

Geometric and Excited-State Properties of 1,4-Bis(benzothiazolylvinyl)benzene Interacting with 2,2',2''-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole] Studied by a Density-Functional Tight-Binding Method

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The energetics and luminescent property of a guest molecule, 1,4-bis(benzothiazolylvinyl)benzene (BT), interacting with a host molecule, 2,2',2''-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole] (TPBI), in organic light-emitting diodes are studied by performing excited-state calculations using a time-dependent density-functional tight-binding method complemented with dispersion energy. It is found that the overlap between the TPBI emission and the BT absorption spectra shows an efficient energy transfer from the host molecule to the guest molecule when they are excited. The planar BT molecule becomes distorted when it is mixed with TPBI, resulting in a blue luminescence around 475 nm. The separation of the TPBI + BT mixture on a graphite surface is found to be energetically favorable, consistent with experimental observation.

Introduction

Organic light-emitting diodes (OLEDs) have the potential to become the next generation of full-color flat-panel displays.¹ Improving the performance of OLEDs is an ongoing task in the attempt to commercialize this technology. Many highly fluorescent materials have been developed to fulfill the need for the three basic colors red, green, and blue for a full-color display. The interfacial structures, charge injection, transport, and luminescent mechanisms in OLEDs have been well studied. The morphology, surface, and interfacial electronic structure have been investigated intensively using various available techniques such as scanning electronic microscopy (SEM) and ultraviolet photoelectron spectroscopy (UPS).

Heterocycles containing oxazole, oxadiazole, benzazole, and benzoxazole moieties have been found in the molecular structures of many fluorescent agents.² The benzothiazole and its derivative 1,4-bis(benzothiazolylvinyl)benzene (BT) have been found to give a high fluorescence quantum yield.³ Recently, the self-assembling behavior of the guest molecule BT, the host molecule TPBI (2,2',2''-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole]), and their mixture deposited on the highly oriented pyrolytic graphite (HOPG) surface has been studied by the STM method.⁴ It has been found that BT and its derivative *m*-BT form an ordered pattern and the methyl groups in *m*-BT result in a larger interrow spacing than that of BT. Because of the steric configuration of TPBI, it is difficult for this host molecule to form two-dimensional ordered structures. BT and TPBI molecules mix homogeneously at room temperature, whereas at a higher temperature, BT molecules migrate and agglomerate to form ordered domains. Aggregation of BT molecules in TPBI at higher temperatures might be one important cause of OLED degradation, as is supported by the results of photoluminance (PL) measurement.

However, the details of the structure of the mixed host and guest molecules were not clear in the STM image, especially the procedure of their adsorption on the graphite surface. In this paper, we study the interaction between the BT and TPBI molecules, their self-assembly behavior on the HOPG surface, and the emission spectrum of BT at its different structure, by performing quantum-mechanical calculations using a self-consistent-charge density-functional tight-binding method (SCC-DFTB).⁵ We aim to provide understanding at the atomic level of the interaction and to promote molecular design for OLEDs with improved performance.

Theoretical Method and Molecular Models

The DFTB method is a second-order perturbation approach to density-functional theory.^{6–8} The Hamiltonian is represented in a minimal basis of atomic orbitals, to which further approximations are applied. On this basis, the diagonal elements were chosen to be the Kohn–Sham atomic eigenvalues, and the nondiagonal elements were calculated in a two-center approximation. First derivatives of interatomic forces were analytically calculated, and second derivatives of the energy with respect to atomic positions were calculated numerically. To describe the van der Waals (vdW) interaction between two separated fragments, an empirical dispersion term was added to the DFTB total energy^{8,9} (acronym DFTB-D). For weakly interacting systems including hydrogen bonding, DFTB-D has been applied successfully to the investigation of biomolecules^{10,11} and the interaction between water clusters and graphite.¹² To also access excited-state properties, the DFTB method has been extended in the spirit of time-dependent DFT.¹³ The resulting scheme, here referred to as TD-DFTB, has been shown to provide optical spectra for molecules, clusters, and amorphous systems in good accord with experiment.^{14–16} In

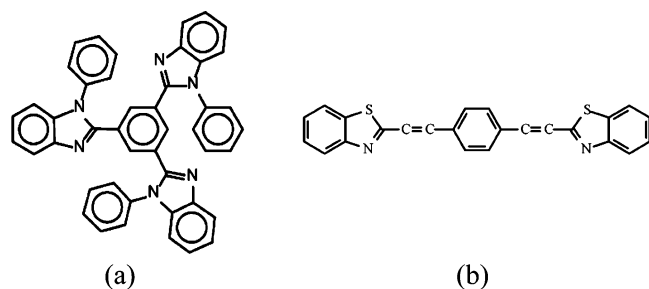


Figure 1. Schematic representation of the molecular structures of (a) TPBI and (b) BT.

