4.0	-6.12	-1.76	6.30	1.57
	DEE, 4.24	-6.12	-1.76	6.29	1.59
	CB, 5.70	-6.13	-1.77	6.22	1.69
	DCE,10.13	-6.15	-1.78	6.13	1.81
	ACN, 35.69	-6.17	-1.79	6.04	1.93
	Water, 78.36	-6.17	-1.79	6.02	1.96
HAC, no. Ref. 1 (IP, EA)					
86 (5.50, 2.30)	vacuum, 1	-4.98	-1.16	5.99	0.06
	Toluene, 2.37	-5.02	-1.21	5.37	0.83
	ε =4.0	-5.05	-1.25	5.19	1.08
	DEE,4.24	-5.05	-1.25	5.18	1.11
	CB, 5.70	-5.07	-1.26	5.12	1.21
	DCE, 10.13	-5.08	-1.29	5.04	1.34
	ACN, 35.69	-5.10	-1.31	4.97	1.46
	Water, 78.36	-5.11	-1.32	4.96	1.49
91 (6.30, 3.20)	vacuum, 1	-5.65	-1.60	6.65	0.39
	Toluene, 2.37	-5.67	-1.54	6.01	1.09
	ε =4.0	-5.69	-1.53	5.83	1.32
	DEE, 4.24	-5.69	-1.53	5.81	1.34
	CB, 5.70	-5.70	-1.53	5.75	1.43
	DCE, 10.13	-5.71	-1.52	5.67	1.55
	ACN, 35.69	-5.73	-1.52	5.61	1.66
	Water, 78.36	-5.73	-1.52	5.59	1.69

and the EA for those three molecules namely, the electron acceptors 40 (1,3,5-tris(phenyl-2-pyridylamino)benzene) and 169 (2,4,6-tris[di(2-pyridyl)amino]-1,3,5-triazine), and the hole acceptor 91 (4,4'-di(N-carbazolyl)biphenyl, CBP). In addition, and with the objective of checking the methods, the IP and EA of two molecules, one of each group, lying in the right region, i.e., 170 (2,4,6-tris(carbazolo)-1,3,5-triazine, TRZ2) and 86 (TPD) were also calculated. DFT calculations were carried out using the B3LYP method,[15–18]and the base Def2TZVPP,[19,20] that we checked to be large enough for our purposes. In addition, and aiming to simulate the effect of the amorphous solid, we incorporated a polarized continuum model (PCM).[14] Although recent extensions of this model have allowed to incorporate crystallinity,[21] we believe that a continuum model is more appropiate to describe amorphous solids. The dielectric constant ϵ (the ratio of the permittivity of a substance to the permittivity of free space) of the continuum medium was varied in the range 1-78 (ϵ=1 corresponds to a single molecule in vacuum); actually, the dielectric constant of molecular materials is known to lie within the range 1-6.[22–24] We have checked this to be an essential ingredient to obtain correct values for both IP and EA. These magnitudes were calculated using the standard expressions, IP=$E^+ - E^0$ and EA=$E^0 - E^-$, where E^0 is the ground state energy of the neutral molecule, while $E^\pm$, are the molecule ground states with minus or plus one electron. Both were calculated with the geometry of the neutral molecule. All these calculations have been done with the Gaussian09 package.[25]

The results for IP and EA of the five molecules mentioned above are reported in Table 1, along with the data gathered in ref. 1. In addition, the energies of the HOMO y LUMO molecular orbitals are also shown. It is first noted the significant effect that increasing ϵ has. While the IP for all molecules decreases in approximately 1 eV when ϵ is increased from its value in free space up to 78, the absolute value of the HOMO increases only very slightly in the same range. In addition, for $\epsilon \geq 10.13$ a crossover to overscreening[26] takes place in such a way that beyond that value of the dielectric constant HOMO>IP (absolute values) for all



