

## Theory of magnesium/Alq<sub>3</sub> interaction in organic light emitting devices

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The interaction between the magnesium (Mg) atom and Alq<sub>3</sub> molecule in organic light emitting devices has been theoretically studied using the PM3 method of the molecular orbital theory. It has been shown that various interactions can happen when the Mg atom approaches the Alq<sub>3</sub> molecule, leading to significant changes in the molecular geometry and electronic structure of Alq<sub>3</sub>. The resulting configurations with insertion of Mg into the central part of the Alq<sub>3</sub> molecule are found to be energetically more favorable than those with Mg forming bond(s) with a benzene ring of Alq<sub>3</sub>. In agreement with recent experiments, this result shows that the interaction between Mg and the Alq<sub>3</sub> molecule depends on the order of deposition. Interestingly, the density of states calculated for these systems reveals that the creation of the new electronic gap states observed in the experiments is mainly relating to the aluminum atomic orbital due to interaction, instead of a direct contribution of Mg. © 1999 American Institute of Physics. [S0003-6951(99)01411-4]

In the past decade, organic materials have been shown to exhibit outstanding optoelectronic properties that are unattainable with conventional semiconductor materials.<sup>1</sup> Particularly, the remarkable discoveries of efficient electroluminescence (EL) from organic molecules<sup>2,3</sup> and conjugated polymers<sup>4</sup> have stimulated intensive research on the photo-physics and device physics of organic materials. In a typical organic light emitting device (OLED), an organic layer is placed next to a metal, forming a metal/organic interface. The metal/organic interaction has been found to be critical in determining device performance. The strong coupling between the geometric and electronic structures of organic materials suggests that important modifications of the band structure may occur as a result of this interaction. Previous studies of the interaction between aluminum and conjugated polymers have reported the formation of covalent Al-C bonds and a reduction in the  $\pi$  conjugation of organic polymers.<sup>5</sup> Applications involving metal/organic thin-film interfaces constitute a field of growing technological importance.<sup>6</sup>

For the OLED based on small molecules, Alq<sub>3</sub> is particularly chosen as the key organic material because it is prototypical and represents the state-of-the-art electron transport/emitting layer. The interactions between the metallic atoms of the cathode such as Mg, Au, Ca, or Al and the Alq<sub>3</sub> molecule at the interface are particularly important. Recent UV photoemission spectroscopic (UPS) measurements<sup>7</sup> of the Au and Mg/Alq<sub>3</sub> interfaces have shown that the metal Fermi levels are pinned at 1.7 eV above the highest occupied

molecular orbital (HOMO) energy level of Alq<sub>3</sub> despite a big difference between the metal work functions. A parallel study by Rajagopal and Kahn<sup>8</sup> reported that Mg deposition onto Alq<sub>3</sub> led to a broad "doped" interface and new electronic gap states, while Alq<sub>3</sub> deposition onto Mg gave negligible influence.

The semiempirical molecular orbital approaches such as modified neglect of differential overlap MNDO/PM3 and INDO,<sup>9-11</sup> and the density functional theory (DFT)<sup>12</sup> have been used to study the electronic structure of some organic molecules, and valuable information has been obtained. In contrast, many theoretical studies have been made in combination with experiments for conjugated polymer related systems.<sup>13</sup> To our knowledge, no theoretical work pertaining to Mg/Alq<sub>3</sub> interactions has been reported. This work aims to fill such a deficiency and provide an understanding at the molecular level of the Mg/Alq<sub>3</sub> system. Particular attention is paid to the interaction/reaction, the origin of new electronic states, and the charge transfer and dipole at the Mg/Alq<sub>3</sub> interface.

The PM3 parametrization<sup>14</sup> of the MNDO semiempirical Hamiltonian<sup>15</sup> was used in this study for all calculations. Higher level calculations with *ab initio* or density functional theories which we previously applied to other systems<sup>16-18</sup> were not used, due to the limitation of computation for the large size and the many possible configurations of the present systems. The DOS was calculated based on the electronic density obtained with the above-described theoretical method.<sup>19</sup> The DOS was projected onto atomic orbitals in order to deduce how the individual atoms contribute to the total electronic structures.

