Electronic states of vapor deposited electron and hole transport agents and luminescent materials for light-emitting diodes

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The electronic states of vapor-deposited materials used in electroluminescent devices were measured by ultraviolet and x-ray photoelectron spectroscopy, UV-visible absorbance, and photoluminescence spectroscopy. The combination of these measurements on ultrathin films of these materials allows (1) the determination of the energy (with respect to vacuum) of the highest occupied molecular orbital (HO) and the ionization potential (IP), and (2) the estimation of the lowest unoccupied molecular orbital (LU) energy and an approximation of the electron affinity, (EA). The knowledge of the binding energies of these states is important for the understanding of light-emitting diode properties and the potential optimization of such devices. The luminescent material tris(8-hydroxy-quinoline) aluminum has an IP of 5.9 eV and an apparent EA smaller than 3.5 eV. The IP of both hole transport agents, tri-p-tolylamine and 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane, is 5.4 eV and their EA is estimated to be smaller than 1.8 eV. The electron transport agents 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, 2-t-butyl-9,10-n,n'-dicyano-anthraquinonediimine and dicyano-diphenylsulfone differ in IP from 7.1 to 7.6 eV and the EA for these materials are estimated to be smaller than 3.5, 4.9 and 5.5 eV, respectively.

I. INTRODUCTION

Since the first usage of organic materials for light-emitting devices (LEDs) by Tang *et al.*[1(a)] and Adachi *et al.*[1(b)] and the discovery by Friend *et al.*[2] that the polymer poly(p-phenylene-vinylene) (PPV) can be employed for LEDs, significant effort has gone into the improvement of such devices, and to increasing our theoretical understanding of their operation. As in inorganic devices, the operation of an LED based on organic materials is discussed in the context of occupied and unoccupied electronic states and the recombination of injected holes and electrons from these states to produce an emitted photon (Fig.1).[3] Under forward bias holes are injected from an electrode (commonly indium-tin-oxide, ITO) into the occupied states of a hole transport agent (HTA). The holes are transported through this layer to a luminescent material (LM). Electrons are injected from a metal or metal alloy into the unoccupied electron states of an electron transport agent (ETA) or the luminescent material may be in direct contact with this cathode. The electrons and holes recombine and photons are emitted. Whether this recombination takes place in the LM layer or at the LM/ETA or HTA/LM interface depends on the experimental conditions, such as bias voltage, band gap, barrier heights, and charge transport properties.

For most organic materials used in LEDs the energies of the electronic states are not well-known.[3] The goal of this article is to begin to fill the gap of experimental data for a few already widely used or promising LMs, HTAs, and ETAs. Similar data for oligomers of the phenylene-vinylene type, where the corresponding polymer, PPV, is already in use in LEDs; and for a series of oligorylenes, which also promise applications as LMs, have been measured by us, and are discussed elsewhere.[4,5]

The method used for the estimation of the energy of the occupied electronic states is ultraviolet photoelectron spectroscopy (UPS). The combination of UPS, UV-vis absorbance and photoluminescence spectroscopy allows a determination of the binding energy of the states responsible for the absorbance and luminescence (mainly excitons in organic materials) and the approximation of the energies for the unoccupied electronic states.[4] The knowledge of these states allows a discussion of possible optimization of materials for LEDs in order to decrease the driving voltage of the devices and ensure balanced injection conditions for electrons and holes.[3] Another possibility for the application of these data is to discuss the formation of the heterojunctions where recombination takes place, in order to avoid quenching of the electroluminescence near the conducting injection electrodes of ultrathin film LEDs.[3]

II. EXPERIMENT

A. Materials and sample preparation

The following materials were used in this investigation as shown in the attached scheme.

