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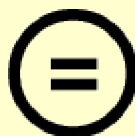
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Master's Thesis

Chemical Degradation of OLED Host Materials:
The Role of Non-Local Interaction
in Electronic Excited States

Seunghyun Lee

Department of Physics

Graduate School of UNIST

2019

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Seunghyun Lee

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Approved by

Advisor

Noejung Park

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Seunghyun Lee

This certifies that the thesis/dissertation of Seunghyun Lee is approved.

12.11. 2018 of submission

Signature

Advisor: Noejung Park

Signature

Jungwoo Yoo

Signature

Junhyeok Bang

Abstract

Organic light-emitting devices (OLEDs) have been attracted to both academia and industry, because of their wide applications and remarkable advances in display. Despite the conspicuous advances in OLEDs and even their successful implementation in commercial displays, device degradation issues still remain as one of the most important problems. Because degradation occurs mostly in operating conditions, the underlying mechanism is considered to be linked to carriers in excited states. While several theoretical and experimental studies have focused on the mechanisms of OLED degradation, the microscopic role of the excited carrier remains elusive. In this work, I study how chemical degradation is driven by the excited carrier in OLED materials, using occupation-constrained density functional theory calculations. The results show that the C-N bond is a weak link of OLED molecules both in the electronic ground and excited states, and the rupture of the bond is the main cause of the chemical degradation in short lifetime. While the excited carrier generally weakens the bond, the effect can be mitigated by the non-local interaction with the other bonding and anti-bonding states. The results suggest that the presence of such a non-local interaction can contribute to an enhancement of the chemical stability of the materials in operating environments.

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II. Introduction

2.1 OLED degradation

After the first discovery of organic light emitting devices (OLEDs)¹, its significantly development has continued over the past half century, and now OLED has been commercialized in various displays and lighting applications.²⁻⁴ That is mainly because of its excellence in display technologies with deep & full colors, thin, light-weight, and flexible display.⁵ Additionally, the fabrication cost of OLEDs have significantly been reduced, and higher quantum efficiencies have been achieved which led to a lower power consumption.⁶ Despite these good properties and advantages, because OLED materials have short lifetime which result from the degradation problem, it is still difficult to fully commercialize OLED products particularly for large-scaled displays.⁷ Understanding the degradation mechanisms is very important and essential for developing appropriate control strategies to mitigate degradation problems.

The mechanisms of degradation can be generally classified by two categories from inside and outside of OLED. Firstly, there are some external factors commonly observed such as the influence of water and oxygen, voltage increase, and temperature effects. Because of the presence of water and oxygen, various processes in OLED are initiated: photo- and electrochemical reactions resulting in oxidation of organic materials⁸⁻⁹, and humidity-induced crystallization.¹⁰ As voltage increase accompanies the degradation of OLEDs, injection barriers between adjacent layers are increased by voltage rise.¹¹⁻¹² In addition, higher than a critical temperature of materials will accelerate and induce the device degradation.¹³⁻¹⁸

Furthermore, there are some internal factors which are not easier to investigate than external mechanisms. Accumulation of non-radiative recombination centers, unbalanced charge and position of the recombination zone, and electro- or photochemical reactions can be commonly observed as internal degradation mechanisms. While the accumulation of degraded molecules or fixed charges occurs in operating system, the efficiency of emitting light gets lower by acting as non-radiative the recombination centers.¹⁹⁻²⁵ Since charges migrate from a layer to another layer, appropriate charge balance lead to recombination efficiency in emitting layer.²⁶⁻²⁷ Also, depending on the position of recombination zone, the density of the excited carrier which leads to degradation can be changed.²⁸⁻²⁹ Lastly, chemical reactions are caused by electrochemical processes such as decomposition of anode and cathode, and oxidation of organic materials, and by photochemical processes such as the effect of the

excited carriers created by recombination, energy transfer, or light absorption.³⁰ In particular, the excited carrier is regarded as a major role in the device degradation.⁷

In OLED operating progress, OLED can be described as electroluminescent phosphor in the emission layer.³¹ Due to the presence of excited carriers, the chemical reaction can occur frequently with high energy of the excited carrier in the emission layer.³² When there is direct excitation to a repulsive potential, molecules can be deactivated as a result of bond dissociation.³³ Previous works have calculated the bond dissociation energies of OLED materials to analyze a tendency of chemical degradation.⁶ However, most of calculations has been done in the electronic ground state, while the OLED degradation mostly happens in the working condition, which is likely in the electronic excited state.³⁴⁻³⁵ Therefore, the calculation of neutral and charged states in the ground state is not enough to explain the OLED degradation. Here, I consider that the effect of the electronic excitation on the chemical degradation of OLED molecules and moieties.

As a result of bond dissociation of a molecule by chemical reaction, they are divided up into fragments called as moiety then this result leads to loss of their own properties. This dissociation process also can cause additional degradation by producing charged fragments or radicals which can react with surrounding molecules. So, their outcomes become new molecules which are not proper materials for OLEDs.³⁰ Through these processes, OLED materials lose their own function then this degradation result in the short lifetime of devices.

