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Effect of acceptor on efficiencies of exciplex-type organic light emitting diodes

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The relationship between the electroluminescent (EL) efficiencies of interfacial exciplex emission and the lowest unoccupied molecular orbital (LUMO) of the acceptors systematically investigated. A nearly linear relationship was observed between LUMOs of acceptors and exciplex efficiency for a fixed donor of 4,4′,4″-tris[3-methyl-phenyl(phenyl)amino]-triphenylamine in exciplex-type devices. This result indicates that the lower the LUMO of the acceptor is, the higher the EL efficiency of the exciplex is. The effect of acceptor on the efficiencies of exciplex-type devices is attributable to the interactions between the donor and acceptor molecules, which were closely related to the matched LUMOs and intermolecular conformations overlap between donor and acceptor molecules. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2762298]

The electroluminescence (EL) that originates from the interactions of donor and acceptor molecules at the organic/organic interface or solid intermolecular contacts in some multilayer organic light emitting devices[1–4] (OLEDs) is called exciplex emission. Exciplex is a kind of excited state complex formed between donor D and acceptor A, with one in the excited state and the other in the ground state. On one hand, exciplex usually leads to the redshifted emission and broadened spectrum relative to the emissions of the individual acceptor or donor. Therefore, for pure homochromatic OLEDs, exciplexes should be avoided. Some methods for eliminating the boring exciplex emission have been reported. They are the insertion of a hole transport material with high highest occupied molecular orbital (HOMO) between the donor and acceptor interface,[2,5] or the employment of doping or blending techniques to reduce the probability of exciplex formation.[6,7] On the other hand, exciplexes have been exploited to develop bifunctional devices with photovoltaic and EL performances,[8–10] to tune the OLED emission color,[1,11] and to design white OLEDs.[12] The major problem in utilizing these effects in devices is to find systems that work with high exciplex EL efficiency,[13] so investigation of the active factors for efficient exciplex emission is a subject of significance though it has been rarely studied yet.

It is well known that the donor with lower HOMO would be in favor of donating an electron and that the wavelength of the exciplex emission usually reflects the energy difference between the lowest unoccupied molecular orbital (LUMO) of the acceptor and the HOMO of the donor.[14] These results indicate that the LUMO of the acceptor is an important factor which determines the emissive wavelength of the exciplex.

In this letter, we investigated the effect of the LUMO of acceptors on the EL efficiencies of exciplex emissions based on D-A interfacial type devices, in which 4,4′,4″-tris[methyl-pheny(phenyl)amino]-triphenylamine (*m*-MTDATA), with HOMO of 5.1 eV and LUMO of 1.9 eV,[15] was used as a donor and several compounds with various LUMO levels were chosen as acceptors. The acceptors studied include tris(8-hydroxyquinoline) aluminum (Alq_3), 9,10-di-(2-naphthyl)anthracene (ADN), 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI), 2-(biphenyl4yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP). Among these systems, the EL emissions of the *m*-MTDATA-Alq_3,[16] *m*-MTDATA-TPBI,[17] *m*-MTDATA-PBD,[13] and *m*-MTDATA-BCP systems[18] have been confirmed as exciplex emissions.

All devices were fabricated by thermal deposition of materials in vacuum of 3.0×10^{-4} Pa. Indium tin oxide (ITO)-coated glass substrates with sheet resistance of 30 Ω/□ were used as anodes, which were routinely cleaned, followed by O_2 plasma surface treatment for 5 min prior to organic film deposition. Devices with structure of ITO/*m*-MTDATA (60 nm)/acceptors (40 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (100 nm) were fabricated, in which the exciplex-exciton is

