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# The structural characterization and its influence on photoluminescence of lithium tetra-(8-hydroxy-quinolinato) Boron

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Lithium tetra-(8-hydroxy-quinolinato) boron ($LiBq_4$) is one kind of blue light-emitting material with good performances. In this paper, $LiBq_4$ sample was synthesized and purified. The purity is up to 97.6%. In order to investigate the influence of $LiBq_4$ structure on its optical characteristics, especially on the shift of photoluminescence (PL) central wavelength, compared with that of tris-(8-hydroquinoline) aluminum ($Alq_3$), a joint experiment based on a combination of X-ray diffraction (XRD) spectrum, infrared absorption (IRA) spectrum, hydrogen nuclear magnetic resonance (HNMR) spectrum, absorption and photoluminescence spectra of $LiBq_4$ was performed. IRA and HNMR spectra generally make certain the molecular structure, and illuminate the interaction among the atoms in $LiBq_4$. Absorption and photoluminescence spectra qualitatively suggest the basic optical characteristic of $LiBq_4$ and that the emitted light results from 8-hydroxyquinoline rings. By comparing $LiBq_4$ with $Alq_3$, the conclusion that besides B—N covalent bond, B—O is another important factor which heavily influence on the PL peak can be drawn. Furthermore, the influence of $LiBq_4$'s special coupling manner on PL peak is demonstrated too. © *2006 Springer Science + Business Media, Inc.*

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## 1. Introduction

In 1987, the organic light-emitting device (OLED) with high luminescence efficiency was firstly reported by Tang and Vanslyke [1]. Since then, the interest in OLED has considerably increased [2–9]. Due to the excellent performances, E.g., low cost, wide viewing angle and rapid video response rate etc [2–5], a lot of organic materials have been tested in an effort to obtain different color light emitting. In these materials, 8-hydroxyquinoline chelates are notable. By changing the different metal atoms as the central atom, different color light emitting can be achieved. For example, the well known green-light-emitting material, tris-(8-hydroquinoline) aluminum ($Alq_3$), now is widely used in OLED. Up to now, great progress has been made in red and green OLED [6–9], while regretfully it is not so successful in blue OLED due to the wide band gap of the materials adopted. Nevertheless, a few blue photoluminescent boron-containing polymers, small molecules and electron-transporting organoboron compounds have been reported [10–12]. In view of the special role of 8-hydroxyquinoline chelates in OLED, the boron (B) atom is also tried to be introduced as the central atom of 8-hydroxyquinoline chelates and it has made great success in blue OLED [13]. The intensity of emitting light is strong, while the central wavelength is much shorter (blue shift) than that of $Alq_3$. This is quite interesting and will be illuminated in this work. In order to investigate the PL characteristics, especially to find the influence of central atom (boron) on PL peak, several spectra were measured and analyzed carefully. The interactions among atoms, especially that of central atom *B* with O, N atoms, are discussed in detail. At last, some useful conclusions are drawn.

## 2. Experiment

Firstly, the absolute ethanol was further dehydrated by pure $Mg(OH)_2$. Then stir 0.43 g (20 mmol) lithium borohydride ($LiBH_4$) and 11.6 g (80 mmol) 8-hydroxyquinoline (HQ) into 30 ml and 150 ml dehydrated absolute ethanol respectively. The former appears white suspending liquid, labeled as A. The latter is brown

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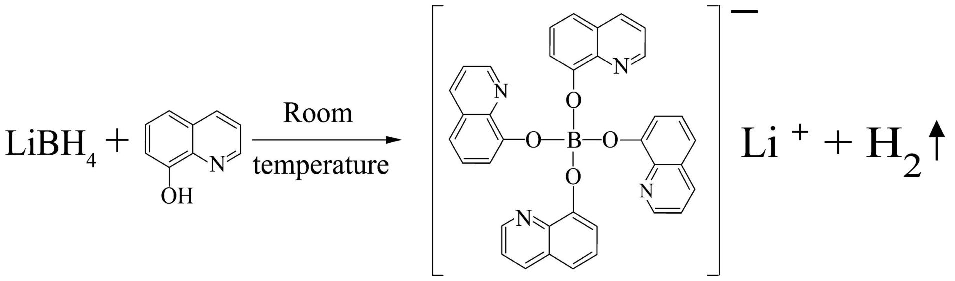