In the ground state, dissociation is a local process, and moiety itself describes well the nature of degradation processes. Some researches of the binding energy have been performed for not only molecule but moiety as well.^{6, 30} Through calculation of binding energy of moiety, we can understand the dissociation mechanism with bonding effect of materials from a fundamental perspective. Many researches only have paid attention to the local dissociation mechanism of either molecule or moiety, however, no one has been interested in the incidental part which is the difference between molecule and moiety. This part can be described as non-local interaction of OLED materials. By comparing dissociation mechanisms between molecule and moiety, we can understand the effect of non-local interaction in dissociation mechanisms.

2.2 OLED structure

OLED structure is composed of many layers which are hole injection layer (HIL), hole transport layer (HTL), electron injection layer (EIL), electron transport layer (ETL), and emission layer (EML)

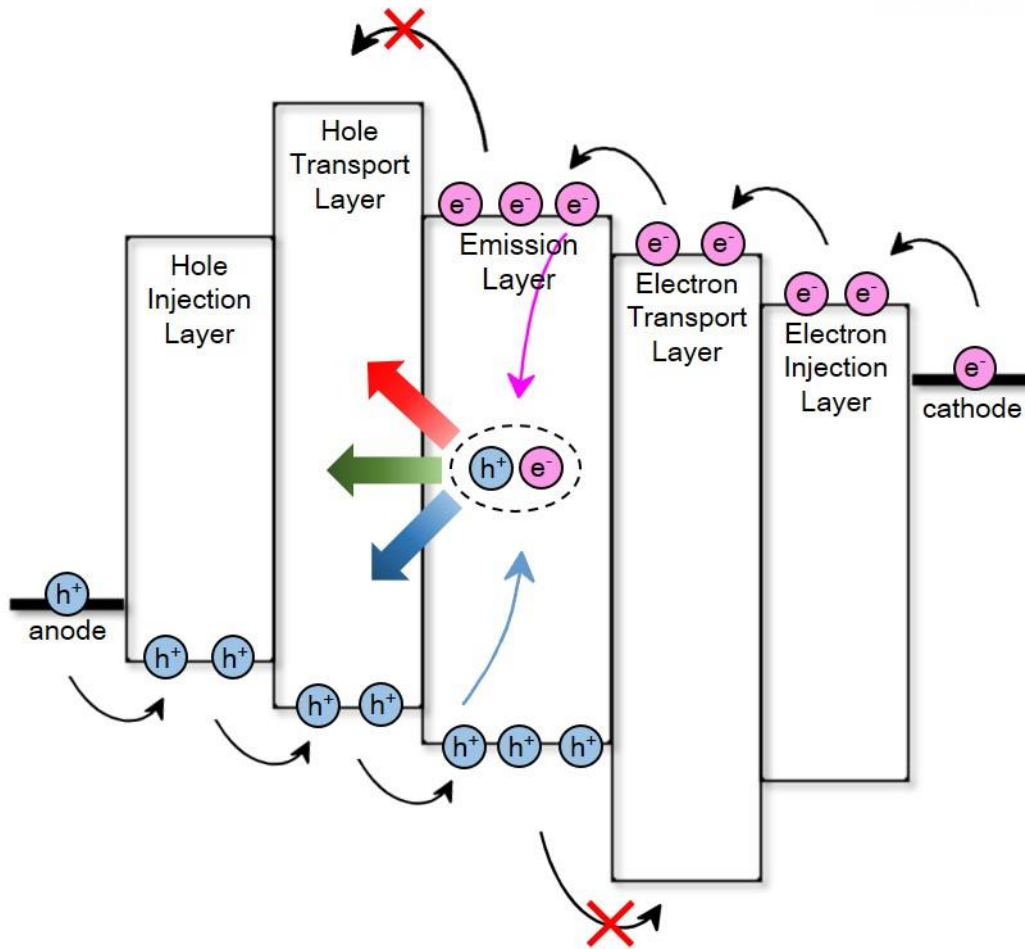


Figure 1. The Schematic diagram of OLED structures and operation procedure.

and anode, cathode for injecting current. Each of the layers composed of organic materials has their own functions.³⁶ HIL and EIL receive holes and electrons from anode and cathode, respectively.

The role of HTL and ETL is to move the holes and electrons from injection layer to EML. To get good mobility of carriers, suitable energy levels of materials are very important. When an electron moves from layer to another layer, the requirement of small energy barriers from EIL to EML is needed for high transportability. And the requirement of a large energy barrier from EML to HTL is essential to block that the electron climb over HTL.³⁷ The same requirements are applied on the holes. The schematic representation of an OLED structure is shown in figure 1.

