

The effect of metal electron cloud on the luminescence characteristics of organic ligands: An experimental and theoretical investigation

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The luminescence processes of metal complexes are complicated by intramolecular charge (energy) transfer from the metal to the ligand or from the ligand to the metal. The charge transfer strongly influences the excited state of the ligand and its luminescence characteristics. The luminescence characteristics of tris(8-hydroxyquinoline) aluminum (Alq₃) and tris(8-hydroxyquinoline) gallium (Gaq₃) are investigated to reveal the effect of the metal ion on the ligand. Emission from the complexes shows a significant red shift as the size of the metal ion increases from Al to Ga because of more efficient charge transfer from the metal to the ligand. Theoretical calculations on the structure and transition characteristics of the excited states of Alq₃ and Gaq₃ were performed. The calculated emission wavelength agrees with the experimental value and the effect of the metal electron cloud on the emission wavelength is clarified.

luminescence, charge transfer, computational modeling

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Organic semiconductor materials attract significant attention because of their huge potential as the active layer in optical electronics applications, such as organic light emitting diodes (OLEDs), organic thin film transistors and organic solar cells [1–4]. The realization of high performance organic optoelectronic devices strongly depends on the development of novel materials. Some basic and key issues that strongly affect the performance of organic electronic devices, such as charge carriers and transfer, exciton dissociation, molecular arrangement on different substrates and evaporation conditions, have been studied intensively [5–7]. However, the dynamic process of the conversion between electricity and light in a single molecule is still not clearly understood.

Since Tang and VanSlyke [8] first reported that the metal complex tris(8-hydroxyquinoline) aluminum (Alq₃) exhibited efficient green light emission more than twenty years ago, Alq₃ has become one of the most popular materials in OLEDs. Following the success of Alq₃, a series of metal complexes with the same ligand, including 8-hydroxyquinolalithium [9], tris(8-hydroxyquinoline) gallium (Gaq₃) [10], and bis(8-hydroxyquinoline) zinc [11], have been synthesized and used as the active layer in organic electronics. Metal complexes can be classified as one of the following two kinds: (i) complexes that exhibit relatively intense luminescence in the solid state and in solution at room temperature because of metal-to-ligand charge transfer (MLCT) transitions, with the ligand as the luminescent center [12], or (ii) complexes whose luminescence arises from ligand-

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to-metal charge transfer transitions, with the metal ions as the luminescent center [13]. The former could be classified as fluorescent and phosphorescent materials, according to the effect of the metal ion on the electronic spin of the excited state of the ligand. Phosphorescent materials are the most effective because they can harvest both singlet and triplet excitons for the heavy ion effect, which leads to the potential for achieving 100% internal quantum efficiency [14,15]. The luminescence of the ligand is strongly affected by the electron cloud overlapping between the ligand and metal ion. For organic materials with the metal ion as the luminescent center, transition metal ions are always chelated with ligands that possess broad and intense absorption bands. The luminescence of the transition metal ion originates from the intramolecular energy transfer of excitation energy from not only the triplet state but also the singlet state of the ligand [16]. Lehn [17] named this phenomenon the "antenna effect" and proposed that such complexes could be seen as molecular light conversion devices because they are able to transform light absorbed by the ligand into light emitted by the metal ion via intramolecular energy transfer. Regardless of the direction of charge transfer, the overlap of the electron cloud between the metal and ligand strongly determines the efficiency of intramolecular charge transfer. It is known that the radius of electrons around the nucleus increases with atomic number in the same group, while the restriction on outer electrons by the nucleus becomes weaker. This means that the charge transfer (related to the overlap of the electron cloud) may be more efficient within metal complexes containing chelated ligands. For complexes containing the same ligand coordinated to different metal ions, such as copper phthalocyanine [18], zinc phthalocyanine [19], tin phthalocyanine and cobalt phthalocyanine [20,21], the diversity of their optical and electrical characteristics can be attributed to the effect of the metal ion on the phthalocyanine ligand.

In this paper, the effects of the metal electron cloud on the luminescent characteristics of the fluorescent materials Alq_3 and Gaq_3 were investigated. Experimental results revealed that the emission wavelength of Gaq_3 is longer than that of Alq_3 despite their similar molecular structure, and that emission occurs on the same ligand with different electron cloud structures. Although a previous study indicated

that the emission properties of the ligand dominate the fluorescence of the complexes [22], this study showed that the central metal ion does influence the emission properties of these materials. Quantum chemistry calculations were used to examine the geometric and electronic structure of the lowest excited states of the two molecules to interpret the effect of charge transfer from the metal to the ligand on the luminescence characteristics of organic semiconductors chelated to metal ions.

