

유기 발광 다이오드 내부의 라디칼 반응 가능성 검사

Feasibility Test for Radical reactions in Organic Light Emitting Diode

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Abstract : Feasibility test for radical reactions in organic light emitting diode(OLED) has been applied on OLED consisting of hole transport layer(HTL) and electron transport layer(ETL). Organic molecules such as 4,4',-Bis[N-(1-naphthyl)-N-phenylamino] biphenyl(NPD) and 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine(m-MTDATA) are chosen for hole transport layer(HTL) and Bathocuproine(BCP) for electron transport layer(ETL) in this study. Informations on energy and shape of frontier orbitals and data on radical reactions of simple aromatics from semiconductor(TiO₂) photocatalysis have provided basis for determining feasibility for radical reactions in OLED. The outcome of our feasibility test would be useful in designing optimum molecule for organic layer with a view to extending the lifetime of OLED.

Keywords : density functional theory, electroluminescence device, frontier orbitals, radical reaction, semiconductor photocatalysis

I. Introduction

Organic light emitting diodes(OLEDs) are superior to LCD due to higher picture quality, faster response, wider viewing angle, better outdoor readability, and slimness; however, the same cannot be said about the reliability and durability, as yet.

Various efforts are being made to extend the lifetime of OLED, and encapsulation is a common manufacturing practice that has contributed significantly to that end. The aim of encapsulation engineering is to keep the enclosure free of oxygen and water as much as possible, since they are linked to oxidation of the organic layers [1], however, there have not been studies which show the adverse effect of water molecules on the lifetime of OLED clearly, to my knowledge.

In seemingly different yet related topic of semiconductor photocatalysis, where electrons and holes are created optically followed by electron-hole recombination, and decomposition of organic compounds by radicals are known to occur, the role of water molecules has been studied extensively [2,3]. In OLED, in comparison, holes and electrons are injected into the inner organic layers through which they travel, and some of them recombine in certain organic layer.

Now that we have established grounds for resemblance between semiconductor photocatalyst and OLED operations, we proceed to investigate the feasibility for radical reactions in OLED while paying attention to oxygen and water. In subsequent applications, we have chosen 4,4',-Bis[N-(1-naphthyl)-N-phenylamino]biphenyl(NPD) and 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine(m-MTDATA) for hole transport layer and Bathocuproine(BCP;2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) for electron transport layer.

II. Experimental

Details of our experiments on semiconductor photocatalysis of benzene and toluene are described elsewhere [4].

The reaction was carried out in a batch type glass vessel at 1

atm and ambient temperature. Air flowed through a mass flow controller into the saturator placed in a constant temperature bath at 20°C and 1 atm, and was mixed with 90% air coming from another mass flow controller in order to obtain predetermined concentrations of aromatic compounds in air. The aromatic mixture flowed into and out of a 10 L batch reactor initially to allow adsorption to take place in the reactor.

Samples of outlet mixture were periodically analyzed with a gas chromatograph(GC) equipped with a flame ionization detector and a capillary column to be compared with the target composition. When the target composition was achieved, the inlet and outlet of the reactor were closed, and photocatalytic decomposition of the aromatic compound was carried out in the reactor. During the experiment gas samples were taken at 30 min. interval for GC analysis to monitor variations in the concentration of the aromatic compound.

The photocatalyst used in this study was sol type titanium dioxide(15% TiO₂) suspended in alcoholic solvent, and this was mixed with silicon binder solution of pH 3.5 to increase the coherence of titanium dioxide on the substrate, aluminum plate. Aluminum plate was coated with TiO₂ using a bar-coater, which was dried at 120°C for 30 min. in the air without calcinations. Three 8 W UV lamps were used for the irradiation of TiO₂ coated aluminum plate.

As to the molecular orbital calculations, quantum mechanical calculations based on density functional theory(DFT) are employed with B3LYP/6-31G* density functional model. All the calculations in this study are carried out using SPARTAN '06, version 1.0.1 [5].

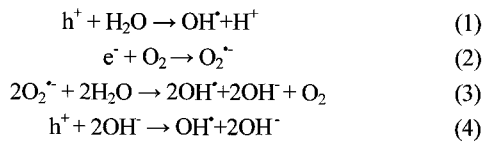
III. Results and Discussion

Semiconductor photocatalysis we refer to in this study is based on TiO₂, and UV excitation is required to generate valence electrons and conduction holes due to its bandgap of ~3.2 eV, and subsequent electron-hole recombination is known to occur on the order of 25 ns [6]. Those electrons and holes of electron-hole pairs with their reducing and oxidizing ability, respectively, are capable of attacking organic molecules on the surface of TiO₂ either directly or indirectly as follows.

