Excitation Spectra of Dibenzoborole Containing π-Electron Systems: Controlling the Electronic Spectra by Changing the $p_\pi-\pi^*$ Conjugation

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We report time-dependent density functional theory calculations of the vertical excitation energies for the singlet states of three-coordinate 5H-dibenzoborole (DBB) derivatives and four-coordinate 5-fluoro-5H-dibenzoborole ion (FDBB) derivatives. These molecules show remarkable hypsochromic (blue) shifts in their fluorescence spectra and bathochromic (red) shifts in their absorption spectra when the bridging boron atoms change their coordination number from three to four. We constructed a series of derivatives of DBB and FDBB and studied how the energies of the electronic excitations change. The states with prominent oscillator strength in all of the DBB and FDBB derivatives show similar shifts of their excitation energies upon coordination. The three-coordinate DBB derivative 5-(2,4,6-triisopropylphenyl)-2,8-dimethoxy-3,7-bis[*p*-(*N,N*-diphenylamino)phenyl]-5H-dibenzo[*d,b*]borole has an intense absorption at 3.25 eV, which shifts in the four-coordinate FDBB derivative 5-fluro-5-(2,4,6-triisopropylphenyl)-2,8-dimethoxy-3,7-bis[*p*-(*N,N*-dip henylamino)-phenyl]-5H-dibenzo[d,b]borole ion to 3.17 eV. The experimental absorption peaks are 3.43 and 3.31 eV, respectively. In addition, we investigated and analyzed the nature of these electronic excitations using attachment/detachment density plots, with which we characterized the changes in electron density that arose from the excitations.

Introduction

Boron-containing π-conjugated extended systems have been investigated both experimentally and theoretically for the last fifteen years because of their extensive applications in opto-electronics and in materials that can be used in information processing.[1−14] Some suggested applications for using boron-containing molecular devices include chemical sensors, fluorescence switches and probes, nonlinear optical devices, molecular photonic wires, optical gates, optoelectronic devices, and photonic devices. Some of these materials show remarkable fluorescence phenomena and were recently used in the fabrication of molecular switches.[15−17] Boron-containing π-conjugated systems also have been investigated for use in the design, synthesis, and characterization of material and technological applications.[18−23]

In this paper, we report a series of theoretical calculations on the structural properties and excited electronic spectra of a series of dibenzoborole derivatives. Three-coordinate 5H-dibenzoborole (DBB) and four-coordinate 5-fluoro-5H-dibenzoborole anion (FDBB) represent the basic skeleton structures for the series. The three-coordinate and four-coordinate DBB/FDBB compounds exhibit remarkable fluorescence/absorption changes, which can be employed to create an "on/off" fluorescence device controllable by changing the $p_\pi-\pi^*$ conjugation. The $p_\pi-\pi^*$ conjugation between the vacant p_z orbital on a three-coordinated boron atom and the π^* orbital of the attached carbon π-conjugated moiety is responsible for this unique property.[24−30] In the system the "on/off" control of the $p_\pi-\pi^*$ conjugation by the addition of a donor molecule, such as a fluoride ion, changes the lowest-unoccupied molecular orbital (LUMO)
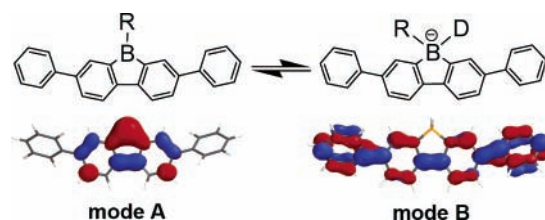
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Figure 1. The "on/off" control of the $p_\pi-\pi^*$ conjugation in the LUMO of DBB/FDBB π-electron systems. Adapted from ref 25.

