

Charge-transfer states and white emission in organic light-emitting diodes: a theoretical investigation

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This work is dedicated to the memory of Michael J. Rice, whose independent and rigorous mind has been a continuous inspiration over the years

Abstract

Efficient white light emission has been recently reported in an electroluminescent device where the active material is a complex made of *N,N'*-bis(α -naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) and a boron–fluorine derivative of 1,6-bis(2-hydroxy-5-methylphenyl)pyridine ((mdppy)BF). Here, we investigate theoretically the intermolecular charge transfer in the materials. The interfacial layer is modeled on the basis of a simple dimer structure, for which the lowest excited states are described in the framework of a correlated quantum-chemical semiempirical technique. From the analysis of the calculated excited-state wavefunctions, we find that the lowest excited state possesses significant contributions from charge-transfer excitations from the donor (NPB) to the acceptor ((mdppy)BF). The influence of intermolecular distance and medium polarization are also explored.

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1. Introduction

Considerable interest is given to organic electroluminescent devices (OLEDs) due to their potential applications namely in large-area flat display technology. An advantage of organic materials is the possibility to tune the color of the emitted light over the entire visible range [1–9]. Among the strategies explored to achieve color-tunable emission, white light-emitting devices have attracted much attention since they allow easy color selection through the use of appropriate filters [10]; these devices can also be used as paper-thin light sources or as backlight in liquid crystal displays.

Several methods of producing white light from polymer or small-molecule organic devices have been demonstrated [11–15]. White emission in these devices can be produced

by either energy-transfer or charge-transfer (CT) processes. In the former scheme, excitation energies can partly funnel from higher energy sites to lower energy sites through a sequence of hopping processes; provided all the sites can decay radiatively with sizeable efficiencies, light emission can in principle cover the full visible range. In the latter scheme, either inter- or intramolecular charge-transfer excited states are generated that can subsequently decay radiatively at a lower energy than the localized molecular excited state; in this case, the energy distribution of emissive species is believed to arise from the sensitivity of the charge-separated excited-state energy on the actual morphology and effective electric field at the interface of molecular blends.

Recently, Liu et al. have demonstrated that the luminescent complex of the boron–fluorine derivative of 1,6-bis(2-hydroxy-5-methylphenyl)pyridine ((mdppy)BF) and *N,N'*-bis(α -naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) (see Fig. 1) yield white light emission at high efficiencies when used as the active material in an OLED structure [16]. In solution, both molecules show strong photoluminescence at about 450 nm (in the blue); therefore, the possibility of an energy transfer mechanism can be ruled

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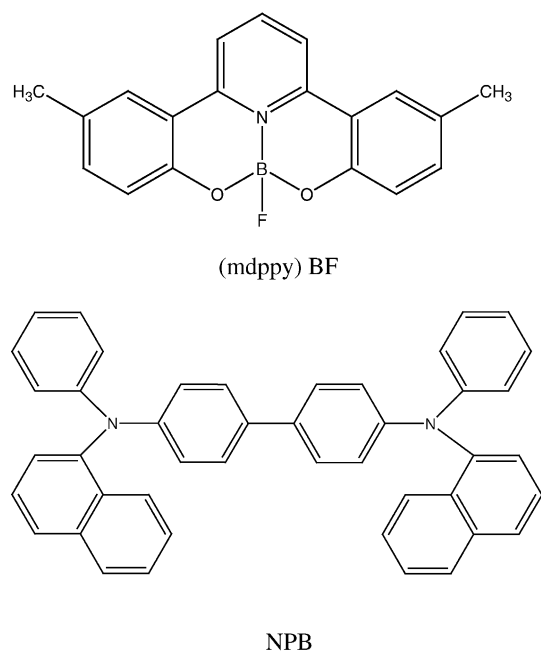


Fig. 1. DFT-B3LYP/6-31G-optimized molecular geometries of (mdppy)BF and NPB.

out. Understanding at the microscopic level the underlying mechanism for the white emission in this complex calls for a detailed quantum-chemical characterization.