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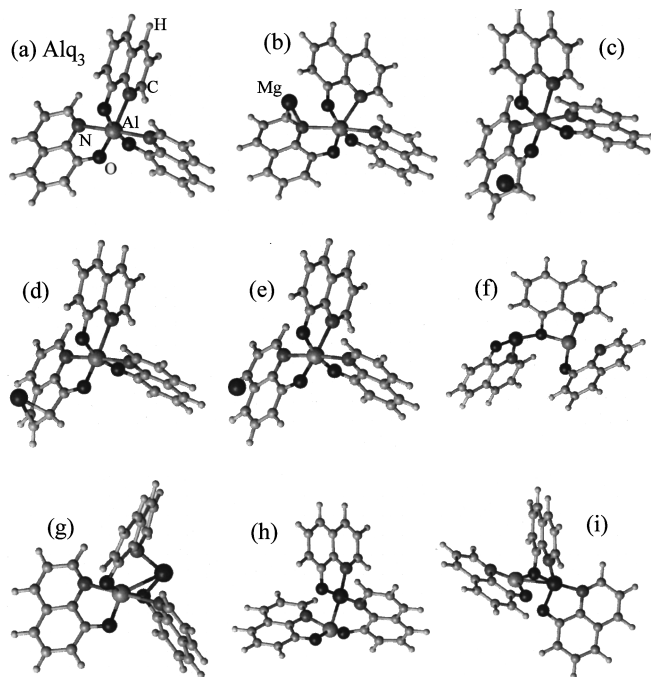


FIG. 1. The structural geometries of Alq<sub>3</sub> (a) and eight Mg–Alq<sub>3</sub> interaction systems (b)–(i).

The structure of Alq<sub>3</sub> has been well determined. In this study, we used the same isomer studied by others,<sup>9–12</sup> as shown in Fig. 1(a). Its three-dimensional structural characteristics suggest that (i) if the Mg is deposited onto the Alq<sub>3</sub>, the Mg can interact with any atom in the molecule since there is no screening for any of them except the Al atom, whereas (ii) if the Alq<sub>3</sub> is deposited onto a flat Mg surface, interactions may only occur between the outside benzene rings and the surface Mg atoms. Following the above, we placed individual Mg atoms into different sites near the representative atoms of the Alq<sub>3</sub> molecule, namely, Al, O, N, and C. Geometric optimization using the PM3 method was carried out for each corresponding complex. The consequential structures were analyzed to reveal the interactions. Figures 1(b)–1(i) show eight representative structures selected from 18 possible cases considered in this study of the Mg–Alq<sub>3</sub> system. Structures (b)–(e) represent the cases where Mg interacts with a benzene ring. For such cases, the addition of Mg results in simple bonding and thus, only slight structural deviations from the original Alq<sub>3</sub> molecule in (a). For structures (f)–(i), Mg is inserted close to the core of the Alq<sub>3</sub> molecule or forms a bond with the Al atom, because the Mg is placed near the N or O atom or both and

also the central Al atom. Therefore, the ensuing changes in structural configuration are substantive.

Table I lists the heats of formation of the considered interaction systems in Fig. 1. A comparison of these values reveals that when the Mg atom is inserted into the central part of the Alq<sub>3</sub> molecule [cases (f)–(i)] the resultant structures are more energetically favorable. Therefore, if Mg is deposited onto Alq<sub>3</sub>, these structures are most likely to be formed. In contrast, when the Mg bonds to the carbon atoms within an individual quinoline unit [cases (b)–(e)], the structures produced are less energetically favorable even when a bond is also formed between the Mg and a nitrogen atom [case (b)]. Nevertheless, the latter structures still correspond to metastable configurations and thus may also be formed by deposition, although their occurrences are expected to be less probable.

