

Characterization of electronic structure of aluminum (III) bis(2-methyl-8-quinolinato)-4-phenylphenolate (BAIq) for phosphorescent organic light emitting devices

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Abstract

The structure of the triplet host material, aluminum (III) bis(2-methyl-8-quinolinato)-4-phenylphenolate (BAIq), has been optimized by density functional theory (DFT) with B3LYP methods to study the electronic distribution of its HOMO and LUMO energy states. Calculated triplet bandgap energy of BAIq is shown to be consistent with the experimental data. By analyzing the partial density states (PDOS) of these ligands contributing to the total density of states (TDOS), it is concluded that the HOMO and LUMO orbitals of BAIq are mainly localized on the 4-phenylphenol and 2-methyl-8-hydroxyquinoline ligands, respectively. © 2005 Elsevier B.V. All rights reserved.

Phosphorescent organic light-emitting devices (PHOLEDs) can achieve near 100% internal quantum efficiency [1]. However, a number of stability issues are still to be resolved, before full scale commercialization can commence. As reported previously, the choice of hole blocking layer in PHOLEDs can seriously impact on their operational lifetime [2]. For example, green emitting *fac-tris*(2-phenylpyridine)iridium [Ir(ppy)₃] doped PHOLEDs employing an aluminum (III) bis(2-methyl-8-quinolinato)phenolate (PAIq) hole blocking layer was reported to produce high efficiency (18 cd/A) but with low device stability with a projected $t_{1/2}$ of only ~1075 h at an initial luminance (L_0) of 500 cd/m². But, devices employing aluminum (III) bis(2-methyl-8-quinolinato)-4-phenylphenolate (BAIq) has, on the other hand, achieved an EL efficiency of 19 cd/A with nearly ten fold improvement on life time of $t_{1/2}$ ~ 10000 h (L_0 ~ 500 cd/m²) [2]. Recently, Tsuji et al. [3] reported

that BAIq could also be used as host material in devices doped with red phosphorescent dopant bis(2-(2'-benzo [4,5-a]thienyl)pyridinato-N,C^{3'})iridium(acetylacetonate) (Btp)₂Iracac and prolonged operational lifetime with comparable efficiency.

There have been a number of theoretical electronic structural studies of OLED materials in the literatures, but most dealt with Alq₃ which is the archtypical host electron transport materials for fluorescent OLEDs [4]. Andreoni and co-workers [5] has characterized the structural and electronic properties of Alq₃ in both neutral and charged states, which provided a complete picture of the orbital structure of Alq₃ using density functional theory (DFT) calculations, photoemission and near-edge X-ray absorption fine structure (NEXAFS). Johansson et al. [6] has used a combination of X-ray and UPS with DFT calculations to discuss the interaction of Alq₃ with Li and K. Recently, the geometrical and electronic structures of Alq₃ interacting with Mg and Al have also been studied using DFT [7,8]. The observed infrared spectrum of Alq₃ has been found in

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good match with the theoretical results [9,10]. There is some resemblance between the BAQ and Alq₃ molecules, which are shown in Fig. 1, but to the best of our knowledge, there is no theoretical study on the structure and molecular orbitals of BAQ, however.

In this Letter, the electronic structures of BAQ and its ground state are compared with Alq₃ molecule. The calculated infrared spectrum of BAQ is found to be in good agreement with the experimental data. The triplet gap of BAQ which is the energy of the transition of T₁ → S₀ has been calculated and found to be larger than that of Alq₃. The electronic structure of BAQ has been de-convoluted by density of states (DOS) analysis, particularly in studying the electron density distribution with respect to its HOMO and LUMO energy states. We expect based on this work, the information provided on the electronic structure of BAQ could significantly aid the design and molecular engineering of improved phosphorescent host and hole blocking materials of the future.