In this work, we consider a dimer structure consisting of two interacting (mdppy)BF and NPB molecules to model the interface between the two materials. By means of correlated quantum-chemical calculations, we show that due to the mismatched electronic structures of the two molecules, charge-transfer excitations occur at energies close to those of excitations localized on the donor and acceptor molecules; it is the mixing between these two types of excitations that

provides both the CT character and a significant oscillator strength to exciplex-type states.

2. Theoretical methodology

The molecular geometries of the (mdppy)BF and NPB isolated molecules have been optimized at the DFT level using the B3LYP functional and the 6-31G basis set [17]; they are sketched in Fig. 1. The interface layer is modeled as a dimer, using the following simple procedure: the intramolecular geometrical parameters of the donor and acceptor moieties are kept at their DFT values in the isolated molecules; these are used to build donor–acceptor supramolecular systems assuming different initial orientations and distances between the interacting units. The total energy of the dimer is calculated through the semiempirical Austin model 1 (AM1) as implemented in AMPAC [18]. We find the packing mode shown in Fig. 2 as the most favored one. Note, however, that: (i) other conformations are also accessible at relatively small energy expenses; and (ii) in the actual material, a number of different intermolecular separations and relative orientations of the molecules are likely present at the interface. Thus, the dimer model used in this work should be regarded as a rough guess of the actual interfacial geometric arrangement.

To investigate the dependence of the results on the choice of intermolecular geometric parameters, we have repeated the same calculations when systematically varying the intermolecular distance. The influence of applying a static electric field was also explored; the presence of such field is meant to account for both the effective internal field induced by the surrounding molecules and/or the external field present in a working OLED device. Again, the amplitude of the applied electric field has to be regarded here as a tunable parameter taking into account the fact that in the

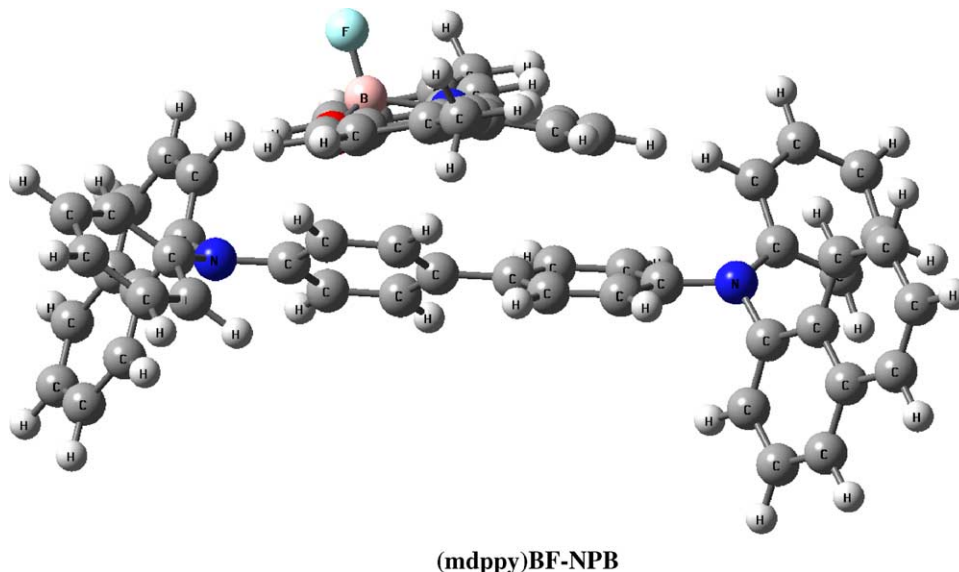


Fig. 2. Stacking mode in the bimolecular system of (mdppy)BF and NPB, as obtained from AM1 supramolecular calculations.

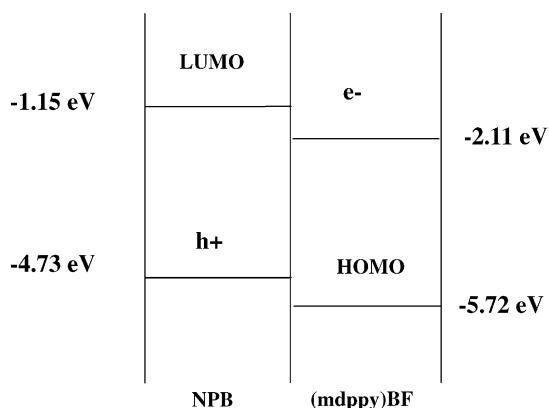


Fig. 3. DFT-B3LYP/6-31G HOMO and LUMO energies of isolated (mdppy)BF and NPB molecules.

molecular blend the microscopic environment at the interface is not uniform.