delocalization from "mode A" to "mode B," as shown in Figure 1. The resulting LUMO in mode B is still delocalized over the carbon framework, though, as in a normal π-conjugated system. The previously studied DBB and FBDD derivatives,[15] the three-coordinate 5-(2,4,6-triisopropylphenyl)-2,8-dimethoxy-3,7-bis-[*p*-(*N,N*-diphenylamino)phenyl]-5H-dibenzo[*d,b*]borole and the four-coordinate 5-fluoro-5-(2,4,6-triisopropylphenyl)-2,8-dimethoxy-3,7-bis[*p*-(*N,N*-diphenylamino)phenyl]-5H-dibenzo[*d,b*]borole anion are listed in Tables 1 and 2 and in Figures 2 and 3 as molecules **7** and **18**, respectively. Few experimental results have been reported for the absorption and fluorescence spectra of DBB compounds.[15,31,32] In addition, only two theoretical studies of electronic spectrum of DBB compounds have been reported.[33,34]

Computational Details and Methods

Density functional theory (DFT)[35−38] has become a prominent tool in computational chemistry to predict a variety of ground-state properties of molecules. DFT does not require significantly more computer resources than a Hartree−Fock calculation and therefore, in general, is much more efficient than the post-Hartree−Fock methods. Since DFT methods have been accepted

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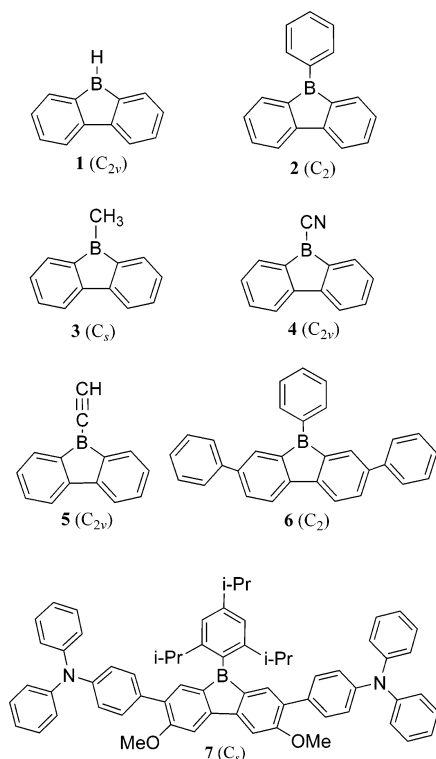*J. Phys. Chem. A, Vol. 110, No. 7, 2006* **2435**

Figure 2. Structures of the three-coordinate DBB derivatives.

TABLE 1: TDDFT Excitation Energies (in eV) for the Most Intense Excitations in the Three-Coordinate BBD Derivatives Calculated Using B3LYP/6-31+G*

	attached groups				energy and
no.	R$_1$	R$_2$	X	state	oscillator strength
1	H	H	H	3B$_2$	4.84 (0.91)
2	H	—ph	H	4B	4.75 (0.67)
3	H	—CH$_3$	H	4A″	4.85 (0.91)
4	H	—CN	H	3B$_2$	4.79 (0.75)
5	H	—C≡CH	H	3B$_2$	4.77 (0.76)
6	—ph	—ph	H	5B	4.04 (1.31)
7	—phNph2	—(2,4,6-Tri*i*-Pr)ph	—Ome	4A″	3.25 (0.97)

TABLE 2: TDDFT Excitation Energies (in eV) for the Most Intense Excitations in the Four-Coordinate FDBB Derivatives Calculated Using B3LYP/6-31+G*

	attached groups					energy and
no.	R$_1$	R$_2$	X	D	state	oscillator strength
8	H	H	H	F	1A″	4.17 (0.25)
9	H	—ph	H	F	1A″	4.17 (0.23)
10	H	—CH$_3$	H	F	1A″	4.15 (0.26)
11	H	—CH$_3$	H	—CH$_3$	1B$_2$	4.19 (0.30)
12	H	—CH$_3$	H	—CN	1A″	4.26 (0.29)
13	H	—CN	H	—CN	1B$_2$	4.32 (0.24)
14	H	—CN	H	F	1A″	4.25 (0.27)
15	H	H	H	—CN	1A″	4.27 (0.28)
16	H	—C≡CH	H	F	1A″	4.20 (0.26)
17	—ph	—ph	H	F	1A″	3.38 (0.91)
18	—phNph2	—(2,4,6-Tri*i*-Pr)ph	—OMe	F	2A	3.17 (1.15)