1 Experimental

Indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 60 Ω/\square were cleaned in an ultrasonic bath containing acetone, ethanol and deionized water sequentially. The organic semiconductors, Alq_3 , Gaq_3 and N,N' -bis-(1-naphthyl)- N,N' -1-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) were purchased from Shanghai HanFeng Chemical Scientific Co., Ltd. Thin films of these materials were fabricated by thermal evaporation at a rate of about 0.6 $\text{\AA}/\text{s}$ under a high vacuum of 2×10^{-4} Pa. The thicknesses of the deposited films were measured with a quartz-crystal microbalance. The top Al electrode (100 nm) was prepared by thermal evaporation with a shadow mask. The active emission area of the devices was about 0.1 cm^2 . Spectra were measured on a Spex Fluorolog-3 spectrophotometer (Jobin Yvon) under ambient atmosphere. The optical power and current-voltage (I - V) characteristics were measured with I - V - L measurement system and a Keithley source meter 2410. The chemical structures of the organic materials used are shown in Figure 1.

2 Computational methods

Studies of the excited state properties using the configuration interaction singles (CIS) method tend to overestimate the electronic transition energies. Multi-reference approaches such as coupled-cluster with single and double excitations (CCSD) [23], and complete active space self-consistent field (CASSCF) [24–26] methods allow very accurate estimates but are limited to small systems because

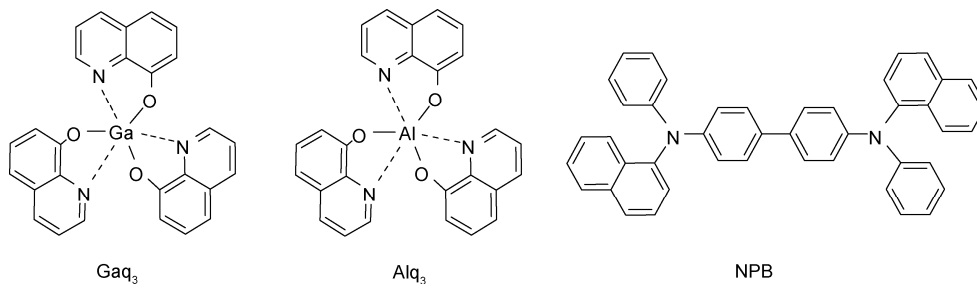


Figure 1 The chemical structures of Gaq_3 , Alq_3 and NPB.

of their large computational cost [27]. An alternative approach that is feasible to use is time-dependent density functional theory (TD-DFT) [28]. In particular, the recent availability of TD-DFT analytical gradients provides direct access to the structure and properties of electronically excited states at a reasonable computational cost and with reliable accuracy.

In this study, the first singlet excited state (S_1) structures of the molecules were optimized using TD-DFT methods. The Kohn-Sham equation was calculated with the hybrid B3LYP function [29], which is considered as a standard for DFT calculations [30]. Vertical transition energies were evaluated at the TD-B3LYP level of theory. The LANL2DZ [31] basis set, which includes effective core potentials, was used for both Alq_3 and Gaq_3 . All of the calculations were carried out using the Gaussian 09 program.

3 Results and discussion

The photoluminescence (PL) and absorption spectra of thin films of Alq_3 and Gaq_3 on quartz substrates are shown in Figure 2. These two materials show absorption peaks in similar positions but with different absorption coefficients. The thin films of Alq_3 exhibit stronger absorption at about 270 and 400 nm than those of Gaq_3 with the same thickness. The weaker absorption of the thin films of Gaq_3 results in poorer PL performance; in Figure 2, the PL intensity of Gaq_3 is normalized with that of Alq_3 under the same measurement conditions. For Alq_3 and Gaq_3 , the emission results from radiative decay of the excited singlet state of the 8-hydroxyquinoline ligands, which is influenced by the metal ion. Charge transfer from the Ga ion to 8-hydroxyquinoline should be more effective than that from the Al ion. The PL emission peak of Gaq_3 appears at about 546 nm, which is at much longer wavelength than that of Alq_3 at 520 nm. The difference can be attributed to the different shape of the frontier molecular orbitals of 8-hydroxyquinoline due to the presence of the chelated metal ion, which is rationalized as follows. It is generally considered that central metal ions play two kinds of roles: (i) decreasing intramolecular vibration and increasing the energy of the radiative transition; and (ii) modulating the excited state of the ligand through charge transfer. Uncoordinated 8-hydroxyquinoline does not show any emission because of its intramolecular freedom (not given in this paper). The introduction of metal ions effectively reduces the loss of intramolecular energy and facilitates strong emission.