On the basis of the supramolecular geometric structures, the electronic excited states of the whole system were studied by combining the intermediate neglect of diatomic overlap (INDO) Hamiltonian [19] to a single configuration interaction (SCI) formalism. The CI active space has been built by promoting a single electron from one of the M highest occupied levels to one of the N lowest unoccupied levels; here, we have chosen $M = 50$ and $N = 50$ given that such a choice of active space leads to converged excitation energies. The results are analyzed by means of the Zoa software [20].

3. Results and discussion

3.1. Charge-transfer excited states

Fig. 3 shows the relative one-electron energy levels of the isolated (mdppy)BF and NPB molecules, as obtained at the DFT-B3LYP/6-31G level. The energy difference between the HOMO levels of (mdppy)BF and NPB is 0.98 eV; that between the LUMO levels is 0.96 eV. This simple frontier orbital picture suggests that a charge-transfer excitation can in principle contribute to the lowest excited state, provided intermolecular interactions are significant. In this case, we expect the lowest excited state to be dominated by an electron transition from the frontier molecular orbitals, with the HOMO being essentially localized on NPB and the LUMO concentrated mostly on (mdppy)BF. If the intermolecular interactions are large enough that they lead to a significant mixing between such CT excitations and localized excitations on the donor and/or acceptor, this will result in low-lying dipole-allowed excited states; radiative decay from such states could contribute to the long-wavelength emission spectrum, a key component for a white light source.

When considering various geometric structures of the dimer, we find that there usually exists a CT excited state located at a lower energy than the localized molecular ex-

cited states, vide infra. In order to understand the nature of this excitation, we have adopted the following scheme to analyze the electron–hole wavefunction. In the single CI approach, an electron is promoted from an occupied MO to a virtual MO; the many-body wavefunction is then a linear combination of all the single excitations and we can express an excited state as:

$$|e\rangle = \sum_{i,a} \frac{Z_{i,a}^e (|i_{\uparrow} \rightarrow a_{\uparrow}\rangle + |i_{\downarrow} \rightarrow a_{\downarrow}\rangle)}{\sqrt{2}} \quad (1)$$

where $|e\rangle$ is the excited state, $i(a)$ is the occupied (virtual) molecular orbital index, $|i_{\uparrow} \rightarrow a_{\uparrow}\rangle$ represents a determinant with an electron in MO i with spin up promoted to MO a . In the spatial representation, the excited-state wavefunction can be projected into the electron–hole coordinate space in the following way:

$$\Psi^e(x_e, x_h) = \frac{1}{\sqrt{2}} \sum_{i,a} Z_{i,a}^e (\varphi_i(x_e) \varphi_a(x_h) + \varphi_a(x_e) \varphi_i(x_h)) \quad (2)$$

where the φ 's are molecular orbitals.

We have previously applied this formulation to study the localized and delocalized electronic excitations in phenylene-based conjugated polymers; this contributed to the emergence of a coherent picture on the origin of the frequency-dependent photo-current action spectra in these materials [21]. A similar scheme has been applied by other groups in analyzing the excited-state structure of porphyrin and ladder-type conjugated polymers [22].

To illustrate the nature of the electronic excitations, we have generated a two-dimensional grid where the horizontal axis x represents the coordinate of the electron and the vertical axis y , the coordinate of the hole; each point on the grid then represents a possible electron–hole pair. An excited state obtained from SCI can be viewed as a linear combination of all the generated electron–hole pairs, with the brightest regions on the grid corresponding to the highest probabilities. Having the bright spots occurring for similar x – y values means that the electron and hole remain close to each other in the transition process. If the bright spots occur for x and y values very different from one another, it indicates that the electron and hole are well separated. Note that each point on the grid is an instantaneous representation of the excited state; it does not necessarily describe the charge distribution in the excited state but rather reflects the transition density distribution. In the upper panel of Fig. 4, we depict the exciton wavefunction analysis results for the lowest excited state of the complex in the geometry of Fig. 2. This state has a CT character since we observe that the bright spots are found in areas with rather different x and y values, i.e., the electron and hole are well separated.

