

# Metal–Alq<sub>3</sub> Complexes: The Nature of the Chemical Bonding

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**Abstract:** Alq<sub>3</sub> (tris(8-hydroxyquinolino)aluminum) is the most widely used electroluminescent molecule in organic light-emitting devices. An urgent strong need exists currently to understand its chemistry and its reactivity, especially to those metals that constitute the cathodes commonly used. Complexes with single metal atoms are expected to form in metal-doped Alq<sub>3</sub> layers as well as at several stages of the functioning of the device. These, however, elude characterization via experiment only. The present study provides such a characterization by means of a series of calculations using density functional theory with gradient-corrected functionals of complexes with Li, Al, and Ca. Very clear results emerge that allow us to understand the nature of the interaction of the organic with such metal atoms and to identify the common as well as the metal-specific electronic and structural characteristics of each of them. Moreover, these calculations shed light on the specific and non-trivial effects that the formation of these chemical species can have on the intrinsic properties of the organic material.

More than a decade has elapsed since the first demonstration that Alq<sub>3</sub> (tris(8-hydroxyquinolino)aluminum) could be used as an efficient electroluminescent material.<sup>1</sup> By now, Alq<sub>3</sub> has become the prototype of a whole class of electroluminescent units currently in use in organic light-emitting diodes (OLEDs), and a strong need exists to deepen our knowledge of its chemistry, severely limited so far by experimental difficulties. Intense research efforts are now especially focused on unraveling the chemistry of its interaction with electron-injecting materials, whose key role has also emerged. In particular, metal–Alq<sub>3</sub> complexes are often invoked to rationalize spectroscopic data and are expected to form at the cathode/organic interface (see e.g., ref 2) in the early stages of metal deposition or during degradation processes,<sup>3</sup> and in the metal-doped organic layers.<sup>4,5</sup> However, experimental attempts have so far failed to provide any characterization of such complexes. The theoretical study we present here succeeds in providing such a characterization for complexes of Alq<sub>3</sub> with individual metal atoms, identifying the common as well as the metal-specific electronic and structural properties, and thus establishing the crucial effects they can induce in the organic.

Basic questions are open: Can Alq<sub>3</sub> indeed form such complexes? If so, which is the correct picture of the bonding? Which configurations offer possible sites for attack from the metal? How and to what extent are the properties of the molecule affected? We have carried out ab initio calculations based on density functional theory (DFT)<sup>6</sup> that are able to give a reliable answer to all these questions.

We consider Alq<sub>3</sub> interacting with individual atoms of Li, Al, and Ca,<sup>7,8</sup> namely of metals that constitute (in alloys or not) commonly used cathodes. We take as reference our recent calculations<sup>9</sup> of the structural and electronic properties of Alq<sub>3</sub>, using the same computational method, the results of which were corroborated by comparison with experimental data on solid films.<sup>10,11</sup> This study clarified the relationship between geometry and electronic structure and the effects of hole and electron injection. It also emphasized similarities and differences between the two geometrical isomers of Alq<sub>3</sub>, called facial and meridional. In particular, the facial isomer turned out to be less stable than the meridional by ~4 kcal/mol and to have a slightly higher electron affinity (by ~2 kcal/mol). The coexistence of these isomers in amorphous Alq<sub>3</sub>, of which the thin films in the device are formed, was thus argued, in agreement with previous suggestions.<sup>12,13</sup>

(7) The wave function basis set consists of plane waves with a 70 Ry cutoff. Corrections for spurious interactions among the periodically repeated images are made following Barnett and Landman (Barnett, R. N.; Landman, U. *Phys. Rev. B* **1993**, *48*, 2081). The CPMD code in the parallel 2.5 version (IBM Corp. copyright) developed by J. Hutter was used.

(8) The computational scheme applied here has previously been successfully used for other cases of organic molecules interacting with metal atoms. An example are metallofullerenes, whose results are reviewed in the following: Andreoni, W.; Curioni, A. *Appl. Phys. A* **1998**, *66*, 299.

(9) Curioni, A.; Boero, M.; Andreoni, W. *Chem. Phys. Lett.* **1998**, *294*, 263.