In the EML, there are not only guest emitting materials but also host materials. The host materials can provide good charge carriers mobility for both holes from HTL and electrons from ETL. Because of the presence of host materials, EML can have less triplet-triplet annihilation and concentration quenching which result in low efficiency. So, the host material performs a significant role of light emission by acting as an exciton formation center that transfer emission energy to the emitters. Because of these critical role of host materials, understanding of degradation mechanisms of host materials gives us huge improvements in OLED. For appropriate host materials, some requirements are necessary: (i) High triplet energy for avoiding energy transfer back from emitting materials to host materials. (ii) High charge-carrier mobility for providing efficient carrier recombination. (iii) Adequate energy level with adjacent transport layers for ensuring good charge injection.³⁴ Host materials have two types according to charge carrier transporting features that are electron-transport-type and hole-transport-type. I calculated the hole-transport-type host materials which have hole transport nature and are composed of electron-donating moiety.³⁸

2.3 OLED materials

In order to investigate the dissociation mechanism, I choose the molecules which have good properties and have been widely used as host ingredients in EML of OLEDs. Carbazole derivatives are one of most widely used as hosts of OLEDs due to their enough high triplet energies and good hole transporting properties.^{10, 11} A 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP) is one of the most common carbazole based hole-transport-type host materials for OLEDs.^{7, 12-15} 4,4'-bis(9-carbazolyl)-2,2'-dimethyl-biphenyl (CDBP), 4,4'-bis(9-carbazolyl)-3,3'-dimethyl-biphenyl (o-CDBP), derivatives of CBP are also host materials with high triplet energies and improved thermal stability.^{10, 16, 17} In addition, I consider hole-transport materials in HTL which are N,N'-Bis(3-methylphenyl)-N,N'-diphenyl

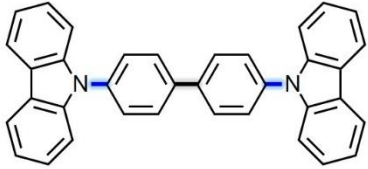
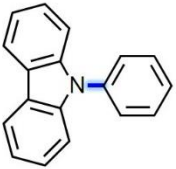
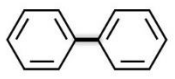
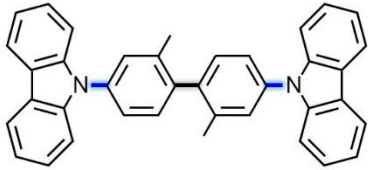
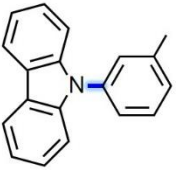
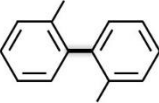
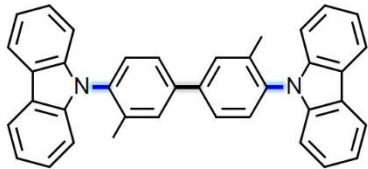

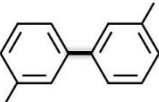
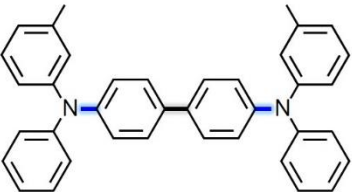
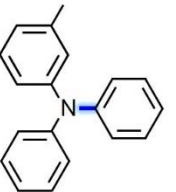

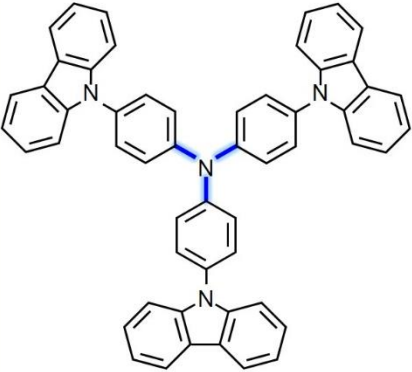
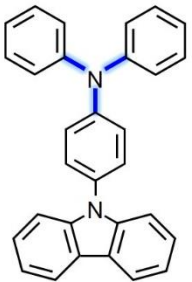
	Molecule	Moiety	
		C-N	C-C
CBP			
CDBP			
o-CDBP			
TPD			
TCTA			

Figure 2. Chemical structures of the CBP, CDBP, o-CDBP, TPD, and TCTA molecules and their moieties classified by the bond characters which are C-N and C-C

benzidine (TPD) and Tris(4-carbazoyl-9-ylphenyl)amine (TCTA). These two hole-transport materials are selected for additional comparative analysis because of a similar bond character with host materials.

Here, I calculate the bond dissociation energies to investigate the stability of OLED materials. By calculating bond energies, we can analyze which bond is the weakest bond in materials and how strong it is. The lower bond energy means the weaker bond which indicates that more likely to be dissociated. As shown in Figure 2, materials are linked with a lot of bonds which are carbon-carbon(C) and carbon-nitrogen(N) in materials. I consider the exocyclic C-N bond and C-C bond cleavages because they are known to undergo dissociation with bonding energies in the same energy range as the first singlet excited state.^{30-31, 33-34, 39} The bonds corresponding to the dissociation mechanism are marked with blue and black thick lines for C-N and C-C, respectively in Figure 2. The dissociation of endocyclic bonds in benzene rings and carbazole ring are excluded, because they have higher bond dissociation energies than single bonds between fragments.^{31, 33}

Structures of moieties are configured to have the same bond dissociation role with molecules. This means that the other parts far from the corresponding bond are removed and only the parts which adjoin the bond are considered as moiety. And the moieties are not just fragments of molecules, but free radicals are filled with hydrogens. So, these moieties can exist on their own in a natural state without reacting. The structures of moieties are shown in Figure 2.