Figure 3. Structures of the four-coordinate DBB derivatives.

as an inexpensive and reasonably accurate method that rectifies many of the problems inherent in the Hartree−Fock approximation, great interest has arisen in extending DFT to excited electronic states. Currently, the most successful and widely used method to calculate excitation energies within DFT is time-dependent DFT (TDDFT).[39−45] In recent years TDDFT has emerged as a reliable standard tool for the theoretical treatment of electronic excitation spectra, and recent work demonstrates the good accuracy for a wide range of systems.[46,47] The primary advantage of TDDFT is that it can be applied to fairly large
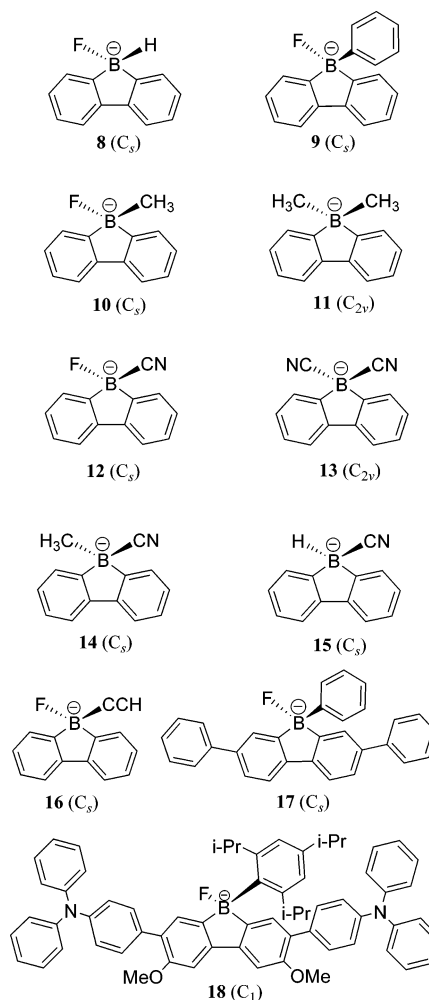
systems,[48,49] with a much smaller computational cost than the wave-function-based post-Hartree−Fock ab initio methods. Although in principle TDDFT can be an exact theory, in practice it is an approximate method due to the use of the adiabatic approximation[39,40] and the approximate nature of the standard (TD) exchange-correlation functionals used. Standard density functionals do not yield a potential with the correct long-range Coulomb tail.[50−56] Therefore, excited states that sample this tail (for example, diffuse Rydberg states and some charge-transfer excited states) are not given accurately.[50,51] Hence, TDDFT can only be safely employed for low-lying valence excited states that are well below the first Rydberg state of the molecule.

To help understand the nature of the electronic excitations, we have performed attachment/detachment density analyses on the states with oscillator strengths of greater than 0.1. The attachment/detachment density plots[57,58] pictorially represent the hole and particle densities of an electronic transition and thus can be used to characterize the excitations. The difference density matrix is diagonalized and decomposed into its negative and positive semi-definite parts. The negative part is called the detachment density matrix, because this part corresponds to the ground-state density that is removed during the excitation. The positive part is the attachment density, which is the density added upon excitation. In other words, the detachment density is that part of ground-state density, which is replaced by the attachment density to form the excited-state density. As a result the attachment/detachment density plots define the nature of transition.[59−63]

