Quantum Chemical Study of the OLED Materials Tris[4'-(1''-phenylbenzimidazol-2''-yl)phenyl] Derivatives of Amine and Benzene

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Since its discovery by Tang and Van Slyke¹ and by Burroughes and co-workers,² organic light-emitting diode (OLED) is under intensive study as a very promising material for low-cost large-area light-emitting display technology.³⁻¹⁵ Several types of OLED, including conjugated polymers,⁵⁻⁷ metal complexes,^{8,11} and dyes^{9,10} have demonstrated desirable optoelectronic properties, such the emitting wavelength and efficiency, thermal stability, and amorphous film formation property. Synthetic aspects of the OLED investigation have been largely on a trial and error basis, mostly depending on empirical rules, such as the prediction of emitting wavelengths based on HOMO and LUMO energy levels. If the relationship between the optoelectronic properties and molecular structures of OLED is systematically understood, designing of the light-emitting materials would be more facile and economical.

Quantum chemical investigations that have tremendously affected synthetic chemistry through studies of structure-property relationship and underlying mechanism seem to have been much less helpful for studying OLED materials in this respect, probably due to the large size of molecules. Recent progress in quantum chemical methods, especially the advent of density functional theory (DFT) and time-dependent DFT (TDDFT), now allows systematic calcu-

lations for the structure and properties of OLED materials both in electronically ground and excited states to provide invaluable knowledge for photoabsorption and emission, and charge carrier mobility.

In the present work, we study the tris[4'-(1''-phenylbenzimidazol-2''-yl)phenyl] derivatives of amine (TPBPA: tri[4-(1'-phenylbenzimidazol-2'-yl)phenyl]amine) and benzene (TPBPB: 1,3,5-tris[4'-(1''-phenylbenzimidazol-2''-yl)phenyl]benzene) that were observed to have very useful emission properties.^{16,17} We describe their geometry and the electronic spectra, finding that the calculated electronic absorption and emission spectra of the two OLED materials agree very well with experimental observations.

Structures of the electronic ground states are obtained by using the B3LYP (Becke's three parameter hybrid method¹⁸ and the correlation functional by Lee, Yang and Parr¹⁹) method with the 6-31g(d) basis set implemented in Gaussian 03 set of programs.²⁰ The energy of the electronic excited states is calculated by using the TDDFT (B3LYP) and single-excitation CIS (CI-Single excitations) with the 6-31g(d) basis set. Stationary structures are obtained by verifying that all the harmonic frequencies are real. Default options are employed for all optimizations. No symmetry constraints are imposed during the optimizations.

Figure 1. Structures of TPBPA and TPBPB in electronic ground states.

Table 1. Absorption and emission properties of TPBPA and TPBPB

	TPBPA		TPBPB	
	absorption	emission	absorption	emission
Transition energy (eV)	3.22 (3.37) ^a	2.99 (2.91) ^a	3.79 (3.92) ^a	3.26 (3.22) ^a
Transition wavelength (nm)	385.1 (368) ^a	415.2 (427) ^a	327.6 (316) ^a	397.1 (383) ^a
Oscillator strength	0.87	1.14	1.43	1.65
HOMO-LUMO Gap (eV)	3.69		4.20	

^aExperimental: Refs. 16, 17

Figure 1 presents the structures of TPBPA and TPBPB in ground electronic states that are of C_3 symmetry. The angles in TPBPA and TPBPB are quite similar, except for some dihedral angles. In TPBPA, The distances between the three carbon atoms C_1 , C_2 , C_3 forming an equilateral triangle are all 2.459 Å. Since the distance between this triangle and the central N atom (N_c) is only 0.0068 Å, these four atoms essentially form a plane. Similarly, the distance between the central benzene ring and the three carbons C_1 , C_2 , C_3 in TPBPB is calculated to be 0.0024 Å, indicating that the three carbon atoms C_1 , C_2 , C_3 and the central phenyl ring lie

virtually in a plane.

One of the most important properties of OLED materials is the photoabsorption and emission spectra, especially the emission wavelengths with regard to the intense efforts to develop “blue emitters”. Table 1 presents the calculated absorption and emission properties of TPBPA and TPBPB in comparison with experimental observations. The absorption wavelengths are calculated as vertical excitation from the electronic ground state structure to the excited state calculated by the TD-DFT(B3LYP)/6-31G(d) method. The emission wavelengths are obtained as vertical transition

Figure 2. Absorption spectra of TPBPA and TPBPB (a) calculated⁽¹⁾ (b) experimental. ⁽¹⁾Calculated spectra were fitted by using GaussSum-1.0.5 (FWHM = 3000).