The molecular geometries of the ground state BAQ were optimized using ab initio density functional theory (DFT) with the B3LYP (Becke three-parameter Lee–Yang–Parr) [11,12] exchange correlation function with 6-31G* basis sets, in GAUSSIAN 03. Calculation of density of states (DOS) is based on the output coefficient

matrix of wave functions and the discrete peaks were broadened using Gaussian functions with a broadening parameter of 0.5 eV. The orbital characters in partial density of states (PDOS) plots are determined by Mulliken population analysis [13]. The decomposition technique of PDOS is used to reveal the detailed information of the electronic structures of the BAQ molecule. The triplet gap is determined by the energy difference between the unrestricted triplet state and the restricted singlet state in the optimized triplet state geometry. Experimental UV–vis spectra were measured by Hewlett Packard 8453, the electrochemical properties were obtained using cyclic voltammetry by CH instrument CHI 604A and infrared spectra were obtained by Nicolet AVATAR 320 FTIR spectrometer.

The BAQ molecule is structurally composed of two molecules of 2-methyl-8-hydroxyquinoline and a 4-phenylphenol ligand coordinated by a central aluminum (III) cation. As the detailed structure of BAQ has not been experimentally determined, it is necessary to search for the global minimum structure by designing many possible initial structures according to their possible spatial arrangements. The ground state geometries of BAQ are optimized using the hybrid B3LYP approximation with a 6-31G* basis set, with Fig. 1b showing the lowest optimized geometrical structure. We found the three

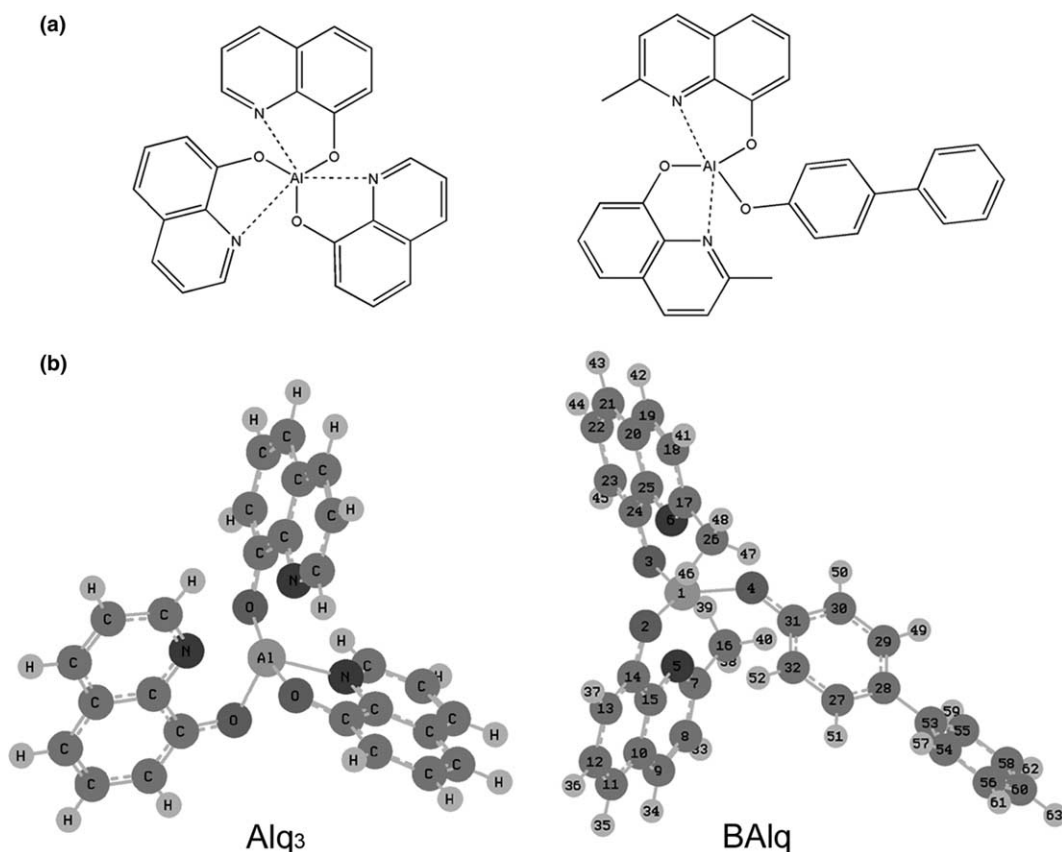


Fig. 1. Molecular structures of Alq₃ and BAQ.

coordinated oxygen atoms are almost coplanar with the O–Al–O angles around 120° , and the remaining two nitrogen atoms lie perpendicular to the AlO_3 mean plane. For comparison, the experimental and theoretical infrared spectra are given in Fig. 2 and there is good agreement to substantiate that the optimized molecular structure of BALq is valid and reasonable.

