J. Phys. Chem. A **2007,** *111,* 2739−2744

Theoretical Study on Photophysical Properties of Phenolpyridyl Boron Complexes

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Received: November 19, 2006; In Final Form: January 15, 2007

Organoboron complexes have potential application in organic light-emitting devices (OLEDs). Our group has synthesized four phenolpyridyl boron complexes (*Inorg. Chem.* **2006**, *45*, 2788), which can function as an electron transport materials (ETM), white and blue emitters, and exhibit high efficiency and stability. To reveal the relationship between the properties and structures of these functional materials, theoretical analysis of spectral properties and electronic structures of these complexes was systematically characterized with the B3LYP and 6-31G* basis set. The calculated absorption and emission spectra of these systems are in good agreement with the experimental ones. It is clear seen that these transitions are charge transferred along 2,6-bis(2-hydroxyphenyl)pyridyl boron moiety, and the contribution of boron atom in these compounds to the main transition orbitals is vanishingly small. The substitution of methyl and methoxyl for hydrogen does not change the absorption wavelengths and transition natures, but influences the radioactive efficiencies and electron transport properties, which are observed and discussed in detail. Furthermore, large red shifts of fluorescence are caused by replacing the hydrogen with CN or NO_2 groups, which indicates that they are potential candidates as green-light-emitting materials. These results are favorable to further understanding the photophysical properties of this kind of complexes.

1. Introduction

Since Tang and Vanslyke developed efficient multilayered organic light-emitting diodes (OLEDs) using tris-(8-hydroxyquinoline) aluminum (Alq_3) as the emission and electron transport material,[1] OLEDs have received extensive attention for the potential use in the next-generation full-color flat-panel displays,[2,3] and some have already been commercialized.[4] Nevertheless, the widespread use of OLED-based displays relies on wide availability of high-performance red/green/blue (RGB) light-emitting materials. OLEDs based on small molecules typically comprise three layers—the electron transport layer, the emitter layer, and the hole transport layer, to facilitate charge transport and charge recombination, and enhance the overall efficiency of the devices.[5−7] The other commonly used strategy in enhancing device efficiency is to dope emitters into hosting layers.[8] Although very bright and efficient OLEDs have been achieved by using multilayer device structures or the doping strategy, from a manufacturing point of view, devices have fewer layers and do not require doping are much more desirable because they simplify the fabrication process, allow better control of the uniformity of the device, and minimize the problems of interfacial diffusions.[9] One way to reduce the number of layers in OLEDs is to use molecules that are capable of functioning as efficient emitters as well as charge-transport materials, i.e., bifunctional or multifunctional molecules.[10]

The development of high-performance materials is a key issue for the fabrication of high-performance organic EL devices. The most well-known electron transport material used in OLEDs known to date is Alq_3, in which three 8-hydroxyquinolato (q) ligands chelate to the Al(III) ion in an octahedral environment.[11] Alq_3 is also a good green emitter in OLEDs. Moreover, Zhang and Frenking have studied Alq_3 by quantum chemical analysis, which is very helpful for understanding its chemical bonds and photophysical properties.[12] Recent study finds that three-coordinate organoboron compounds have emerged as promising materials for OLEDs. For example, Shirota and others have reported several three-coordinate organoboron compounds as electron transport/hole-blocking materials for OLEDs.[13−20] Our investigation on boron compounds was therefore motivated by their potential application in OLEDs. In our previous work, we have reported white light emission EL devices which come from exciplex by introducing mixed phenolpyridine functional groups to tetrahedral coordinated boron compounds that exhibited electron mobility and emitting properties.[21,22] To improve the performance of the boron compounds, we modified the boron molecule by attaching the triphenylamine group to the boron center by B−C bond to produce a novel molecule, which can be used as an emitting material to fabricate an efficient single-layer electroluminescent device.[23] Our theoretical studies show that 2,6-bis(2-hydroxyphenyl)pyridine boron ((dppy)BF) functions as an electron transport group and triphenylamine as a hole transport group. Moreover, the charge transport ability for the two types of carriers is not only high but also nearly balanced.[24] Recently, our group have synthesized four mixed phenol-pyridine derivatives 2,6-bis(2-hydroxyphenyl)pyridyl boron naphthalene (**1**), 2,6-bis(2-hydroxy-5-methylphenyl)-pyridyl boron naphthalene (**2**), 2,6-bis(2-hydroxyphenyl)pyridyl boron 2-methoxylbenzene (**3**), and 2,6-bis(2-hydroxy-5-methylphenyl)pyridyl boron 2-methoxylbenzene (**4**). These compounds can function as an electron transport material (ETM)