(10) Fujii, I.; Hirayama, N.; Ohtani, J.; Kodama, K. *Anal. Sci.* **1996**, *12*, 153. Schmidbauer, H.; Lettenbauer, J.; Wilkinson, D. L.; Muller, G.; Kumberger, O. *Z. Naturforsch. B* **1991**, *46*, 901.

(11) Curioni, A.; Andreoni, W.; Treusch, R.; Himpfel, F. J.; Haskal, E.; Seidler, P.; Heske, C.; Kakar, S.; van Buuren, T.; Terminello, L. *J. Appl. Phys. Lett.* **1998**, *72*, 1575.

(12) Burrows, P. E.; Shen, Z.; Bulovic, V.; McCarty, D. M.; Forrest, S. R.; Cronin, J. A.; Thompson, M. E. *J. Appl. Phys.* **1996**, *79*, 7991.

(13) The morphology of the amorphous thin films of Alq<sub>3</sub> is not fully understood yet. Structural studies show that it is complex and that phase heterogeneity is present, which also depends on the substrate (Brinkman, M.; Biscarini, F., private communication). Scanning tunneling microscopy of Alq<sub>3</sub> on metal surfaces demonstrates that both the luminescence spectrum (Alvarado, S. F.; Libioulle, L.; Seidler, P. F. *Synth. Met.* **1997**, *91*, 69) and the measured electron-injection threshold (Alvarado, S. F.; Rossi, L.; Seidler, P. F., to be published) can only be explained in terms of two isomeric forms of Alq<sub>3</sub>.

(1) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

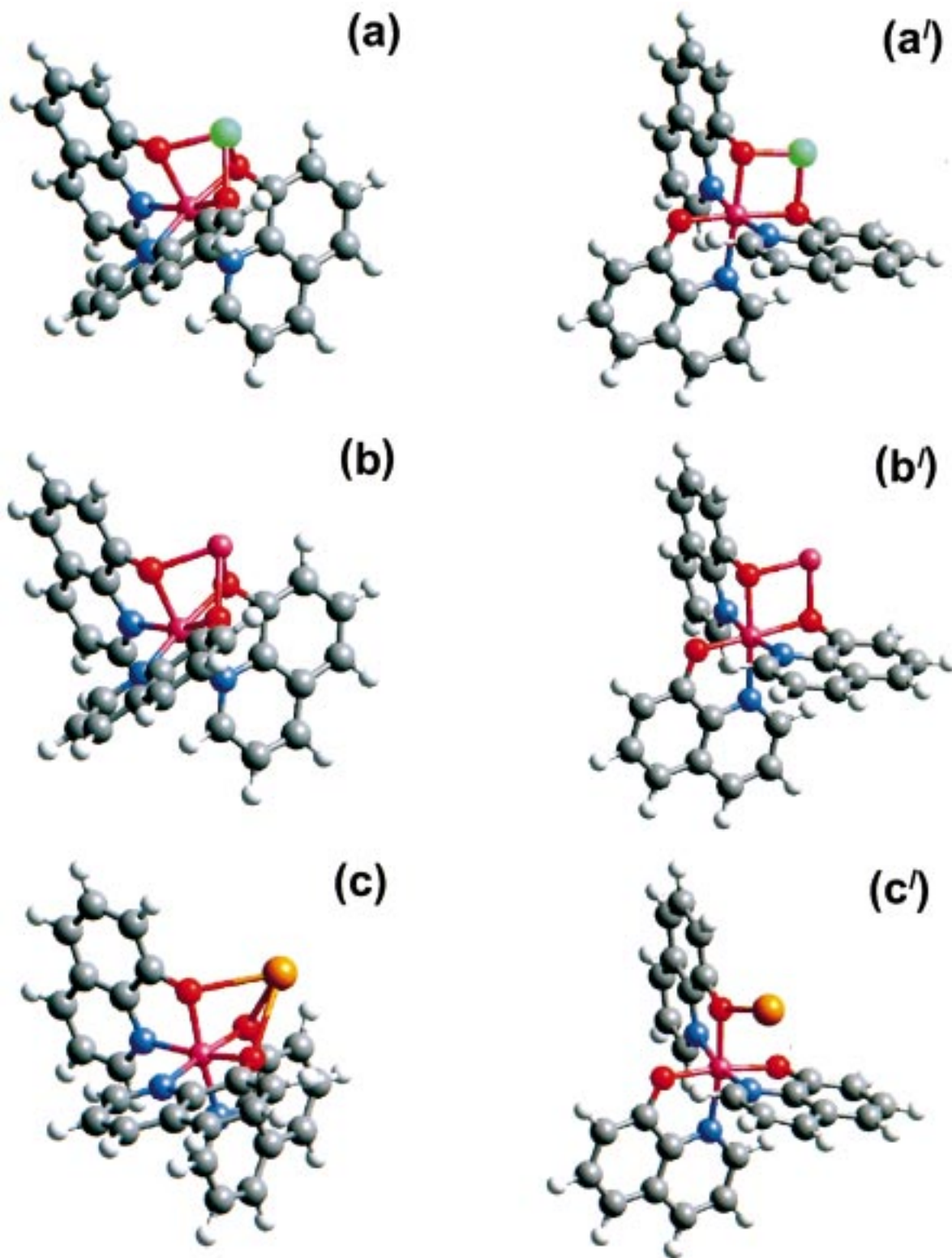
(2) Choong, V.-E.; et al. *Appl. Phys. Lett.* **1998**, *72*, 2689.