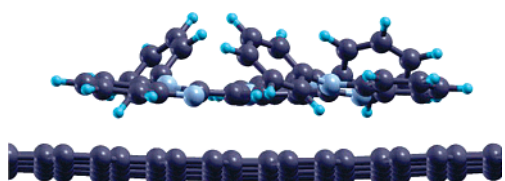


Figure 2. Optimized structure of TPBI adsorbed on a graphite surface.

general, DFTB closely approximates DFT, but runs $\sim 10^3$ to 10^4 times faster.⁵

The molecular structures of BT and TPBI are shown in Figure 1. The geometries of isolated BT and TPBI molecules were optimized by a conjugated gradient method with a rigid convergence criterion of 10^{-5} au. When considering the interaction of mixed guest and host BT and TPBI molecules or their adsorption on an HOPG surface, the weak vdW force was also taken into account because, in these systems, this force plays an important role in determining their structure and the attractive energies. The calculation of adsorption behavior on the graphite surface was carried out using a supercell approximation with a rectangle graphite cell with $a = 29.82$ Å, $b = 24.60$ Å, and $c = 20$ Å, which is the distance between graphite surfaces and is large enough that the graphite surfaces do not interact with each other. The UV/vis absorption and emission spectra were calculated using the optimized molecular structure in both isolated and mixed states.

Results and Discussion

Because of the geometry obstacles, TPBI cannot form an ordered structure on a graphite surface (see Figure 2). During the optimization, it was found that the three benzimidazole planes tend to be parallel to the graphite surface so as to reach maximum attraction energy and bend the phenyl group upside down. The distance between the TPBI and the graphite is in the range of 3.0 Å, which indicates a physical absorption type. The adsorption of the BT molecule on graphite is also of the physical type; however, since the planar structure did not change during the adsorption, it is easy to form large-scale ordered structures, as observed in the STM experiment.⁴

The absorption spectrum (Figure 3a) of the isolated BT was calculated at the optimized structure, while the emission spectrum was computed at the minimum of the first excited-state potential energy surface. The calculated Stokes shift was about 70 nm, which is close to the experimentally observed data of BT in solution.³ However, the emission energy was underestimated. In the experiment, the BT molecule emitted blue light at the 480 nm peak position. However, the DFTB method predicted a longer wavelength of around 550 nm. Nevertheless, the calculated TPBI emission spectrum is in good agreement with the experimental results (Figure 3b).

To further investigate the origin of the discrepancy between theory and experiment, we considered the four isoenergy

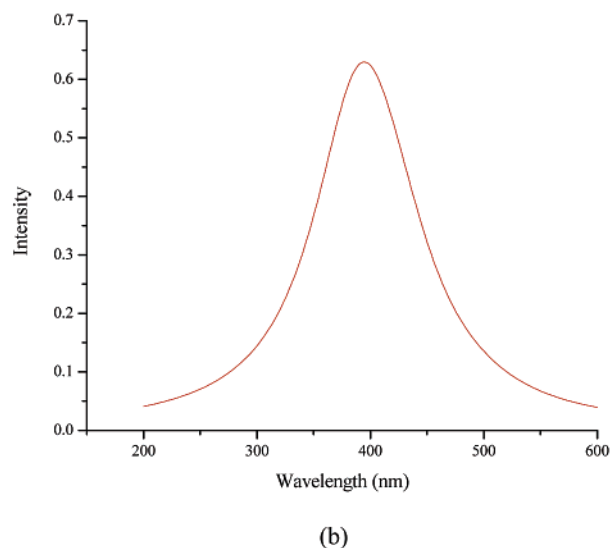
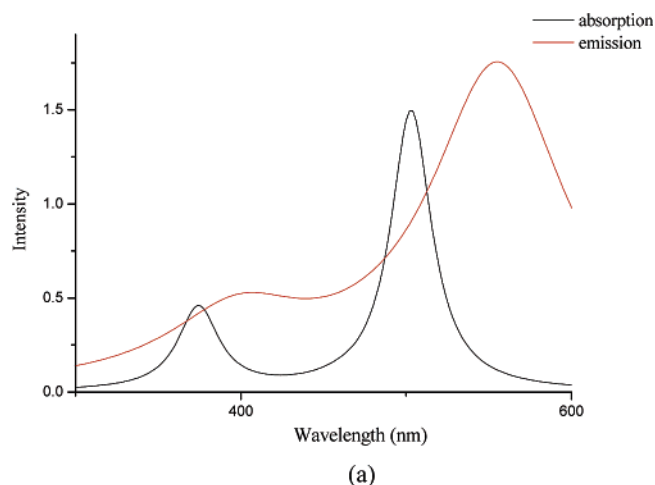