Figure 3 shows the electroluminescence (EL) power dependence of OLEDs with the structure ITO/NPB/ Gaq_3 /Al and ITO/NPB/ Alq_3 /Al on the driving voltage. The EL intensity of the Alq_3 device is stronger than that of the Gaq_3 device under the same driving voltage. The EL intensity depends on not only the balance of charge carriers injected

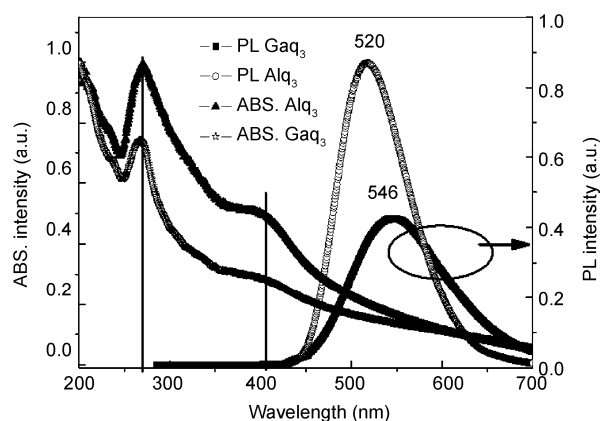


Figure 2 Absorption and PL spectra of thin films of Gaq_3 and Alq_3 on quartz substrates.

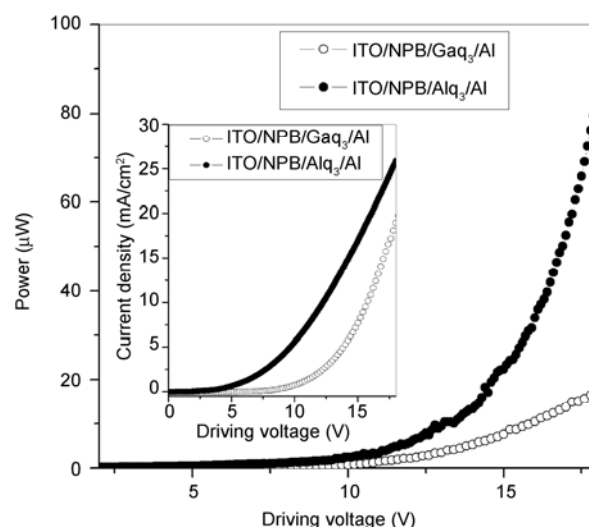


Figure 3 Optical power dependence of devices containing Gaq_3 or Alq_3 on the driving voltage. The inset shows the J - V characteristics of these devices.

from both electrodes but also the internal quantum efficiency of the emissive materials. The inset in Figure 3 shows the current density dependence on the driving voltage for these two kinds of devices. The PL experimental results show that luminescent efficiency of Alq_3 is higher than that of Gaq_3 . For these two kinds of EL devices, the charge carrier recombination zone is confined in the Alq_3 or Gaq_3 layer and the NPB layer acted as a hole transporting layer. Both devices should have a similar amount of holes injected because the hole injection process from anode is the same; however, the current density of the device containing Alq_3 as the active layer is larger than that of the device with Gaq_3 , which is attributed to the injection of more electrons from the cathode to the Alq_3 layer.

In Table 1, the experimental and theoretical emission wavelengths (in nm) for Alq_3 and Gaq_3 , which were computed using the TD-B3LYP/LANL2DZ method based on the

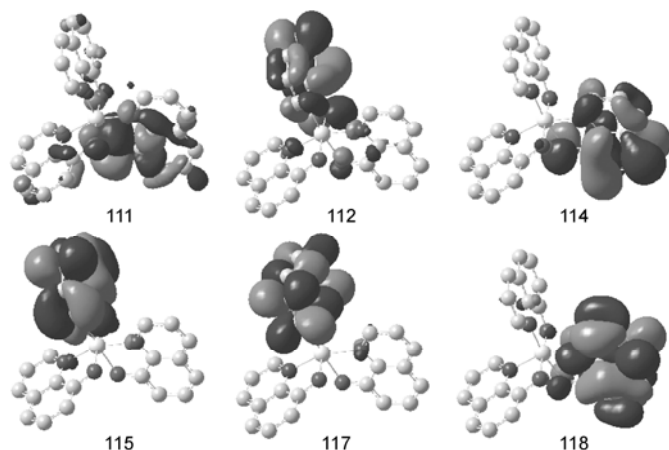
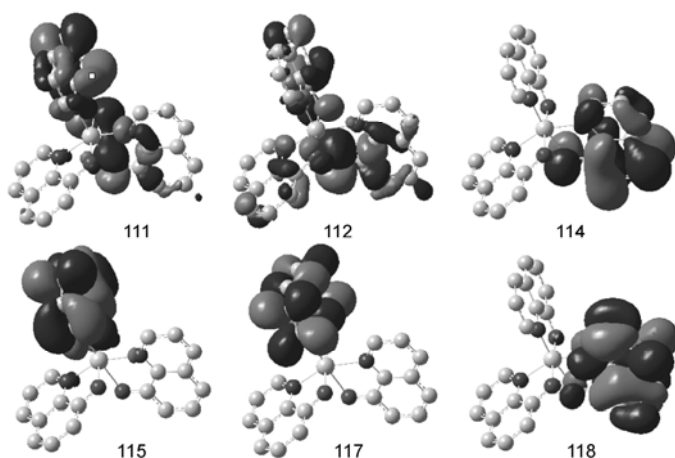
Table 1 Emission wavelengths (in nm) from theoretical calculations and experimental observation