(3) Rajagopal, A.; Kahn, A. *J. Appl. Phys.* **1998**, *84*, 355.

(4) Kido, J.; Matsumoto, T. *Appl. Phys. Lett.* **1998**, *73*, 2866.

(5) Huang, M. B.; et al. *Appl. Phys. Lett.* **1998**, *72*, 2914.

(6) Gradient-corrected exchange and correlation functionals are used, from Becke (Becke, A. D. *Phys. Rev. A* **1998**, *38*, 3098) and Lee–Yang–Parr (Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785), respectively. Norm-conserving nonlocal pseudopotentials are used for all elements. In particular, those of Li and Ca include nonlinear core corrections.



**Figure 1.** Minimum energy structures for the Li (a,a'), Al (b,b'), and Ca (c,c') complexes with  $Alq_3$  in the two geometrical isomers (facial, meridional). The colors used are green for Li, pink for Al, yellow for Ca, red for oxygen, blue for nitrogen, black for carbon, and light gray for hydrogen.

We let the atom probe different parts of the molecule by placing it at several locations and optimizing the structure locally. Further confirmation of the resulting geometries was obtained with Car–Parrinello molecular dynamics.<sup>14</sup> The environments of interest were the Al–ligand octahedral coordination shell and the quinolate ligands. We were able to establish that, in all cases (Li, Al, Ca, and both isomers of  $Alq_3$ ), the oxygens constitute the centers of strongest attraction for the metal atom, and moreover that in the thus-formed metal

complexes, the relative stability of the two molecular isomers is inverted, with the facial one being more stable by at least 10 kcal/mol. Isomerization from the meridional isomer is likely to occur, given the physical conditions at which the interaction takes place (see ref 15). In fact, the co-deposition of the organic and the metal in the fabrication of doped layers is a gas-phase high-temperature process, and the deposition of the metal on the organic refers to thermally activated organic surfaces.

(14) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1998**, *55*, 2471.

**Table 1.** Binding Energies (kcal/mol) of the Metal–Alq<sub>3</sub> Complexes in the Optimized Configurations for Both Molecular Isomers

facial isomer		meridional isomer	
metal	BE	metal	BE
Li	51	Li	39.5
Al	51	Al	37.1
Ca	23	Ca	11

The detailed results are presented in Figure 1 for the optimal configurations of the six cases, in Table 1 for the corresponding binding energies (BEs), in Figure 2 for the differential densities in the optimal configuration, and in Figure 3 for the diagram of the Kohn–Sham (KS) energy levels. We use the latter for the classification of the orbitals around the gap region of Alq<sub>3</sub>.<sup>16</sup>

We recall that Alq<sub>3</sub> has a relatively high electron affinity ( $\sim 1$  eV) and a relatively high ionization potential ( $IP \approx 5.7$  eV), whereas the probe atoms have similar first ionization potentials of 5.4 (lithium), 6.0 (aluminum), and 6.1 eV (calcium) but much lower electron affinities (0.6, 0.4, and 0.02 eV, respectively).<sup>17</sup> Thus, simple arguments such as the one based on the Mulliken electronegativity would predict a somewhat higher tendency for an electron to escape from the metal atom to the molecule than vice versa.