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According to the above reactions, hole is capable of generating hydroxyl radical(OH[·]), the powerful oxidizing species, by oxidizing water directly, whereas electron reacts with oxygen first to produce superoxide anion radical, which then reacts with water to generate hydroxyl radical. From these reactions the role that water and oxygen play in generating hydroxyl radical, the major species responsible for initiating decomposition reactions of various aliphatic and aromatic compounds, is obvious [6], and it is true that water and oxygen or more importantly water molecules must be present in the reaction environment for the photocatalysis to occur.

On the other hand, water and oxygen must be avoided in OLED operations for the very reasons that are useful for the semiconductor photocatalysis. Studies have shown formation of crevasses in the organic layer by oxygen and hydrogen evolved from water electrolysis, oxidation of Al electrode by O₂, and self-degradation of some electroluminescence(EL) polymers by oxygen radicals [1,7]. It is to be noted that the formation of crevasses in the organic layer by oxygen gas is not chemical change but morphological change.

Assuming that encapsulation material is not perfectly hermetic, H₂O and O₂ molecules are expected to be present inside the enclosure, even if very small, and some of them are likely to diffuse into the organic layers. Now the question is whether H₂O and/or O₂ will generate hydroxyl radicals in these various organic layers as they do in TiO₂ following UV excitation. We start addressing this question by examining the feasibility of reaction (1) in hole transport layer and the feasibility of reactions (2) and (3) in electron transport layer.

In the case of TiO₂, valence hole is estimated at ~ -7 eV [8], and highest occupied molecular orbital(HOMO) of water molecule is calculated at -7.92 eV, and there exists energy gap of ~0.92 eV,

표 1. 반응물의 분자 궤도함수 에너지.

Table 1. Molecular orbital energies of reactants.

Reactants	HOMO (eV)
NPD	-5.5
m-MTDATA	-5.1
BCP	-6.5
H ₂ O	-7.92*
OH [·]	-8.95*

*Calculated in this work

표 2. 벤젠과 톨루엔의 광촉매 분해반응 속도상수와 분자 궤도함수 에너지.

Table 2. Photocatalytic decomposition rate constants and Molecular Orbital energies of benzene and toluene.

	HOMO (eV)	rate constant (min ⁻¹)
benzene	-6.70	6.79 x 10 ⁻⁴
toluene	-6.40	3.97 x 10 ⁻⁴

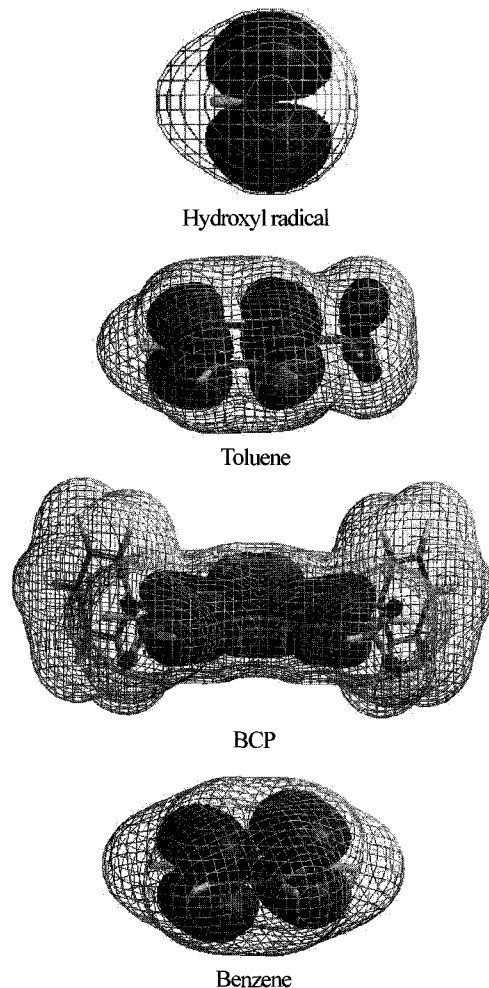


그림 1. 벤젠, 톨루엔, BCP의 HOMO 및 히드록시 라디칼의 SOMO 그리고 전자 밀도 표면.

Fig. 1. Electron density surfaces and HOMOs of benzene, toluene, BCP and SOMO of hydroxyl radical.

which allows reaction (1) to occur in view of the OH[·]-mediated photocatalytic decomposition mechanism [9]. In comparison, we examine NPD and m-MTDATA, the two organic molecules developed for hole transport layer [10], from Table 1, and find that HOMO energies are higher than the energy of valence hole in TiO₂, thereby making the energy gap with respect to water larger. In terms of energy consideration only, larger energy gap between frontier orbitals of two reacting species in hole transport layer is not in favor of reaction (1), according to the frontier orbital theory, and there is a supporting evidence in a study by Kondakov et al. [11]. In an experiment on a holes-only device(75nm NPD | 20 nm CBP | 30 nm NPD | 20 nm copper phthalocyanine), where NPD was hole transport layer, they did not detect any sign of degradation of compounds [11].