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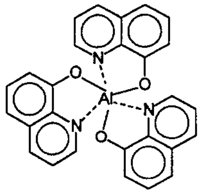
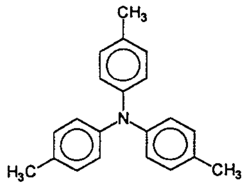
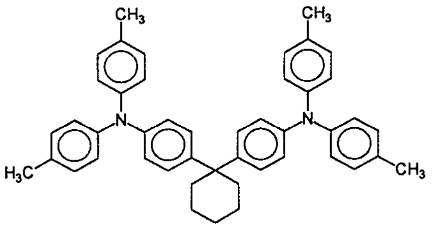


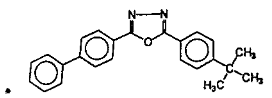
Alq3



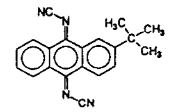
TTA



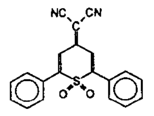
TAPC



butyl-PBD



DCAQ



DPS

The luminescent material was tris(8-hydroxy-quinoline) aluminum[1,6] (Alq_3), the hole transport agents were tri-p-tolylamine[7] (TTA) and 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane[1,7,8] (TAPC), and the electron transport agents were 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (butyl-PBD),[3,9] 2-tert-butyl-9,10-n,n'-dicyano-anthraquinonediimine (DCAQ)[10] and a type of dicyano substituted diphenylsulfone (DPS), a prototypical electron transport agent. These materials were donated by C. Tang at KODAK. All materials, with the exception of Alq_3, were used as delivered without further purification. Alq_3 was purified by gradient sublimation with a maximum temperature of 305 °C.[1(a)]

Thin solid films of these materials were deposited from Knudsen cell sources at base pressures of less than 10^{-7} Torr atop atomically clean, polycrystalline gold and silver foils, which were argon sputter-cleaned immediately before the evaporation process. The deposition temperatures were measured with a type *K* thermocouple and are all in the range between 120 and 260 °C. The materials were held in the Knudsen cell at the deposition temperatures for at least 15 min. before beginning the deposition on the clean substrates. In this way final outgassing and purification of each substance preceded each deposition. Film thickness and growth rates were monitored by a quartz crystal microbalance (resonant frequency=10 MHz) mounted within the deposition chamber. For UV-vis absorbance and photoluminescence spectroscopy films were deposited on 1-mm-thick sapphire substrates, 1 cm in diameter (ROLYN). The sapphire substrates were cleaned in an ultrasonic bath with water (Milli-Q quality) and methanol and subsequently dried with nitrogen.

B. Photoelectron spectroscopy

Photoelectron spectroscopy data were acquired at room temperature with a VG ESCALAB MKII spectrometer. The occupied electronic states were measured with HeI (21.2 eV) radiation (UPS). In this mode the number of photoelectrons detected at each kinetic energy is proportional to the joint density of states between the initial and final states of the electrons, superimposed on a background of secondary elec-

