A boron-containing molecule as an efficient electron-transporting material with low-power consumption

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We theoretically propose a boron-containing molecule, hexaboracyclophane (HBCP), as an electron-transporting (ET) material with low-power loss. We calculate the vibronic coupling of HBCP, comparing them with those of other ET materials, tris-(8-hydroxyquinoline) aluminum(III) (Alq_3) and tris[3-(3-pyridyl)mesityl]borane (3TPYMB). Using the nonequilibrium Green's function method to evaluate their single molecular ET properties, we show that HBCP exhibits more efficient and lower-power consumption than Alq_3 and 3TPYMB. HBCP has suitable highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels as an electron-transport layer when Alq_3 is employed as an emitter. © *2010 American Institute of Physics*.
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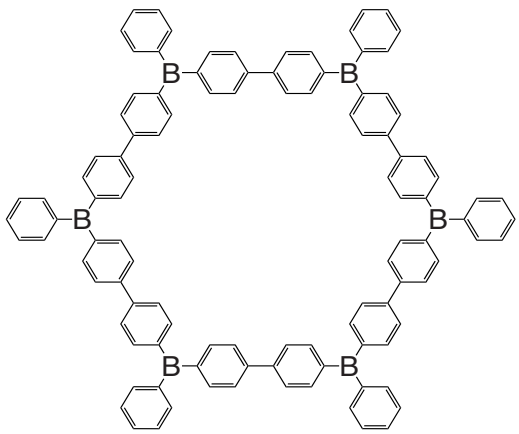
Organic light-emitting diodes (OLEDs) have been of great interest because of their potential application for large-area full-color flat-panel displays. To enhance device efficiency it is necessary to develop electron-transporting materials with high-electron mobility and improve charge balance in OLEDs.[1] Alq_3 is one of the most widely used electron-transporting material in OLEDs and also used as a green emitter.[2,3] On the other hand, various boron-containing π-conjugated systems have electron-transporting property,[4–9] suggesting that boron plays a key role in electron-transporting process. Recently, Tanaka *et al.*[9] have reported that tris[3-(3-pyridyl)mesityl]borane (3TPYMB) exhibits electron mobility about ten times higher than that of Alq_3 and has hole-blocking property.

One of the factors that controls the electron mobility is intramolecular vibronic coupling (electron–molecular vibration interaction). Inelastic scattering due to vibronic coupling not only inhibits electron transport and reduces electron mobility but also causes Joule heat or power loss. Crystallization or melting of organic materials due to Joule heat is an origin of the instability of OLEDs.[10] Hence, molecules with weak vibronic coupling are favorable for electron-transporting material. In this letter, we theoretically propose a boron-containing electron-transporting material, hexaboracyclophane (HBCP) (Fig. 1) and compare its vibronic coupling, electron-transporting property, and hole-blocking character with those of *mer*-Alq_3 and 3TPYMB.

The strength of vibronic coupling of the i^{th} mode is controlled by the vibronic coupling constant (VCC) V_i. V_i can be expressed as $V_i = \int \Delta\rho \times v_i d\tau$, where $\Delta\rho$ is an electron-density difference between neutral and anion states and v_i is one-electron part of the derivative of the nuclear-electronic potential with respect to the i^{th} normal coordinate.[11] Note that only totally symmetric modes couple to the electronic states and have nonzero V_i values. Geometry optimization and vibrational analysis for neutral *mer*-Alq_3, 3TPYMB, and HBCP were done at the B3LYP/3–21G level of theory. We assumed C_1, C_3, and D_6 symmetries for *mer*-Alq_3, 3TPYMB, and HBCP, respectively. The electronic structures of anionic states for these molecules were calculated at the UB3LYP/3–21G level of theory using the optimized geometries of the neutral states. A scaling factor of 0.963 (Ref. 12) was used for B3LYP/3–21G theoretical frequencies. All the *ab initio* calculations were done using GAUSSIAN 03 software.[13] We calculated current through a single *mer*-Alq_3/3TPYMB/HBCP molecule employing the nonequilibrium Green's function (NEGF) method taking into account inelastic scattering due to vibronic coupling.[14]

Figures 2(a)–2(c) show VCCs of *mer*-Alq_3, 3TPYMB, and HBCP. *mer*-Alq_3 has the largest V_i and exhibits the strongest vibronic coupling among them. Since *mer*-Alq_3 belongs to C_1 symmetry, all the vibrational modes (150 modes) have nonzero V_i. Low-symmetry molecular structure and not small V_i values lead to stronger vibronic coupling of *mer*-Alq_3 than those of 3TPYMB and HBCP. However, the



HBCP

FIG. 1. Chemical structure of HBCP.