The optical gap of BALq measured by UV–vis spectrometer is 3.44 eV (360 nm), which is larger than Alq_3 with 3.20 eV (388 nm). The calculated optical gaps for BALq and Alq_3 are 3.38 and 3.28 eV, respectively, with BALq slightly larger, which is consistent with the observed experimental data. This is mainly derived from the fact that BALq has a lower HOMO than Alq_3 (Table 1) but their LUMO levels remain similar. The calculated Alq_3 molecule [14–16] is considered as a *meridional* isomer here, since it is derived from the experimentally observed crystal structure [17]. The HOMO of BALq is lower than that of Alq_3 by about 0.2 eV, therefore injection of hole into BALq molecule is more difficult than Alq_3 which confines excitons in the emission layer for higher efficiency.

In addition, the operating lifetime of phosphorescent OLED has been improved by inserting thin BALq as hole blocking layer [2]. Recently, BALq has also been

employed as triplet host material for the red PHOLED with high efficiency and long operational lifetime without the additional hole blocking layer [3]. For comparison, devices using Alq_3 as host material produced low efficiency because it has a lower triplet bandgap energy (2.00 eV) than that of $(\text{Btp})_2\text{Iracac}$ (2.02 eV [18]) and its exciton-formation zone in this device is also narrower. Indeed, we found that the calculated triplet energy gap of BALq is larger than that of Alq_3 by about 0.42 eV, and the calculated Alq_3 triplet gap of 2.00 eV is consistent with the experimental value of 2.05 eV [19]. The calculated BALq triplet gap of 2.42 eV is near the experimental BCP triplet gap of 2.5 eV [20] which is expected to have sufficiently triplet energy for exothermic energy-transfer to the red dopant of $(\text{Btp})_2\text{Iracac}$.

The total density of states (TDOS) and partial density of states (PDOS) which reflects the projection of DOS to individual atoms of the BALq molecule are presented in Fig. 3 in which the TDOS is expressed as a solid line and the PDOS of 4-phenylphenol and 2-methyl-8-hydroxyquinoline are expressed as dashed and dotted lines, respectively. By analyzing PDOS of these ligands contributing to the TDOS, it is concluded that the HOMO and LUMO orbitals of BALq are essentially localized on the 4-phenylphenol and 2-methyl-8-hydroxyquinoline ligands, respectively.

The plot of electron distribution in general is dependent on the *iso*-surface parameter which only gives qualitative analysis. Here, we have used PDOS to plot the electron distribution on HOMO and LUMO energy states not only for qualitative analysis but also quantitatively (Fig. 4). The two 2-methyl-8-hydroxyquinoline

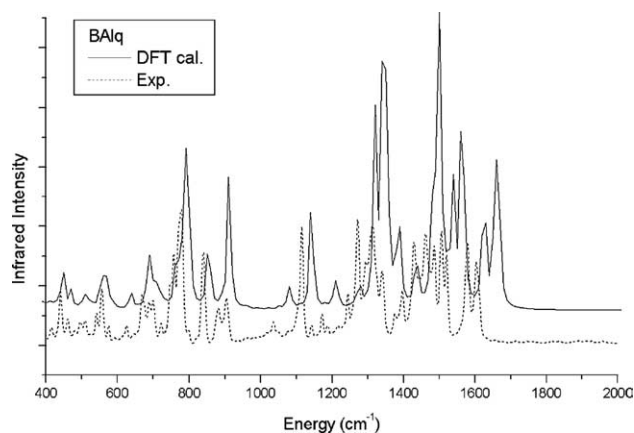


Fig. 2. Theoretical and experiment infrared spectra of BALq.