*Figure 1* Synthetic reaction equation of $LiBq_4$.

solution, labeled as B. It is noted that all the reactants should be of high purity. Then put B solution into A liquid drop by drop, at the same time, the magnetic force stir was applied and kept for two hours after all B solution is added. At the beginning, there is some precipitate appears and eventually the white yellow suspending liquid was obtained. Afterwards, the liquid was filtered, and then dried in the evacuated chamber. At last, the white powder, namely $LiBq_4$ was obtained. The reaction equation is shown in Fig. 1.

The originally obtained sample was crude and should be purified. Here the extraction is adopted. The sample was put into micro-Soxhlet's extractor and the high-purified ether was adopted as the dissolvent to purify it continuously for more than 48 h. At last, the impurities in $LiBq_4$ power were fully dissolved by ether and then filtered. The purified sample shows white powder at room temperature and it is chemically stable in the dry atmosphere.

## 3. Discussion

### 3.1. The X-ray diffraction spectra of $LiBq_4$

In order to qualitatively testify the purity of $LiBq_4$, X-ray diffraction (XRD) experiment was carried out at room temperature and the Cu-K$\alpha$ radiation source ($\lambda = 1541.8$ Å) in the Rigaku D/max-2400 XRD spectrometer is used. The result is schematically illustrated in Fig. 2.

Except the XRD spectrum of $LiBq_4$, the spectrum of the reactant $LiBH_4$ was also shown in Fig. 2. It's evident that the peaks in Fig. 2c absolutely disappear in Fig. 2b, which can fairy lead to the conclusion that there is no $LiBH_4$ reactant in $LiBq_4$ powder. Taking into account the fact that the other reactant, 8-hydroxyquinoline, is soluble in ether, it should had been completely filtered in the course of purification, thus the conclusion that the purity of $LiBq_4$ powder was very high can be drawn. In addition, the sharp peaks were shown in Fig. 2, which suggest that the sample was slightly crystallized. $LiBq_4$ powder was polycrystalline or amorphous.

### 3.2. Purity test

The rigorous test of $LiBq_4$ purity has also been performed by means of Vario EL Elementary Analytic Instrument. Table I shows the theoretically calculated results at the first line while the measured results at the second. Comparing the results, it can find that the percentages of N, O and H atoms of obtained $LiBq_4$ powder all are agreed well with the theoretical results, indicating that the purity is very high. Finally, by means of the Varian Vista-5060 liquid chromatograph, the purity of 97.6% of $LiBq_4$ was obtained.

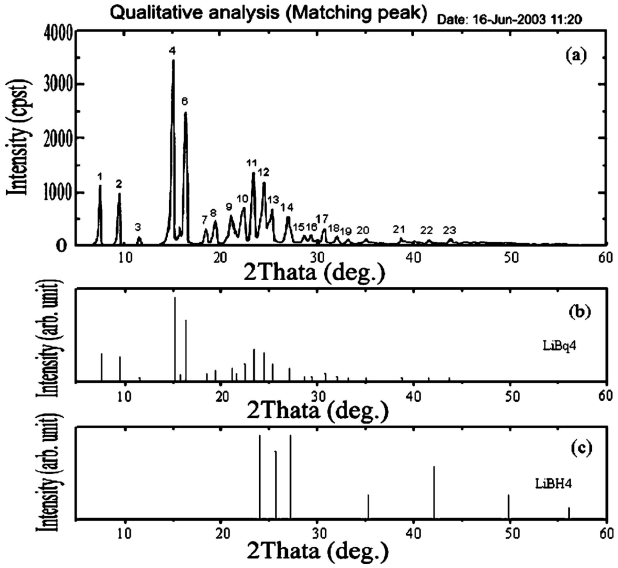


*Figure 2* X-ray diffraction (XRD) spectra of $LiBq_4$ powder.