Figure 3. Calculated (a) adsorption and emission spectra of BT and (b) emission spectrum of TPBI. The peaks were broadened by a Lorentzian line-shape modification with a 15 nm half-width.

structures of BT shown in Figure 4 and checked whether one of these structures will give an emission peak at 480 nm. Starting from the structure shown in Figure 4a, we obtained the one shown in Figure 4b by rotating the σ bond in the left benzothiazole group by 180° . By further rotating the benzothiazolylvinyl group in the structure shown in Figure 4b around the σ bond connected with benzene, we obtained the one in Figure 4c. Figure 4d shows a structure in which the benzothiazolylvinyl group of the structure in Figure 4b rotates 180° and then the benzothiazole group rotates 180° further. All these molecules are planar.

However, the calculated emission spectra of these four isoenergy structures were almost identical to the one shown in Figure 3b. Another possible reason for the discrepancy between the experimental and theoretical results is the solid-state effect in the experiment. To simulate the influence of other molecules on the one under study, we carried out the following three-step simulation. First, three BT molecules stacking face-to-face with initial 3.0 Å separations (shown in Figure 5) were optimized. The optimized structures show that the three BT molecules stay parallel to each other with a nearest distance between them of 3.36 Å. Second, after the optimized structures were obtained, the center BT molecule was selected for further optical property study, and the other two BT molecules were replaced by the net charge as that obtained in the optimized structure. This is

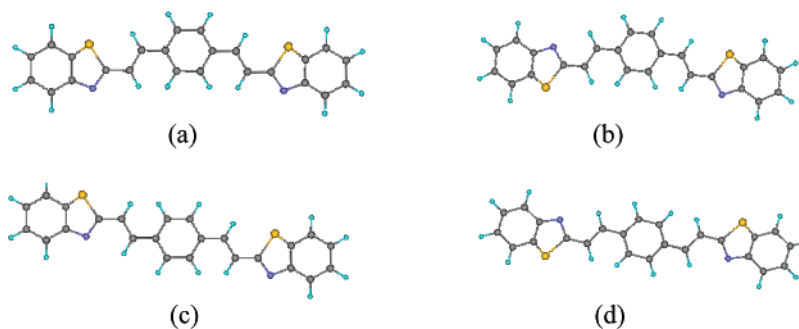


Figure 4. Schematic representation of the four isoenergy BT molecular structures.

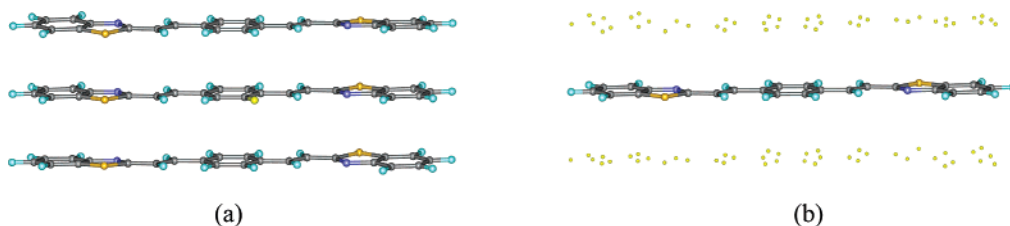


Figure 5. (a) Three optimized BT molecules and (b) calculated BT molecule with net charges surrounding the center BT molecules.

because of the absence of chemical bonding among the BT molecules due to the large separation so that the influence on its optical properties is mainly due to the static electronic interaction. Third, the selected BT molecule was calculated for its emission spectrum in an environment of surrounding atomic Mulliken charge at the position of the other BT molecules. Because of the weak π - π interaction, the center BT molecule shows a geometry nearly identical to that of the isolated BT molecule, indicating that the interactions with the other two BT molecules are negligible. The emission spectrum calculated locates at a peak position similar to that of the isolated molecule, though the intensity was slightly decreased.