In the lower panel of Fig. 4, we illustrate the INDO frontier orbitals of the complex. The LUMO is centered on the NPB molecule, while the HOMO and HOMO-1 are

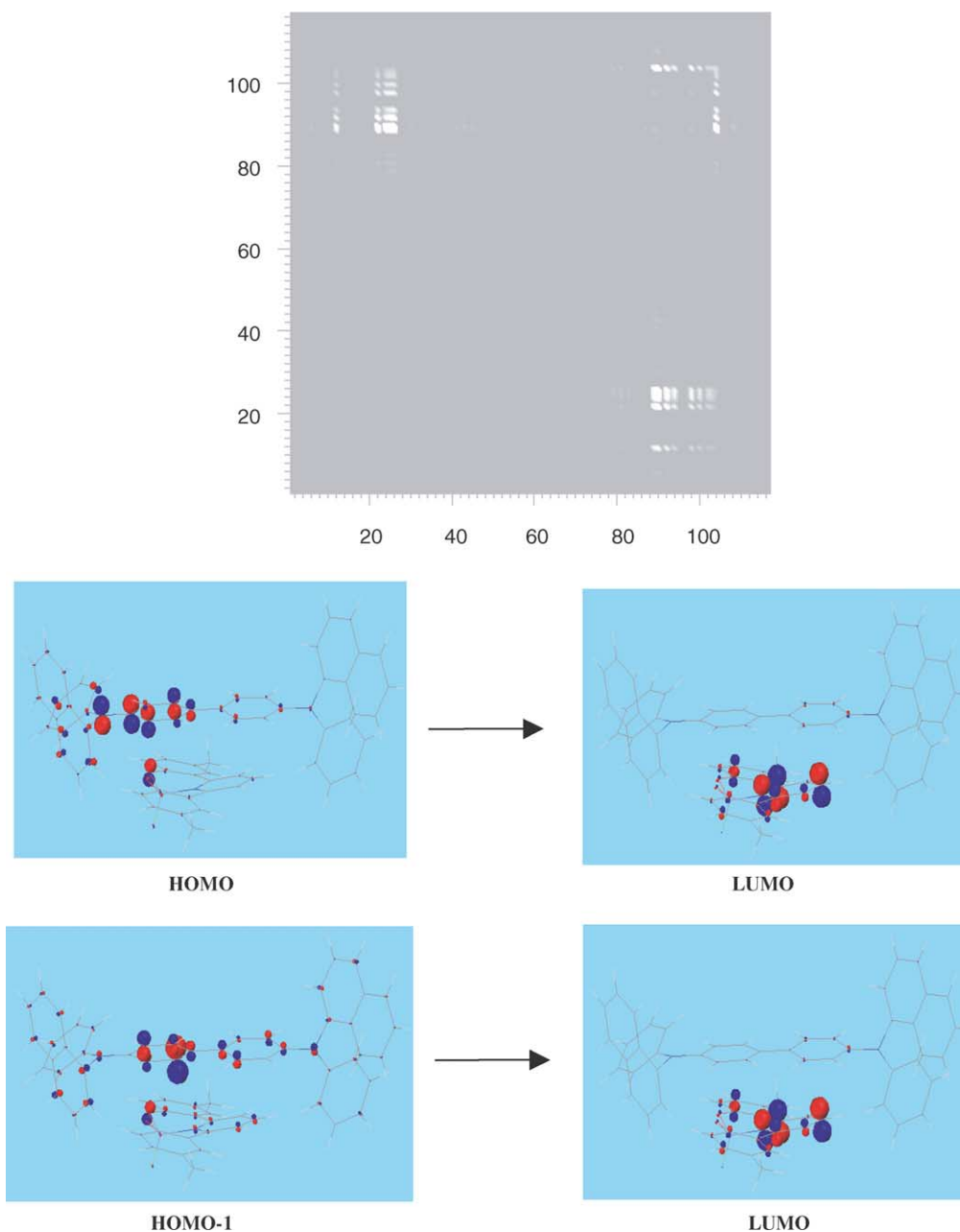


Fig. 4. Description of the electron-hole pair distribution for the lowest excited state of the complex in the geometry of Fig. 2, where the average separation between molecular planes is on the order of 3.2 Å (upper panel). The INDO frontier molecular orbitals contributing to the excitation are depicted in the lower panel.