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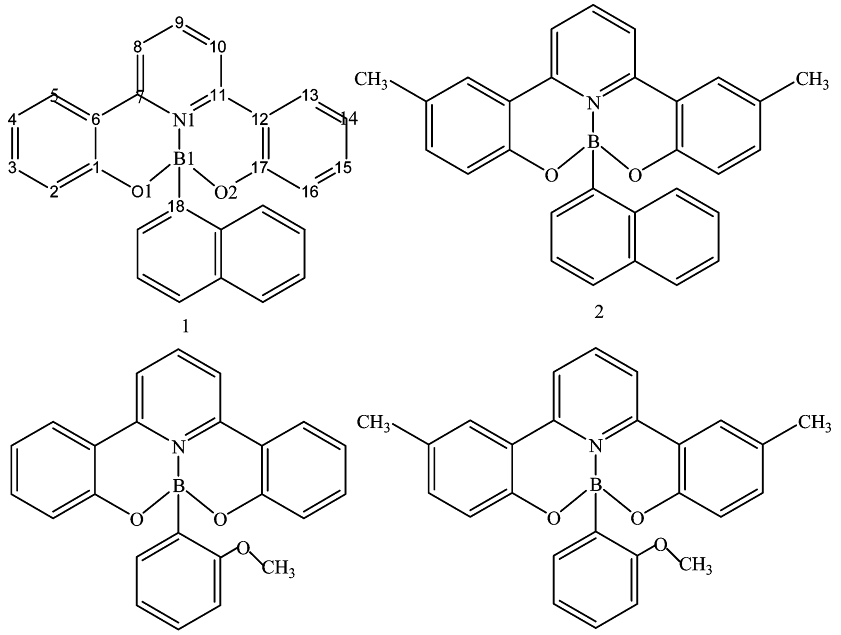
10.1021/jp067685v CCC: $37.00



1 2 3 4

Figure 1. Molecular structures of studied systems 1−4.

TABLE 1: Selected Bond Lengths (Å) for Systems 1 and 4: Ground States (S_0) and First Exited States (S_1)

	$1S_0$	exp	$1S_1$	$4\ S_0$	exp	$4S_1$
B(1)−O(1)	1.465	1.447	1.470 (−0.005)	1.472	1.478	1.478 (−0.006)
B(1)−O(2)	1.466	1.459	1.471 (−0.005)	1.459	1.460	1.467 (−0.008)
B(1)−N(1)	1.617	1.594	1.550 (0.067)	1.621	1.613	1.541 (0.080)
B(1)−C(18)	1.624	1.614	1.634 (−0.010)	1.631	1.624	1.642 (−0.007)
O(2)−C(17)	1.333	1.339	1.297 (0.036)	1.341	1.354	1.288 (0.053)
O(1)−C(1)	1.341	1.349	1.315 (0.026)	1.348	1.357	1.289 (0.059)
N(1)−C(11)	1.366	1.352	1.383 (−0.017)	1.364	1.371	1.385 (−0.021)
N(1)−C(7)	1.369	1.376	1.387 (−0.017)	1.367	1.374	1.386 (−0.019)

and emitter material and exhibit high efficiency and stability.[25] In this paper, we focus on studying photophysical properties of these systems and revealing the relationship between the properties and structures of these functional materials with the assistance of quantum-chemical calculations.