In this work, I present a computational study of the dissociation of the C-N bond and the C-C bond for molecules and moieties. The results are obtained by Density Functional Theory (DFT) and I calculate the differences of bond dissociation energy (BDE) for molecules and moieties in the ground and the excited state. I investigate the effect of non-local interaction in excited states by comparing molecule and moiety systems. Through energy level analysis, I confirm that the effect of non-local interactions can be analyzed by level repulsion. The results indicate that the calculation of bond energies should consider the overall structure of the molecule, rather than only the moiety.

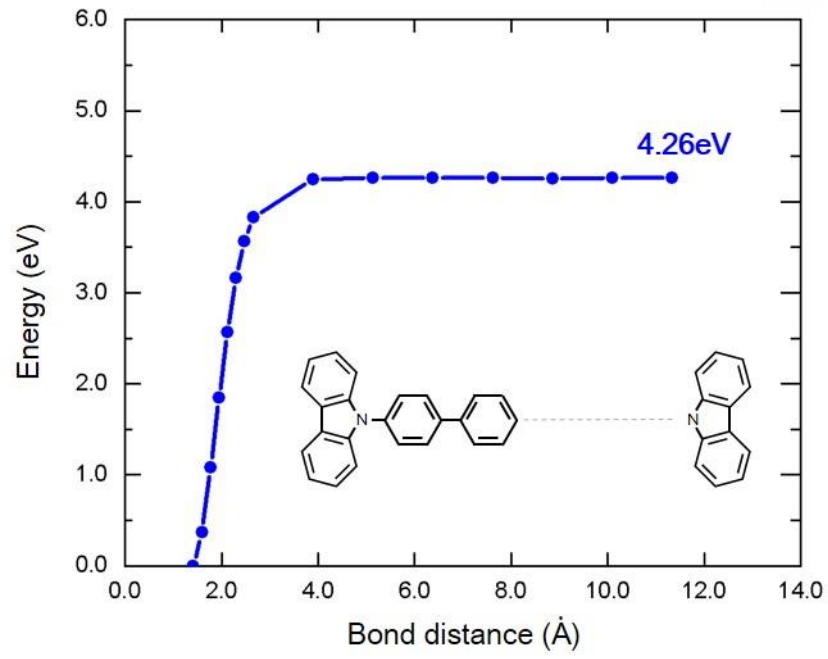


Figure 3. Bond dissociation energies via bond distance for the C-N bond of the CBP molecule

III. Computational details

3.1 Computational methods & electronic and geometric structure

To perform the first-principle calculations, I used the Density Functional Theory (DFT) implemented in Vienna Ab-initio Simulation Package (VASP, version 5.4.1) source code.⁴⁰ Perdew-Burke-Ernzerhof (PBE) type gradient-correlated functional was employed for exchange-correlation functional.⁴¹ The plane-wave basis set with an energy cutoff of 400 eV was used in the expansion of the Kohn-Sham wavefunctions. The atomic pseudopotentials were used with the Projector Augmented Wave (PAW) method in order to describe the core-valence interaction.⁴² The k-point for geometry optimizations and band structure were sampled 1x1x1 by using the Monkhorst-Pack sampling. The structure of OLED molecules and moieties were composed in enough large unit-cell. To prevent interaction between molecules, I set the distance between atoms and other atoms in adjacent molecules more than 10Å at least.

3.2 Bond dissociation energy

The linear interpolation method is used for calculating bond dissociation energies for OLED materials. The results of energy distribution are obtained like Figure 3. Figure 3 is an example of C-N bond dissociation of the CBP molecule. Because the results of bond dissociation energies are obtained without barriers, calculation with a linear interpolation method is enough to get the bond dissociation energies. The results of bond energies are obtained by relaxation with fixed two atoms corresponding to the dissociation bond. The direction of dissociation corresponds to the direction of bond and the distances of separated atoms are calculated until more than 11Å.

3.3 Calculation in electronic excited state

In the electronic ground state, the electronic structure can be represented with Figure 4(a). As shown in Figure 4(a), the levels are filled with electrons until highest occupied molecular orbital (HOMO) in ground state. When the current is applied in OLED materials, electrons and holes are flowed into the excited levels and HOMO levels respectively as shown in Figure 4(b). At that time, the excited carriers are relaxed to the lowest unoccupied molecular orbital (LUMO) level within about a few pico-seconds

