

Organometallic Chemistry at the Magnesium–Tris(8-hydroxyquinolino)aluminum Interface

Chongfei Shen,[†] Ian G. Hill,[†] Antoine Kahn,^{*,†} and Jeffrey Schwartz^{*,‡}

Department of Electrical Engineering, Princeton University
Princeton, New Jersey 08544-5263

Department of Chemistry, Princeton University
Princeton, New Jersey 08544-1009

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Modern organic light emitting diode (OLED) devices are typically prepared in part by vapor phase deposition of a low work function metal cathode onto an organic electron carrier/photoemitter. Tris(8-hydroxyquinolino)aluminum (Alq₃, **1**) is a commonly used electron carrier/photoemitter, and it is reasonable to propose that chemical reduction of Alq₃ (with concomitant formation of metallic cations) can occur as a result of metal atom deposition, by analogy with well-known reduction processes of aromatic compounds which can be accomplished by activated or dissolved alkali and alkaline earth metals. Since the products of Alq₃ reduction might vary in structure according to the deposited metal, the choice of cathodic metal may affect the performance of an OLED not only obviously, because of work function considerations, but also subtly, because of details of chemistry at the Alq₃/cathode interface. It is not surprising, then, that analysis of possible chemical reactions between Alq₃ and several atomic alkali and alkaline earth metals (Li, K, Mg, and Ca) has been of considerable interest recently, both from theoretical and experimental perspectives.^{1–4} Two items are noteworthy because of their absence from these reports. First, while they focus strongly on the expected shift to *lower* core level binding energies for the nitrogen atoms of the reduced quinolate ligands, these studies either ignore any core level binding energy shifts for the oxygens of the ligands or suggest that such shifts are minor (and no mention is made of binding energy shifts for the central Al atom, either). Most surprising is that, while Mg (as Mg/Ag) is the most commonly used OLED contact with Alq₃, no experimental studies correlating the chemistry of Mg atom deposition on Alq₃ with spectroscopic observations have been reported. Since chemical reduction of polynuclear aromatic hydrocarbons with activated Mg can take a course quite different from that of Li, K, and Ca, the operationally significant Mg contact may in fact be structurally unrelated to these recently described models based on these other metals. We have now studied the deposition of this operationally key metal (and also of Al) onto thin films of Alq₃, and we find, by XPS and UPS analysis, a strong shift to *higher* binding core level energies occurs both at the ligand oxygens and at the central Al atom of the Alq₃, which can be explained using simple organometallic models based on “solution”-derived observations.

All procedures were carried out in an ultrahigh vacuum system consisting of three inter-connected chambers, which were used for surface preparation, film growth, and analysis, respectively. A 100 Å thick film of Alq₃ was deposited on a gold substrate by

[†] Department of Electrical Engineering.

[‡] Department of Chemistry.

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(5) XPS and UPS spectra were collected with a Perkin-Elmer double-pass cylindrical mirror analyzer. Resolution for the UPS and XPS measurements were 0.15 and 0.7 eV, respectively. Energy scales were calibrated using the Fermi edge of a clean gold surface and the Mg(2p) core level of a freshly deposited Mg layer. Al K α irradiation was used to collect O(1s), C(1s), and N(1s) data, and Zr M ζ irradiation was used for Mg(2p) and Al(2p) measurements.

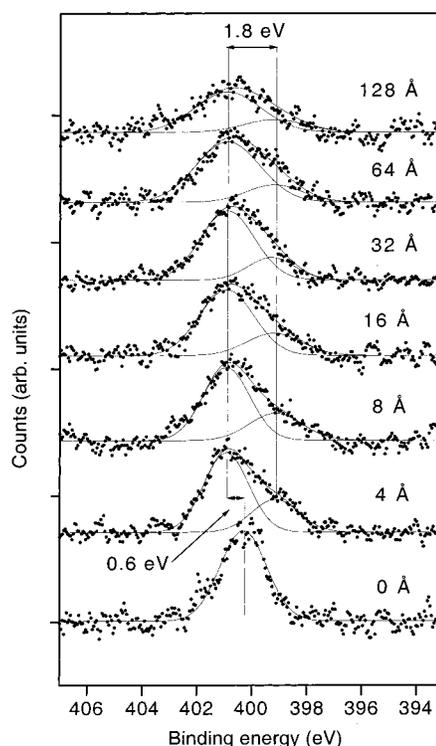


Figure 1. N(1s) XPS spectra of Alq₃ with increasing Mg exposure.