Table 1

The singlet and triplet energy gap of molecules of BALq and Alq_3 have been calculated to compare with experimental data

		Alq_3	BALq
HOMO/LUMO (eV)	B3LYP/6-31G*	5.01/1.73	5.12/1.74
	Exp. ^b	5.7/3.0	5.9/3.0
HOMO–LUMO (eV)	B3LYP/6-31G*	3.28	3.38
	Exp. ^a	3.2	3.44
Triplet gap (eV)	B3LYP/6-31G*	2.00	2.42
	Exp.	2.05	Non

^a The absorption gap of experimental data were measured by UV–vis.

^b IEEE J. Sel. Top. Quantum Electron. 10 (2004) 101.

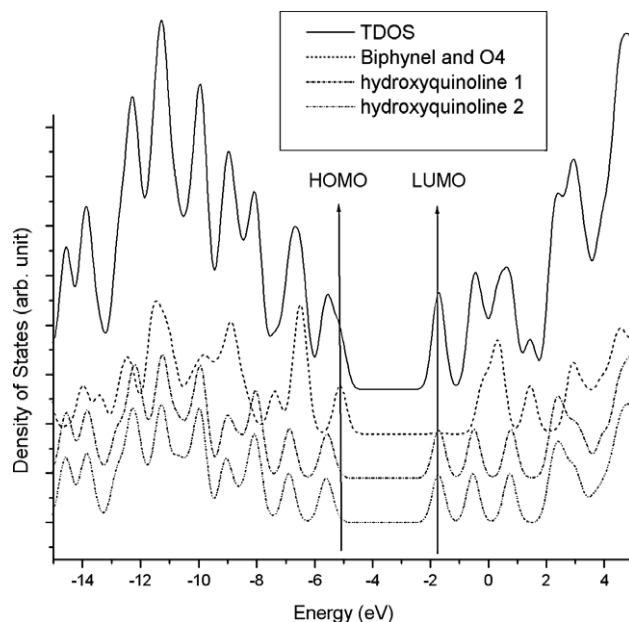


Fig. 3. Total DOS of BALq versus the PDOS of 4-phenylphenol and 2-methyl-8-hydroxyquinoline.