Figures 2(a)–2(i) depict the corresponding DOS for the considered systems. The DOS of the Alq<sub>3</sub> molecule, which is expressed as a thick solid line in Fig. 2(a), is almost identical to those reported by others.<sup>9,10</sup> The broadening parameters are 0.27 eV for all the DOS in Fig. 2 plotted with the thick line and 0.60 eV for the DOS in Fig. 2(a) plotted with the fine line. The difference in the binding energy of the DOS peaks is mainly because we did not align the DOS according to the UPS spectrum which was aligned in the other reports.<sup>9,10</sup> In addition, the calculated DOS feature of Alq<sub>3</sub> as indicated with the fine line in Fig. 2(a) is also similar to that from the DFT calculation.<sup>12</sup> Nevertheless, the present calculations are able to reflect the essential electronic features of the Alq<sub>3</sub> molecule which leads us to believe that the present approach is similarly applicable to the systems containing the Mg atom, the neighboring element of Al in the periodic table of elements.

In analyzing the calculated DOS, we found that joining Mg to the Alq<sub>3</sub> results in significant changes in the electronic structures, particularly for the cases where the Mg atom is inserted into the central part of the Alq<sub>3</sub> molecule. The results suggest that the broadening feature of the UPS spectrum<sup>7,8</sup> is mainly attributed to the DOS changes caused by the various metal-molecular interactions that occur when the Mg is deposited onto the Alq<sub>3</sub>.

Further, we have identified the origin of the new electronic states above the HOMO in the UPS experiments induced due to the deposition of Mg onto Alq<sub>3</sub>.<sup>8</sup> By projecting the DOS onto the atomic orbitals, we have observed that when Mg is inserted into the central part of Alq<sub>3</sub> [cases (f)–(i)], the atomic orbitals of Al are the main contributors to the new electronic gap states. When Mg is deposited elsewhere

TABLE I. Calculated heats of formation, atomic net charges on Mg, and dipole moment of Mg–Alq<sub>3</sub> complex. (a)–(i) correspond to the configurations in Fig. 1.

Models		(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
Heats of formation (eV)		-3.9534	-2.4448	-1.7427	-1.8053	-2.3688	-5.1872	-2.9886	-3.7165	-5.6280
Charges (a.u.) at Mg			0.5562	0.1857	0.3617	0.0232	0.8654	0.2102	0.7704	0.6029
Coordinates of Mg	X		3.0423	-3.2478	-4.4835	-4.3576	2.0552	-1.7833	0.6460	1.1941
	Y		1.0592	-2.0971	-0.0271	-0.2504	0.9231	0.2146	0.1064	0.3639
	Z		-0.2761	2.3927	-1.8885	-1.9532	-0.5713	-1.5253	-0.5052	-0.0801
Dipole moments	X	-0.7026	-1.1909	1.9418	1.1091	1.7445	2.0956	-0.2642	2.5008	0.2528
	Y	0.9596	2.1883	0.4824	-0.6647	-0.4941	2.5141	0.3072	2.8378	2.6955
	Z	0.7441	-0.6355	-1.7971	0.2428	1.8000	1.0655	-0.2499	-1.0158	1.6440