thermal evaporation from an Al₂O₃ crucible. Magnesium was then deposited incrementally on the Alq₃ film. XPS and UPS measurements were performed following each successive deposition event; the base pressure was maintained between 10⁻⁸ and 10⁻¹⁰ Torr, for deposition and analysis, respectively. XPS data were collected using achromatic Al K α (1486.6 eV) or Zr M ζ (151.4 eV) irradiation produced by a VSW double-anode source. Valence state data (UPS) were obtained using the He(I) ultraviolet emission (21.2 eV) line.⁵ Changes in Mg(2p), C(1s), N(1s), O(1s), and Al(2p) core level binding energies (BE) were measured as a function of exposure of Alq₃ to Mg vapor. Analysis following initial Mg deposition (4 Å) showed the Mg(2p) peak to consist primarily of a high binding energy component (BE = 51.6 eV), corresponding to Mg(II), and a smaller component at BE = 49.3 eV. This latter peak grew with increasing exposure, and is assigned to metallic Mg. Peaks for C(1s), N(1s) and O(1s) all shifted by 0.6 ± 0.1 eV to higher BE after initial exposure to Mg, which is attributed to a shift of the whole molecular level structure of the organic film initially aligned with the Au substrate (see Table 1 in Supporting Information). While the peak shape and half-width for the C(1s) and Al(2p) peaks remained nearly constant regardless of Mg exposure, the N(1s) and O(1s) peak shapes changed considerably. Consistent with reports of K and Li deposition onto Alq₃,^{3,4} reaction with Mg gave rise to a new, *lower* binding energy N(1s) peak component (experimental BE = 399.1 eV; corrected BE = 398.5 eV; Figure 1). But in contrast, a new O(1s) peak component also appeared, which was shifted by 1.4 eV (corrected for molecular level realignment) to *higher* binding energy vs Alq₃ (experimental BE = 533.7 eV; corrected BE = 533.1 eV; Figure 2). The Al(2p) signal also shifted to higher binding energy (experimental BE = 75.5 eV; corrected BE = 74.9 eV). In agreement with previous measurements,^{6,7} UPS measurements show that, while deposition of 2 Å of Mg onto Alq₃ attenuates spectral features, several peaks remain identifiable and are shifted (by realignment of molecular levels) to higher binding energies by ~0.6 eV. A new state, at approximately 1.5 eV above the (corrected) HOMO of Alq₃, was also detected

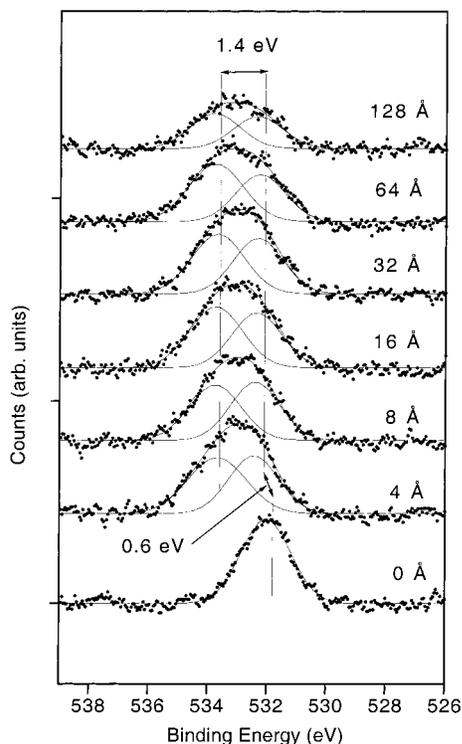


Figure 2. O(1s) XPS spectra of Alq₃ with increasing Mg exposure.

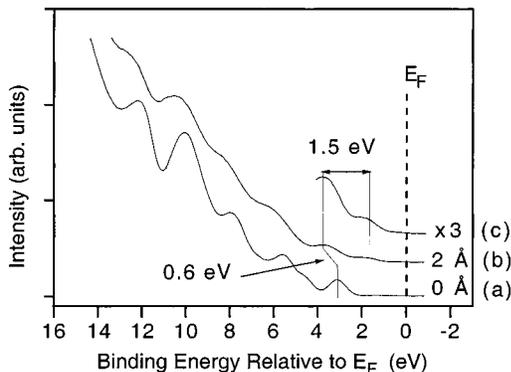
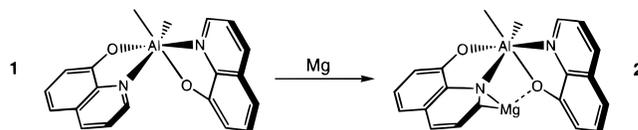


Figure 3. UPS spectrum of (a) clean Alq₃, (b) following deposition of 2 Å of Mg, and (c) following deposition of 2 Å of Mg, expanded.