TABLE 3: Other TDDFT Electronic Excitations (in eV) below 5.0 eV That Have Oscillator Strengths of at Least 0.1 Calculated Using B3LYP/6-31+G*

molecule	state, energy, and oscillator strength
2	2A 3.82 (0.29), 4B 4.75 (0.67)
4	2B$_2$ 3.46 (0.10), 2A$_1$ 4.55 (0.11), 3B$_2$ 4.79 (0.75)
5	1A$_1$ 4.08 (0.11), 2A$_1$ 4.62 (0.12), 3B$_2$ 4.77 (0.76)
6	3A 3.83 (0.26), 5B 4.04 (1.31), 6B 4.25 (0.29)
7	1A″ 2.33(0.14), 4A″ 3.25 (0.97), 7A″ 3.71 (0.41), 8A″ 3.89 (0.38), 9A″ 3.95 (0.26), 12A″ 4.21 (0.52)
13	1B$_2$ 4.32 (0.24), 2B$_2$ 4.49 (0.11)
17	1A″ 3.38 (0.91), 9A$^{"}$ 4.47 (0.13)
18	2A 3.17 (1.15), 5A 3.36 (0.18), 20A 3.92 (0.17), 22A 3.95 (0.11), 25A 3.96 (0.12), 26A 3.97 (0.10)

All of the calculations were performed with a development version of the Q-Chem[64] quantum chemistry program. The geometry optimizations of the ground states of DBB and FDBB derivatives were performed with the B3LYP functional,[65,66] which has been shown to be effective at accurately predicting geometries and ground-state energies. All calculations have been carried out using the 6-31+G* basis set.[67−69] This basis set should be sufficient for these calculations, considering the size of the molecules studied and considering that geometry optimizations and vibrational frequency calculations were carried out. The biggest of these systems, molecules **7** and **18**, contain 131 atoms, 486 electrons, and 1452 basis functions and 132 atoms, 496 electrons, and 1471 basis functions, respectively. After the optimized structures were obtained, TDDFT calculations were carried out using the same functional and basis set. The attachment/detachment densities were also calculated with the same functional and basis set and then plotted for all significant excitations.

Results and Discussion

In this section we present and discuss the results for the excitation energies of both the three-coordinate DBB and four-coordinate FDBB derivatives. The three-coordinate boron in DBB is inherently electron poor and is a strong π-electron acceptor because of its vacant p$_z$ orbital; this orbital can also lead to significant delocalization when conjugated with an adjacent organic π-system. The boron p$_z$ orbital is readily attacked by an electron pair from a donor molecule to form a four-coordinate boron compound. After the attack, which changes the hybridization from sp^2 to sp^3, the bridging boron atom no longer participates effectively in the conjugation of the adjacent π-system. The vacant p$_z$ orbital on the boron atom of DBB, along with the π* orbital of attached carbon π-conjugated moieties, is responsible for this p$_\pi$−π* conjugation. The addition of a donor molecule, in this case a fluoride ion, changes the LUMO delocalization and breaks the p$_\pi$−π* conjugation. The nature of the p$_\pi$−π* conjugation of three-coordinate and four-coordinate systems is easily interpreted by plotting the LUMO orbitals, as shown in Figure 1.

The most intense vertical singlet excitation energies for all of the DBB derivatives are shown in Table 1 and those for all of the FDBB derivatives are shown in Table 2. These molecules are represented graphically in Figure 2 for the DBB derivatives and Figure 3 for the FDBB derivatives. Our choice of molecules allowed us to investigate the effects of various electron-donating and -withdrawing groups on the excitation energies. For this aim, we used −CH$_3$, −CN, −C≡CH, and −ph as subsistuent groups. In addition to their most intense excitations, some of the molecules show extra electronic excitations with significant oscillator strength. In Table 3, we summarize those other excitation energies for the DBB and FDBB derivatives. All

electronic excitation energies below 5.0 eV for the molecules we studied are located in the Supporting Information. This somewhat arbitrary cutoff was chosen to eliminate those states with substantial Rydberg character (as indicated by their attachment densities) that possessed significant oscillator strength.

