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Time-dependent density functional theory study on electronic and spectroscopic properties for Ph₂Bq and its complexes

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Abstract The molecular structures of the ground state and the first singlet excited state for diphenylboron analogs of Alq₃ [Ph₂Bq where q is 8-hydroxyquinoline (QH)] and its three derivatives were optimized with the Density Functional Theory and ab initio “configuration interaction with single excitations” method, respectively. The frontier molecular orbital characteristics of Ph₂Bq were analyzed systematically in order to study the electronic transition mechanism. Electronic and spectroscopic properties of complexes have been investigated with Time-Dependent Density Functional Theory, which indicates that the emissions of Ph₂Bq and its derivatives originate from the electronic $\pi \rightarrow \pi^*$ transitions within the QH ligands. That means that one might tune the emission wavelengths and improve charge transfer properties through the effect of substituent on the 8-hydroxyquinoline ligand. Similar calculations were carried out for isolated QH and its three derivatives for comparison. We found that the highest occupied molecular orbital and the lowest unoccupied molecular orbital of Ph₂Bq are similar to those of QH and their spectroscopic properties change similarly when they are substituted by the same group, which suggests that one can search possibility of a red or blue emission from Ph₂Bq derivatives by analyzing QH and its derivatives.

Keywords Ph₂Bq · Organic electroluminescence · TD-DFT · Spectrum

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1 Introduction

Organic light-emitting diodes (OLEDs) are currently under intense investigation for application in next generation display technologies. OLEDs are heterojunction devices in which layers of organic transport materials are usually incorporated into devices as amorphous thin solid films [1]. Tris(8-quinolinolato)aluminum (Alq₃) has been a key compound for organic electroluminescence (EL) devices [2–9] since the first realization of a multilayered EL device by Tang and Van Slyke [10]. With an aim to further optimize its applications in OLEDs, many complexes with similar emissive properties to Alq₃ but different molecular geometries have been prepared and studied [11–14]. Recently, Anderson et al. [15] reported the synthesis of diphenylboron analogs of Alq₃ [Ph₂Bq where q is 8-hydroxyquinoline (QH)] and their absorption and emission (photoluminescence and electroluminescence) characteristics in solution and in the solid state. Solution photoluminescence of Ph₂Bq is about 15 nm shorter than that of Alq₃ and its quantum efficiency is higher. Color tuning of the OLED is a key technology to develop a full-color flat-panel display. It is interesting to look for a reasonable method to tune and predict the emissive color of Ph₂Bq and its derivatives. The molecular structures calculated are shown in Fig. 1.

In the present work, we try to predict the ground-state and excited-state geometries and evaluate the transition energies for Ph₂Bq, QH, and their derivatives. Hartree-Fock (HF) and B3LYP methods were used to optimize the ground-state geometries, respectively. The excited-state geometries were optimized at the ab initio configuration interaction singles (CIS) level of theory. The transition energies were calculated at the ground-state and excited-state geometries using the density functional levels of theory, and some results were compared with the available experimental data [15]. In this work, we try to find a reasonable way to tune and predict the emission wavelengths of Ph₂Bq and its derivatives through studying the emission wavelengths of QH and its derivatives.

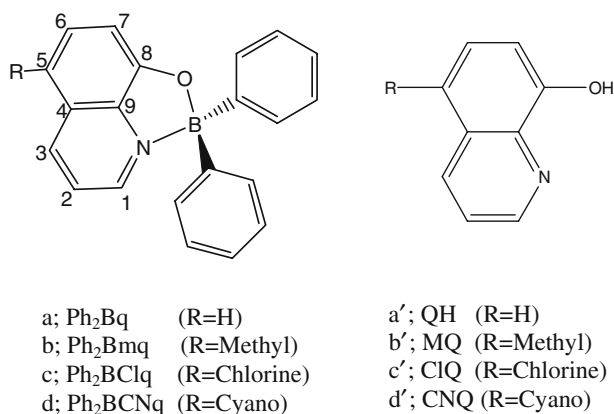


Fig. 1 Calculation structures of Ph₂Bq, 8-hydroxyquinoline (QH), and their substituted derivatives R=CH₃, Cl, CN