localized on the (mdppy)BF molecule. From the INDO-SCI calculations on the complex geometry of Fig. 2, the lowest excited state consists of 83% HOMO to LUMO transition and 12% HOMO-1 to LUMO transition. This confirms that there are dimer configurations for which a charge-transfer state can be the lowest excited state for the complex.

3.2. Effect of intermolecular distance

We now study the nature of this CT state with respect to the relative separation of the two molecules; this separation

plays a crucial role on the energetics of charge-separated versus localized excitations. In the complex shown in Fig. 2, the two main molecular planes are nearly parallel to each other; thus, the distance between these planes is expected to affect significantly the CT. Here, we have kept the same relative orientations and varied the distance between the planes from 3 to 15 Å. We define the CT probability, ρ , as the probability of having the electron in one molecule and the hole in the other molecule: $\rho = 1$, thus means that in the excited state the charges are fully separated, while for $\rho = 0$, the excitation corresponds to a localized molecular excited

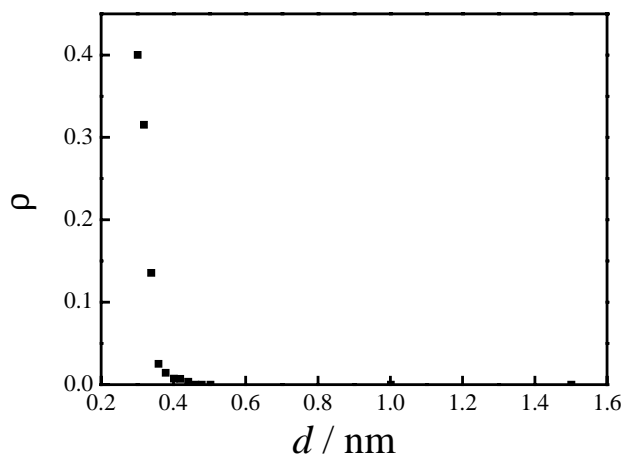


Fig. 5. Charge-transfer probability, ρ , as a function of the distance between molecular planes of (mdppy)BF and NPB.

state. Other relevant characteristics include the energy and oscillator strength for the lowest excited state.

Fig. 5 shows that the CT probability ρ increases with decreasing distance between the two molecules. Specifically, it is clear that as d gets smaller than 3.8 \AA , there is an abrupt increase in ρ , indicating a clear charge-transfer transition. For d between 4.0 and 4.5 \AA , the value of ρ is small and decreases slowly with increasing d ; thus, the lowest excited state is mostly a localized species with slight CT character for d larger than 4.6 \AA .

Fig. 6 gives the evolution of the lowest excitation energy with respect to intermolecular distance. It is interesting to note that the evolution fully correlates that in Fig. 5: the charge-transfer state is stabilized for intermolecular distances lower than 4.5 \AA . Fig. 7 illustrates the evolution of the oscillator strength for the lowest excited state with respect to transition energy. The localized molecular excitations are stronger; however, interestingly, at short distances, the oscillator strength of the CT state slightly increases with

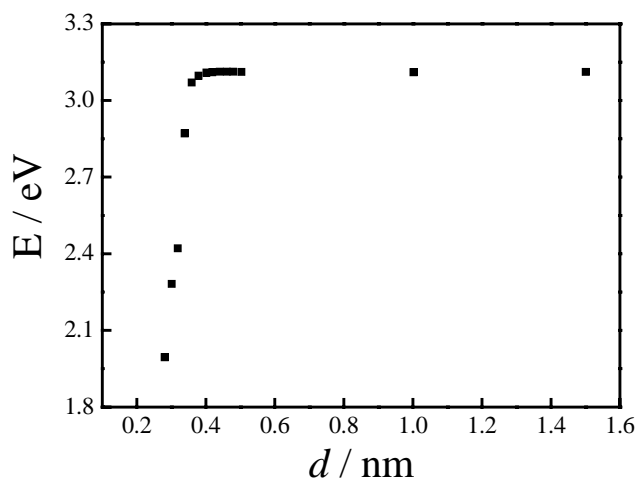


Fig. 6. Energy of the lowest singlet excited state as a function of intermolecular distance.