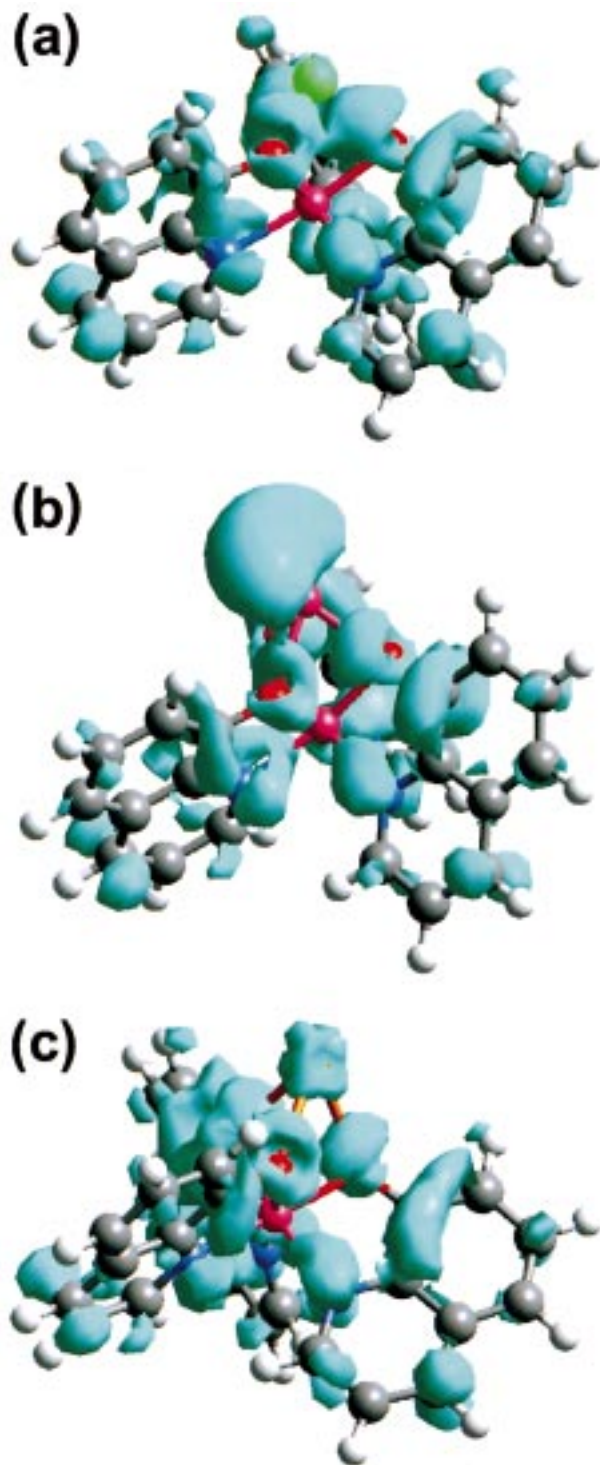
Complete electron transfer takes place from lithium. However, the charge distribution (see Figure 2a) differs from that in the radical anion (see ref 9). The excess electron is still localized on the pyridyl side of the ligands, but a strong polarization is induced on the oxygen lone pairs by the positive ion ( $Li-O \approx 1.99$  Å). The deformation of the Al coordination shell is also much more pronounced. In the radical anion, the mere addition of one electron drives a small increase of the Al–O distance ( $\Delta(Al-O) \approx 0.02$  Å) and a more significant decrease of the Al–N distance ( $\Delta(Al-N) \approx -0.035$  Å). Here, these values are  $\approx 0.08$  and  $\approx -0.12$  Å, respectively. The highly ionic character of the bonding is, to a great extent, independent of the specific configuration of the complex, but it also largely explains why those with lithium near the oxygen sites are energetically more favorable, and why the facial isomer, by providing a higher Li–O coordination than the meridional (three vs two; see Figure 1a'), stabilizes the Li ion more. In the meridional configuration, in fact, the binding is weaker by 11 kcal/mol. As indicated in Figure 3, the nature of the occupied states with lower binding energy is not modified with respect to that of Alq<sub>3</sub>.