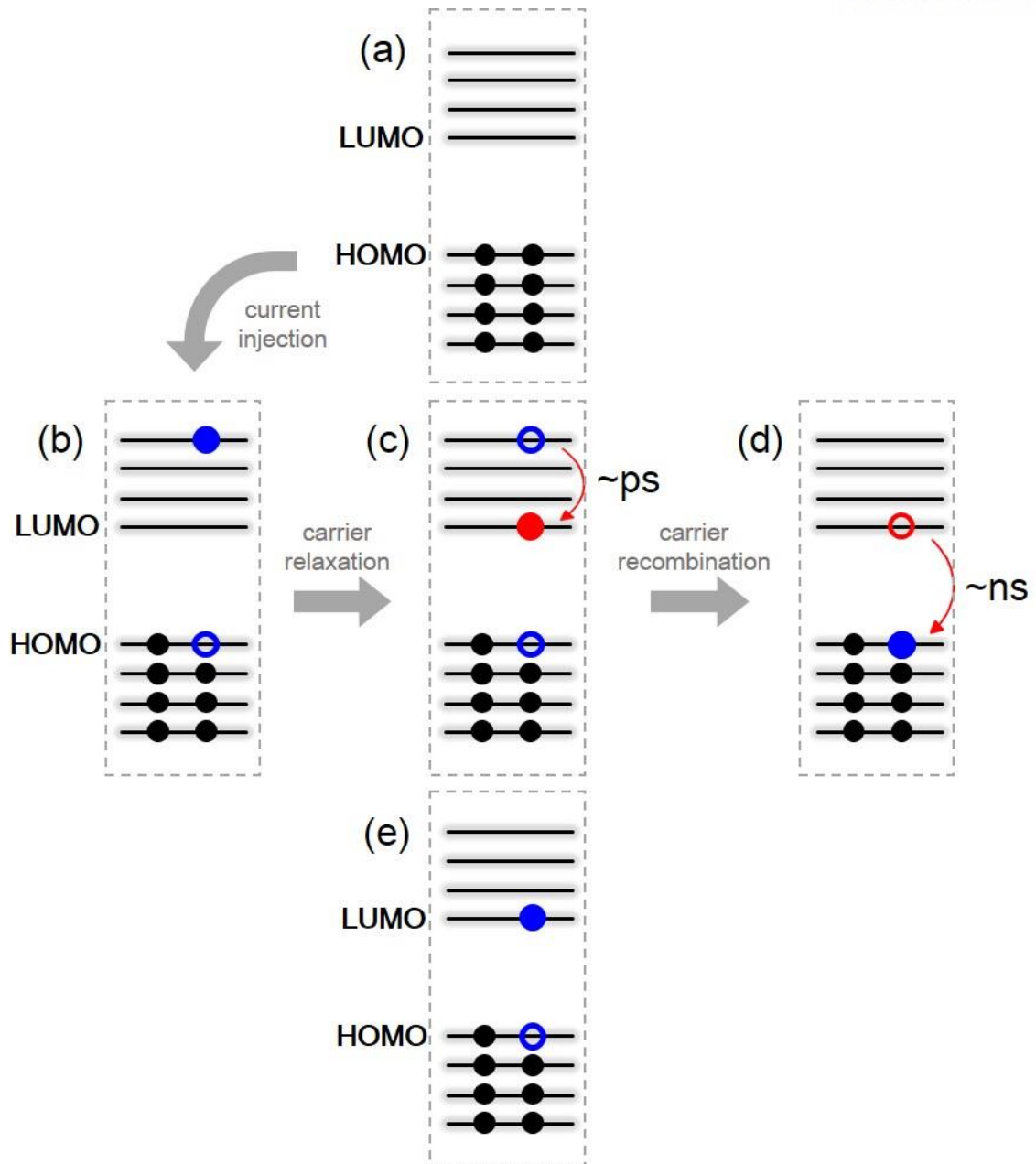


Figure 4. Electronic structures: (a) in ground state, (b) when currents are applied in OLED, (c) when excited carriers are relaxed, (d) when excited carriers are recombined, (e) in excited state

like figure 4(c). After that, the excited carriers in LUMO levels are recombined with holes in HOMO levels within hundreds of nano-seconds like figure 4(d). Because of the time scale differences between carrier relaxation and recombination, the electronic structure in excited states can be described as figure 4(e) in the OLED operating process.

Therefore, I used the occupation-constrained DFT method to calculate the bond energies in electronic excited states. By using occupation-constrained DFT, I can express partial occupancies for all bands of electronic structure. For all cases in excited states, electronic structures are set as one electron is moved from HOMO level to LUMO level.⁴³⁻⁴⁴ This is a reasonable description of the excited carrier in the quasi-equilibrium condition⁴⁵⁻⁴⁶, where the chemical degradation usually occurs.

IV. Results and discussion

4.1 C-N and C-C bond energies in ground state

The materials' degradation can usually be attributed to microscopic bond breakings on chemical reactions, and the bond dissociation energy (BDE) can be a typical factor in determining the stability of materials. Before we calculate BDEs of molecules, I first investigate which bonds of molecules are dissociated one by one. In the case of the CBP molecule, I calculate BDEs of the exocyclic C-N bond between the carbazole and the phenyl, the C-C bond between the phenyls. For the CDBP molecule, the exocyclic C-N bond between the carbazole and the 2,2'-dimethylbiphenyl moiety, the C-C bond between the 2,2'-dimethylbiphenyls are considered. For the o-CDBP molecule, the exocyclic C-N bond between the carbazole and 3,3'-dimethylbiphenyl moiety, the C-C bond between the 3,3'-dimethylbiphenyl moieties are considered. For the TPD molecule, the exocyclic C-N bond between 3-methylphenyl moiety and phenylbenzidine, the C-C bond between the 3-methylphenyls are considered. For TCTA molecule, the C-N bond between 4-carbazoyl and 9-ylphenyl moiety is considered.