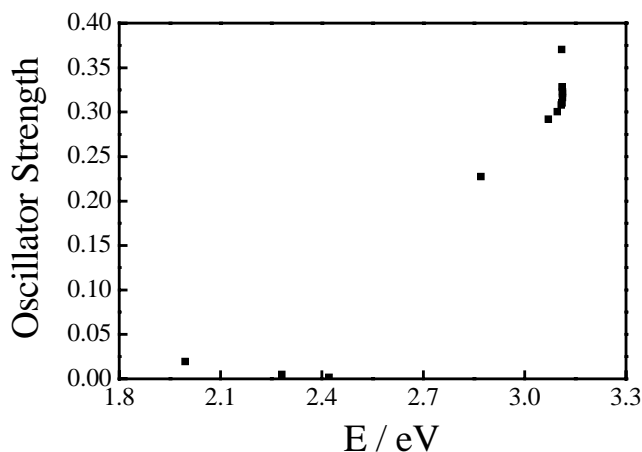


Fig. 7. Relationship between transition energy and oscillator strength for the lowest singlet excited state. Each point corresponds to a specific intermolecular distance.

decreasing transition energy. This can be rationalized in the following way: as the distance between the interacting units is getting shorter, the energy of the CT state is lowered, the average electron–hole separation becomes smaller. Thus, such intermolecular CT states could play a role in white emission. If in the actual materials there exists a distribution of dimers, the emission of the CT states can contribute to the long-wavelength emission and the molecular excited states to the short-wavelength emission.

3.3. Effect of electric field

Admittedly, the model for the complex considered here is a crude representation of the interfacial layer. In reality, the surroundings play an important role, through packing, local field, and polarization effects. As a very first step towards modeling these effects, we have simply applied to the complex a uniform static electric field going from NPB to (mdppy)BF. The instantaneous electron and hole separation distance in a CT state is expected to be significantly influenced by the electric field. Fig. 8 shows the evolution of the lowest CT state energy when the electric field increases from 0 to $5 \times 10^7 \text{ V/cm}$ for an intermolecular distance $d = 4.0 \text{ \AA}$. The CT energy decreases smoothly with field, as must be expected. Fig. 9 illustrates the energy difference between the first charge-transfer excited state and the lowest excited state found at zero-field, as a function of electric field strength for an intermolecular distance $d = 4.0 \text{ \AA}$. At this distance and without electric field, the lowest excited state is mostly a molecular exciton mixed with a small portion of CT; the full CT state is identified by the wavefunction analysis and is about 0.38 eV above the molecular exciton state. We observe that, as the field strength increases, the CT state becomes lower in energy than the molecular excited state (their difference Δ starts at $+0.38 \text{ eV}$, then goes down and becomes negative). However, beyond a field strength around $3.6 \times 10^7 \text{ V/cm}$, Δ starts to increase again. This expresses

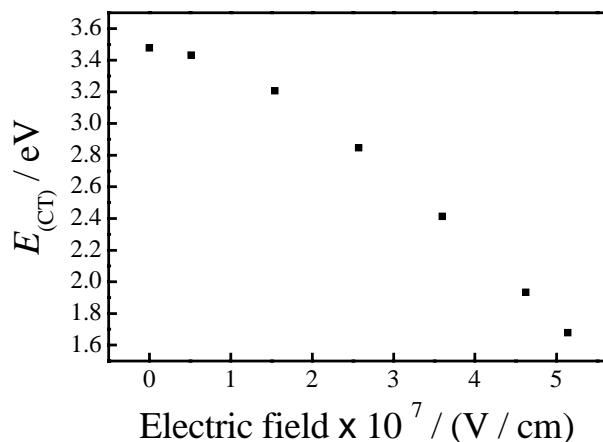


Fig. 8. Energy of the first charge-transfer excited state as a function of electric field for $d = 4 \text{ \AA}$.