We further considered other reasons such as the geometry distortion of the BT molecule. Since the C-C σ bonds are easy to rotate, it is reasonable to assume that the BT molecule will not keep its lowest energy planar structure in the solid state. We therefore assumed that the σ bonds in the two benzothiazolylvinyl groups rotate 30° , 45° , and 90° , respectively, and analyzed the corresponding changes in the spectrum. Their energies were 3.26, 6.97, and 15.19 kcal/mol higher, respectively, than those of the planar structure. Figure 6a shows the calculated absorption spectrum for the different σ bond rotation angles.

The absorption spectrum shows that when the rotation angle reaches 90° —that is, when the benzothiazole group is perpendicular to the center benzene ring—the peak shifts to the blue, from the original 550 nm of the planar molecule to 350 nm. This high sensitivity of the optical spectrum to the rotation angle suggests that the distortion of the BT planarity will lead to an emission at the experimental value of 480 nm at a certain distortion angle. In fact, as shown in Figure 6b, when the σ -bond-connected benzothiazole group rotated 55° relative to the benzene plane, the calculated emission position was predicted to be the same as the experimental data. To investigate the real OLED device where the guest BT molecule serves as a dopant to the host TPBI molecule, several models that include BT and TPBI were optimized with particular consideration of the vdW force. Figure 7b shows one of the optimized structures that present a significant geometry distortion of the BT molecule, where the aromatic rings of BT and TPBI have moved closer due to the electronic attraction between them.

The structure of the BT + TPBI mixture and the emission spectrum of BT molecules with different σ bond distortion angles indicate that the distortion would make BT generate luminescence in the blue region, as observed in the experiment. It is interesting to note that, in all our TPBI and BT mixed models, all BT molecules were distorted by TPBI when they moved closer. Thus, we may modify BT at the σ bond with, for example, a methyl group to accelerate its distortion while keeping its optical properties unchanged. In the adsorption procedure of the BT and TPBI mixture on a graphite surface at room temperature, no ordered structure was observed in the STM experiment, which indicates that the BT and TPBI remain mixed and the BT molecule remains distorted.

One of the requirements that should be satisfied for the OLED device is an efficient energy transfer from the excited host to the guest molecule. This can be elucidated by analysis of the molecular orbitals of the BT and TPBI mixture; an example is the one shown in Figure 8.¹⁷ The HOMO and LUMO orbital images of the BT and TPBI mixture show that the HOMO is mainly located on the TPBI molecule while the LUMO is carried by the BT molecule, which indicates a charge transfer from the TPBI to the BT when they are excited. The analysis of the adsorption spectrum of the mixture (Figure 8) shows that the peak with the highest intensity should correspond to the HOMO to LUMO excitation, which is at 2.455 eV in our calculation. In fact, once the BT molecule accepts an electron from the TPBI, its total energy will increase by -2.01 eV.

Since the amorphous structure of the BT and TPBI mixed layer adsorbed on the graphite surface, it is impossible to give a definite binding energy of the BT + TPBI + graphite surface (abbreviation G_s) system. As an estimation, the largest binding energies of different combinations of BT, TPBI, and G_s were calculated and are shown in Table 1. These values were obtained by considering the configuration which has the largest π - π contact area; for example, the binding energy of BT + BT was obtained by putting two BT molecules parallel to each other and face-to-face, as shown in Figure 5a. The TPBI + G_s configuration is shown in Figure 2, where the benzimidazole groups are close to the graphite surface, denoted as facing graphite. If the TPBI is put on the opposite site, the binding energy is smaller than that of the former since the phenyl groups