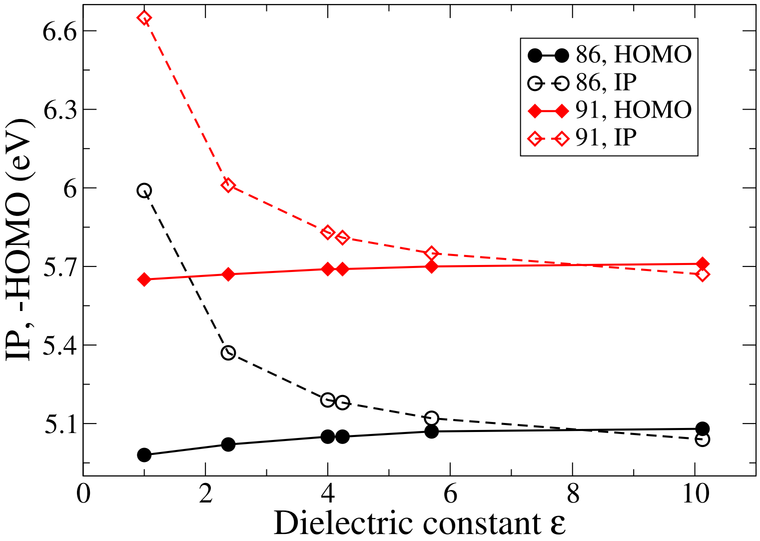


Figure 3: (Color online) Experimental (filled symbols) and calculated (empty symbols) values of IP and EA for the three molecules whose experimental data placed them out of their respective "right" regions (40, 169 and 91 in Fig. 1 and Table 1) plus two molecules (170 and 86 in Table 1) lying in the right region.

molecules. Just the opposite occurs for $\epsilon < 10.13$.

Fig. 3 depicts the calculated HOMO and IP for the five molecules mentioned above and dielectric constant $\epsilon \leq 10.13$. It is noted that beyond $\epsilon = 4$ the IP and -HOMO already become very similar; actually, they differ in less than 0.2 for the five molecules (see Table 1). In the foregoing discussion, results for this value of ϵ will be considered (note that in the amorphous solids it is widely accepted that -HOMO=IP, see ref. 1). It is remarkable that the two molecules (170 and 86) whose experimental IP place them in their respective "right" regions, show calculated values that do not remove them from that region. The electron acceptor molecule 170 has an experimental IP of 6 eV and a calculated IP of 6.3 eV, deeper inside the "right" (electron) region, while the hole acceptor molecule 86 in turn has an experimental (calculated) IP of 5.5 (5.19) that again places this molecule deeper into the hole region. Regarding the three failures mentioned above, it is noted the large increase in the IP of molecule 169 (compare the experimental value of 5.07 eV with the calculated one 6.49 eV) that places this molecule deep into the right region. Finally, although the IP of molecule 40 (91) is increased (decreased) in 0.68 (0.47) eV it is not enough to place them deep into their respective "right" regions but rather both still lie near the borderline, one in the right side (40) and the other (91) in the wrong side. These results suggest that some of the experimental data gathered in ref 1 may need to be revised.

The objective of this work was trying to identify one or several *intrinsic* parameters of amorphous molecular materials that could univocally determine whether they will be electron- or hole-acceptors. Plotting experimental results for the electron affinity against the ionization potential of hole- and electron-acceptor amorphous materials (25 of each group)[1] it is readily concluded that IP=5.7 eV might be the borderline of those two groups, the EA apparently playing a minor role. Only three molecules lie deep into their respective "wrong" regions. In order to discard any error in the experimental data or their interpretation, DFT calculations incorporating the polarized continuum model with dielectric constant in the range covered by these materials (2-6) were carried out for those three failures plus two molecules whose experimental IP places them in the right region. The calculated IPs for the three failures are at variance with the experiments but almost fully compatible with their character (as hole- or electron-acceptors). Instead the IP results for the other two molecules keep them in their right region. As the experimental data reported in ref. 1 were obtained using as cathode either Mg, Al or an alloy of the two metals, we evaluated the performance of Mg and Al as cathodes by plotting the barrier height that those metals pose for holes versus that they pose for electrons, concluding that performances of the two metals are very different. This is compatible with the work functions of Mg and Al, namely, 3.7 and 4.2 eV, respectively, and suggests that IP=5.7 eV may well be a valid "borderline" for cathodes having work functions within a range wider than 3.7-4.2 eV.

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