The situation changes in part for aluminum and calcium because of their diminished tendency to transfer electrons. The optimal configuration is still provided by the oxygen shell of

(15) Proton NMR of Alq<sub>3</sub> in solution (Baker, B. C.; Sawyer, D. T. *Anal. Chem.* **1968**, *40*, 1947) is consistent with either meridional-to-facial isomerization or a rapid exchange of the ligands, occurring at  $\sim 100$  °C.

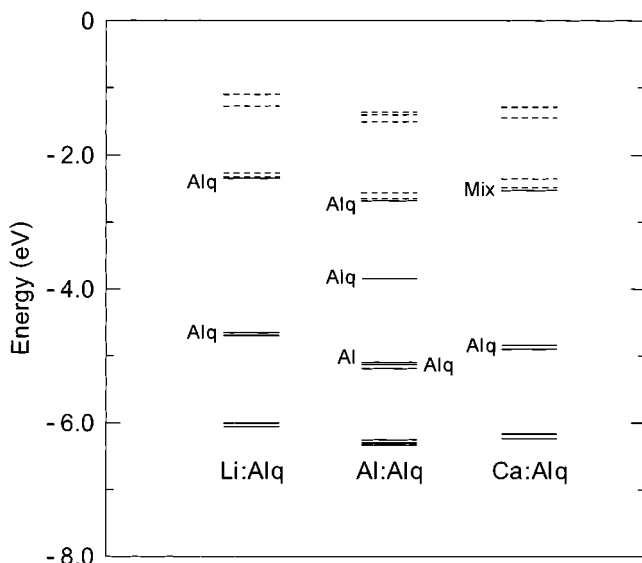
(16) This KS level diagram is only to be considered as a one-electron scheme that helps identify the orbitals involved in the bonding and the differences among the three complexes, and bears an indication of the appearance of "new" states induced by the interaction of the metal atom. We recall that, apart from the case of the HOMO level in the case of exact DFT, the orbital energies do not correspond to measurable values. However, this KS diagram for the occupied states offers a good approximation to the photoemission spectrum of Alq<sub>3</sub>.<sup>11</sup> It is well known that, on the contrary, differences between KS levels do not correspond to the electronic excitation energies. This is the case, in particular, of the HOMO–LUMO gap of the KS diagram.

(17) Experimental values for IPs of Li, Al, and Ca are 5.392, 5.986, and 6.113 eV, respectively. The corresponding BLYP values are 5.30, 5.93, and 6.11 eV. Experimental values for EAs of Li, Al, and Ca are 0.618, 0.441, and 0.018 eV, respectively. The corresponding BLYP values are 0.64, 0.23, and 0.0 eV. Measured values are taken from the following: *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Ed.; CRC Press: Cleveland, OH, 1995; pp 10–205 (IP), 10–180 (EA).



**Figure 2.** Isodensity hypersurface of valence electron density differences  $\Delta\rho(\vec{r}) = \rho(\text{Me:Alq}_3)(\vec{r}) - \rho(\text{Me})(\vec{r}) - \rho(\text{Alq}_3)(\vec{r})$  for Me = Li (a), Al (b), and Ca (c), with Alq<sub>3</sub> in the facial isomer. The isodensity value plotted is 0.005 e/au.<sup>3</sup>

the facial isomer (Figure 1b,c), with however a less symmetrical position of the metal atoms that are also kept farther away by electron repulsion, consistent with the larger ionic size ( $Al-O \approx 2.09$  Å;  $Ca-O \approx 2.60$  Å). Bond length variations are slightly different from those induced by lithium (for Al and Ca respectively,  $\Delta(Al-O) \approx 0.09$  and  $0.07$  Å,  $\Delta(Al-N) \approx -0.15$  and  $-0.11$  Å). The difference electron densities in Figure 2b,c show the progressive change of the bonding character from highly ionic for the lithium complex to predominantly covalent for the calcium complex. In the case of aluminum, the BE is



**Figure 3.** Kohn-Sham energy level diagram (in eV) of the metal-Alq<sub>3</sub> complexes with Alq<sub>3</sub> in the facial isomer. Labels denote the character of the KS orbital (Alq<sub>3</sub> or mixed metal-Alq<sub>3</sub> (MIX)). Note the additional level in Al:Alq, where Al indicates that the dominant character is metal-like. Dashed lines indicate empty states.