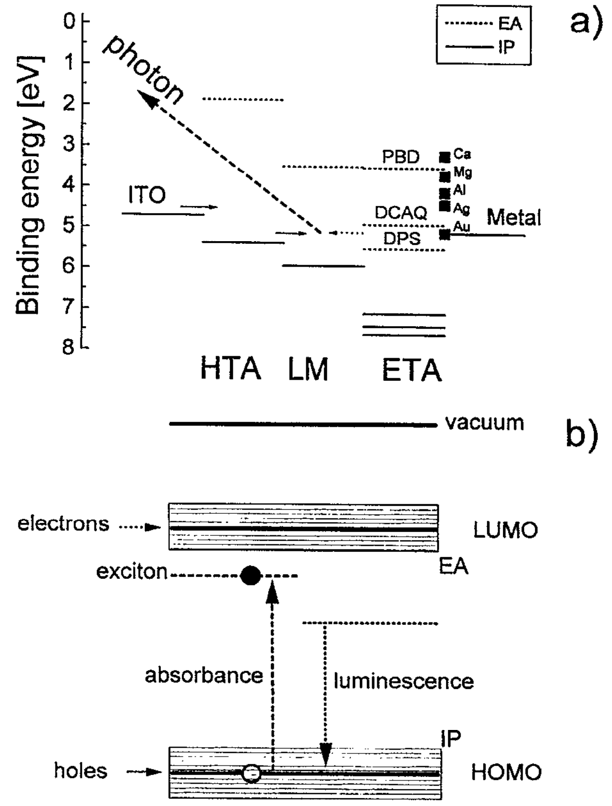


FIG. 1. (a) Energy levels of an idealized LED (without bias). Holes are injected from an external electrode into the occupied (—IP) states of a HTA and electrons are injected into unoccupied (- - - EA) electron states of an ETA. The charges combine in a LM layer and a photon is emitted. The energetic positions are taken from the results described in the article, the multiple lines for the ETA correspond to the three different ETAs investigated. The Fermi-levels of ITO, typically used as the hole injector, and metals (Au, Ag, Al, Ca, Mg), which are used for electron injection, are also given. (b) Important energy levels for the operation of a light-emitting diode. Ionization potential, IP, and electron affinity, EA, are determined from the width of the HOMO and LUMO. EA can be approximated from the absorbance state (exciton state), and differs from it only by the exciton binding energy. The energetic position of the luminescence state determines the luminescence maximum.

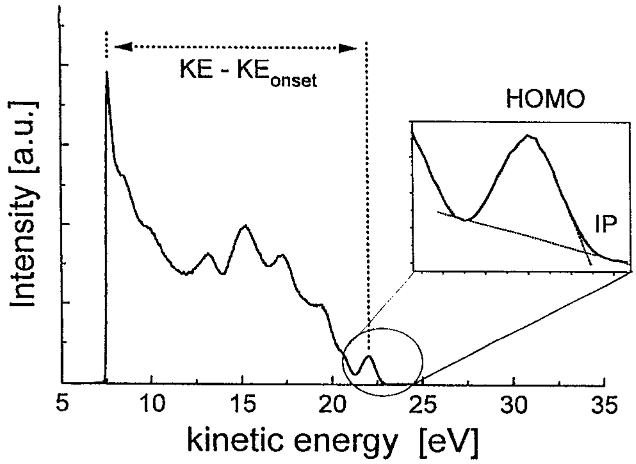


FIG. 2. Number of photoelectrons as a function of their kinetic energy for a 210-Å-thick film of Alq_3 vapor deposited on silver. The absolute binding energy of the HOMO vs vacuum, BE, can be determined from this UPS experiment from the difference in the kinetic energy of the HOMO, KE, and the onset of secondary electrons, KE^{onset}: BE= $h\nu$-(KE - KE^{onset}). The inset shows the approximation of the ionization potential, IP, from the width of the HOMO peak.

trons. The number of photoelectrons as a function of binding energy can be considered to be a first approximation as a representation of the density of states (DOS) of the occupied electron levels. For survey scans the signal was measured in steps of 0.05 eV, while for the determination of peaks and onset of secondary electrons steps of 0.01 eV were used. The electron analyzer was set to a constant retardation ratio of 4.

The absolute binding energy, BE_{vac} of the occupied states was measured versus vacuum as described in a previous paper (see also Fig. 2) by using a negative bias voltage (typically -5.00 ± 0.01 V) at the sample:[4]

$$BE_{vac} = h\nu - (KE - KE^{onset}). \tag{1}$$

Here $h\nu$ is the photon energy (21.2 eV), KE is the position of the peak under investigation and KE^{onset} is the onset of the secondary electrons on the low kinetic energy side of the spectrum.[4] The well-defined peaks in the raw data were fit with a Gaussian peak shape after subtraction of a linear background. From the point of inflection of the HOMO peak a linear extrapolation down to the baseline was used to approximate the ionization potential (IP) of the material in the solid state (see inset in Fig. 2). The IP is defined as the minimum energy necessary to bring an electron from the material into vacuum and is usually measured by using different photon energies and extrapolating down to the low energy limit.[11] We use only one photon energy, therefore we can obtain only an upper limit for the true IP with our method. The comparison between the IP measured as described in Reference 11 with the method used here showed a difference of ca. 0.2 ± 0.1 eV for different perylene derivatives.[4] This deviation is close to the experimental error of ±0.15 eV in the determination of the binding energies by UPS and can be expected to hold for other aromatic molecules.