2 Calculation details

The ground-state (S_0) structures of the molecules studied here were optimized using the Kohn-Sham density functional theory (DFT) with 6-31G(d) basis set and the Becke three-parameter hybrid exchange-correlation functional known as B3LYP [16, 17]. To obtain the excited-state structures, the HF method was also used to optimize the S_0 structures. The ab initio CIS [18–20] method was adopted to obtain the first singlet excited-state (S_1) structures of the molecules based on the S_0 structures optimized using HF method. To obtain estimates of the vertical electronic transition energies which include some account of electron correlation, time-dependent density functional theory (TD-DFT) using the hybrid B3LYP functional was used [21]. The split-valence polarized 6-31G(d) basis set was employed. Typically, the lowest ten singlet roots were calculated to obtain the vertical transition energies. All calculations were carried out with the program package GAUSSIAN98 [22].

3 Results and discussion

3.1 Ground-state and excited-state structures

The ground geometries of Ph₂Bq and its derivatives were optimized with C_s point group symmetry constraints. The B–N bond lengths in Ph₂Bq and its derivatives are between 1.671 and 1.675 Å obtained using B3LYP method. The bond lengths of B–O are 1.523, 1.519, 1.521, and 1.528 Å for Ph₂Bq, Ph₂Bmq, Ph₂BClq, and Ph₂BCNq systems. The electron-donating methyl and chlorine groups increase the electron population on oxygen, which contributes to strengthening the coordination to B. In contrast, the electron-withdrawing cyano group decreases the electron population on oxygen. The B–N and B–O bond lengths in Ph₂Bq are, respectively, shorter than the Al–N and Al–O bond lengths in Alq₃, which means that boron-ligand bond is more covalent than that of aluminum-ligand [6]. Therefore, boron compounds are generally much more stable than the aluminum

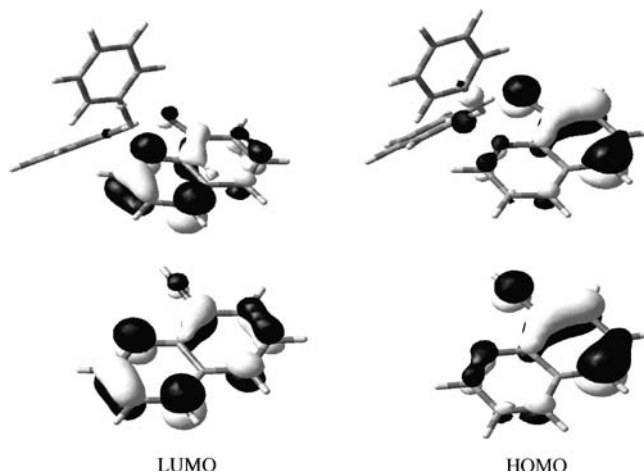


Fig. 2 Contour plots of the HOMO and LUMO obtained with the B3LYP/6-31G(d) method for Ph₂Bq and QH in the ground state

compounds, making them an attractive and potentially useful class of compounds for OLEDs.

Configuration interaction single optimizations were carried out for the S_1 states mentioned above. Interestingly, the QH ligands distort appreciably, while the others remain close to their ground-state for Ph₂Bq and its derivatives. This indicates that the emission properties of the QH ligand dominate the fluorescence of the complexes. It is well known that the structural shift is predominantly localized on one ligand for Alq₃ [6]. The differences of bond lengths between ground state and emission state for Alq₃, Ph₂Bq, and QH were compared in Table 1. The comparison of structural shifts among Alq₃, Ph₂Bq, and QH reveals that the structural changes of the QH ligand within Alq₃ and Ph₂Bq are very similar to the changes of the isolated QH molecule, which suggests that they may have a similar electronic transition mechanism.