remarkably close to that of lithium,<sup>18</sup> but the bonding character is significantly different. Also in the optimal configuration, in fact (see Figure 2b), the 3p electron is not fully transferred to the Alq<sub>3</sub> states, as suggested by examination of the orbital character of the electronic structure. In fact, 3s-3p hybridization takes place, which favors bonding through coupling with the oxygen lone pairs. As can be seen from the KS diagram in Figure 3, the structure of the levels near the gap changes. Clearly, loss of symmetry splits the highest occupied molecular orbital (HOMO) level of Alq<sub>3</sub>. The interaction with the metal atom is such that one of the Alq<sub>3</sub> HOMOs is repelled to higher energy, and a state with predominant Al character appears in the same energy range as the other two. In the calcium complex, the coupling of the oxygen lone pairs with the metal orbital (4s) is less effective, owing to its weak polarizability (high s-p promotion energy), its relative energy position, and its spatial spreading. As a result, the hybrid state with prevalent Ca 4s character is quasi-degenerate with the lowest unoccupied molecular orbitals (LUMOs) of the molecule and constitutes the doubly occupied HOMO of the complex. This emerges from the density difference plot in Figure 2c.<sup>19</sup> The KS level diagram is modified accordingly (Figure 3). In addition, the BE of this complex is much lower than in the Al case.

Despite the decrease of ionicity in the bonding character, the relative isomer stability is the same as for the lithium case. In fact, the energetically favored location in the meridional isomer (Figure 1b,c) also corresponds to the vicinity of the oxygen atoms and implies the same binding mechanism as the one described for the facial. Owing to the higher directionality, configurations with 2- and 1-fold coordination with oxygen are separated by ~2 kcal. The bond strength is diminished by more than 10 kcal/mol (Table 1). Thus, the interaction of Alq<sub>3</sub> with Li, Al, and Ca definitely inverts the thermodynamical stability of its two geometrical isomers with one (the facial) now strongly favored. This fact has been completely overlooked so far but

(18) Efficient binding of Al to Alq<sub>3</sub> is in agreement with the observed good intermixing in the fabrication of Al-Alq<sub>3</sub> layers (ref 5).

(19) Spin-polarized exchange-correlation functionals have been used to explicitly include the possibility of having ionic configurations with the Ca<sup>+</sup> radical.

can entail several important consequences for the specific function of the molecular units as light emitters.<sup>20</sup>

One should not neglect that, depending on the experimental conditions, the metal atom can visit other parts of the molecule and be trapped in other minima of the potential energy surface. In the facial isomer, for instance, the face where the three nitrogens lie is a possible such environment: only lithium, however, whose interaction is predominantly ionic, is still strongly bound there (40 kcal/mol). The BEs of the Al and Ca complexes, instead, are only 4 and 1 kcal/mol, respectively. The interaction of the  $\pi$  states of the quinolate rings is attractive for both lithium (BE  $\approx$  22 kcal/mol) and aluminum (BE  $\approx$  25 kcal/mol), but not for calcium, which is unbound. The same chemical trend is found in the case of the meridional isomer. These findings thus invalidate previous suggestions that Ca<sup>2+</sup> ions form at the first stages of deposition and stabilize Alq<sub>3</sub> radical anions,<sup>2,21</sup> and that the first attack takes place in the vicinity of the nitrogens.<sup>2</sup>

The BEs just calculated for these complexes should be compared with those of the metal dimers, whose formation can, in principle, be competitive. These are about 26 kcal/mol for lithium, 32 kcal/mol for aluminum, and 11 kcal/mol for calcium.<sup>22</sup> In all cases, the metal Alq<sub>3</sub> units are more stable thermodynamically. However, the trend is clear.

