Theoretical Study on Photophysical and Charge Transport Properties of 1,6-Bis(2-hydroxyphenol)pyridylboron Bis(4-*n*-butylphenyl)phenyleneamine Compound

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The absorption and emission spectra of 1,6-bis(2-hydroxyphenol)pyridylboron bis(4-*n*-butylphenyl)phenyleneamine were systematically calculated by time-dependent density functional theory (TD-DFT) level. These results are in good agreement with experiment ones. The charge transport properties were investigated within the framework of the charge hopping model. The results show that 1,6-bis(2-hydroxyphenyl)pyridineboron ((dppy)BF) functions as a electron transport group and triphenylamine as a hole transport group; the charge transport ability for the two types of carriers is not only high but also nearly balanced, which explains why it is an efficient single-layer electroluminescent device. On the basis of the large second-order polarizability value and high transparency, this compound has the possibility to be an excellent second-order nonlinear optical material. The main origin of this large second-order nonlinear optical response is charge transfer from the triphenylamine group to (dppy)BF.

1. Introduction

Organic light-emitting diodes (OLEDs) are of interest for displays because they show promise for low cost, they are large area devices, and they are compatible with low processing temperatures and flexible substrates. As a consequence, there have been increasing interest and research activities in this field, and enormous progress has been made in the improvements of color range, luminance efficiency, and device reliability.[1] The continued emergence for these applications will mainly depend on performance enhancement in such materials. The efficiency of OLEDs is determined by charge injection and transport, charge carrier balance, radiative decay of excitons, and light extraction. However, charge transport in organic materials is one of the most important properties in the performance of OLEDs,[2] organic field effect transistors,[3] and organic solar cells.[4] For OLEDs, the location of the electron−hole recombination zone where excitons are created and light is emitted is directly affected by the mobilities of electrons and holes in the materials.[5] An unbalanced charge transport results in an excess of one carrier type that does not contribute to light emission, and it can also result in an enhanced nonradiative recombination because of interactions of excitons with the charge carriers. Moreover, charge transport is one of the main limiting factors in determining operating voltage and luminance efficiency. High charge mobilities also reduce the resistance of the devices, leading to higher efficiency. Therefore, both efficiency and balance of charge transport within the organic layer(s) play a key role for the OLEDs. Understanding the relationship between molecular structure and charge transport properties of a material is a key point for providing guideline for device design, and a great theoretical research effort is currently being made in this regard.[6]

An OLED has an organic electroluminescence (EL) medium consisting of extremely thin layers (<0.2 μm in combined thickness) sandwiched by two electrodes. In a basic three-layer OLED structure, one organic layer is specifically chosen to transport holes, one organic layer is specifically chosen to transport electrons and the other organic layer is chosen to light. However, fabrication of multilayer devices is often tedious, difficult and more expensive than single-layer devices. In view of this, fabrication of single-layer device is a challenge of the next generation of high-performance OLEDs. In this device, the molecule acts as both efficient emitters and charge transport materials. Our group has fabricated a efficient single-layer device by using the 1,6-bis(2-hydroxyphenol)pyridylboron bis(4-*n*-butyl-phenyl)phenyleneamine ((dppy)BTPA) compound.[7] The reason this material exhibits high efficiency has remained illusive. Furthermore, a fundamental understanding of charge transport in organic molecules for potential applications as electronic device elements is very significant. In this paper, our goal is to shed light, with the help of quantum-chemical calculations, on photophysical properities of compound (dppy)-BTPA compound and elucidate why it is an efficient single-layer electroluminescent device.