At first, I calculate the C-N and C-C bond dissociation energies for OLED molecules in electronic ground state. The calculated C-N and C-C BDEs for molecules are shown in Figure 5 with blue and black circles, respectively. The C-N bond and the C-C bond dissociation energies for molecules lies in the range of 3.82-4.26eV and 5.64-5.93eV, respectively. The average of C-N BDEs for molecules is as low as around 1.8eV less than the average of C-C BDEs. This result shows that the C-N bond is more likely to be dissociated than the C-C bond for these molecules in ground state. In addition, the results of BDEs are similar values depending on whether these are the C-N bond or the C-C bond. From this result, we can guess a tendency for local bond effect depending on bond characters.

To figure out this, the moieties which are the fragments of molecules are only considered for looking into bond effect without incidental parts of molecules. So, the parts far from the dissociation bonds are excluded and the parts corresponding to dissociation bonds are only considered in moieties. Through comparison with the dissociation energies of molecules and moieties, we can figure out that the bond effect depends on bond characters in ground state.

For calculations of moiety, let me enumerate the composition of moieties one by one. In the case of CBP moiety, the structures are made of the combination of carbazole and phenyl for the C-N bond dissociation case and the combination of 3-methylphenyls for the C-C bond dissociation case. In the case of CDBP moiety, the structures are made of the combination of carbazole and 2,2'-dimethyl-

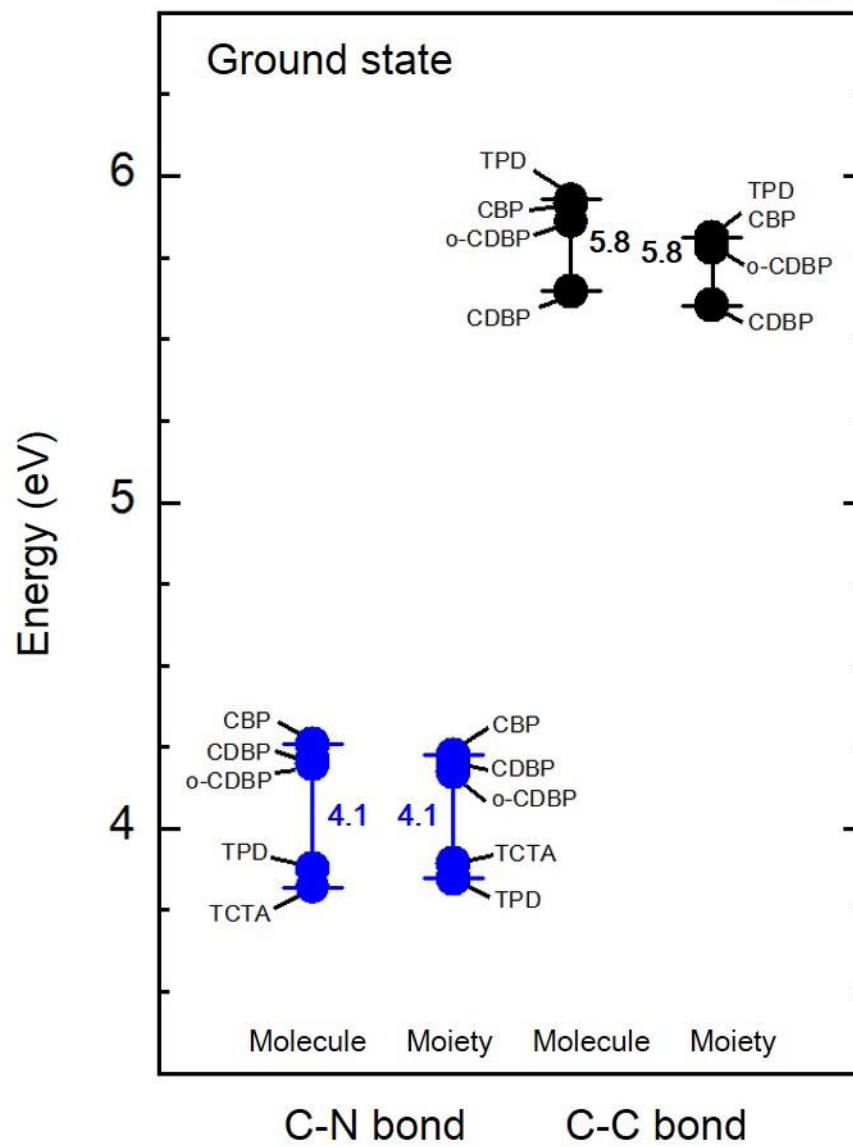


Figure 5. Bond energies of molecules and moieties for C-N and C-C bonds in the ground state

biphenyl moiety for C-N bond dissociation case and the combination of 2,2'-dimethyl-biphenyl moieties for the C-C bond dissociation case. In the case of o-CDBP, the structures are made of the combination of carbazole and 3,3'-dimethyl-biphenyl moiety for the C-N bond dissociation case and the combination of 3,3'-dimethyl-biphenyl moieties for the C-C bond dissociation case. For TPD moiety, the structures are made of the combination of 3-methylphenyl moiety and phenylbenzidine for the C-N bond dissociation case and the combination of 3-methylphenyls for the C-C bond dissociation case. For TCTA moiety, the structure is made of combination of 4-carbazoyl and 9-ylphenyl moiety for the C-N bond dissociation case.