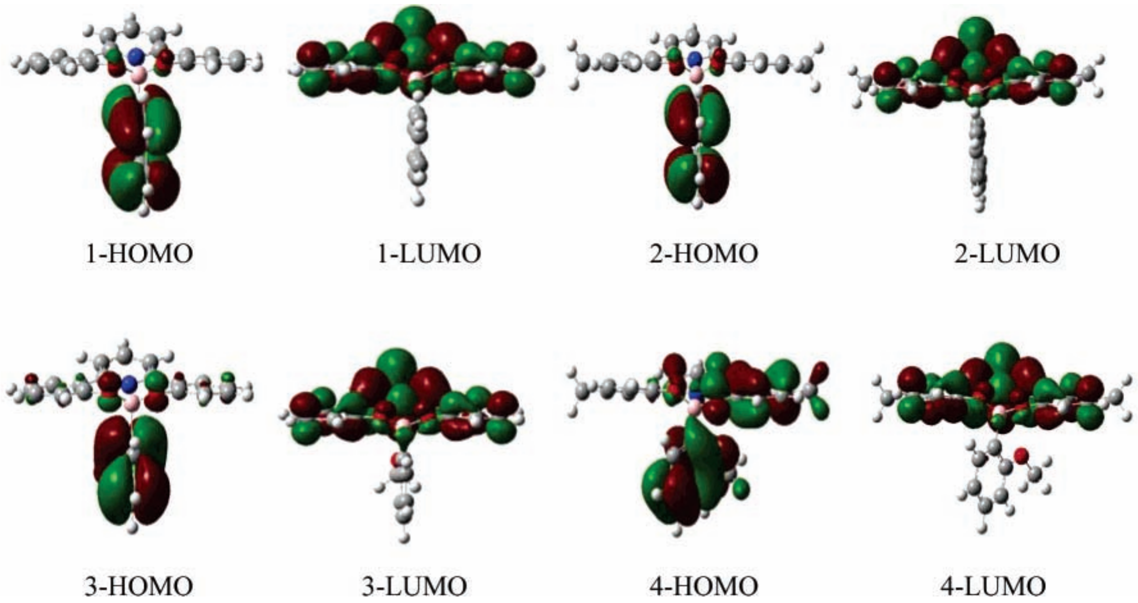
2. Calculational Details

All calculations are performed at the density functional theory level with the B3LYP functional, involving the gradient correction of the exchange functional by Becke[26,27] and the correction functional by Lee, Yang, and Parr,[28] employing 6-31G* basis set using Gaussian 03 program suite.[29] No symmetry or internal coordinate constraints were applied during optimization. The anion states were optimized with an unrestricted B3LYP functional within the same basis set. The single-excitation configuration interaction (CIS)[30] method is adopted to obtain the first singlet excited-state (S_1) structures, based on the ground state (S_0) structures. 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, recent works demonstrate TDDFT method have good accuracy for a wide range of organometallic systems.[31] Our group[32] has also proven that TDDFT method is a more reliable method to study the absorption and emission transition energies, compared with CIS and Zerner's intermediate neglect of differential overlap (ZINDO) methods. Thus, the absorption and emission energies of our models were systematically investigated by time-dependent density-functional theory (TD−DFT).

3. Results and Discussion

3.1. Molecular Structures. The optimized geometrical structures of the studied systems 1−4 are shown in Figure 1. The selected bond lengths of systems 1 and 4 are given in Table 1, associated with data from experimental determinations. The results are found to be in good agreement with the experimental ones. This indicates that the adopted basis set and functional are feasible to the studied systems. Comparison has been made between systems 1 and 4. The substitution of methyl and methoxyl for hydrogen leads to an increase of bond lengths for system 4 compared with system 1, which might decrease the rigidity and increase the possibility of vibration relaxation. Furthermore, the bond lengths in systems 2 and 3 also are slightly longer than that of system 1. Subsequently, we studied the excited states structures of systems 1 and 4. The first singlet excited-state (S_1) structures were optimized at the 6-31G*/CIS ab initio level. The main bond distances and changes of them (in parenthesis) from S_0 to S_1 state are shown in Table 1. The pronounced geometrical changes for systems 1 and 4 are the B−N and C−O bonds. Moreover, the variation of excited-state bond lengths for system 1 is slightly smaller than that of system 4, which means that system 1 appears to be more rigid with respect to excitation.

3.2. Frontier Molecular Orbitals. Molecular charge transporting property is related to the distribution of HOMO and LUMO.[33] In general, a more delocalized LUMO would allow better intermolecular orbitals overlap which would lead to easier electron transport by hopping. On the other hand, the more localized LUMO will not be favorable for electron transport. A


1-HOMO 1-LUMO 2-HOMO 2-LUMO

3-HOMO 3-LUMO 4-HOMO 4-LUMO

Figure 2. The frontier molecular orbitals of studied systems 1−4.

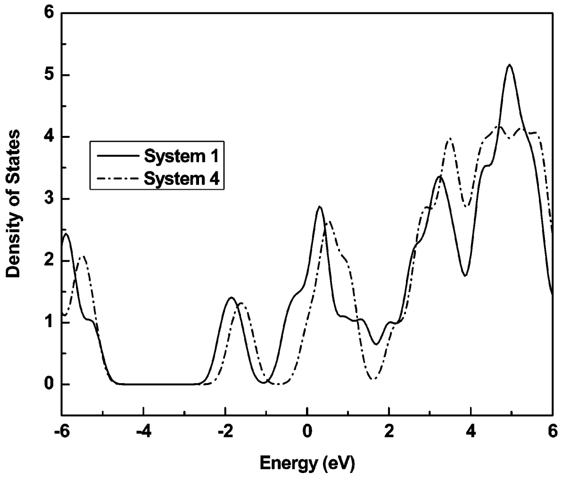


Figure 3. Total of density of states of systems 1 and 4.