2. Method and Computational Details

All calculations are performed at the density functional theory level with the B3LYP functional, involving the gradient correction of the exchange functional by Becke[8] and the correction functional by Lee, Yang and Parr,[9] employing a 6-31G* basis set using the Gaussian 03 program suite.[10] No symmetry or internal coordinate constraints were applied during optimization. The cation and anion states were optimized with an unrestricted B3LYP functional. The single-excitation configuration interaction (CIS)[11] method is adopted to obtain the

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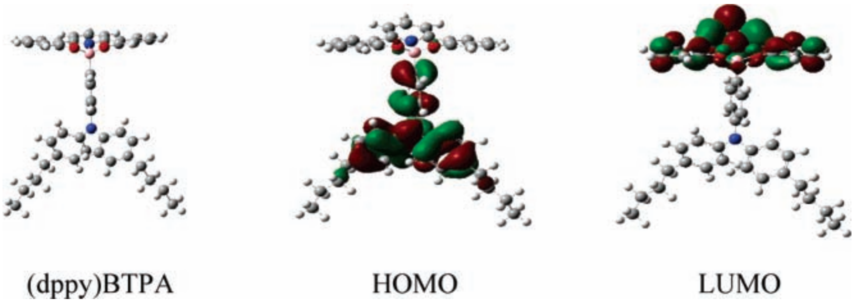

Figure 1. Molecular structure and the frontier molecular orbital of compound (dppy)BTPA.

first singlet excited-state (S_1) structures, based on the ground-state (S_0) structures. The absorption and emission energies were systematically investigated by time-dependent density functional theory (TD-DFT). Since the frontier molecular orbitals play a vital role in the process of charge transport, a sketch of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is shown in Figure 1. The HOMO is mainly localized on triphenylamine and the LUMO is localized on 1,6-bis(2-hydroxyphenyl)pyridineboron ((dppy)-BF).

There are two widely used theories for describing the charge mobilities in organic material, namely the band theory[12] and hopping model.[13] The hopping model is suitable to our case, because the intermolecular interactions are weak for the most thin-film amorphous materials in OLEDs. In this case, the charge transport mechanism can be described as involving a self-exchange electron transfer from a charged oligomer to an adjacent neutral oligomer. According to the semiclassical electron-transfer theory,[14] the electron-transfer rate, k_{ET}, can be described to a good approximation as

$$k_{ET} = \frac{4\pi^2}{h}\frac{1}{\sqrt{4\pi\lambda k_B T}}t^2 \exp\left(-\frac{\lambda}{4k_B T}\right) \tag{1}$$

where λ is the reorganization energy, t is the transfer integral, T is the temperature, and h and k_B are the Planck and Boltamann constants. The intermolecular transfer integral t characterizes the strength of electronic coupling between the two oligomers; the reorganization energy λ corresponds to the sum of geometry relaxation energies upon going from the neutral-state geometry to the charged-state geometry and vice versa. The reorganization energy is the sum of two energetic terms: the inner reorganization energy of the molecule and the reorganization energy of surrounding medium. In this case, the latter contribution can be neglected, so that the structural differences between the equilibrium configurations of π-conjugated units in neutral and ionic states become the dominant ones.[6f] There are two major parameters appearing in eq 1 that determine the electron-transfer rate: (i) the intermolecular transfer integral t, which should be maximized; (ii) the reorganization energy λ, which needs to be small for the efficient transport.

3. Results and Discussion

3.1. Electronic Spectrum. The optical properties of the compound (dppy)BTPA was examined both by absorption and emission spectroscopy at room temperature. This compound exhibits an intense absorption band at 304 nm and a moderately intense absorption band at 375 nm measured in chloroform. Upon irradiation by UV light (λ_{ext} = 365 nm), compound (dppy)BTPA exhibits bright yellow emission in chloroform, the emission maximum is at 550 nm (Figure 2).

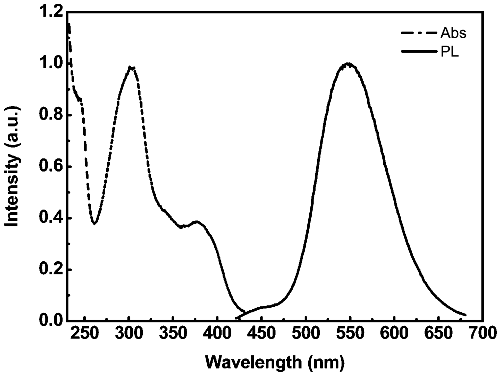

Figure 2. Absorption and emission spectrum measured in chloroform.