The thin film growth chamber was connected directly to the photoelectron spectrometer. The films were moved between the chambers without breaking vacuum after completion of growth of each different film thickness. In this way it was ensured that the results do not depend on the film thickness. The results given in the text and Table I are determined as an average over sufficiently thick films on both gold and silver substrates. The use of two different substrates eliminates the influence of the substrate on the UPS data.

To determine if molecules decompose during the vacuum evaporation, x-ray photoelectron spectroscopy (Al Kα radiation, $h\nu$=1486.7 eV, 240 W) was employed to measure the stoichiometry of the compounds in the films. The photoemission peaks were obtained at a constant analyzer energy of 50 eV in steps of 0.1 eV. The peak intensities were determined from the raw data by using standard background correction schemes and integration of the area remaining under the peak.[12] Relative atomic ratios of the elemental constituents of the films were determined as previously described, by correcting the areas of each peak for escape depth, photoemission probability and the energy dependence of the analyzer transmission function.[12]

C. Optical measurements

UV-visible absorbance spectra were taken with a HITACHI U-2000 two-beam spectrophotometer with a resolution of 1 nm. The fluorescence spectra were obtained with a SPEX Fluorolog-2 spectrophotometer. The angle between excitation and detection was 30 °C. An identical clean sap-

TABLE I. Binding energies of occupied electronic orbitals and optical levels determined by UPS and optical spectroscopy.

Compound	HOMO [eV] 0.15 eV	Ionization potential IP [eV] ±.15 eV	(0-0 phonon) Photo-luminescence maximum[a] [eV]	Photo-luminescence state[b] [eV] ±0.15 eV	Lowest energy absorbance maximum[a] [eV]	Absorbance state,[b] approximating EA [eV]±0.15 eV
Alq_3	6.65	5.93	2.40	4.25	3.17 eV	3.48
TTA	5.85	5.37	3.26(2.86)	2.59	4.01	1.84
TPAC	5.85	5.37	3.26	2.59	4.01	1.84
butyl-PBD	7.62	7.08	3.30(3.15)	4.32	4.08(4.57)	3.54
DCAQ	8.43	7.62	2.91(2.65)	5.52	3.56(4.48)	4.87
DPS	8.24	7.43	2.40	5.84	2.77(3.15)	5.47

[a] Values in parentheses indicate the photon energy of the transition with maximum fluorescence or absorbance.
[b] Binding energy of optical states estimated by: optical state energy=HOMO-optical transition energy.

phire wafer was used as a reference to correct for the substrate absorbance or emission in both methods. Infrared spectra of materials in KBr-pellets were measured with a Nicolet Magna-IR 550 FT-IR spectrometer.

A Hewlett Packard 5988A mass spectrometer, with electron ionization at 70 eV, was used for mass spectrometry of Alq_3.

III. RESULTS AND DISCUSSION

A. Luminescent materials

Figure 2 shows as an example the photoelectron spectrum of the LM Alq_3 There are several photoemission peaks distinguishable within the spectrum. The one with the highest kinetic energy is generally attributed to the HOMO. The binding energy versus vacuum is determined from the experiment as described in the experimental section and as shown schematically in Fig. 2. The HOMO and the extrapolated ionization potential, IP (measured from the onset for photoemission), are obtained in this manner for all compounds under investigation and are given in Table I. The HOMO of Alq_3 is at 6.65 eV with respect to vacuum and the onset of occupied states, the IP, is at 5.93 eV. The IPs of different metal quinolines have also been reported by Hamada *et al.*[13] They found a value of 5.66 eV for Alq_3. This is in reasonable agreement with our upper limit for the IP, considering the deviation of 0.2 ± 0.1 eV expected for the different methods of measuring such energies, and differences in spectrometers.