### 3.3. Infrared absorption spectra of $LiBq_4$

Infrared absorption (IRA) is meaningful to study the structure of $LiBq_4$. In this experiment, the powder specimen of $LiBq_4$ is compacted into pellet with KBr and NEXUS 670 FT-IR infrared spectrophotometer from Nicolet Company is used. The spectra of $LiBq_4$ are illustrated in Fig. 3.

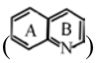
Notably, the IRA analysis for Heterocyclic Aromatic Compounds is similar to that for Carbocycle Aromatic Compounds. The heteroatoms in it are allowed to be taken as substituents [14]. For example, quinoline (
) can

TABLE I Results of elementary analysis.

| | Element | C | H | N |
|---|---|---|---|---|
| Percentage composition | Theoretical results | 72.75% | 4.07% | 9.43% |
| | First time results | 72.58% | 4.18% | 9.48% |
| | Second time results | 72.73% | 4.12% | 9.38% |

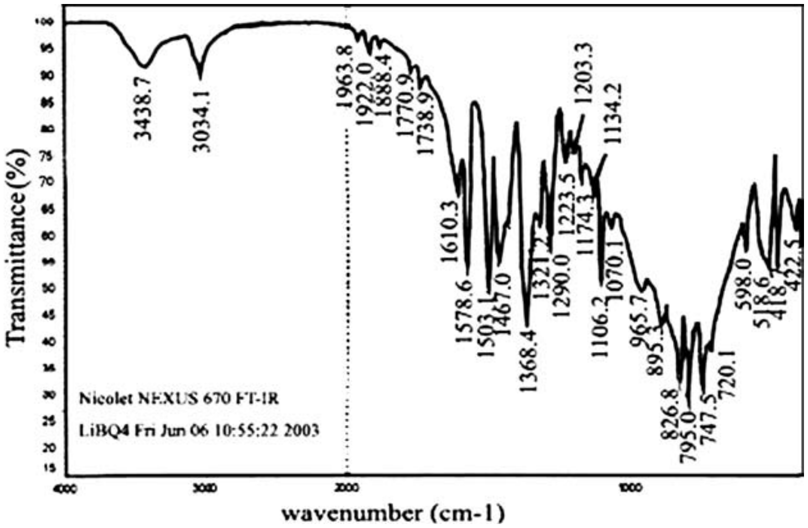


*Figure 3* Infrared absorption (IRA) spectra of $LiBq_4$.

be treated as a complex consisting of one "*A*" ring and one "*B*" ring, in which, "*A*" ring is a benzene ring with 1, 2 position replaced by other atoms, while for "*B*" ring, the replaced positions are 1, 2, 3 position.

The spectra in Fig. 3 are carefully analyzed as follows. The broad characteristic absorption centered at 3439 $cm^{-1}$ corresponds to the stretching vibration of $HO^-$. It suggests that there are still some hydrogen ions around O atoms, which accords with the fact that B–O is covalent bond [16]. Another peak located at 3034 $cm^{-1}$ results from the stretching vibration of C–H bond in aromatic ring. In the area of 2000–1650 $cm^{-1}$ (5–6 $\mu$m absorption band), several weak peaks are presented. It corresponds to the flexural oscillation absorption of –C–H in quinoline rings. In addition, the absorption in this area agrees well with that of "A" ring, indicating that "A" ring exists. Along with the prominent peaks at 795, 747 $cm^{-1}$, it further implies the existence of quinoline rings. Some moderate intensity peaks locate at 1610 $cm^{-1}$, 1579 $cm^{-1}$, 1503 $cm^{-1}$, 1467 $cm^{-1}$, which are the characteristic of the absorption vibration of the aromatic ring skeleton, suggesting that the conjugate action of aromatic rings in molecule is very strong and all electron orbits of quinolinic rings are $\pi$-bonding hybridizations. Another strong peak at 1368 $cm^{-1}$ is assigned to the vibration absorption of B–O or B–N. It is finally inferred to be B–O by the comparison with $LiBq_{m4}$ [15]. The stretching vibration of –C–N of quinoline rings results in the absorption peak at 1321 $cm^{-1}$. The peaks from stretching vibration of –C–O at 1290, 1233 $cm^{-1}$ are weaker, while the peaks of the planar flexural vibrations of C–H of benzene ring at 1202, 1174, 1134, 1070 $cm^{-1}$ are stronger than the homologous peaks of HQ [Spectral Data Base System, No = 1559, IR-NIDA-00925], indicating that the strong coordinate action of B–O– heavily affects both O bonding and the proton electronic environment in the molecule. This is also confirmed by the analysis of HNMR in the following section. The characteristic absorption peaks of quinoline rings are shown in the area of 800–600 $cm^{-1}$. The absorption in far-infrared region of 400–600 $cm^{-1}$ originates from the vibration between B atom and the 8-hydroxyquinoline ligands.