Molecule **1**, which is DBB, has a prominent absorption peak at 4.84 eV, and molecule **8**, which is FDBB, has its main absorption at 4.17 eV. All the pairs of molecules show this basic pattern that, when a molecule goes from a three-coordinate boron system to a four-coordinate boron system, the absorption shows a red shift. The three-coordinate DBB derivatives **1**−**5** show prominent absorption peaks gathered around 4.8 eV. The four-coordinate FDBB derivatives **8**−**16** show prominent absorptions gathered around 4.2 eV. Molecules **6**, **7**, **17**, and **18** also show the same pattern but with lower energies. Because of their attached phenyl groups, these molecules have much more extended π systems. In addition, these molecules show some extra peaks arising from the inclusion of the additional phenyl groups. However, they keep a similar pattern of red shifts for their main excitations. Since the excitation energies for the major absorption lines did not vary significantly, we can conclude that the primary features of the excitation spectra depend on the basic DBB structure and not on the identities of the attached groups.

To investigate the nature of these electronic excitations, we performed attachment/detachment density calculations.[57,59] Figures 4 and 5 give the attachment/detachment densities for the most intense excitations of molecules **1**, **7**, **8**, and **18**. The plots show the 90% density enclosure isosurface. For better illustration, the values were scaled up by a factor of 100. The electron density that remains unchanged between the ground state and the excited state during excitation does not appear in the density plots. The plots[58] represent the attachment/detachment densities of the electronic excitations that belong to the most intense peaks and that are subject to a red shift in the absorption spectra when the coordination number of the borons changes. The detachment densities are placed above the arrow, and the attachment densities are shown below the arrow. Figure 4a shows the attachment/detachment densities of molecule **1,** which is the basic borole skeleton. We can compare its attachment/detachment densities with the attachment/detachment densities of molecule **7** (Figure 4b), which was the experimentally studied system.[15] Here we see that the attachment/detachment densities around the basic borole skeleton are very similar in both molecules, which means that the electron density comes from analogous initial locations and goes into analogous final locations. Thus, we can assign the two peaks as arising from the same physical excitation, and therefore the prominent peak of the spectrum of the molecule **7** arises from the basic borole skeleton. Further, we can see the same nature in the attachment/detachment densities for all of the electronic excitations that appear in Table 1. The attachment/detachment density plots for these molecules are included in the Supporting Information.

Figure 5a shows the attachment/detachment densities for molecule **8**, which is the four-coordinate FDBB basic skeleton compound. Figure 5b shows the attachment/detachment densities for molecule **18**, which was the other experimentally studied system.[15] We again interpret parts a and b of Figure 5 as showing similar attachment/detachment densities around the borole ring system, meaning these excitations also have similar electronic character. Here we have chosen to focus on only the attachment/detachment density plots that belong to the most prominent peaks for molecules **1**, **7**, **8**, and **18**. Attachment/detachment density plots for all the excitations listed in Tables 1−3 appear in the Supporting Information section. Notice that
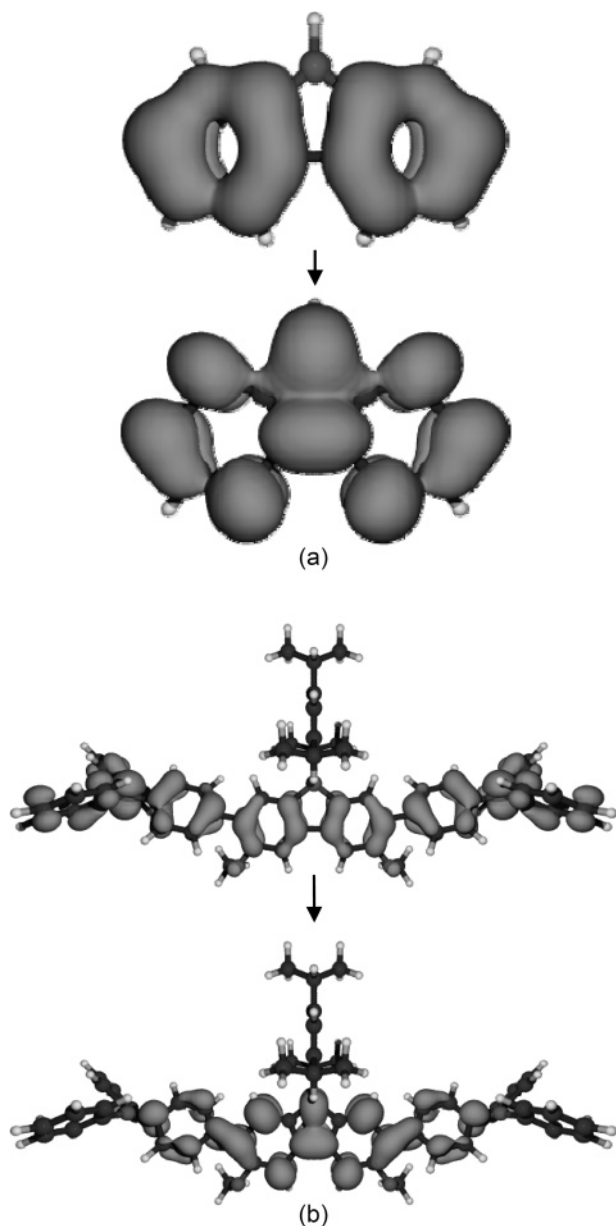
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Figure 4. Calculated attachment/detachment densities for molecules (a) **1** and (b) **7**.