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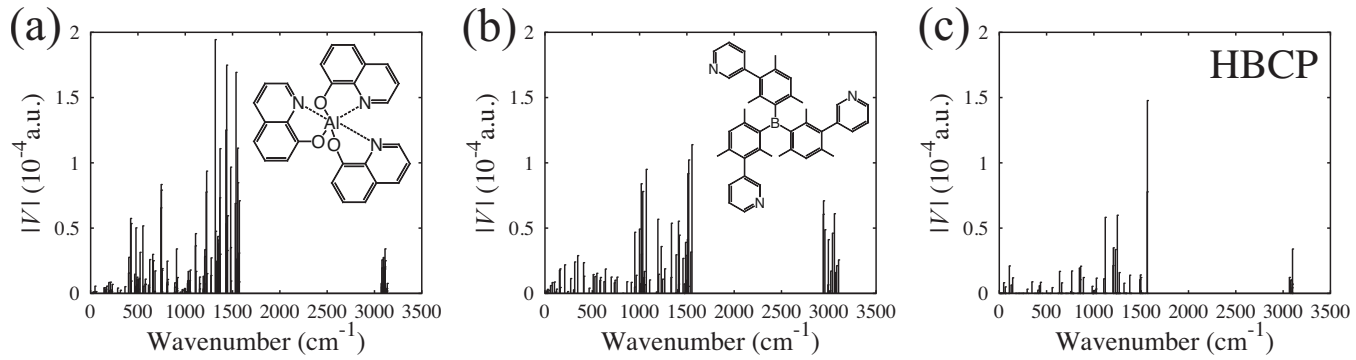

FIG. 2. VCCs of (a) *mer*-Alq_3, (b) 3TPYMB, and (c) HBCP.

largest V_i of *mer*-Alq_3 is at most 2.0×10^{-4} a.u., which is small compared with biphenyl, fluorene, and carbazole,[15] indicating that the vibronic coupling in *mer*-Alq_3 is weak as a π-conjugated system.

The largest V_i of 3TPYMB is about 1.2×10^{-4} a.u. [Fig. 2(b)]. This value is quite small and comparable to the vibronic coupling in the cationic state of *N*,*N*′-bis(3-methylphenyl) -*N*,*N*′-diphenyl - [1,1′-biphenyl]-4,4′-diamine,[11] which is a widely used hole-transporting material in OLEDs. The number of vibrational modes of 3TPYMB (258 modes) is larger than that of *mer*-Alq_3. However, the number of totally symmetric modes of 3TPYMB (86 modes) is smaller than that of *mer*-Alq_3 because of the existence of the C_3 axis. The smaller V_i values and number of totally symmetric modes are responsible for the weaker vibronic coupling in 3TPYMB than in *mer*-Alq_3.

Figure 2(c) shows V_i of HBCP. Although HBCP has the largest molecular size and the number of vibrational modes (570 modes) among the three molecules, it has the smallest number of totally symmetric modes (46 modes) because of its high symmetry. Thus, high symmetry reduces the number of totally symmetric modes, and consequently, weakens the vibronic coupling as a whole. Furthermore, the largest V_i of HBCP is relatively small (1.6×10^{-4} a.u.) and the other V_i values are of the order of 1×10^{-5} a.u. and quite small. The high symmetry and small V_i values of HBCP make it a promising candidate for an electron-transporting material.

Figure 3 shows highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of *mer*-Alq_3, 3TPYMB, and HBCP calculated at the B3LYP/3–21G level of theory and Fermi energy of the Mg:Ag electrode, which is a typical cathode for OLEDs. The Fermi energy shown here is the experimental work function of the Mg:Ag alloy with the opposite sign.[16] The HOMO/LUMO energy level of HBCP is lower than that of 3TPYMB and hence, HBCP is expected to be a better electron-injecting and hole-blocking material than 3TPYMB when *mer*-Alq_3 is used as an emitting layer.

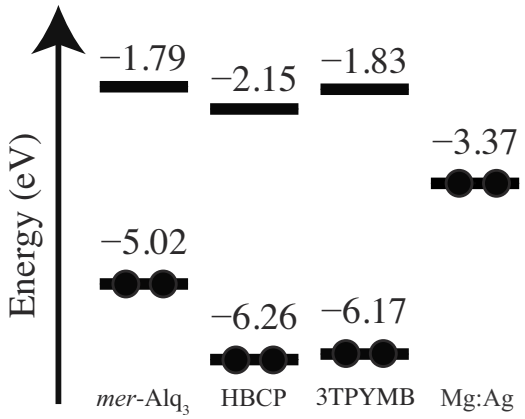

FIG. 3. HOMO/LUMO energy-level diagrams for *mer*-Alq_3, 3TPYMB, and HBCP calculated at the B3LYP/3–21G level of theory. The experimental work function with opposite sign of an Mg:Ag alloy (see Ref. 16) is shown as the Fermi energy of Mg:Ag electrode surface.