3.2 The frontier molecular orbitals

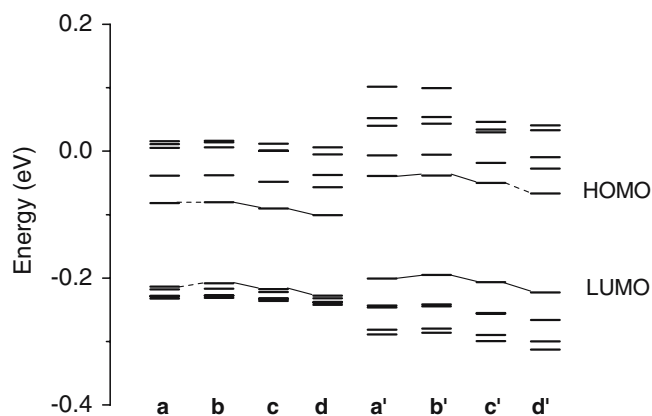
It is well known that the electron mobility is important for luminescence. Of all the electrons in a molecule, those residing in the frontier orbitals are least bound to the molecule and thus are most closely related to the charge transport properties of the material. In Fig. 2, we plotted the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Ph₂Bq and QH molecules. As one may see, the HOMO and the LUMO of Ph₂Bq largely preserve the electronic characteristic of individual QH with little contribution from the central atom (B), which is similar to Alq₃ [23, 24]. The highest occupied π orbital is mainly located on the phenolate side and the lowest unoccupied π^* orbital is mainly located on the pyridyl side for Ph₂Bq and QH molecules. Thus similar tendency of spectral property is expected, when they are substituted by the same group.

As the Fig. 3 shows, the HOMO–LUMO gaps of Ph₂Bq and its derivatives are smaller than those of the isolated ligands. Besides, when Ph₂Bq and QH are substituted by the

Table 1 Bond distance in fac-Alq₃, Ph₂Bq, and 8-hydroxyquinoline (QH) in the first excited state optimized with the CIS/6-31G(d) method

	Ligand	C1–C2	C2–C3	C5–C6	C6–C7	C7–C8	C1–N	C8–O
fac-Alq ₃ ^a	A	1.410 (0.001)	1.367 (0.002)	1.370 (0.001)	1.411 (0.000)	1.372 (0.001)	1.310 (0.001)	1.322 (0.000)
	B	1.409 (−0.001)	1.366 (0.001)	1.369 (0.000)	1.411 (0.000)	1.372 (0.000)	1.309 (−0.001)	1.323 (0.001)
	C	1.366 (−0.044)	1.414 (0.048)	1.417 (0.047)	1.366 (−0.045)	1.434 (0.063)	1.383 (0.074)	1.276 (−0.047)
Ph ₂ Bq	Q	1.361 (−0.049)	1.421 (0.055)	1.423 (0.059)	1.365 (−0.056)	1.429 (0.067)	1.375 (0.075)	1.271 (−0.044)
	QH	–	1.366 (−0.051)	1.415 (0.059)	1.424 (0.067)	1.363 (−0.050)	1.422 (0.059)	1.361 (0.069)

Values in parentheses are differences in bond distances in the ground and first excited states (a positive value means an increase), Å unit
^aRef. [6]

**Fig. 3** Energy levels obtained with B3LYP/6-31G(d) method for Ph₂Bq, QH, and their derivatives**Table 2** Absorption wavelengths (λ_{\max} in nm) computed at the various density functional theory (DFT) levels of theory using B3LYP geometries for Ph₂Bq

Methods	λ_{\max}
Local density approximation	
SVWN	513
Pure gradient-corrected	
BLYP	517
BP86	509
BPW91	479
Hybrid	
B3LYP	416
B3P86	414
B3PW91	414
MPW1PW91	400
Experimental	395

same group, the shifts of HOMO and LUMO energy level are similar. The gaps increase in the complexes substituted by electron-donating methyl and chlorine groups while decrease in the complexes substituted by electron-withdrawing cyano group.