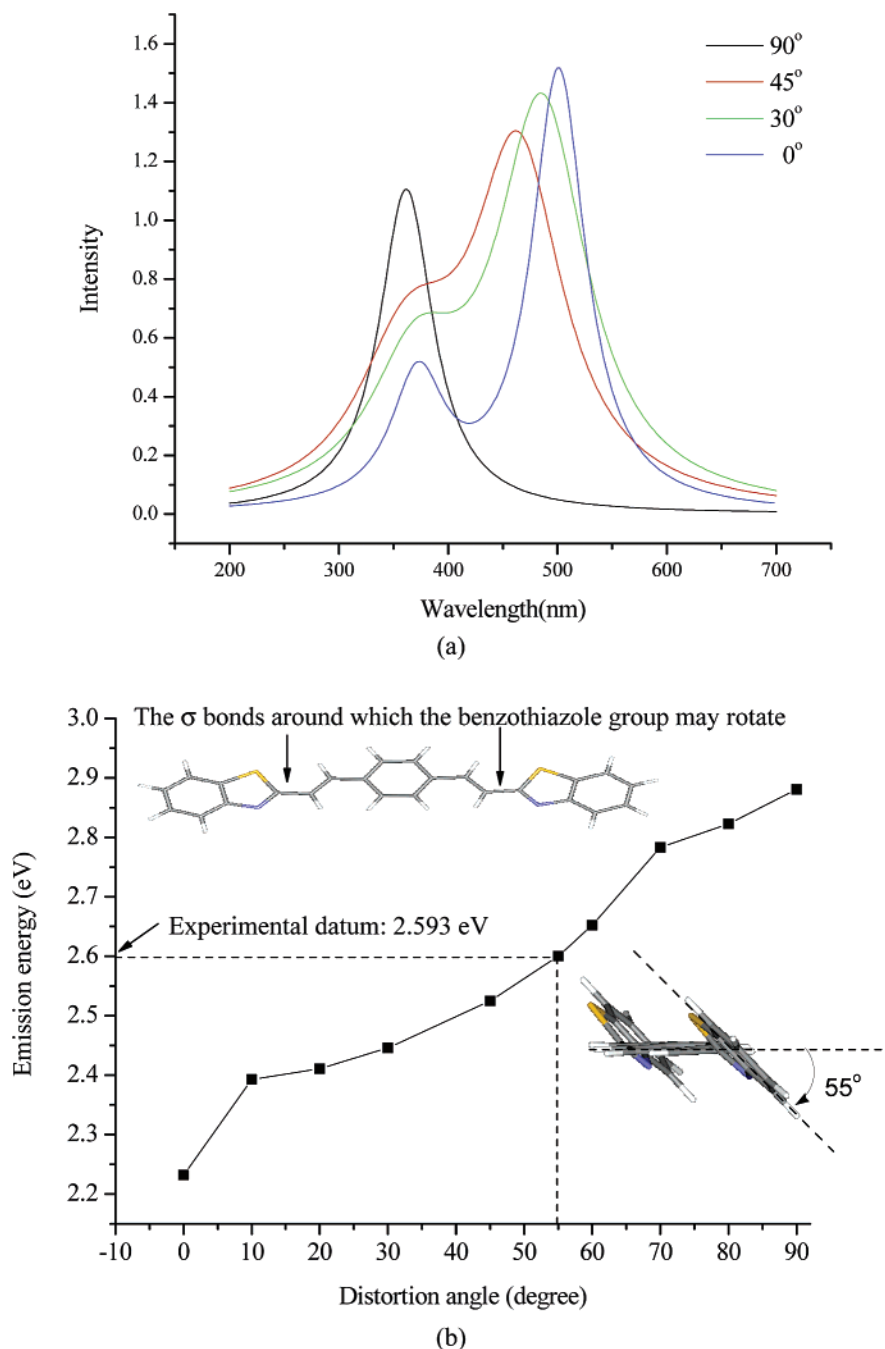


Figure 6. (a) Calculated absorption spectrum of BT for different σ bond rotation angles. (b) Emission peak energy as a function of the σ bond rotation angle.

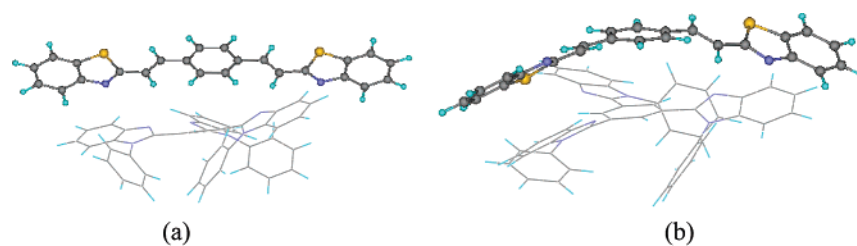


Figure 7. Representations of the BT and TPBI mixture: (a) initial structure and (b) equilibrium structure.

have less contact area than the benzimidazole groups. The BT + TPBI configuration is shown in Figure 7b, which indicates that BT benzothiazole groups were bent to be parallel to the two benzimidazole groups of the TPBI molecule. For TPBI + TPBI, we found a configuration that allows phenyl groups on two TPBI molecules to face each other, and this configuration

has the largest binding energy. The configuration of BT + TPBI + G_s is the complex that contains a BT molecule above a TPBI molecule facing the graphite surface as shown in Figure 2.