TABLE 1: Absorption and Emission Energy (nm), Oscillators Strengths, Major Contribution, and Experimental Data

	experiment	theory	f	major contribution
absorption	304	312	0.2769	HOMO → LUMO+4
absorption	375	384	0.0015	HOMO → LUMO
emission	550	576	0.0325	HOMO → LUMO

TABLE 2: Transfer Integral *t*(h) for Hole and *t*(e) for Electron of the Studied Molecule in Each Pathway

pathway	I	II	III	IV	V	VI	VII	VIII
t(h)/10^{-4} eV	17.7	62.6	844.9	13.6	183.7	289.8	178.3	24.7
t(e)/10^{-4} eV	12.3	295.3	504.8	537.4	268.1	112.9	24.5	213.6

Time-dependent density functional theory (TDDFT) has emerged as the currently most applied method for molecular computations due to its balance between accuracy and efficiency. Moreover, Han et al.[15] and our group[16] have proved that the TD-DFT method provides the most reliable results for the absorption and emission transition energies, compared with CIS and Zerner's intermediate neglect of differential overlap (ZINDO) methods. In Table 2, we summarize the absorption energies, emission energy, oscillator strength, and major contribution for the studied compound, as compared to experimental data. This result shows an intense absorption band at 312 nm and a moderately intense absorption band at 384 nm. This indicates that the B3LYP excitation energies and oscillator strength are in good agreement with the experimental ones. The main contribution of the corresponding maximal absorption corresponds to the promotion of one electron from HOMO to LUMO+4. A crucial feature is that the HOMO are localized mainly on triphenylamine and LUMO on the compound (dppy)-BF. Based on the structure obtained from the CIS method, emission spectrum is calculated by TDDFT method. Theoretical value (576 nm) is agreement to the experimental one (550 nm). This emission corresponds to the promotion of one electron from HOMO to LUMO (Figure 4). The absorption and emission properties mainly were determined by charge transfer between triphenylamine group and (dppy)BF.

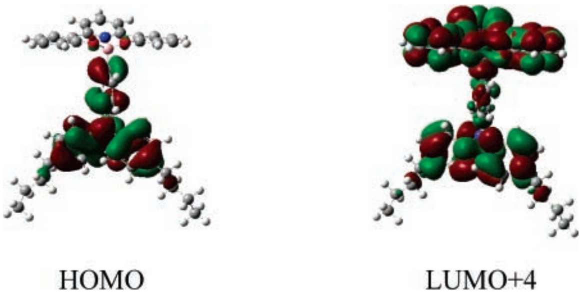

Figure 3. Molecular orbitals involved into the main absorption transition.

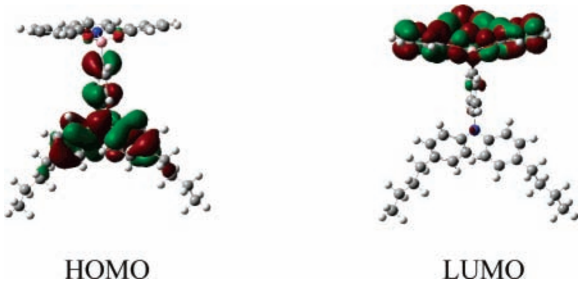

Figure 4. Molecular orbitals involved into the emission transition.

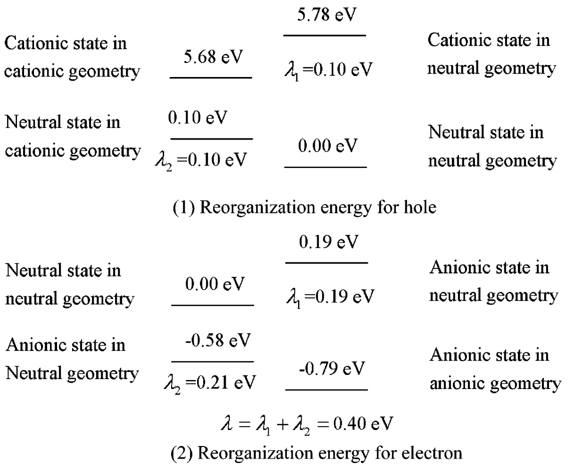

Figure 5. Sketch map of reorganization energy for compound (dppy)-BTPA.