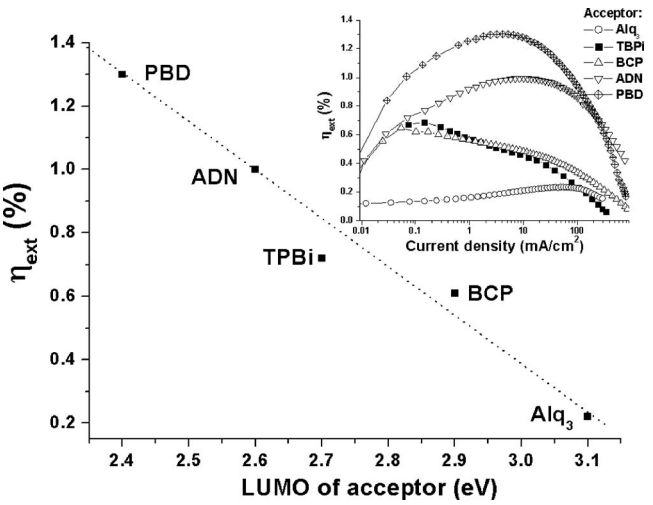

FIG. 1. Relationship between the η_{ext} of exciplex emission and LUMO levels of the acceptors for devices with structure of ITO/*m*-MTDATA (60 nm)/acceptor (40 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al; the inset is the corresponding η_{ext} of exciplex emission vs current density.

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TABLE I. HOMO-LUMO of various acceptor materials, exciplex emission peaks, and η_{ext}, which are obtained from devices based on donor of *m*-MTDATA. LUMO-HOMO data are cited from literatures (see Refs. 19–22).

Acceptor materials	Alq_3	BCP	ADN	TPBi	PBD
LUMO-HOMO (eV)	3.1–5.8	3.0–6.4	2.6–5.8	2.7–6.2	2.4–6.1
η_{ext}(%)	0.22	0.6	1.0	0.71	1.3
Exciplex emission peak (nm) at 5 V	554	543	532	538	528

formed at the interface between *m*-MTDATA and various acceptor layers. A shadow mask overlapped with the anode was used to define the cathode by 3×3 mm^2 in dimension. The characteristics of luminance–current density–voltage were measured by a Keithley source meter, and the EL spectra were measured with a Hitachi MPF-4 fluorescence spectrophotometer.

Figure 1 shows the dependences of the external quantum efficiency (η_{ext}) of exciplex emission on the LUMOs of acceptors, and the inset presents the corresponding relationship between the exciplex η_{ext} and the current density. Table I lists the HOMO-LUMO levels of the acceptor materials, exciplex emissive peaks, and the respective maximum η_{ext}. As Fig. 1 and Table I show, a nearly linear relationship between η_{ext} and the LUMO of acceptor was observed, i.e., $\eta_{ext}=kx+b$, where $k=-1.5$ and $b=4.9$ for *m*-MTDATA based exciplex-type devices. It is also suggested that the η_{ext} of exciplex emission is almost independent of the luminescence efficiencies and the electron mobility of the acceptors. For example, the EL efficiency is about 3.0 cd/A for Alq_3 emission and is less than 2 cd/A for ADN emission,[19] respectively, the electron mobility of ADN is much lower than that of Alq_3. However, the efficiency of exciplex emission in ADN-based device is higher than in Alq_3-based one, ~3.0 cd/A ($\eta_{ext}=1.0\%$) for the former and only 0.75 cd/A ($\eta_{ext}=0.22$) for the latter. Similar cases were also observed in BCP- and TPBI-based devices. In PBD-based device of ITO/*m*-MTDATA/PBD/Alq_3/LiF/Al, the η_{ext} of exciplex emission was only 0.5%, by the insertion of a 5 nm mixture layer of *m*-MTDATA and PBD with ratio of 1:1 between the D-A interface, as high as 1.3% of exciplex emission in η_{ext} was obtained, which fits well with the relationship of $\eta_{ext}=kx+b$.