Photoluminescence (PL) quenching in Alq<sub>3</sub> upon metal deposition has often been ascribed to the presence of new states induced by the interaction with the metal in the gap of the organic. Photoemission spectra can, in principle, locate the binding energy of the additional electron in these complexes relative to that of the most weakly bound electron in Alq<sub>3</sub>. This corresponds within a good approximation to the difference between the IP of the two molecular entities (the Alq<sub>3</sub>-metal complex and Alq<sub>3</sub>), a quantity that DFT calculations can accurately provide. Such values are 2.2 eV in Li:Alq<sub>3</sub>, 2.0 eV in Ca:Alq<sub>3</sub>, and 1.8 eV in Al:Alq<sub>3</sub>,<sup>23</sup> thus significantly smaller than the (measured) band gap of solid Alq (about 3 eV).<sup>24</sup> However, from the discussion above (see also Figure 3), a clear difference emerges between the three cases considered here, concerning the origin of the additional level. In fact, in all cases, lithium essentially transfers one electron to the Alq<sub>3</sub> LUMO, while this is strongly modified by calcium whenever it binds. (This fact was not appreciated in previous attempts to interpret the observed PL quenching.<sup>2</sup>) The strongest modification should, however, correspond to aluminum, where also the HOMOs are strongly perturbed and thus induce also a new HOMO-derived state lying deeper in the gap of the organic.

The insight we have gained here into the nature of the interaction of Li, Al, and Ca with Alq<sub>3</sub> allows us also to make predictions on the behavior of other metals and their ability to form the type of complexes we have discussed. We can expect that magnesium,<sup>25,26</sup> for instance, has a lower affinity for Alq<sub>3</sub>

(20) Curioni A.; Andreoni, W., in preparation.

(21) Choong V.-E.; et al. *J. Vac. Sci. Technol. A* **1998**, *16*, 1838.

(22) *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Ed.; CRC Press: Cleveland, OH, 1995; pp 9-51.

(23) We recall that simple KS diagrams such as the one in Figure 3 cannot be used for such purposes for the following reasons: (i) HOMO levels are not a reliable measure of the IPs in either the local or the semilocal approximation for the exchange-correlation functionals; (ii) the HOMO-LUMO gap of the molecule does not correspond to the real gap in the molecule, which is given by the difference between the IP and the EA; and (iii) the gap in the solid (which is the one of interest as this is the real system to which measurements refer) and that in the molecule do not match, owing to the stabilization of both the additional charges in the solid state. Indeed, for Alq<sub>3</sub>, they differ by about 2 eV.

(24) Campbell, I. H.; Smith, D. L. *Appl. Phys. Lett.* **1999**, *74*, 561.

(25) Mg is a commonly used electron-injecting material once alloyed with Ag.

than calcium, mainly owing to its high IP, whereas complexes with sodium, despite its lower IP, should be less thermodynamically stable than those with lithium but at least as much as those with calcium.

The study of the nature of the chemical bonding of the systems we have considered in this paper is an essential step

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(26) An investigation of Mg–Alq<sub>3</sub> complexes on a parametrization model 3 (PM3) of an MNDO Hamiltonian has recently appeared (Zhang, R. Q.; Hou, X. Y.; Lee, S. T. *Appl. Phys. Lett.* **1999**, *74*, 1612). The low performance of PM3 for Alq<sub>3</sub> and the absence of any discussion of the chemical bonding of these species (e.g., of a clarification of the factors that determine the relative structural stability) seriously affects the validity and usefulness of this work. The poor performance in the determination of the structure of Alq<sub>3</sub> itself and the problem of transferability of semiempirical schemes to Alq<sub>3</sub> has been shown and discussed in ref 9. The lack of accuracy of the specific parametrization used by Zhang et al. for the electronic properties clearly emerges from a simple comparison of the density of states (DOS) in Zhang et al. with that calculated with our scheme and compared to experiment.<sup>11</sup> Concerning the Mg complex, Zhang et al. limit themselves to report a number of geometries for the meridional isomer and the corresponding DOS. None of these, however, corresponds to the ones of lower energy that we find for this isomer in the three cases.

toward the microscopic understanding of LEDs based on Alq<sub>3</sub> and its derivatives. The relevance of the calculations emerges also from the fact that these species affect the functionality of the organic molecules but, being metastable in real conditions, elude direct experimental investigation. It is also worth pointing out that, contrary to previous assumptions (see, e.g., ref 26), these systems are by no means representative of the interaction of Alq<sub>3</sub> with clean and defect-free metal surfaces, whose nature and strength are drastically different.<sup>27</sup> On the other hand, the interest in such unusual metal–organometallic complexes goes well beyond the specific field of OLEDs. In fact, similar entities are expected to come into play at the interfaces of diverse multicomponent electronic devices.

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(27) Curioni, A.; Andreoni, W., to be published.