It is recognized that UPS spectra do not give a real picture of the occupied density of states, but rather a convolution of occupied and unoccupied states.[4,5] For many metal complexes, especially where the frontier orbitals of the metals are far removed from vacuum, UPS data can be used at least in a comparative sense to compare HOMO positions among materials which are known to create thin film heterojunctions. These assumptions are certainly also reasonable for aromatic molecules, such as those presented here, where the HOMO levels are likely to be filled π orbitals, with little nonbonding-electron character.

Table I also contains the absorbance and photoluminescence maxima measured for Alq_3 thin films comparable to those in Figure 2. These data have already been reported for several of the compounds discussed here.[1,6–10] Nevertheless, in this investigation thin films were prepared on sapphire substrates within the same chamber, at the same deposition pressure, as the samples prepared for the UPS measurements. This was done to ensure that all data were obtained and compared for materials with the same preparation conditions and hence the same microstructure in the thin films. The optical spectra for Alq_3 are given in Figure 3. Maximum photoluminescence occurs at 517 nm (2.40 eV) and the absorbance spectrum shows a characteristic maximum at 390 nm (3.17 eV). The difference between excitation and emission energies for Alq_3in the solid state is therefore 0.78 eV.

Figure 4 depicts the energy diagram of the occupied electron levels and the optical levels of Alq_3 determined from these data. The absolute binding energy of the optical states is estimated by subtracting the transition energies from the ground state, i.e., the HOMO energy. The energy of the photoluminescence state is therefore estimated at 4.25 eV and the absorbance (exciton) state is estimated to be located at 3.48 eV. These optical data are in general agreement with other published results.[1,6]

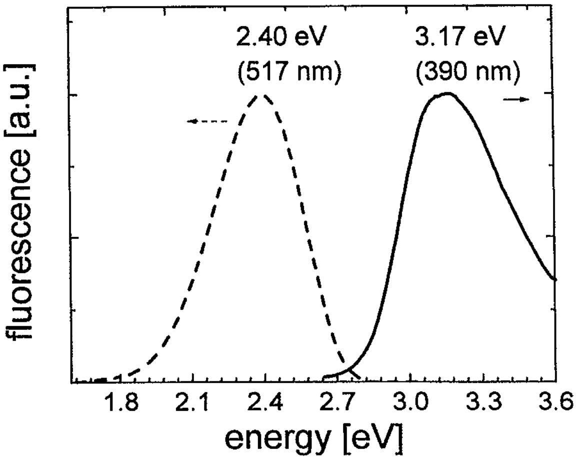


FIG. 3. The absorbance and photoluminescence spectra of a vapor-deposited Alq_3 film (250 Å) on sapphire. From these data the lowest energy absorbance peak and highest energy photoluminescence peak are determined.

The optical data can be used to approximate the electron affinity, EA, of such materials in thin solid films. The EA is defined as the first unoccupied energy level which injected electrons would occupy (e.g., in an LED). In absorbance/luminescence events, electrons are not photoexcited directly into the LUMO, but typically form an exciton state with holes in the HOMO [see Fig. 1(b)]. The binding energy of the excitons, i.e., the energy difference between the absorbance state and the LUMO is usually not known. It is therefore not possible to use the absorbance ("optical band gap") as a direct measure of the electronic band gap (HOMO-LUMO difference). However, the energetic position of the absorbance states allows an estimation of the upper limit for the electron affinity [Fig. 1(b)]. The results of this approxi-

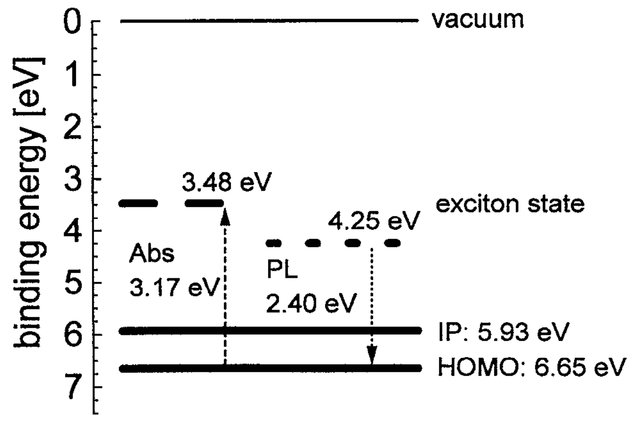


FIG. 4. Absolute binding energy of the frontier orbitals and optical levels for Alq_3 as determined by the combination of UPS and optical spectroscopy.

mation are given in Table I for the materials under investigation. The EA of Alq_3 will therefore be smaller than 3.48 eV.