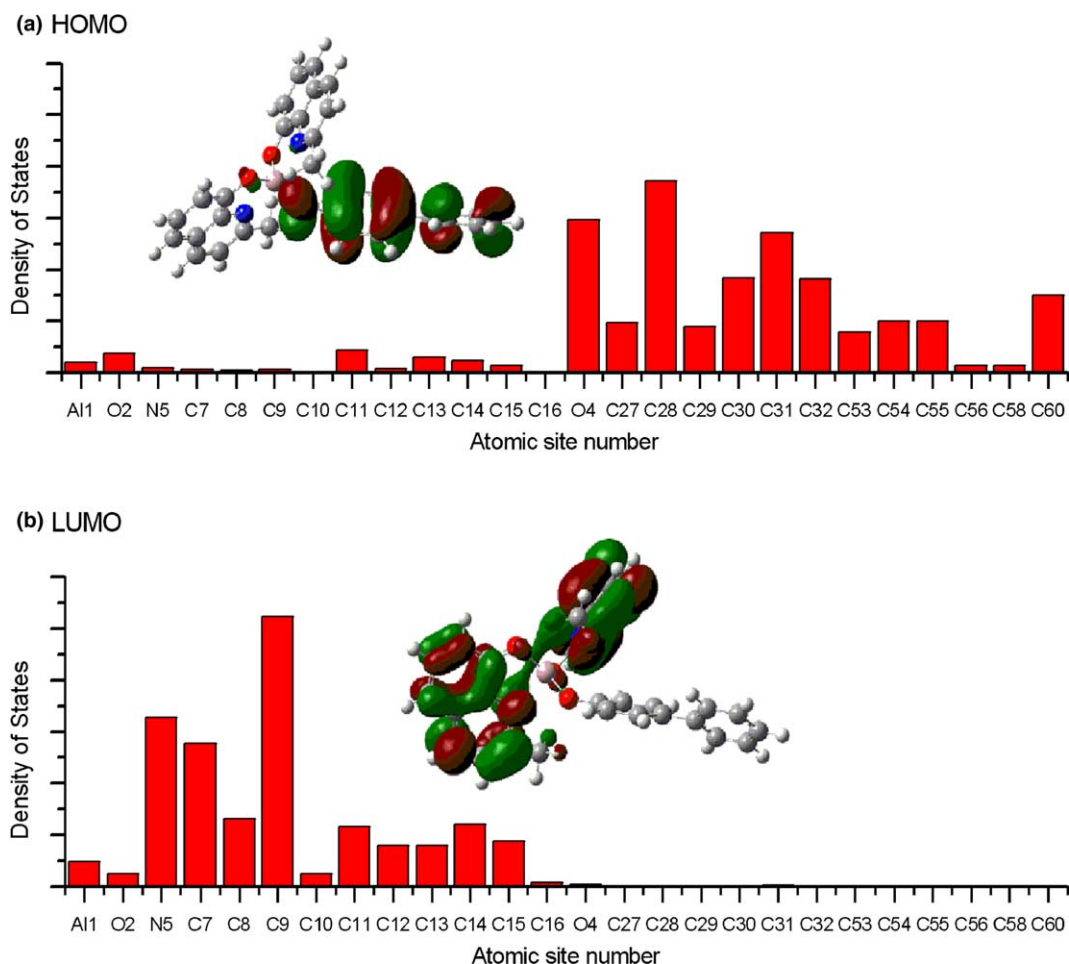


Fig. 4. Calculated electron distribution of: (a) HOMO and (b) LUMO of BALq. The quantification of the electron distribution on HOMO and LUMO energy states by PDOS are also shown.

ligands have almost identical electronic structure (Fig. 3), hence the atomic projected density states which omit one of the two 2-methyl-8-hydroxyquinoline ligands is shown in Fig. 4. The HOMO of BALq is found to mainly localize on the 4-phenylphenol site (Fig. 4a), the O4 with its three adjacent carbon atoms and the C28 appears to possess the most population. In addition, molecular hole-transporting property is related to the distribution of HOMO [21]. A more delocalized HOMO would suggest that the charge would be more easily moved around the molecule and in turn it would lead to improved intermolecular charge-transport. On the other hand, the more localized HOMO will not be favorable for hole-transport. Hence, from this calculation, it is predicted that the localized HOMO of BALq will decrease the frequency of intermolecular hole-hopping and carrier mobility. That is due to the fact that there are three hoping sites (phenoxide of 8-hydroxyquinoline) for each Alq₃ molecule, but there is merely one hoping site (4-phenylphenoxide) for each BALq molecule. These results suggest that the trapped holes in BALq are more probable to transfer to the HOMO states of (Btp)₂Ira-

cac, and hence provide a simple mechanistic model to explain the recent report on improved EL efficiency and stability using BALq as triplet host for the red dopant (Btp)₂Iracac without needing the additional hole blocking layer.

Fig. 4b shows the electronic clouds of the LUMO which are found to localize on the pyridine ring in the two 2-methyl-8-hydroxyquinoline ligands. By analyzing and comparing the DOS of BALq and Alq₃ molecules, the electron distribution of their LUMOs are similar with N5, C7 and C9 having denser population. Detailed electronic structures of the neutral Alq₃ molecules have been described in previous studies [21] which show that both the HOMO and LUMO orbitals of Alq₃ predominantly localize on the phenoxide and pyridyl moieties of the 8-hydroxyquinoline ligand, respectively. On the contrary, the phenoxide orbital states of BALq are on the HOMO-1 energy state which is one energy level below HOMO.

In summary, the present study shows the optimized structure of BALq molecule along with its HOMO and LUMO de-convoluted by PDOS analysis. Calculated

triplet gap of BALq is 2.42 eV which is larger than Alq₃ by about 0.42 eV. This result is consistent with what has been published in the literature. Different from that of Alq₃, the localized HOMO state of BALq molecule is on the 4-phenylphenol site, which may provide a good opportunity for synthetic chemists to modify the molecular structure of BALq and to further improve its EL performance in PHOLEDs as triplet host or hole blocking molecule. A simple mechanistic model is also presented to explain the recent report on improved EL efficiency and stability using BALq as triplet host for the red dopant (Btp)₂Iracac without needing the additional hole blocking layer.

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