3.2. Charge Transport. The internal reorganization energies for hole and electron transfer calculated by the DFT B3LYP/6-31G* method. Our calculations of the reorganization energy associated with different geometries of these two states are based on the hopping model schematically illustrated in Figure 5. The energy of optimized neutral compound (dppy)BTPA was used as reference and was set to zero, the others with respect to this reference are also listed. The reorganization energy computed for hole λ(h) is 0.20 eV, while for electron λ(e) is 0.40 eV. The value of λ(h) is smaller than that of TPD which is a typical hole transport material.[13d] The value of λ(e) is slightly larger than that of Alq which is a typical electron transport material.[5] This indicates that the compound (dppy)BTPA could be a good carrier transport material from the standpoint of reorganization energy. The slightly smaller λ(h) would suggest that the carrier mobilities of the hole are larger than that of the electron. The bond length modifications on going from neutral to negatively charged compound are mainly localized on the compound (dppy)BF. While those modifications on going from neutral to positively charged compound are mainly localized on triphenylamine. This indicates that compound (dppy)BF is functioned as a electron transport group and triphenylamine as a hole transport group. In our previous work, the (dppy)BF complex is a emitter material and has a superior electron mobility.[17] The triphenylamine group is known to be a superior hole mobility.[18] This implies that the functions of both (dppy)BF and triphenylamine do not alter in the (dppy)BTPA. And this is also in accordance with the frontier molecular orbitals (Figure 1). This indicates that (dppy)BTPA would act as both charge transport and emitters material. As a whole, the average bond length modifications upon oxidation (0.005) are much smaller than that upon reduction (0.014). The larger reorganization energy of the anion is rationalized by the fact that the geometry modifications upon reduction are more pronounced than upon oxidation. This indicates that the larger reorganization energy results from the larger bond length modifications.

The relative positions of the two molecules in the hopping complexes are necessary for calculating transfer integral for our studied compound in an amorphous film. An amorphous material can be considered as a collection of molecules with relative positions similar to that in crystalline state without long range order. A charge on a [(dppy)BTPA] can hop to others related by translational symmetry in neighboring unit cells. The charge can also hop to other molecules related by inversion symmetry in addition to translational symmetries in neighboring unit cells. The hopping pathways are shown in Figure 6. The direct coupling scheme HF−KT[19] was employed to calculate the transfer integral. Energy splitting values were calculated as the energy differences between HOMO and HOMO-1 (for hole transfer) or between LUMO and LUMO+1 (for electron transfer) of the hopping complex. *t* is half of the energy splitting. According to KT, a large value for *t*(h)/*t*(e) results from good overlap of the HOMOs and LUMOs of the two interacting partners. The transfer integral of I is 1 order of magnitude smaller than that of III, V, and VI because of longer distance between the two molecules. Among the eight pathways, there are four oligomers with effective overlap for LUMO and four oligomers with effective overlap for HOMO. The statistical average value for transfer integral *t*(e) is 246.1/10^{-4} eV, while for transfer integral *t*(h) is 203.0/10^{-4} eV. This indicates that there exits effective overlap for both HOMO and LUMO. The average value of transfer integral *t*(e) is slightly larger than that of transfer integral *t*(h). This feature does not like the Alq that transfer integral *t*(e) is larger by 1 order of magnitude than transfer integral *t*(h).[5] According to the eq 1, we can find that the two carrier mobilities are almost equivalent.