How good the approximation is depends on the (unknown) binding energy of the excitons. The absorbance maximum is often a broad peak, which does not allow unambiguous determination of the optical band gap, as is often possible in inorganic materials. Another choice for the optical band gap would be the extrapolation to zero absorbance at the high energy side of the absorption. Approximations for the EA based on the different optical band gaps and the HOMO or IP (EA<HOMO/IP-optical band gap) are typically identical within the experimental error to the values obtained as described above.

The photoemission and optical data for the different charge transport materials discussed below were gathered and evaluated as discussed for Alq_3. For optical spectra with more than one peak the different peak positions were determined with a multiple Gaussian fit. For the determination of the optical transition energies and LUMO states and EA the absorbance peak with the lowest energy and the fluorescence peak with the largest energy (0-0 phonon transitions) are chosen. The results can be found in Table I.

B. Hole transport agents

The two HTAs studied here (TTA and TAPC) have essentially the same occupied frontier orbitals. The HOMO for both materials is at 5.85 eV and their IP is found to be 5.37 eV. This is expected from their chemical similarity: TAPC is just two TTA molecules connected by a cyclohexane ring. ITO, with a work function of ca. 4.7 eV, is typically used as the hole injection electrode in LED devices.[1–3] The holes therefore have to overcome a barrier of ca. 0.7 eV between ITO and TTA or TAPC [see Fig. 1(a)]. The IPs of both HTAs are smaller than the IP of Alq_q, so this creates an additional barrier for hole injection between the HTAs and the LM of ca. 0.5 eV [Fig. 1(a)].

The lowest energy absorbance (309 nm, 4.01 eV) and photoluminescence peaks (380 nm, 3.26 eV) are also identical for both hole transport materials. We can therefore approximate the EA for both HTAs to be smaller than 1.84 eV. There is an additional twin peak at about 430–440 nm in the photoluminescence spectra of both molecules. The two molecules, however, have a different Frank-Condon factor. In TAPC the 0-0 phonon peak has the highest fluorescence yield, while in TTA the second peak at 434 nm is stronger than the 0-0 phonon peak. The energy difference between excitation and emission levels is 0.75 eV for both molecules in these thin films.

The very low electron affinities of these hole transport agents causes a high barrier for electron injection from LMs and ETAs, since the EAs of these materials, as discussed below, are much larger [Fig. 1(a)]. This is a necessary property for hole transport agents in organic LEDs, in order to confine electrons to the luminescent layer.

C. Electron transport agents

The three investigated ETAs have all HOMOs and IPs below 7.0 eV binding energy. The optical band gap for these materials differs by more than 140 nm, and the absorbance state (and EA) therefore varies significantly from 3.56 to 5.48 eV.

The HOMO-1 in Butyl-PBD is at 8.25 eV, very close to the HOMO at 7.62 eV. These two peaks are difficult to resolve because their photoemission bands typically have a fwhm of 0.65 eV. The IP of this ETA is 7.08 eV. The lowest energy absorbance at 404 nm (4.07 eV) leads to an absorbance state at 3.55 eV. The binding energy of the unoccupied states is therefore estimated to be below 3.55 eV. The maximum absorbance of butyl-PBD is at 272 nm (4.56 eV). The difference between the excitation and emission energies in this material is 0.78 eV in the solid state, with the maximum fluorescence at 394 nm (3.15 eV) and the 0-0 phonon fluorescence at 376 nm (3.30 eV).