sketch of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is shown in Figure 2. For systems 1−3, the HOMO is mainly localized on either benzene or naphthalene moiety. However, for system 4, the HOMO is delocalized on the both benzene and 2,6-bis(2-hydroxy-5-methylphenyl)pyridyl boron moiety. The LUMO is mainly localized on 2,6-bis(2-hydroxy-5-methylphenyl)pyridyl boron moiety for systems 1−4, showing that the substitution of methyl and methoxyl for hydrogen does not cause a significant change in LUMO distribution. But it can tune the distribution of the HOMO orbital for system 4. Our previous study shows that systems 1−4 can function as both an electron transport materials (ETM) and emitter materials in electroluminescent (EL) devices. To obtain high quantum efficiency in OLEDs device, the material requires high electron carrier mobility. Our calculations suggest that systems 1−3 have similar electron carrier mobilities, while system 4 could not be an effective ETM due to its considerably delocalized HOMO electron density, which might enhance hole transport ability and result in an unbalanced charge transport, and enhance nonradiative recombination because of interactions of excitons with the charge carriers. Furthermore, the total density of states (DOS) of systems 1 and 4 has been compared in Figure 3. The energies of LUMO are −2.01 and −1.77 eV for systems 1 and 4, respectively, and it is obvious that system 1 has more DOS on LUMO than system 4 has. This character suggests that system 1 can accommodate more electrons in LUMO, and thus system 1 has larger electron mobility compared to system 4.

TABLE 2: Calculated Ground-State Properties for the Systems 1−4: S_1 Excitation Energies (eV), Oscillator Strengths (*f*), Main Contribution (Configuration Interaction Expansion Coefficients Are in Parentheses), and Ground-State Dipoles (D)

	absorption	exp. absorption	f	main contribution	dipole
1	309	281	0.2287	HOMO-4 → LUMO (67%)	5.2985
2	310	282	0.1986	HOMO-4 → LUMO (67%)	5.3743
3	303	286	0.1734	HOMO-4 → LUMO (67%)	5.4610
4	307	287	0.1653	HOMO-4 → LUMO (71%)	5.1373

3.3. Electronic Spectrum. The S_1 excitation energies, oscillator strengths, and ground-state dipole moments have been calculated and listed in Table 2. All of the S_1 transitions are characterized by electron promotion from the HOMO-4 to the LUMO and are polarized along the 2,6-bis(2-hydroxy-5-methylphenyl)pyridyl boron moiety (Figure 4). The calculated transition energies agree with the experimental results. From Table 2 and Figure 4, we can draw the following conclusions: (1) These orbitals are π symmetry characters, and so the main UV−visible absorption features are best described as $\pi \rightarrow \pi^*$ transitions. Furthermore, the boron atom in these molecules have vanishingly small contribution to the main transition orbitals. (2) All the systems have similar absorption wavelengths and the same transition natures. This character indicates that the attachment of methyl and methoxyl does not change the absorption wavelengths and transition natures. (3) The oscillator strengths of these systems decrease as follows: 1 > 2 > 3 > 4. The oscillator strength[34] for an electronic transition is proportional to the transition moment. The transition moments of systems 1−4 are 1.5285, 1.4219, 1.3152, and 1.1674 au, respectively. The transition moment reflects the transition probability from the ground state to the excited state. This means the transition probability of these systems decrease as follows: 1 > 2 > 3 > 4. In general, the higher the transition probability to the first excited state, the greater the emission probability and fluorescence kinetic constant which can be obtained.[35] The substitution of methyl and methoxyl for hydrogen significantly reduces transition probability. Our results suggest that efficiency