In studies on electron injection and transport in tris (8-hydroxyquinoline) aluminum (Alq₃), Kiy et al. [12] reported observation of Mott Gurney law in Alq₃ films and showed that even small traces of atmospheric gases led to the disappearance of a space charge limited conduction, thereby identifying atmospheric gases as electron trapping centers. Accordingly, water and oxygen molecules, which are present in electron transport

layer either as impurities from the manufacturing process or by diffusion after encapsulation, would encounter injected electrons from the cathode and proceed to form hydroxyl radicals via reactions (2) and (3). This means that the possibility for attack of organic molecules by hydroxyl radicals is highly likely in electron transport layer unlike the situation in hole transport layer.

Table 2 shows decomposition rate constants for benzene and toluene from our photocatalytic experiment on TiO_2 [4], together with calculated HOMO energies.

According to the frontier orbital theory [13-16], interactions between HOMO in one of the reactant species and LUMO in the other species determine the chemical reactivity essentially. Thus, only the interactions between HOMO and LUMO for the aromatic compound and oxidants need to be considered in the photocatalytic decomposition of aromatic compound.

In view of the frontier orbital theory, the difference in decomposition rates can be explained by the difference in energy gap between HOMO of aromatic and singly occupied molecular orbital (SOMO) of OH^\cdot , since the difference in the steric factors between two aromatics is negligible.

Thus, benzene with gap of 2.25 eV is predicted to decompose faster than toluene with energy of 2.55 eV, which is in agreement with our experimental observation.

Bathocuproine (BCP) in Table 1 is organic molecule commonly used for electron transport layer, and its HOMO energy of -6.5 eV [17] is between that of benzene and toluene in Table 2. Based on energy consideration only, decomposition of BCP in OH^\cdot -mediated reaction mechanism [9] is expected to occur. To get a better picture for the reaction, electron density surfaces and HOMOs of benzene, toluene, BCP and SOMO of hydroxyl radical are shown in Fig. 1.

In decomposition reaction of benzene and toluene, attack of hydroxyl radicals will be toward the plane of the ring, since approaches to the side yield no reaction due to unfavorable overlap of orbitals. Compared to benzene and toluene, BCP shows higher delocalization of electron density over larger conjugated rings and higher steric hinderance due to phenyl rings and methyl groups attached to 1,10-phenanthroline moiety; however, steric hinderance is most effective in the sideways attack to the 1,10-phenanthroline plane, the same type of uneffective attack as in benzene and toluene as far as reaction is concerned.

In summary, our consideration of energy and shape of molecular orbitals in Fig. 1 has given strong support for decomposition of BCP by hydroxyl radicals in electron transport layer. Moreover, Joule heating which is known to occur in EL devices [18] will promote such a reaction.

IV. Conclusions

We have investigated feasibility of radical reactions in hole transport layer and electron transport layer in typical OLED, in analogy to radical reactions in photocatalysis on TiO_2 . In hole transport layer, feasibility test of radical reactions is focused on generation of hydroxyl radicals between either NPD or m-MTDATA and water molecule. Our analysis of energy gap of frontier orbitals in view of simple aromatics such as benzene and toluene and observation of no chemical decomposition in holes-only EL device in the literature [11] do not support feasibility of radical reaction in hole transport layer, although feasibility due to

various types of hole traps cannot be ruled out.

The situation is different in electron transport layer where the mobility of injected electrons in amorphous organic layer is quite slow and electron traps including atmospheric gases are known to exist. In this layer, it is possible that dissolved O_2 is reduced to superoxide anion radical and then reacts with water to generate OH^\cdot . We have chosen BCP for electron transport layer and tested feasibility of reaction with hydroxyl radicals. Our analysis of energy and shape of frontier orbitals in view of decomposition reaction of benzene and toluene supports feasibility of radical reactions in electron transport layer, thus decomposition of BCP.

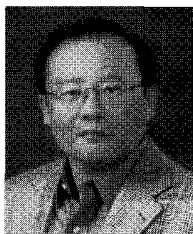
In conclusion, we have shown that OLED, where either NPD or m-MTDATA is hole transport layer and BCP is electron transport layer, is vulnerable to radical attack in the presence of oxygen and water, and electron transport layer is under higher risk of decomposition, in analogy to OH^\cdot -mediated mechanism for the photocatalytic decomposition of benzene and toluene on TiO_2 .

Furthermore, molecular engineering aimed at protecting high electron densities in HOMO of molecules in organic layer against water and/or hydroxyl radical needs to be better implemented with a view to extending the lifetime of OLED.

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