The binding energy between BT and BT is much smaller than that between BT and G_s , which is in agreement with the experimental observation that no face-to-face stacking among

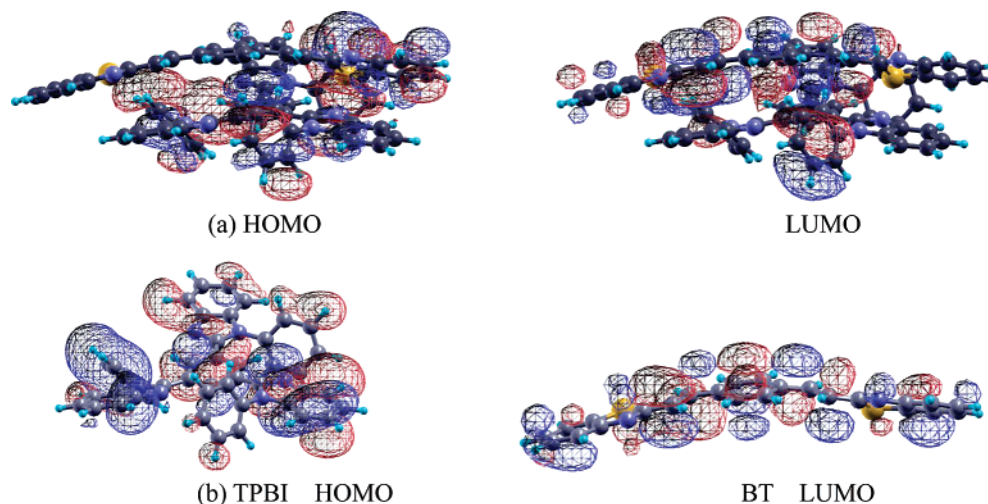


Figure 8. Schematic representations of the HOMO and LUMO of the BT and TPBI mixture and the isolated BT and TPBI molecules.

TABLE 1: Binding Energy (E_b) of Different Combinations of BT, TPBI, and G_s (kcal/mol)

BT + TPBI	BT + BT	TPBI + TPBI	BT + TPBI + G_s	TPBI + G_s	BT + G_s
-56.9	-32.80	-36.5	-92.5	-89.9	-73.3

the BT molecule was formed when they adsorbed on G_s . In our calculation, if two BT molecules are placed side-by-side in a short distance as the initial structure on the graphite surface, they will gradually move together face-to-face in the geometry optimization procedure. It seems that the N and S atoms cannot form an effective hydrogen bond between BT molecules, but the attraction between the aromatic π electrons plays a more important role in the intermolecular interaction. Furthermore, when two BT molecules are set parallel to the graphite surface, they will keep the side-by-side parallel geometry structure due to the attraction between the π electrons and the graphite surface.

Although the binding energy between BT and TPBI is larger than those of BT + BT and TPBI + TPBI, the binding energy of BT + TPBI + G_s is just slightly larger than those of TPBI + G_s and BT + G_s . In terms of lowering the energy, TPBI + G_s and BT + G_s are more favorable than the mixture BT + TPBI + G_s . These results provide a clue to explain the experimental observation⁴ that TPBI and BT would separate and aggregate together at higher temperatures. Unfortunately, a molecular dynamic simulation at the DFTB level to study the agglomeration of BT and TPBI is beyond our current computational capability. However, as shown in Table 1, the relatively small binding energy of BT + TPBI + G_s indicates that the separation of TPBI + BT on the graphite surface is energetically preferred.

Conclusions

By using the TD-DFTB-D method, the interaction between the host TPBI molecule and the guest BT molecule was elucidated. It was found that the isolated planar BT molecule will be distorted when it interacts with TPBI through the vdW and π - π electron attraction forces. The geometry distortion of BT and its interaction with TPBI were found to play an important role in the luminescence properties. The distortion of the BT molecule was activated by the TPBI molecule and

gave blue luminescence around 475 nm. The weak vdW attraction between BT and TPBI adsorbed on the graphite surface was found to be slightly larger than that between each of them and the HOPG substrate. The separation of the TPBI + BT mixture on the graphite surface is energetically preferred. This fact can partly explain the migration and agglomeration at elevated temperatures, which is believed to be one cause of device degradation.

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