The occupied frontier orbitals of DCAQ are at 8.43 eV (HOMO) and 7.62 eV (IP). The absorbance spectrum has maxima at 277 nm (4.48 eV) and 348 nm (3.56 eV). The absorbance state, which is an upper limit for the EA, is therefore estimated to be 4.87 eV. The photoluminescence also shows two distinct peaks at 426 nm (2.91 eV) and 468 nm (2.65 eV). The difference between excitation and emission energies for DCAQ in the solid state is therefore 0.65 eV.

DPS has a HOMO of 8.24 eV and an IP of 7.43 eV. The lowest energy absorbance peak of DPS is at 448 nm (2.77 eV), while its absorbance maximum is at 393 nm (3.16 eV). The 0-0 phonon photoluminescence peak at 516 nm (2.40 eV) is, in contrast, dominant and sharp, with a small shoulder at 625 nm (1.98 eV). The difference in energy between these two levels in DPS is therefore estimated to be 0.37 eV. From these observations we can approximate the absolute binding energy of the absorbance state to be 5.47 eV knowing that the EA will be smaller than that value.

Metals like Ca (work function 3.2 eV), Mg (3.7 eV), Al (4.1 eV) , Ag (4.4 eV) and Au (5.1 eV), and their alloys, are of interest for electrode materials to inject electrons into the ETA. Based on the comparison between the approximated EA energy levels and the metal work functions we predict that for devices constructed using DCAQ and DPS as ETAs it should be possible to use a metal with as high a work function as that for Ag as an electrode [Fig. 1(a)]. This would represent a marked improvement compared to butyl-PBD, where Ca or Mg would appear to be necessary (see Ref. 3) due to the low EA of less than 3.55 eV for butyl-PBD [Fig. 1(a)]. The EAs of DCAQ and DPS are large compared with Alq_3 so we predict they will form a barrier for electron injection into the luminescence layer. Butyl-PBD has, in contrast to that, an EA comparable to Alq_3 Butyl-PBD and DCAQ (or DPS) may be useful to form a staircase electron transport layer, where DCAQ (DPS) allows for easier injection of electrons from a metal electrode with a high work function, while Butyl-PBD is more suited to inject electrons into the LM. A band diagram like that depicted in Fig. 1(a) indicates that the use of Ag (or even Au) as an injection electrode, with the combination of DPS (as ETA) and Alq_3 will allow for a small bias voltage, with electron-hole recom-

TABLE II. Stoichiometric ratios of Alq_3 determined from XPS measurements (15% error).

	C/Al	O/Al	N/Al
Powder sample, nonpurified material	19±3	2.4±0.4	1.1±0.2
Powder sample, purified material	22±3	2.4±0.4	1.9±0.3
Vacuum deposited film, nonpurified material	21±3	2.2±0.3	1.7±0.3
Vacuum deposited film, purified material	17±3	2.1±0.3	1.6±0.2
Expected: Alq_3	27	3	3
Theoretical: Alq_2OH	18	3	2
Theoretical: q_2Al-O-Alq_2	18	2.5	2
Theoretical: Alq_2	18	2	2

bination at the Alq_3/DPS interface, and luminescence coming from DPS. To get luminescence from $Alq_{3/DPS}$ the bias voltage would have to be increased drastically.

D. Alq_3 and HTA/ETA stability during sublimation

To check if the vapor deposition of the material is accompanied by decomposition of these compounds, XPS measurements were carried out to determine relative atomic ratios, to confirm stoichiometry in the near surface region of these thin films. It was generally found that the stoichiometric ratios of the transport materials under investigation are, within experimental error (±15% for XPS), identical to the expected ratios. It can be concluded that the vapor deposited films investigated here are pure and stoichiometric down to the detection limit of XPS (deviations from stoichiometry down to ca. 5% can be detected).