## 3.4. Hydrogen nuclear magnetic resonance (HNMR) spectra of $LiBq_4$

In order to further study the interaction of the central atom (B) with the ligands (8-hydroxyquinoline) in $LiBq_4$ molecule, HNMR experiment (shown in Fig. 4) is quite useful and it was carried out at room temperature by using the Mercury Plus Nuclear Magnetic Resonance Spectrometer under the working frequency of 300 MHZ. Dimethyl Sulfoxide (DMSO) acts as the solvent. Fig. 4 displays two peaks at 2.51 ppm and 3.35 ppm, which result from the solvent DMSO and $H_2O$ respectively. Other peaks ascribe to $LiBq_4$. There are six different sites for protons are presented in Fig. 5, which results from different electronic environment in the quinoline rings of $LiBq_4$ molecule. The corresponding chemical shift is listed in Table II. Considering that the variations of chemical shift ($\Delta\delta$) between $LiBq_4$ and $Alq_3$, and between $LiBq_4$ and HQ are quite helpful to determine the bonding status between B atom and the ligands, both the standard HNMR spectra of HQ [Spectral Data Base System, No = 1559, HSP-40-282] and the HNMR spectra of $Alq_3$ [16] are shown in Table II too.

Firstly, the comparison of $LiBq_4$ with HQ was done. It is clear that the protons in $LiBq_4$ molecule undergo the shift to high field at d,f sites. This is due to the existence of $B^{3+}$ ion, which decreases the density of electron cloud around the d,f protons, hence reduces the shielding effect to external magnetic field. The chemical shift variation $\Delta\delta$ ($\Delta\delta > 0$) between them indicates that the stronger bond of B–O– exists in $LiBq_4$ than that of H–O– in HQ molecule. As for a-c sites, provided that the covalent bond of B–N exists, the resonance peak at c position will move

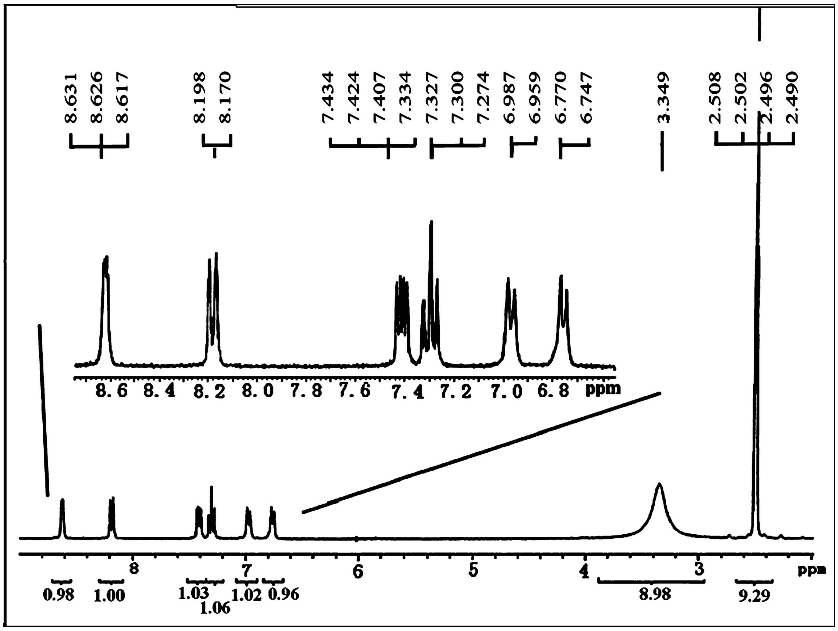


*Figure 4* Hydrogen nuclear magnetic resonance spectra of $LiBq_4$.