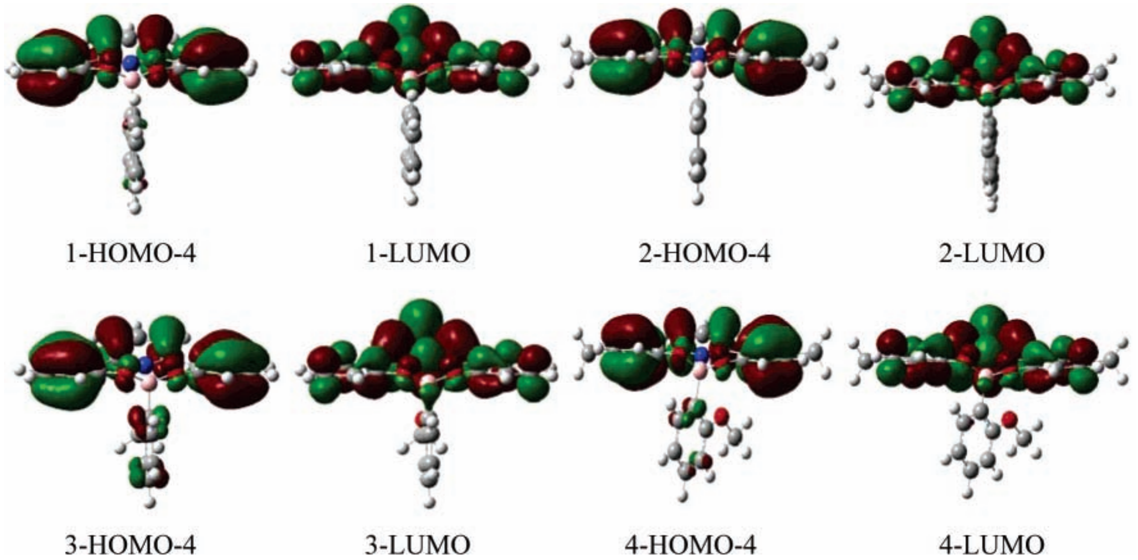


Figure 4. Molecular orbitals involved into the main absorption transition of systems 1−4.

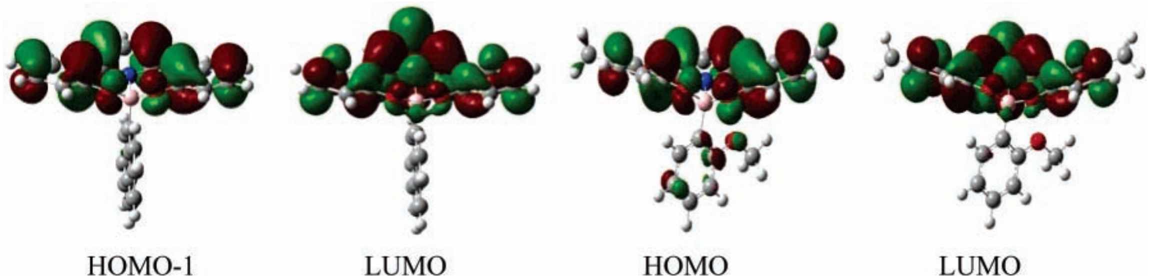


Figure 5. Molecular orbitals involved in the main emission transition of systems 1 and 4.

of our studied systems decreases as follows: 1 > 2 > 3 > 4, which is in accordance with the experimental results. (4) Except system 4, the dipole moments increase as follows: 1 < 2 < 3. Studies show that the charge carrier mobility through the organic thin film strongly depends on dipole moment.[33,36,37] The molecule with larger dipole moment has lower carrier mobility and strongly depends on electric field. Although system 4 has the smaller dipole moment, its rigidity, absorption probability, and density of states are reduced due to the substitution of methyl and methoxyl for hydrogen which might decrease the emission efficiency.

Subsequently, we calculated emission maxima of systems 1−4, which are at 437, 446, 428, and 470 nm, respectively, while experimental values are at 461, 478, 459, and 479 nm. This indicates that our adopted methods can reflect the variable trend of the emission spectra. For systems 1 and 2, the emission corresponds to the promotion of one electron from HOMO-1 to LUMO, while for systems 3 and 4, it corresponds to the promotion of one electron from HOMO to LUMO. Interestingly, these emission transition mainly distribute on the 2,6-bis(2-hydroxy-5-methylphenyl)pyridyl boron moiety and the contribution of boron atom is vanishingly small. To be simple, we only give the transition orbitals of systems 1 and 4 (Figure 5), and the other systems also have similar distributions. The analysis mentioned above show that the emission properties of the 2,6-bis(2-hydroxy-5-methylphenyl)pyridyl boron dominate the fluorescence of these boron compounds.