3.3. The Second-Order Polarizability. On the basis of the result of our calculation, this compound should have larger intramolecular charge transfer under the external electronic field. Moreover, in view of the energy of the UV−vis spectrum, the compound satisfies high transparency in the visible light area according to Gomper's research.[20] This transparency is worthy of remarks in considering practical applications. We anticipate that this compound offers some interesting new opportunities to second-order nonlinear optical materials. The second-order polarizabilty was calculated by using time-dependent density-functional theory (TDDFT) combined with the sum-over-states (SOS) method (TDDFT-SOS). First, 100 excited states were calculated using TDB3LYP model. Then those physical values were then taken as input of the sum-over-states (SOS) formula to calculate the second-order polarizability. Our group has used this method to investigate the NLO properties of a series of compounds.[21] Specific calculating information can be seen in the literature.[21a,e] Although 27 components of the β can be

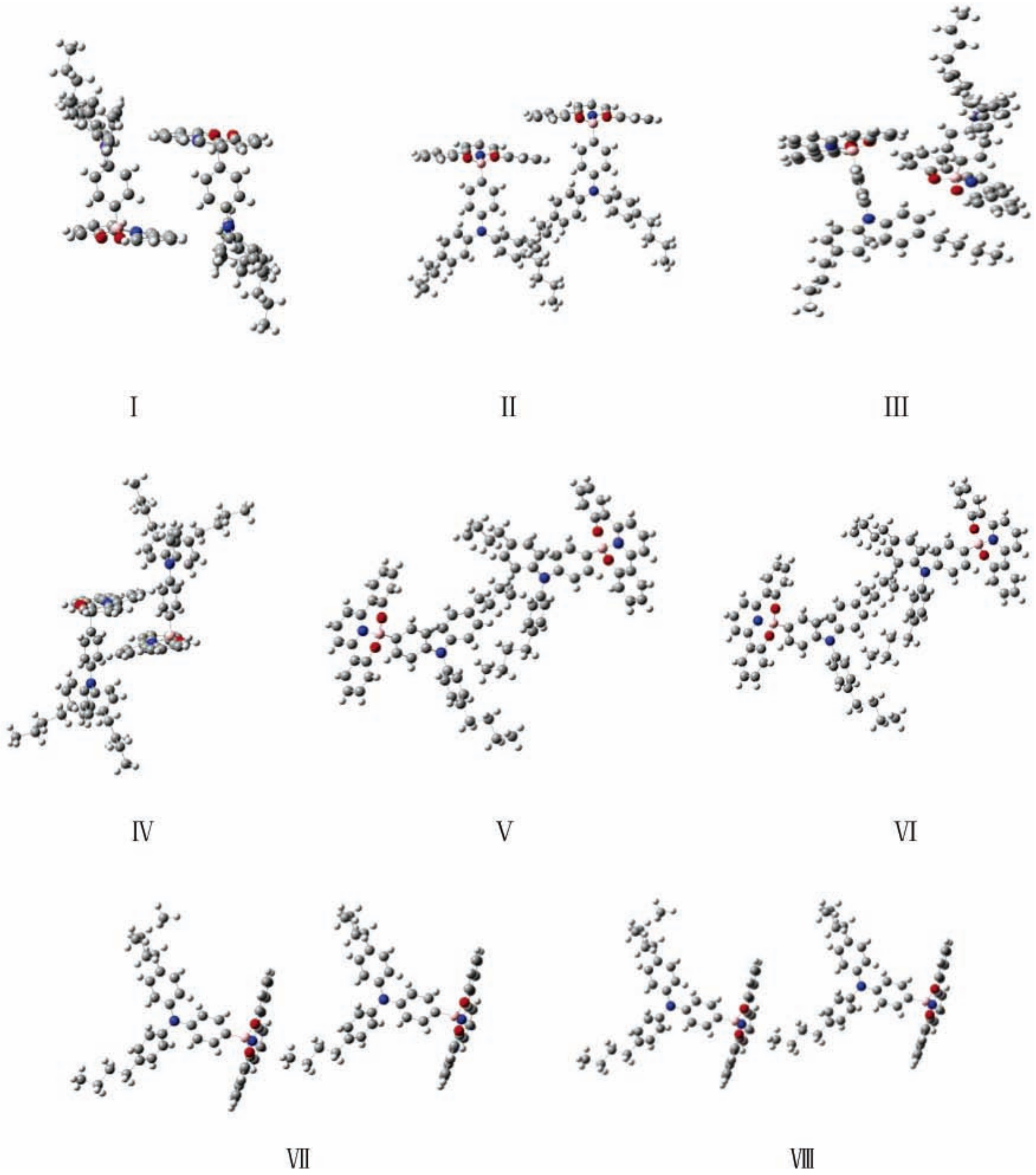

Figure 6. All charge hopping pathways for studied molecule.

computed, only the vector component along the dipole moment direction is sampled experimentally in electric field induced second-harmonic generation (EFISH) experiments. Thus, the β_{vec} is defined as[22]

$$\beta_{\mathrm{vec}} = \sum_{i=1}^{3} \frac{\mu_i \beta_i}{|\mu|}$$

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \qquad (2)$$

The calculated β_{vec}value is 58.1×10^{-30} esu, which is about 400 times larger than the average second-order polarizability of the organic urea molecule[22] and 12 times larger than that measured for highly π-delocalized phenyliminomethylferrocene complex.[23] This indicates that the compound has excellent second-order nonlinear optical response.

From the complex SOS expression, the two-level model that linked between second-order polarizability and a low-lying charge-transfer transition has been established. For the static case, the following expression is employed to estimate β_{CT}:

$$\beta_{\mathrm{CT}} \propto \frac{\Delta\mu f_{\mathrm{gm}}}{{E_{\mathrm{gm}}}^3} \qquad (3)$$