The mechanisms of exciplex formation in OLEDs have been widely reported in the previous papers,[1,13,14,16] the typical opinion was $A^*+D\cdots(D^+A^-)^*$ (exciplex exciton) or $D^*+A\cdots(D^+A^-)^*$ (exciplex exciton), which was judged in terms of the higher energy barrier of electron and hole injections at the D-A interface. However, the efficiency of exciplex emission has been rarely mentioned in these mechanisms. Here, the relationship between the EL efficiency of

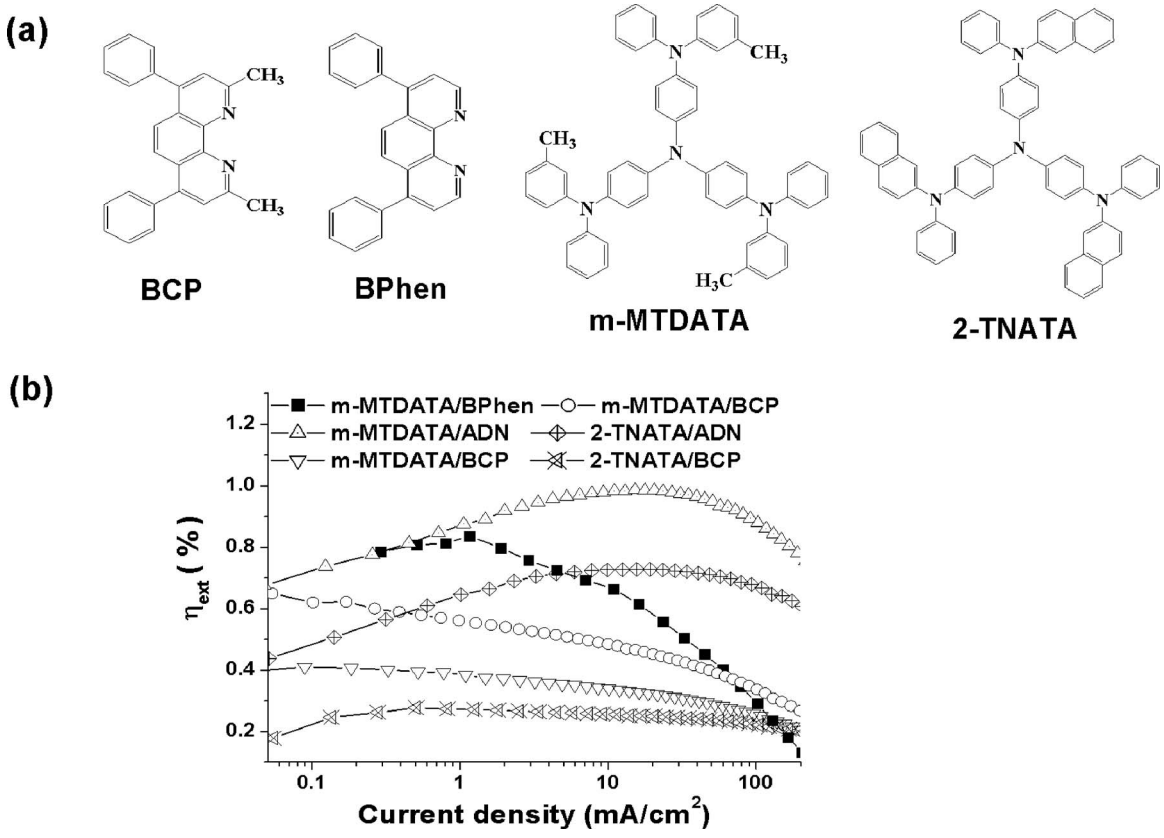

FIG. 2. Molecular structure (a) of acceptor, BCP and BPhe and donor, (*m*-MTDATA and 2-TNATA) used for exciplex-type devices with structure of ITO/donor (60 nm)/acceptor (40 nm) Alq_3 (30 nm)/LiF (1 nm)/Al; the external quantum efficiency of exciplex emission vs current density (b) by fixing the donor, the acceptors are BCP and BPhen, respectively, or by fixing the acceptor, the donors are, respectively, *m*-MTDATA and 2-TNATA for comparison.

exciplex and the LUMO of acceptor is discussed.