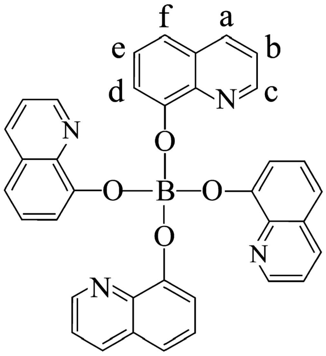


*Figure 5* Molecular structure of $LiBq_4$ and sites of protons.

to lower field, just like that for $Alq_3$ [16]. While in fact it doesn't happen, which implies that B atom in $LiBq_4$ substantively doesn't coordinate with nitrogen (N) atom (similar with the fact that there is no interaction of H–N in HQ). In such circumstances, the $\Delta\delta$ at a-c sites only possibly results from the disturbance of B–O, which means that B–O in "*A*" ring is so strong that it much influence the quinoline ring electronic environment, namely it change the photoluminescence central wavelength of $LiBq_4$, to some extent.

Secondly, the comparison between $LiBq_4$ and $Alq_3$ is performed. Evidently, the chemical shifts of $LiBq_4$ are smaller than that of $Alq_3$ both at a and c sites. Especially at c site, $\Delta\delta$ is big ($\Delta\delta = 0.20$ ppm), suggesting that the covalent bond of Al-N in $Alq_3$ is much stronger than that of B–N in $LiBq_4$. In other words, the covalent bond of B–N in $LiBq_4$ is very weak or inexistent [13]. At d and f sites, commonly the bond of Al–O in $Alq_3$ is electrovalent, which should be much stronger than the covalent bond of B–O in $LiBq_4$, so the chemical shifts of $Alq_3$ should occur at the higher field. But unexpectedly, the experimental results (Table II) show that it is $LiBq_4$ not $Alq_3$ that occurs at higher field position. This may results from the following aspects. Firstly, the chemical bond of Al–O is covalent bond not electrovalent bond in $Alq_3$ [16]. Secondly, being covalent bond, B–O is stronger than Al–O. Thirdly, it originates from the characteristic of atom B itself and the special coupling manner with the ligands.

## 3.5. Absorption spectrum and the photoluminescence (PL) spectrum of $LiBq_4$

The PL and absorption the spectra of $LiBq_4$ film are shown in Fig. 6. They are collected by Jasco FP-777 spectrofluo-

TABLE II The number and the chemical shift of protons at different sites of HQ, $Alq_3$, $LiBq_4$ molecules, respectively.

| Proton sites | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| Resonance area | 1.00 | 0.96 | 0.98 | 1.06 | 1.02 | 1.03 |
| Proton number | 4 | 4 | 4 | 4 | 4 | 4 |
| Chemical shift | | | | | | |
| HQ | 8.148 | 7.426 | 8.783 | 7.191 | 7.453 | 7.330 |
| $Alq_3$ | 8.22 | 7.05–7.51 | 8.83 | 7.05–7.51 | 7.05–7.51 | 7.05–7.51 |
| $LiBq_4$ | 8.198 | 7.327 | 8.631 | 6.770 | 7.394 | 6.987 |

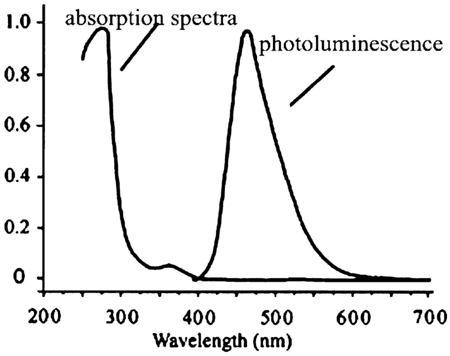


*Figure 6* Normalized (a) photoluminescence and (b) absorption spectra of $LiBq_4$ film.