Figure 5. Calculated attachment/detachment densities for molecules (a) **8** and (b) **18**.

in Figure 4a no detachment density is on the boron atom in molecule **1** but that some attachment density does appear on this boron atom. This means that the empty p$_\pi$ orbital on the boron atom in the three-coordinate molecule participates in the excitation process. When the excitation occurs, electron density goes to the boron atom from elsewhere in the molecule. This gives rise to the intense peak in the three-coordinate molecules. However, neither attachment nor detachment density can be found on the boron atom in molecule **8** in Figure 5a. In the four-coordinate molecules, as can be seen from the density plots, the excitations do not involve density transfer to the boron atoms. Therefore, the intense peaks in the four-coordinate molecules arise from a different origin.

Recently, Yamaguchi et al.[15] have reported both absorption and fluorescence spectra for molecules **7** and **18** in tetrahydro-furan (THF). The three-coordinate molecule **7** shows a first absorption band with a λ_{max} of 2.58 eV and a second band with a λ_{max} of 3.43 eV. Our calculated values for the electronic excitations with prominent oscillator strengths are 2.33 eV for the first band and 3.25 eV for the second band. Experimentally,
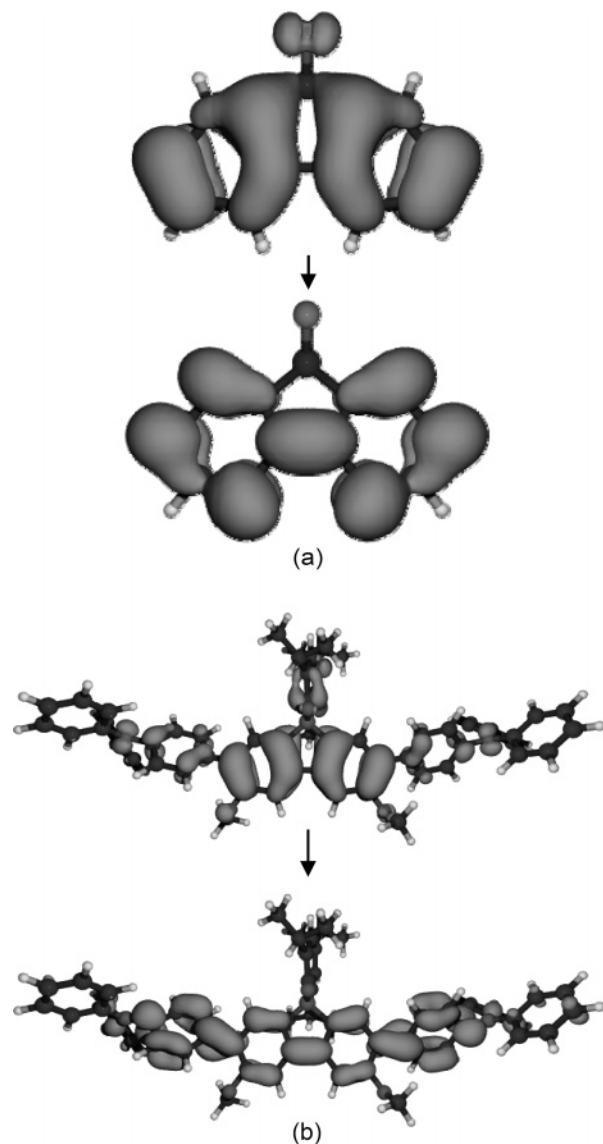
the four-coordinate fluoride-substituted molecule **18** has its first absorption band with a λ_{max} of 3.31 eV. The calculated value from Table 2 is 3.17 eV. All calculated values are within 0.25 eV of the experimental values, which is in reasonably good agreement with the experiment results.