(Figure 3). Both XPS and UPS data indicate that Mg does not readily accumulate on the surface of the Alq₃ film, but rather it diffuses somewhat into that film. Apparently, only when diffusion is no longer rapid (the film of Alq₃ is not entirely reacted), does Mg metal accumulate at the film surface.

The N(1s) peak shifts to lower binding energies recorded following vapor deposition of K or Li onto Alq₃ have been interpreted using a model involving charge transfer from the metal to the LUMO of Alq₃ and coordination of K⁺ or Li⁺ with ligand oxygens.³ A calculational model for reaction of Ca, Al, or Li with Alq₃ comes to similar conclusions, qualitatively.⁴ Our observation of *opposite* binding energy shift trends for N(1s) and

Scheme 1. Reaction of Alq₃ with Mg, Showing Two of the Three Quinolate Ligands



O(1s) are not so easily interpreted in terms of a model in which the quinolate ligands of Alq₃ undergo simple reduction: These calculations show that, even though the LUMO is maximized on the pyridyl ring, some increase in negative charge also accrues to the phenolic ring of the quinolate ligands. In addition, the 1.8 eV shift for N(1s) to lower binding energy measured for deposition of Mg onto Alq₃ is as great as that recorded for K, which is inconsistent with relative first ionization energies for the two metals (7.64 and 4.34 eV, respectively), upon which the ion pair model is based.³ It is also contrary to prediction.⁴

We propose that the trend in core level binding energy changes for N(1s) and the opposite one for O(1s) and Al(2p) can be explained through analogy with structural data for products of reduction of the simple polynuclear aromatic substrate, anthracene, by activated metals: Ion pairs are indeed formed for Li or K,^{8,9} but Mg yields an organomagnesium complex that is characterized by Mg–C bonding.¹⁰ We therefore suggest that the quinolate ligand of Alq₃ may be reduced by reaction with atomic Mg atom to give an organomagnesium derivative, perhaps via an ion pair intermediate. Because “dissolving metal” reduction of quinoline leads primarily to 1,2-dihydroquinoline,¹¹ this organomagnesium product may involve the metal bridging N and C-2 (**2**; Scheme 1). The geometric change at N, concomitant with Mg–amide bond formation, gives rise to the observed N(1s) BE shift.¹² Reduced charge delocalization in **2** (compared with a fully delocalized ligand radical anion⁸) results in only small changes in core binding energies for the carbon atoms before and after reduction, and detection of these changes is not possible, given resolution limitations of our XPS. Finally, coordination of the Mg(II) electrophile to the oxygen of, perhaps, an adjacent quinolate ligand diminishes the donor ability of this oxygen toward the central Al, which accounts for the shifts to higher binding energy recorded in the O(1s) and Al(2p) spectra.

Deposition of Al onto Alq₃ gives rise to XPS binding energy shifts similar to those measured for Mg: the N(1s) and O(1s) core levels move in apparently “opposite” senses. Indeed, the 1.4 eV shift for O(1s) to higher binding energy (corrected BE = 533.1 ± 0.2 eV) is comparable to that recorded for Mg, as is the magnitude of the N(1s) shift (1.8 eV) to lower binding energy (corrected BE = 398.5 ± 0.1 eV). As for Mg, this latter shift is apparently inconsistent with an ion pair model (the first ionization potential for Al is 5.98 eV), and is indeed, contrary to prediction.^{3,4} But it is interesting that organoaluminum derivatives of polynuclear aromatics are well-known¹⁰ and, like Mg, are characterized by metal–carbon bond formation.

Different reducing metals have differing propensities toward carbon–metal bond formation with a given substrate. It therefore seems likely that gross structural differences in products may characterize the chemistry that occurs at the interface between a series of vapor-deposited metals and any reducible organic substrate, and this will depend on the tendency of these metals to form structurally varied organometallic complexes.

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Supporting Information Available: XPS spectra for Mg(2p) and Al(2p) and a table of XPS data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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