Figure 3. Emission spectra of TPBPA and TPBPB (a) calculated⁽¹⁾ (b) experimental. ⁽¹⁾Calculated spectra were fitted by using GaussSum-1.0.5 (FWHM for TPBPA = 2200, for TPBPB = 2800).

Table 2. Calculated coefficients of orbital excitation and population for TPBPA and TPBPB

TPBPA			TPBPB		
Dominant excitation	Coefficient	Population (%)	Dominant excitation	Coefficient	Population (%)
HOMO → LUMO-a	−0.10143	1.06	HOMO-1 → LUMO-a	−0.27882	7.77
HOMO → LUMO-b	0.69352	48.10	HOMO-a → LUMO-a	0.32926	10.84
			HOMO-a → LUMO-b	0.27782	7.72
			HOMO-b → LUMO-a	−0.2779	7.73
			HOMO-b → LUMO-b	0.32931	10.85
			HOMO-b → LUMO+1	−0.15322	2.35
Total population		49.16	Total population		47.26

from the electronic excited state structure optimized by the CIS/6-31G(d) method to the ground state calculated by the TD-DFT(B3LYP/6-31G(d) method. Table 1 shows that calculated absorption (385.1, 327.6 nm) and emission (415.2, 379.1 nm) wavelengths for TPBPA and TPBPB, respectively, are in excellent agreement (to within 5%) with those (368, 316 nm for absorption, 427, 383 nm for emission) experimentally observed. The calculated results may also reproduce the marked blue shift in the emission of TPBPB relative to TPBPA very well. It is worth noting that the

calculated HOMO-LUMO gap (3.67, 4.19 eV) that are frequently employed to describe the observed absorption and emission energies of OLED materials is somewhat less accurate (7-9%) than the calculated $S_0 \rightarrow S_1$ vertical excitation and $S_1 \rightarrow S_0$ emission energies. Figure 2 depicts the calculated absorption frequencies in comparison with experimental spectra, and Figure 3 compares the experimentally observed emission spectra with the calculated emission frequencies.

Natural Bond Orbital (NBOs) analysis may significantly

(1) TPBPA

(2) TPBPB

Figure 4. Shape and energy levels of frontier orbitals in (1) TPBPA and (2) in TPBPB.

help to understand the features of electronic transitions and to unravel the relative frequencies of transition, in the present case, those of TPBPA and TPBPB. It is known that larger conjugation length in the OLED material corresponds to smaller energy gap, and thus to longer absorption and emission wavelength. The difference in conjugate effects in TPBPA and TPBPB may be seen by observing the net charges of the N atoms obtained by NBO analysis (see Figure 1). The net charges of N₁ and N₂ in TPBPA are −0.406, −0.483, respectively, whereas those in TPBPB are −0.404, −0.481, respectively. It seems that these more negative net charges of the N atoms in imidazole rings derive from better delocalization from the central group (N atom in the case of TPBPA) than in TPBPA, and hence results in longer absorption and emission wavelengths in TPBPA than in TPBPB.

Table 2 and Figure 4 present the analysis of the frontier molecular orbitals involved in S₀ → S₁ vertical excitations. The electronic transition in TPBPA is very simple, most of it being due to that from the HOMO to one of the two degenerate LUMO's. It can be seen that the electron density in the LUMO's is localized in the two imidazole rings, whereas in the HOMO it is distributed symmetrically over the three imidazole moieties. The electronic transition in TPBPB, on the other hand, is quite complicated, consisting of many comparable transitions (7–11%) from HOMO-1, HOMO, LUMO and LUMO+1.

In summary, we studied the OLED materials TPBPA, TPBPB to understand the correlation between the structures and the electronic spectra of blue light-emitting materials. We demonstrated that the calculated absorption and emission wavelengths of TPBPA and TPBPB are in excellent agreement with the experimental spectra. We attributed the longer absorption and emission wavelengths observed for TPBPA than for TPBPB to a better delocalization of the electrons. Hopefully, our computational work would help to design OLED materials of better properties.

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