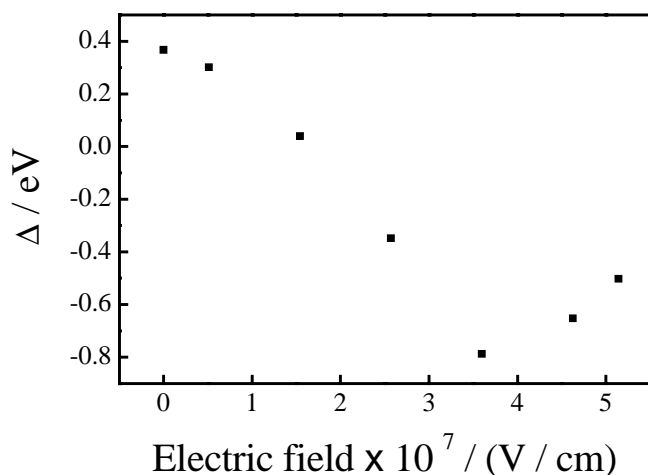


Fig. 9. Evolution of the energy difference between the first charge-transfer excited state and the lowest molecular excited state as a function of electric field for $d = 4 \text{ \AA}$.

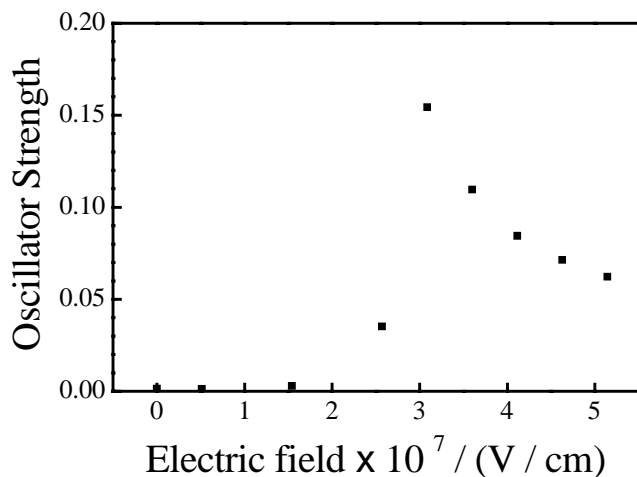


Fig. 10. Oscillator strength of the lowest singlet excited state as a function of electric field for $d = 4 \text{ \AA}$.

the inability of the CT state to keep delocalizing as it is confined within the bimolecular complex of our model.

Fig. 10 illustrates that the oscillator strength for the lowest CT excited state starts increasing with the electric field, then peaks and decreases. In fact, as the field strength is increased, there occur an increasing number of states possessing CT character, borrowing intensity from the lowest CT state.

4. Conclusion

To conclude, we have applied the INDO–SCI method to a bimolecular complex system to rationalize the emission mechanism of a highly efficient white light device ITO/NPB/(mdppy)BF/Al. Our results are consistent with the fact that long-wavelength emission occurs due to exciplex formation at the interfaces between (mdppy)BF and NPB molecules.

By analyzing the instantaneous electron–hole distribution in the excited-state wavefunction, we were able to identify the CT state. We have investigated the nature of the CT state as a function of intermolecular distance and electric field, which serves to mimic the internal and external fields. From frontier molecular orbital analysis, we find that usually the HOMO mostly localizes on NPB and the LUMO on (mdppy)BF. For an intermolecular distance lower than 4 \AA , the CT state is stabilized and can contribute to an emission at much longer wavelength than the molecular exciton. Effects due to internal/external electric fields could further stabilize the CT state and increase its oscillator strength.

It is expected that experimentally there occurs a distribution of dimers or larger aggregates, which present various separations and experience different fields. Even though they are based on an admittedly oversimplified description of the interfacial layers, we believe that our results shed some useful light towards an understanding of the efficient white emission demonstrated in [16].

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