Material	TD-B3LYP/ 6-31G(d)	TD-B3LYP/ LANL2DZ	Orbital transition	Other	Exp.
Alq ₃	506	529	115→112, 118→114	553 ^{a)} , 533 ^{b)} , 543 ^{c)}	520, 519 ^{d)}
Gaq ₃		539	115→111, 115→112, 117→114, 118→114		546

a) Calculated with TD-B3LYP/6-31+G(d,p)//CIS/6-31G [32]; b) calculated with TD-B3LYP/6-31G(d)//CIS/6-31G(d) [33]; c) calculated with TD-B3LYP/6-31G+(d)//CIS/6-31G(d) [33]; d) experimental value [34].

Table 2 Frontier orbital energies (in eV) calculated using TD-B3LYP/6-31G(d)

Material	Orbital energy (eV)					
	111	112	114	115	117	118
Alq ₃	-6.259	-5.987	-4.245	-2.993	-1.333	-1.252
Gaq ₃	-6.095	-5.959	-4.109	-3.102	-1.415	-1.170

**Figure 4** The frontier orbitals of Alq₃ calculated using TDDFT/LANL2DZ level of theory.**Figure 5** The frontier orbitals of Gaq₃ calculated using TDDFT/LANL2DZ level of theory.

optimized geometries at the same theoretical level, are summarized. To the best of our knowledge, this is the first TDDFT study on the excited state of Gaq₃. It can be seen that the emission peak of Gaq₃ is at longer wavelength than that of Alq₃ both theoretically and experimentally. For Alq₃, the predicted emission energy is ca. 2.34 eV, corresponding to ca. 529 nm, which is in close agreement with the experimental value of 2.38 eV (520 nm). Also shown in Table 1 are emission wavelengths calculated using TD-B3LYP/6-31G(d) and data obtained by other groups, which were calculated at the TD-B3LYP level of theory using a spherical 6-31G basis set and optimized geometries obtained using the CIS method. The difference between the calculated data obtained previously and the experimental value is larger than that between our experimental and theoretical results, which indicates that the geometries of the excited states obtained using the CIS method are not as accurate as those calculated by TDDFT [15]. Moreover, the LANL2DZ basis set is more suitable for the calculation of the excited state of Alq₃ than the 6-31G (d) basis set. For Gaq₃, the calculated emission energy is ca. 2.30 eV, corresponding to ca. 539 nm, which is also in good agreement with the experimental result at 2.27 eV (546 nm).

The shapes of the frontier molecular orbitals (FMOs), which are related to the emission wavelength, for the lowest excited states of Alq₃ and Gaq₃ are shown in Figures 4 and 5, respectively. The shape of the FMOs of the S₁ states shows some differences between Alq₃ and Gaq₃, especially for orbitals 111 and 112, which exhibit a larger electronic distribution in Gaq₃ than Alq₃. As seen from Table 1, Alq₃ emission arises from the orbital transitions from 115→112 and 118→114 (Orbital 115 is the highest occupied molecular orbital) and emission from Gaq₃ corresponds to the orbital transitions from 115→111, 115→112, 117→114 and 118→114. Moreover, the orbital energy (Table 2) is higher in Gaq₃ than the equivalent orbital in Alq₃ and the energy gap is smaller in Gaq₃. The difference in the electronic distribution and energy gap determines the energy of the orbital transition, and ultimately the red shift of emission in Gaq₃ is compared with that in Alq₃.

4 Conclusion

The luminescent characteristics of Alq₃ and Gaq₃ were studied by both experimental investigation and theoretical calculation, with the first example of a TDDFT calculation of the excited states of Gaq₃. The difference in the

electronic transition energy between experimental and theoretical values is very small, less than 0.04 eV, which confirms the accuracy of our calculations. It was found that the emission wavelength exhibits a significant red shift as the size of the metal ion increases. The theoretical calculation shows that the differences in the electronic distribution and energy gap cause the red shift of emission from Gaq₃ compared with that from Alq₃.

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