Color tuning of the organic light-emitting devices is a key technology to develop a full-color flat-panel display.[38] Previous study has show that CN and NO_2 groups have obvious influence on the emission properties of some luminescent materials.[39,40] Subsequently, we would like to examine how much the fluorescence of system 1 can be shifted by introducing CN or NO_2 groups. The position of CN or NO_2 groups is the same to that of CH_3 in system 2. Their emission energies were calculated to be 530 and 575 nm, respectively, which can be explained that the introduction of CN and NO_2 groups decreases the LUMO energy level through π orbital interactions. Furthermore, the distributions of frontier orbitals and transition natures are also similar to that of system 1. Further studies on these properties are in progress in our group. We hope that they are potential candidates as green-light-emitting materials in OLEDs.

TABLE 3: Variations of Selected Bond Lengths (Å) for Systems 1−4 in the Anion, Relative to the Neutral Systems

	1	2	3	4
B(1)−O(1)	0.014	−0.007	−0.004	−0.010
B(1)−O(2)	0.013	−0.008	−0.016	−0.003
B(1)−N(1)	−0.067	−0.072	−0.060	−0.080
B(1)−C(18)	0.023	0.040	0.044	0.045
O(2)−C(17)	0.005	−0.017	−0.016	−0.018
O(1)−C(1)	0.006	−0.016	−0.018	−0.016
N(1)−C(11)	0.040	0.030	0.039	0.032
N(1)−C(7)	0.039	0.030	0.031	0.027

3.4. Anion Properties. Our studied systems can act as electron transport materials. To further understand the effects of charge injection on the molecular conformational stability and electron trapped in these molecules, we optimized the anion geometry (i.e., the neutral molecule in the presence of an extra electron). The variations of selected bond lengths relative to the neutral systems are given in Table 3. The main influence of the injection of one negative charge is focused on the change of B(1)−N(1) bond. The optimized structure for anion show small structural changes relative to the natural molecules, which are nearly equal to that of Alq_3.[41] On the basis of the small

TABLE 4: Electron Affinities and Electron Extraction Potentials for Systems 1−4 (in eV)

	EA(v)	EA(a)	EEP
1	−0.627	−0.801	0.755
2	−0.560	−0.735	0.793
3	−0.397	−0.595	0.902
4	−0.382	−0.564	0.942

structural relaxation, we expect that these systems would exhibit a relatively high structural stability versus the injection of one negative charge. Thus, these systems have a better electron transport property.

On the other hand, we calculated vertical electron affinities EA(v), adiabatic electron affinities EA(a), and electron extraction potentials (EEP). Electron affinities can be viewed as the variations of energy adding an electron or extracting a hole. The negative electron affinities imply that adding an electron to the molecule will release energy. The ability to obtain an electron increases with enhancing electron affinities. From Table 4, we can find that accepting an electron of system 1 is much easier than that of system 4. Electron extraction potentials have also the same trend. On the basis of these results, the abilities of accepting electron are in the order of 1 > 2 > 3 > 4 for these systems, which is in agreement with the order of the performance of OLEDs.

4. Conclusion

In this paper, we have optimized ground and excited molecular structures of four phenol-pyridyl boron complexes. The absorption and emission energies have been calculated with time-dependent density-functional theory at the optimized geometries. The fact that the calculated energies are in good agreement with the experimental ones provides support for the utility of adopted method and basis set. These transitions are charge transfer along 2,6-bis(2-hydroxyphenyl)pyridyl boron moiety. Moreover, the contribution of boron atom in these molecules to the main transition orbitals is vanishingly small. The attachment of methyl and methoxyl does not change the absorption wavelengths and transition nature, but changes the transition probability.

To our studied systems, the order (1 > 2 > 3 > 4) of the luminescence quantum yields and performance of OLEDs can be explained from the following two aspects:

(1) The oscillator strengths of these systems decrease as follows: 1 > 2 > 3 > 4. The higher transition probability to the first excited state, the system possesses the greater emission probability and fluorescence kinetic constant will get.

(2) From the standpoint of frontier molecular orbitals, dipole moment, density of states, variations of ground or anion geometries, and electron affinities, the substitution of methyl and methoxyl for hydrogen decreases the abilities of electron injection and electron transport.

Replacing the hydrogen of system 1 with CN or NO_2 groups can cause large red shifts of fluorescence, indicating that they are potential candidates as green-light-emitting materials in OLEDs. We hope that our theoretical study can give some hints to experimentalists for developing a wide variety of useful OLEDs.

Acknowledgment. The authors acknowledge the financial support from the National Natural Science Foundation of China (Project Nos. 20373009, 20573016 and 50225313) and the Major State Basic Research Development Program (2002CB613401). A grant from Science Foundation for Young Teachers of Northeast Normal University (No. 20060307) is also greatly appreciated.

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