The EL efficiency of exciplex should depend on the yields of exciplex exction, which correlate with the interaction between donor and acceptor molecules. It is probable that an electron-transfer process takes place during the interaction, in which the electron-donating molecule is called donor and the electron-accepting molecule is called acceptor. We also noticed that exciplex always takes place when the HOMO of donor is low or the hole injection barrier at the D-A interface is high. High barrier for hole injection would make the hole locate in the donor layer; consequently, the potential energy of hole increases with the increase of the electrical fields. We believe that the donor molecule would react with the hole to form D^+ if the solid-state ionization potential of donor is low and the potential energy of the hole is high enough. The formation of D^+ essentially means that an electron escapes from the donor molecule or the donor molecule donates an electron. The adjacent acceptor molecule accepts the electron to form A^-, which is resonant with D^+, forming metastable exciplex exciton $(D^+-A^-)^*$. In fact, such an electron donating and -accepting process can be regarded as charge transfer from LUMO of the donor to LUMO of the acceptor. Matched LUMO levels between the donor and acceptor would be crucial for achieving efficient electron transfer and A^- formation, which would increase the formation probability of $(D^+-A^-)^*$. As a result, higher exciplex efficiency could be harvested.

Considering that the electron transfer takes place between the donor and acceptor molecules during the exciplex exciton formation, the contact between the donor and acceptor molecules should influence the efficiency of exciplex emission significantly. The results in the system of *m*-MTDATA-PBD just proved it. The LUMO of PBD is 2.4 eV (Ref. 22) but the η_{ext} of exciplex emission was only 0.5% in PBD-based layered device. When inserting a thin mixture layer of *m*-MTDATA and PBD with ratio of 1:1 between D-A interface, the η_{ext} was improved to 1.3%. It is well known that the crystallization temperature of PBD molecules is low and the roughness of PBD film is high, so the contact between the donor and acceptor layers is worse, which is disadvantageous for electron transfer between *m*-MTDATA and PBD molecules. Therefore, the efficiency of exciplex emission is low. The insertion of mixture layer improved the intermolecular conformation overlap between the donor and the acceptor. Consequently the η_{ext} of exciplex emission improved greatly.

Besides compact intermolecular contact, efficient charge transfer between the donor and acceptor is strongly correlated to the electron cloud distributions on their LUMOs. Larger overlapped electron clouds would benefit to the charge transfer.[23] Molecular crystal structures indicate that the electron clouds assemble on the main moiety of the molecules rather than involved substituted groups, so that the substituted groups on either the donor or acceptor molecule would hinder the overlapping between the electron clouds for the mutual contacted molecules. Therefore, charge transfer will be less efficient between substituted molecules with bigger space group, which were testified in the following experiments. BCP and BPhen present similar molecular structure and have almost identical electrical properties such as electron transport and level positions of the HOMOs and LUMOs.[24] As presented in Fig. 2(a), BCP has two additional methyl groups in comparison with BPhen molecule. There are also similar cases for donor materials of *m*-MTDATA and 4,4′,4″-tris[2-naphthyl(phenyl)amino]-triphenylamine (2-TNATA). EL performances of devices based on the donor of *m*-MTDATA with different acceptors of BCP and BPhen, or based on the acceptor of BCP or ADN with different donors of *m*-MTDATA and 2-TNATA are shown in Fig. 2(b), respectively. It is found that the additional spatial blocks on both donor and acceptor molecules lead to 30%–40% loss of the exciplex efficiencies.

In summary, we have investigated the effects of acceptors on the efficiency of exciplex emission systematically. By comparing the performances of exciplex-type devices with varying LUMOs of acceptors for the fixed donor of *m*-MTDATA or the donor/acceptor molecules having identical LUMO and HOMO with different spatial blocks, we found that the electron transfer process from donor to acceptor governs the formation efficiency of exciplex exciton $(D^+-A^-)^*$. Efficient electron transfer between the donor and acceptor requires more matched LUMOs and intermolecular conformations overlap between the donor and acceptor molecules. So, lower LUMO for acceptor and compact donor-acceptor intermolecular contacts would be favored, obtaining efficient exciplex EL emission. The investigation of the effect of acceptor on exciplex efficiency will be beneficial to the design of more efficient exciplex-type devices.

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