Additionally, molecule **7** and **18** show fluorescence peaks at 2.21 and 2.96 eV, respectively, when exposed to 365-nm light.[15] According to our calculations for molecule **7**, as shown in Table 3, the 1A″ state at 2.33 eV has an oscillator strength of 0.14. This energy is close to the location of the measured fluorescence peak. Though the 4A″ state at 3.25 eV gives the most intense absorption peak, we consider it likely that, after excitation, the molecule relaxes from the 4A″ state to the 1A″ state, and therefore the origin of the fluorescence in molecule **7** is the 1A″ state. On the other hand, the most intense peak of molecule **18** is the *first* excited state. Since no other excited states are below the 2A state, the fluorescence must occur from the bright state. Therefore, it appears that the large difference in the fluorescence spectra of molecules **7** and **18** is caused by the fact that the most intense states are the fifth and the first excited states, respectively. Going from a three-coordinate to a four-coordinate boron atom has eliminated the low-lying excited states. This effect appears to be general. From the data in Figure

3 and the Supplementary Information, it can be seen that all of the three-coordinate molecules include a state of intermediate oscillator strength significantly below the bright state. In contrast, for all but one of the four-coordinate molecules, the bright state is the lowest state. The one counterexample, molecule **11**, has a single state with zero oscillator strength only 0.03 eV below the bright state. Therefore, we expect any molecule built upon this dibenzoborole skeleton to show a large blue shift in its fluorescence upon complexation.

Conclusions

Boron-containing organic π-conjugated systems have recently attracted increasing attention as a new class of π-electron materials for optoelectronics. In this work we have computed properties and the ground-state absorption spectra of derivatives of boron-containing organic π-conjugated compounds. Our calculations are in reasonably good agreement with experiment. The coordination number of the bridging boron atom affects the extent of the conjugation system. Therefore, the conjugation can be changed by varying the coordination number. Extension of the conjugation influences both the absorption and fluorescence spectra, with the major differences of the absorption spectra between the three-coordinate DBB molecules and the four-coordinate FDBB anions being a red shift and a decrease in the intensity. It has been shown that the primary properties of the electronic spectrum are based on the basic borole skeleton structure. Comparison of attachment/detachment density plots can explain the nature of electronic excitations that lead to the most intense peaks. The prominent peaks of all DBB derivatives show similar attachment/detachment densities, which means that they arise from similar electronic excitations. The prominent peak of all FDBB derivatives, which is subjected to the red shift, also show similar attachment/detachment densities. Finally, the blue shift in the fluorescence upon complexation can be interpreted as arising from the disappearance of the low-lying excited states in the four-coordinate ions.

Supporting Information Available: This section includes the optimized B3LYP/6-31+G* energies in Hartrees for all molecules, optimized B3LYP/6-31+G* *xyz* coordinates in angstroms for all molecules, calculated TDDFT B3LYP/6-31+G* electronic excited states lower than 5.0 eV for all molecules, and attachment/detachment density plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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