where $\Delta\mu$ is the change of dipole moment between the ground and *m*th excited state, f_{gm} is the oscillator strength of the transition from the ground state (g) to the *m*th excited state (m) and E_{gm} is transition energy. Thus, the second-order polarizability caused by charge transfer, β_{CT} is proportional to the optical intensity and inversely proportional to the cube of transition energy. The calculated value is 31.5×10^{-30} esu by using the two-level model. The contribution of the value calculated from the two-level model to the value obtained from summation over 100 states is about 54%, which has similar trend compared to the literature.[22,24] This indicates that two-level model can be applied to our studied compound and explain the mechanism of the charge transfer. As a result, a larger f_{gm} with a lower E_{gm} will lead to a larger the second-order polarizability. From Table 1 and Figure 2, we can know that charge transfer from triphenylamine group to (dppy)BF plays a key role in the second-order nonlinear optical response.

4. Conclusion

The equilibrium geometries of natural, anionic, and cationic states were optimized by means of the B3LYP method at the 6-31G* basis sets in this paper. The molecular structure of the first singlet excited state (the emission state) was optimized with the CIS method. The absorption and emission energies have been calculated with the TDDFT method at the optimized geometries. The fact that the calculated energies are in good agreement with the experimental ones provides support for the utility of the optimized geometries. The orbital pattern suggests that the absorption and emission transition can be attributed to charge transfer between triphenylamine group and (dppy)BF.

The carrier mobilities of hole are larger than that of electron from the standpoint of reorganization energy, while two carrier mobilities are almost equal from the standpoint of the transfer integral. The transfer integral is the most crucial parameter affecting the charge transport properties, because the k_{ET} is proportional to the square of transfer integral according to eq 1. Therefore, the charge transport ability for the two types of carriers is nearly balanced. This explains why it is an efficient single-layer electroluminescent device. The (dppy)BF is functioned as a electron transport group and triphenylamine as a hole transport group. Thus, combining the excellent hole and electron transport group into one molecule may become an excellent single-layer device in the electroluminescence field. Further studies on these properties are in progress in our group.

In view of the merit of large second-order polarizabilty and high transparency, this compound can become an excellent kind of material in the second-order nonlinear optical field. The analysis shows that the charge transfer from triphenylamine group to (dppy)BF makes dominant contributions to the second-order nonlinear optical response.

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