The only molecule where this was not found to be true is Alq_3. Table II contains the relative atomic ratios of both powder samples and vacuum-deposited thin films of Alq_3, both for the as-received material and for the same material after gradient (entrainer) sublimation. The experimental data do not differ significantly, and suggest that substoichiometric structures like Alq_2, Alq_2OH or a different kind of dimer, q_2Al-O-Alq_2, may be formed. In the latter case two Alq_2 molecules would be attached by an oxygen bridge between two aluminum centers. The typical error of ca. 15% in the stoichiometric ratios does not allow us to distinguish between the three proposed structures. Judging from Ref. 13, where different metal-hydroxy-quinolines are synthesized and characterized, the optical properties and the IP are mainly determined by the quinoline units. It is therefore expected that the optical properties and binding energies of such dimers are not different from Alq_3 itself.

Additional experiments were performed to test the hypothesis of decomposition of Alq_3 during deposition. It was reported recently that Alq_3 denaturates if sublimed repeatedly, but that the products have the same optical properties as the parent molecule.[6(c)] $(Alq_3)_2$ dimers and possible higher oligomers $(Alq_3)_n$ form via a bridge between two ligands of neighbor molecules. Dimers (or higher oligomers) would still give the same stoichiometric ratio as Alq_3, i.e., this denaturation cannot explain our XPS results. Elemental analysis showed that the gradient sublimated material is at least 97% pure, while the non-purified material is only 95% pure. The comparison in Table III shows no evidence for the presence of Alq_2, Alq_2OH, or q_2Al-O-Alq_2. FT-IR characterization of pressed pellet thin films of both Alq_3 materials (purified and nonpurified) were identical. These experiments also show the typical *mer* and *fac* isomer peaks of Alq_3[14] and we have no evidence of a denaturated $(Alq_3)_n$.[6(c)] Electron ionization mass spectroscopy shows for both batches a maximum peak at 315 m/z, corresponding to Alq_2, and a smaller peak (15%) at 459 m/z, which corresponds to Alq_3. Overall, the gradient sublimated sample had a cleaner mass spectrum, indicating a successful purification.

TABLE III. Elemental analysis for Alq_3.

	Al	C	O	N	H
Nonpurified	6.28	69.44	11.48	8.92	3.88
Purified	6.00	70.43	10.82	9.07	3.68
Expected: Alq_3 (MW 459)	5.88	70.59	10.48	9.15	3.92
Theoretical: Alq_2OH (332)	8.13	65.12	14.46	8.43	3.95
Theoretical: q_2Al-O-Alq_2 (647)	8.35	66.87	12.37	8.66	3.74
Theoretical: Alq_2 (315)	8.56	68.57	10.15	8.88	3.84

The comparison between elemental analysis, FT-IR and mass spectroscopy shows that the presence of Alq_2 in the mass spectrometry characterization is an effect of electron damage from the ionization process. The fact that both elemental analysis and FT-IR show the aluminum quinoline to consist of Alq_3 and the evidence for electron beam damage in mass spectrometry strongly suggest that the deviations seen in the stoichiometric ratios measured by XPS are an effect of radiation damage, caused by the high-energy x-ray photons and/or the photoelectrons (up to ca. 1480 keV). This conclusion explains also why the XPS data are nearly identical for both purified and unpurified, powders and vacuum deposited materials (Table II). XPS was therefore conducted for these studies *after* the final UPS measurement for each sample. UPS uses a much smaller photon energy of only 21.2 eV, so we do not expect heavy beam damage to occur. As discussed above, even if a destruction of Alq_3 to Alq_2 or other quinoline-containing products would occur, the optical properties and binding energies of the frontier orbitals are expected to be identical to Alq_3.[13]

IV. CONCLUSION

We have determined the absolute binding energies of the occupied frontier orbitals and estimates for the energies of the optical states in different LMs, HTAs, and ETAs. The information gathered from these spectroscopic studies will be used to discuss possible combinations of the materials to obtain, for example, low driving voltages and to ensure balanced injection of charge carriers into the LM. These investigations are under way and will be reported elsewhere. These measurements are especially significant in comparing the diode performance, and the luminescence and electroluminescence properties of new LED materials based upon synthetic alterations to the Alq_3 and related metal quinolate systems.[15]

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