To investigate a suppression effect of vibronic coupling on electric current we calculated current-voltage (I-V_b) characteristics for a single *mer*-Alq_3/3TPYMB/HBCP molecule using the NEGF method.[14] Here, we considered neighboring molecules in a solid as a part of electrodes and set their Fermi levels to be the HOMO levels shown in Fig. 3. We used the electronic coupling τ=0.5 eV and temperature T=298 K. In the NEGF method, the I-V_b characteristics are influenced by τ and V_i. Since we focus on a suppression effect due to the vibronic coupling on I-V_b characteristics, τ was set to be the same value for the three molecules.

Figure 4(a) shows the I-V_b characteristics for *mer*-Alq_3 (dotted line), 3TPYMB (dashed line), and HBCP (solid line). Significantly, HBCP exhibits the largest I, suggesting that for HBCP, the suppression effect due to vibronic coupling is weak compared with *mer*-Alq_3 and 3TPYMB, and HBCP can be a superior electron-transporting material than *mer*-Alq_3 and 3TPYMB. The large I originates from the high-symmetry and small V_i values of HBCP. Since the vibronic coupling in 3TPYMB is weaker than in *mer*-Alq_3, 3TPYMB exhibits larger I than *mer*-Alq_3. This result is consistent with the experimental observation that 3TPYMB exhibits higher electron mobility than *mer*-Alq_3.[9] The weak vibronic coupling is an origin of the high electron mobility of 3TPYMB. Inelastic scattering due to vibronic coupling causes power loss, in other words, heat generation. Figure 4(b) shows power loss in a single *mer*-Alq_3/3TPYMB/HBCP molecule. The power loss decreases in the following order: *mer*-Alq_3 > 3TPYMB > HBCP, suggesting that molecules with weak vibronic coupling exhibit low power consumption.

In conclusion, we designed the boron-containing molecule with high-symmetry, HBCP. The theoretically designed HBCP exhibits weaker vibronic coupling and higher electron-transporting property than *mer*-Alq_3 and 3TPYMB. Furthermore, since the HOMO/LUMO energy level of HBCP is lower than that of 3TPYMB, HBCP can be a superior electron-injecting and hole-blocking material than 3TPYMB when *mer*-Alq_3 is used as an emitting layer. In

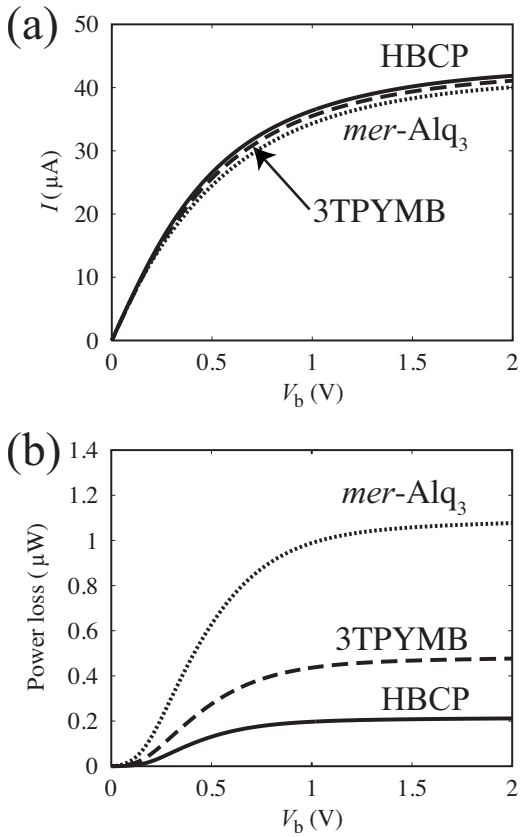

FIG. 4. (a) Current-voltage characteristics and (b) power loss for *mer*-Alq_3 (dotted lines), 3TPYMB (dashed lines), and HBCP (solid lines).

actual synthesis, it is necessary to protect the boron atoms, for instance, by introducing the methyl group at the ortho positions of the phenyl and phenylene groups. Such a chemical modification would change torsion angles between phenyl rings but would not impair the electron-transporting and hole-blocking properties of HBCP so much. We calculated reorganization energies and HOMO/LUMO energy levels at the B3LYP/3–21G and UB3LYP/3–21G levels of theory for one-third-sized fragments of unsubstituted and methyl-substituted HBCP. The difference between the reorganization energies and HOMO/LUMO energy levels for the two molecules are 24 meV and 0.09/0.42 eV, respectively, suggesting that the electron-transporting and hole-blocking properties of HBCP are not influenced significantly by the methyl substitution. Usually, amorphous materials have been used in OLEDs. HBCP might be highly crystalline in nature because of its high symmetry. Amorphous HBCP-based materials would be obtained, for example, by introducing bulky substituents into HBCP.

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