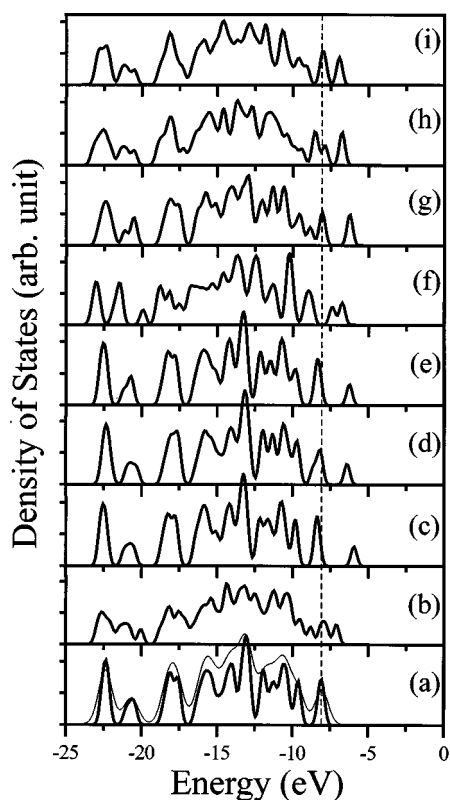


FIG. 2. Calculated DOS of the corresponding Mg-Alq<sub>3</sub> systems given in Fig. 1. The vertical dashed line indicates the HOMO position of the Alq<sub>3</sub> molecule. The states above such a line correspond to the new gap states.

in the Alq<sub>3</sub> molecule [cases (b)–(e)], the atomic orbitals of Mg are the main contributors to the resultant gap states. In the cases where Mg is inserted into the central part of Alq<sub>3</sub>, the atomic orbitals of Mg contribute to the molecular orbitals in the valence band, representing covalent bonding between Mg and its neighboring atoms. In such cases, the HOMO has been reconstructed, with part of Al atomic orbitals contributing to the gap states above the HOMO and thus showing an unsaturated behavior of Al. For other cases, the bonding of the Alq<sub>3</sub> is similar to that without the Mg. The HOMO is essentially composed of the atomic orbitals of the oxygen atom and the carbon atoms of the benzene ring adjacent to the oxygen, as in the case of the virgin Alq<sub>3</sub> molecule. Although the Mg atomic orbitals may contribute to the new gap states as well, the possibility of the free Mg atom forming a complex with the outermost part of the benzene ring is low. On the other hand, when the Alq<sub>3</sub> is deposited onto the Mg metal surface, interaction can only occur between the benzene ring and the many Mg atoms that form the surface. The contribution of the Mg to the DOS in such a case resides in the valence band, which is consistent with the experimental UPS results.<sup>8</sup>

It is worth noting that new gap states were also observed in the Ca/Alq<sub>3</sub> interface and the interfacial interaction depended on the order of deposition.<sup>20</sup> The present calculation on the analogous system may provide some guidance in understanding these results.

In addition, the atomic net charges of Mg obtained by the Mülliken population analysis for the different systems are positive as listed in Table I. The charge transfer naturally results in the formation of an interfacial dipole, which has

been observed experimentally.<sup>7</sup> The calculated dipole moments of the different Mg-Alq<sub>3</sub> complexes are included in Table I. To show the orientations of the dipoles, the corresponding Cartesian coordinates are also listed as reference (the origin of the coordinates lies in the mass center of the complex). The results show that only when the Mg atom is inserted into the central part of the Alq<sub>3</sub> molecule does the dipole moment point towards the direction of the Mg atom within the Alq<sub>3</sub> molecule. Even though the dipoles in many other cases are aimed at areas other than where the Mg atom is situated, those cases are energetically less favorable, according to the calculated heats of formation listed in Table I. When the Mg atom is deposited onto the Alq<sub>3</sub>, the part of the Alq<sub>3</sub> molecule where the Mg is most likely to be incorporated is the side facing the approaching Mg atom. Therefore, generally speaking, the dipole moment should be directed towards where the Mg atom is located.

In conclusion, the Mg is found to favor insertion into the central part of the Alq<sub>3</sub> molecule when forming Mg-Alq<sub>3</sub> complexes, resulting in the reconstruction of electronic structures and the formation of new electronic gap states. Therefore, the dependence of the Mg/Alq<sub>3</sub> interfacial characteristics on the order of deposition<sup>8</sup> is due to the differences in the interaction of Mg with Alq<sub>3</sub> at the central part and benzene ring of the compound. Interestingly, the appearance of new gap states is found to be mainly relating to the aluminum atomic orbital due to interaction, instead of a direct contribution of Mg.

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