3.3 Absorption and emission spectrum properties

With the prerequisite ground-state DFT calculation in hand, we proceeded to time-dependent calculation of all complexes. To predict the characters of low-lying singlet excited state, ten singlet excited states were calculated at the optimized

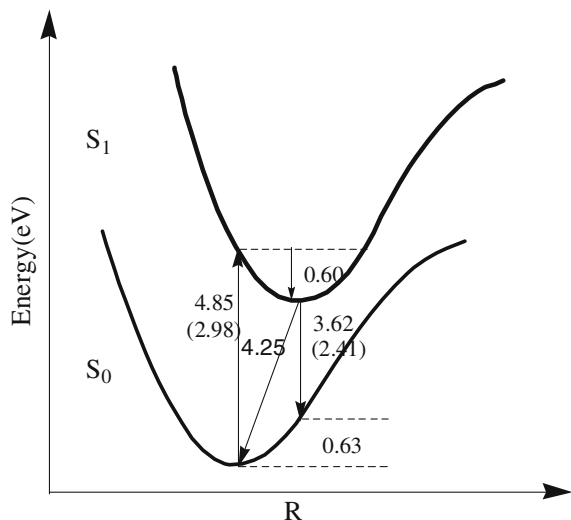
structure of the ground state for each complex. It is well known that TD-DFT calculations are trustworthy for calculating the excitation energies. To determine the functional having the best performance, various functionals – SVWN, BLYP, BP86, BPW91, B3LYP, B3P86, B3PW91, and MPW1PW91 were used to calculate the absorption λ_{\max} values of Ph₂Bq using the 6-31G(d) basis set. As is shown in Table 2, the calculations employing a variety of functional forms indicate that the λ_{\max} values vary significantly according to the employed functionals. The performance of the local density approximation (SVWN) and pure gradient-corrected functionals (BLYP, BP86, BPW91) is found to be poor. The results using the hybrid functionals (B3LYP, B3P86, B3PW91, and MPW1PW91) are much better. Here the B3LYP functional is used to predict the λ_{\max} values. To investigate the effect of the extension of the basis sets, we also used 6-311+G(d,p) and cc-pVTZ basis sets at the B3LYP level of theory by which the calculated absorption λ_{\max} values of Ph₂Bq is 405 and 403 nm, respectively. The enlarged basis sets decrease the λ_{\max} values by 11 and 13 nm. Although the current 6-31G(d) basis set contains some of the basis set truncation errors, we believe that major conclusions of the present work will be affected only slightly by the enlarged basis set.

As shown in the Table 3, the available experimental absorption values are well reproduced by our calculations with the deviations being 21, 21, and 5 nm for Ph₂Bq, ph₂Bmq, and QH, respectively. It is interesting to note that there are similar transition characters between complexes **a**~**d** and complexes **a'**~**d'**. With the exception of Ph₂BCNq whose absorption λ_{\max} value is attributed to HOMO-1→LUMO transition, all absorption λ_{\max} values are assigned to $\pi \rightarrow \pi^*$ transition from HOMO to LUMO being attributed to A'' → A'' transition. The transitions of complexes **a**~**d** are designated intra-ligand charge transfers (ILCT). Compared with the absorption λ_{\max} values of corresponding isolated ligand, the absorption λ_{\max} values of complexes **a**~**d** are red-shifted, which is consistent with the orbital characteristics analyzed above.

Furthermore, the spectrum illustrates the considerable effect that different substituents at the ligand have on the spectral properties of the complexes. There are similar shifts for the absorption λ_{\max} values of Ph₂Bq and QH, when they are substituted by the same group. The λ_{\max} values are red-shifted in the complexes substituted by electron-donating methyl and chlorine groups and blue-shifted in the complex

Table 3 The absorption spectrum with TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) and emission spectrum with TD-B3LYP/6-31G(d)//CIS/6-31G(d) (nm) for calculated models

	Absorption spectrum			Emission spectrum		Stokes shift
	λ/nm	Transition	Character	λ/nm	Transition	
Ph ₂ Bq	416 (395) ^a	A'' → A''	$\pi \rightarrow \pi^*$	514 (505) ^a	A'' → A''	98
Ph ₂ Bmq	434 (413) ^a	A'' → A''	$\pi \rightarrow \pi^*$	553 (529) ^a	A'' → A''	119
Ph ₂ BClq	432	A'' → A''	$\pi \rightarrow \pi^*$	547	A'' → A''	115
Ph ₂ BCNq	409	A'' → A''	$\pi \rightarrow \pi^*$	487	A'' → A''	79
QH	319 (314) ^b	A'' → A''	$\pi \rightarrow \pi^*$	383 (410) ^b	A'' → A''	65
MQ	331	A'' → A''	$\pi \rightarrow \pi^*$	405	A'' → A''	75
ClQ	330	A'' → A''	$\pi \rightarrow \pi^*$	405	A'' → A''	74
CNQ	319	A'' → A''	$\pi \rightarrow \pi^*$	372	A'' → A''	53