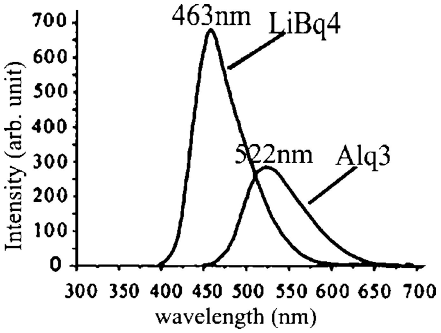


*Figure 7* Photoluminescence spectra of $LiBq_4$ film and $Alq_3$ film.

rometer and UV-360 spectrophotometer respectively. The scan range is from 200 to 700 nm.

$LiBq_4$ PL spectrum Fig. 6a is obtained under an excitation wavelength of 350 nm. The spectrum lies in the blue-light region with the peak locating at 463 nm. The half-peak breadth is about 80 nm. For further study the PL characteristic of $LiBq_4$, under the same condition, the PL spectrum of $Alq_3$ (the purity is 98.6%) is measured and illustrated in Fig. 7. It is clear that the luminescence intensity of $LiBq_4$ is much stronger than that of $Alq_3$, indicating its promising application in OLED. Furthermore, the PL peak of $LiBq_4$ undergoes about 60 nm towards high energy. The shift means that, the central atom B disturbs the light emitting of quinoline ligand, to some extent. This will be discussed in detail in next section.

Besides this, Fig. 7 shows the similar PL spectrum shapes for $LiBq_4$ and $Alq_3$, which results from the similar energy band structure of these two kinds of materials. Taking into account that both B atom and Al atom belong to IIIA, their similar energy structure is anticipated. In addition, the PL spectrum of $LiBq_4$ is broad, quite different from the narrow band from metal ion. So, as well as $Alq_3$, the emitted light from $LiBq_4$ also happens in quinoline rings. $LiBq_4$ is one kind of organic EL material which is strongly disturbed by central atom B.

The absorption the spectrum of $LiBq_4$ is also measured Fig. 6b. The cut-off absorption wavelength is 410 nm, reflecting the energy gap of 3.02 eV between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of $LiBq_4$, quite according with the value reported in other literature [16].

## 4. Results

From Section 3.6, $LiBq_4$ suffers a blue shift to high energy, which implies that the electronic environment in quinoline rings has been greatly influenced by external factors. Based on the discussion of Section 3, the reasons now are analyzed and summarized as follows:

Firstly, as analyzed in HNMR experiment, B–O bond strongly affects the electronic environment in quinoline rings, thus the energy band structure is influenced and the PL peak wavelength is changed. Secondly, it is well known that in the $Mq_3$ ($M$ = Al, Ga and In) complexes, the 8-hydroxyguinoline is functionalized as a bidentate ligand, which further forms chelates complexes with the central metals. The coordination numbers are 6 [17]. However, in $LiBq_4$ molecule, 8-hydroxyquinoline is functionalized as monodentate ligand [13]. Due to the small size of B atom, only four 8-hydroxyguinoline molecules can chelate with the central B atom Fig. 1. Thirdly, as analyzed in HNMR and IRA spectra, there is no coordination bond between B and N atom. This is very important and it distinctly differentiates $LiBq_4$ from other $Mq_3$ ($M$ = Al, Ga and In). It is well known that with the decreasing of covalent bond intensity of metal-nitrogen, the emitting light will shift to shorter wavelength in $Mq_3$ [18]. So, the zero covalent bonding between B and N in $LiBq_4$ molecule further shortens the PL central wavelength.

## 5. Conclusion

In summary, the organic EL material $LiBq_4$ with high purity is synthesized and purified. The molecular structure of $LiBq_4$ is investigated by several kinds of spectra. IRA spectrum qualitatively explicates the properties and structure of $LiBq_4$ molecule. The existence of quinoline rings is confirmed. HNMR spectrum studies on the interactions among the atoms in $LiBq_4$ molecule and suggests that the central atom B only coordinates with O atom, while not with N atom. It points out that except the nature of the B–O bonding, zero interaction of B–N plays very important role for the PL peak blue shift, compared with that of $Alq_3$. That light emitting results from quinoline rings is also testified, which was perturbs by central atom B, to some certain. The PL peak wavelength locates at 463 nm is measured. Base on the analysis above, the factors which influence PL peak is analyzed and the mechanism is demonstrated.

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