The calculated C-N and C-C bond dissociation energies for moieties in ground state are shown in Figure 5 with blue and black striped pattern circles, respectively. The C-N bond and the C-C bond dissociation energies for moieties lies in the range of 3.85-4.22eV and 5.60-5.81eV, respectively. The average of C-N BDEs for moieties is as low as around 1.7eV less than the average of C-C BDEs. Compared to the results of molecules, The BDEs for moieties are almost similar values. These results indicate that the incidental parts have no influence on dissociation mechanisms, that is to say, a local bond effect is applied in ground state.

4.2 C-N and C-C bond energies in excited state

In operating progress, OLED degradation need to be considered in electronic excited state due to the presence of excited carriers. By using occupation-constrained DFT, we describe the electronic structure where an electron is excited from the HOMO level to the LUMO level. I analyze the effect of excitation on the molecule through comparison between the results in ground state and in excited state.

The calculated C-N and C-C BDEs for molecules in excited state are shown in Figure 6 with blue and black circles, respectively. The C-N bond and the C-C bond dissociation energies in excited state for molecules lies in the range of 1.40-1.91eV and 3.05-3.88eV, respectively. Compared to the results in ground state, calculated BDEs in excited state are significantly reduced as much as about 2.3 eV by the effect of excited carriers. This result indicates that OLED molecules are more likely to be dissociated in excited state. In other words, the stability of OLED materials is lower in operating progress. In addition, the average of C-N BDEs for molecules is as low as about 1.8 eV less than the average of C-C BDEs. Both in ground state and in excited state, the results show that C-N bond is a weaker link of molecules than C-C bond. Like as a molecule, to figure out whether the local bond effect exists in excited state, the calculated C-N and C-C BDEs in excited state for moieties are shown in Figure 6 with

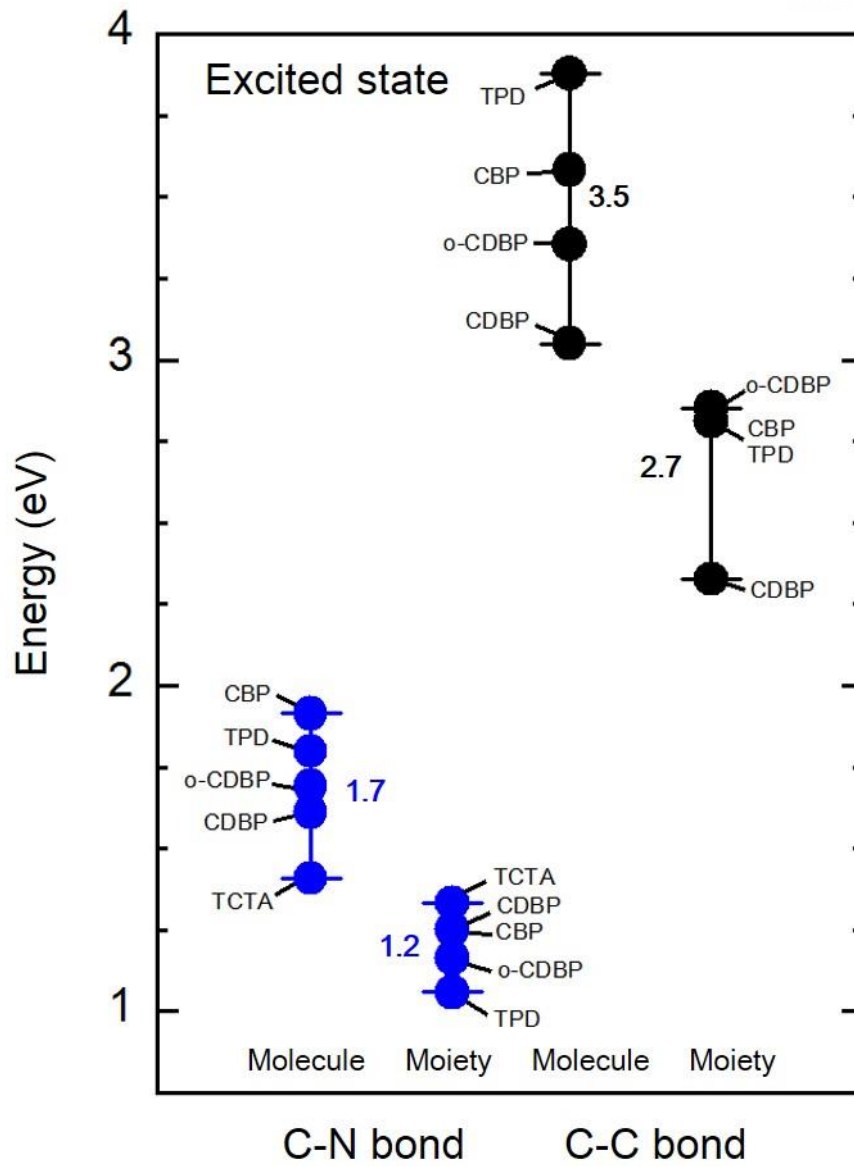


Figure 6. Bond energies of molecules and moieties for C-N and C-C bonds in excited state