^aRef. [15]^bRef. [6]**Fig. 4** Diagram summarizing the CIS/6-31G(d) transition and relaxation energies (in eV) for Ph₂Bq. Parenthetical values correspond to TD-B3LYP/6-31G(d) results for comparison

substituted by electron-withdrawing cyano group. This variation is consistent with the orbital characteristics analyzed above.

Given the intrinsic role that excited-state formation plays in OLED devices, the excited-state property may be as significant as or greater significance than the ground-state property. Taking Ph₂Bq for example, the excited-state properties were studied. From the difference between the HF/6-31G(d) ground-state energy and the CIS/6-31G(d) excited-state energy, the adiabatic excitation energy is estimated to be 4.25 eV (without ZPE corrections) as presented in Fig. 4. The CIS calculation for Ph₂Bq also provides an estimate of the relaxed emission energy from the optimized CIS excited-state structure to the HF ground state ($S_1 \rightarrow S_0$). The emission is calculated to be ca. 342 nm (3.62 eV), which, as with the predicted absorption energies, severely overestimates the energy of the experimental photoluminescence emission at 505 nm [15]. TD-B3LYP/6-31G(d) calculation is carried out for Ph₂Bq at the CIS/6-31G(d)-optimized excited-state structure to obtain more accurate estimate of the emission energy.

The difference between the calculated absorption and emission wavelengths, ca. 85 nm, can be compared to the experimental Stokes shift for Ph₂Bq which is reported at 115 nm [15]. With TD-B3LYP, the emission energy is predicted to be ca. 2.41 eV corresponding to emission at ca. 514 nm, which is in much closer agreement with the experimental observation. The estimated Stokes shift at TD-B3LYP/6-31G(d) level of theory is 98 nm, which is in good agreement with the experimental value, lending support of the excited-state geometry shift described here. The calculated estimates for the absorption and emission energies, computed at the CIS/6-31G(d) and TD-B3LYP/6-31G(d) levels of theory, for Ph₂Bq are summarized in Fig. 4.

As shown in Table 3, the available experimental emission λ_{max} values are well reproduced by our calculations with the deviations being 9, 24, and 33 nm for Ph₂Bq, Ph₂Bmq, and QH, respectively. There are similar shifts for the emission λ_{max} values of Ph₂Bq and QH, when they are substituted by the same group. The emission λ_{max} values are red-shifted in the complexes substituted by electron-donating methyl and chlorine groups and blue-shifted in the complex substituted by electron-withdrawing cyano group.

The available experimental Stokes shifts are also well reproduced by our calculations with the deviations being 12 and 3 nm for Ph₂Bq and Ph₂Bmq. There are similar changes of Stokes shift, when Ph₂Bq and QH are substituted by methyl, chlorine, and cyano groups.

4 Conclusion

The ground-state geometries were optimized at the HF and B3LYP levels of theory, and the CIS method was adopted to obtain the first singlet excited-state (S_1) structures of the molecules. The HOMO and LUMO of Ph₂Bq are similar to those of QH. TD-B3LYP/6-31G(d) level of theory was employed to predict the absorption and emission energies for Ph₂Bq, QH, and their derivatives. When Ph₂Bq and QH are substituted by methyl, chlorine, and cyano groups, the changes of absorption λ_{max} values, emission λ_{max} values, and Stokes shifts are similar. This can further confirm that the emissions of Ph₂Bq and their derivatives originate mainly from

the electronic transitions within QH ligand. So we might tune the emission wavelengths and improve charge transfer properties through the substituent on the QH ligand. In addition, the studies also indicate that the possibility of a red or blue emission from Ph₂Bq derivatives can be predicted by analyzing QH and its derivatives.

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