a blue and black striped pattern circles, respectively. The C-N bond and the C-C bond dissociation energies in excited state for moieties lies in the range of 1.06-1.33eV and 2.33-2.85eV, respectively. Unlike as the results in ground state, the results between the molecule and the moiety do not have a consistent relationship. The lower BDEs for moieties are calculated than molecules. These results indicate that non-local interactions influence on dissociation mechanism, that is to say, the non-local bond effect is applied in excited state.

4.3 Analysis with energy level variation

To understand the role of non-local interaction in excited states, the energy level changes of CBP molecule and moiety via the C-C bond dissociation are shown in Figure 7(a), (b), respectively. In the figures, the black lines indicate HOMO level and the LUMO level. By checking electron charge density, I discovered that the blue lines indicate the levels that are directly involved in dissociation. And illustrations of electron charge density are presented. Fermi energies of molecule and moiety are subtracted from the energy levels.

The binding energies of molecule and moiety can be described by the energy gaps of blue lines. As the molecule and moiety have similar the energy gaps of blue lines, we can understand the binding energies in the bond itself of molecule and moiety are similar in ground state. However, the calculation of binding energies can be applied differently in excited state. It is important to analyze the results from comparison with the HOMO-LUMO gaps in excited state, since the excited carrier moves from HOMO level to LUMO level in the operating process. For the molecule, the lower effect of the excited carrier is applied with lower HOMO-LUMO gap than moiety. Therefore, the bond energies of molecules are calculated with higher energies than moieties. This can be explained with the effect of non-local interactions. Because of more levels from non-local interactions, higher level repulsion is applied in the molecule. Then, the lower HOMO-LUMO gaps are given by the level repulsion of the molecule. Therefore, calculations should be considered with the whole structure of the molecule, when we want to see the dissociation mechanisms in excited states.

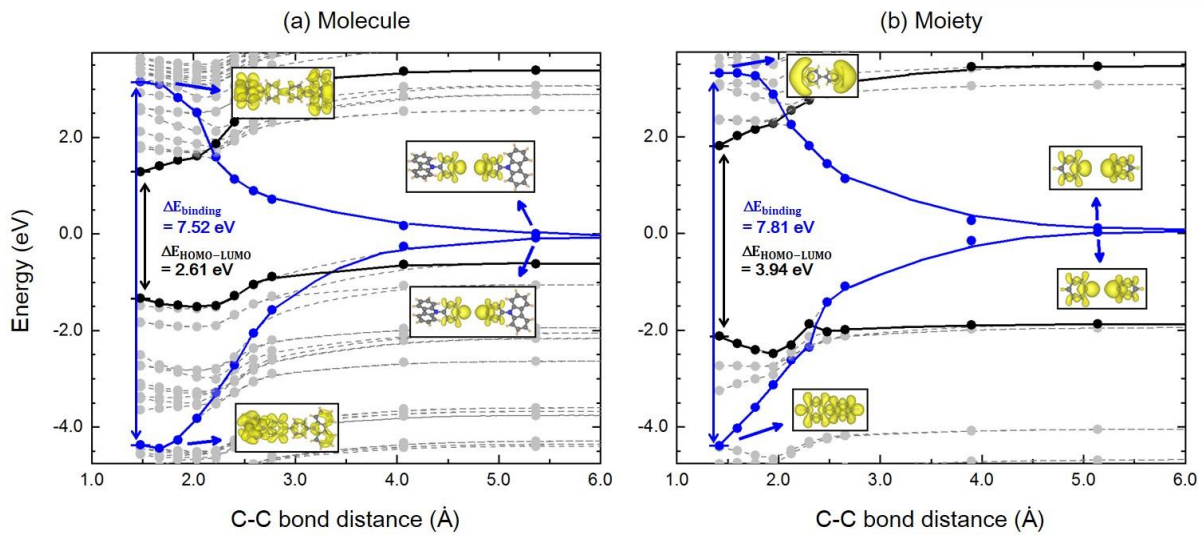


Figure 7. Energy level variations along the reaction pathway for the C-C bond dissociation of the CBP (a) molecule and (b) moiety. Black lines indicate HOMO level (down) and LUMO level (up), respectively. Blue lines indicate the levels directly involved in dissociation with illustrations of the electron charge densities.

V. Conclusion

I studied chemical stability of OLED materials in the device working condition. The electronic structure in excited states is described by the occupation-constrained DFT. I found that the chemical bond is mainly weakened by the excited carriers, and in particular, the C-N bond breaking can possibly be a main cause of chemical degradation. In the electronic ground state, the degradation mechanism can be considered with the local structure of the dissociation bond. However, the effect of the excited carrier depends on the electronic structure of the system, and as a result, in the electronic excited state, the bond dissociation energy is not determined by the bond itself, but by the overall molecular structure.

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