Multilayered Organic Light-Emitting Devices by Solution-Process

Yong-Jin Pu,* Takayuki Chiba, Naoya Aizawa, Hisahiro Sasabe and Junji Kido*

Department of Organic Device Engineering, Research Center for Organic Electronics, Yamagata University, Yonezawa, Yamagata 992-8510, Japan.
pu@yz.yamagata-u.ac.jp; kid@yz.yamagata-u.ac.jp

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1. Introduction
Solution processes such as spin-coating, inkjet-printing, or splay-coating for organic light emitting diodes (OLEDs) are still fascinating due to their potential advantages for a production of large area devices at low cost, although dry deposition processes under vacuum are much ahead of the solution processes from the commercialization point of view. One of the key solutions to improving the performance of the devices is stacking of a number of successive layers of different functional materials. This multilayer architecture allows for the separation of the charge-injecting, charge-transporting, and light-emitting functions to different layers, which leads to a dramatic increase in efficiency and lifetime. We have developed various solution-processable OLED materials. In this review, we report our recent studies on fluorescent emitters[1], phosphorescent emitters[2], host materials[3], cross-linkable host materials[4], and electron injection materials[5] for solution-processed OLEDs.

2. Solution-processable fluorescent emitters
Conjugated polymers have been extensively studied as solution processable emitting materials for OLEDs since 1990[6]. Precise control of molecular weight, end-group structure, and regioregular structure of the conjugated polymers for OLED has been established, but it is not possible to purify structural defects in a polymer chain itself thoroughly. However, monodisperse conjugated oligomers are able to have no structural defects and a better purity from conventional purification methods such as column chromatography, recrystallization, and sublimation, and they can show a high glass transition temperature ($T_g$) and a good film forming ability. We designed bis(difluorenyl)amino-substituted fluorescent dyes 1-4 as solution processable light-emitting dyes (Figure 1). In these compounds, emitting color can be easily controlled by a kind of central dyes, and outer fluorene oligomers can sterically prevent excimer formation between the emitting cores in a neat film. For a practical application, the electron transporting layer has to be common for each color pixel to be deposited without a shadow mask like a deposition of cathode metal. We used BAlq as an common electron transporting layer in a same thickness for each emitting dyes.

Figure 1. Solution-processable fluorescent compounds 1-4.

All compounds were purified from column chromatography, and then thoroughly purified with a train sublimation for OLED application. These sublimable properties are one of advantages compared with the conjugated polymers in the purity point of view, because it is difficult to separate low molecular impurities having similar polarity to the target compounds by column chromatography. In practical, such impurities are regarded as detrimental for device stability. PL
spectra of the films showed the emission color derived from the central dye (1: sky blue, 2: blue green, 3: yellow, and 4: deep red). The outer oligofluorene groups did not affect the emission color because they have a wider energy gap than that of the central dye. The A-conjugations of the fluorene groups and the central dye seem to not be fully delocalized. OLEDs with the configuration as ITO/PEDOT: PSS (40 nm)/1-4 (50 nm)/BAIq (50 nm)/LiF (0.5 nm)/Al (100 nm) were fabricated. PEDOT: PSS and the emitting layer were deposited by spin-coating. BAlq and LiF / Al layer were deposited by evaporation under vacuum successively. EL spectra of the compounds are well congruous with their PL spectrum of the film (Figure 2). Multicolor emissions from conjugated oligomer dyes having well-defined structures were achieved in their OLED fabricated from solution process.

3. Solution-processable phosphorescent emitters

The combination of the solution-process and the phosphorescent compounds can be an ideal choice to achieve low cost and high efficiency in OLEDs in the future. For the solution-process, substitution of functional dendrons on the complex is one of approaches to solubilize it, and P. L. Burn group has been done a lot of pioneering work on the dendrimer OLEDs. The dendron is bulky in volume, so that it can prevent intermolecular interaction between the emitting complexes, resulting in reduction of concentration quenching and high photoluminescence quantum efficiency (PLQE).[7] From the OLED application point of view, those dendrons have to have enough high charge-transporting ability for low driving voltage[9] and have a larger triplet energy level (T1) than that of the core complex not to quench the triplet exciton of the complex.[10] In phosphorescent OLEDs, m-carbazolylbenzene (mCP) is one of well-known and widely-used host materials, because its triplet energy level is enough high (3.0 eV) to confine the phosphorescent emission of the iridium complex, and has bipolar charge-transporting ability.[11] The phosphorescent iridium complex, (mCP)3Ir, attached three mCP dendrons having alkyl groups, and high efficiencies of the OLEDs using that complex. In (mCP)3Ir, mCP dendrons are attached on each phenyl ring of Ir(ppy)3, and (mCP)3Ir is a facial isomer, so that the three mCP dendrons are attached spatially same side in the complex, and surround only half side of Ir(ppy)3. We designed two type of fully surrounded Ir(ppy)3 by six bulky dendrons, (mCP)6Ir and (DAP)6Ir (Figure 3). Both of the complexes showed higher PLQE in a neat film than that of half-surrounded (mCP)3Ir and (DAP)3Ir, well-supporting the results reported in the literature.[7c]

![Figure 3. Chemical structures of the dendronized iridium complex.](image)

<table>
<thead>
<tr>
<th>compound</th>
<th>solution (%)</th>
<th>film (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mCP)3Ir</td>
<td>91</td>
<td>49</td>
</tr>
<tr>
<td>(DAP)3Ir</td>
<td>83</td>
<td>33</td>
</tr>
<tr>
<td>(mCP)6Ir</td>
<td>79</td>
<td>66</td>
</tr>
<tr>
<td>(DAP)6Ir</td>
<td>73</td>
<td>60</td>
</tr>
</tbody>
</table>

![Figure 4. The optimized structures of (a) (mCP)3Ir and (b) (mCP)6Ir by PM 6 calculation.](image)

PLQE of the complexes in the neat film are important parameter to estimate the shielding effect of the surrounding dendrons to Ir(ppy)3. PLQE of
the toluene solution and the films were measured by using an integrating sphere system under 331 nm excitation (Table 1). In a diluted solution, all complexes showed higher PLQE than 70%, which are comparable to 85% of unsubstituted Ir(ppy)3. This result demonstrated that these surrounding dendrons are optically inert and does not affect the emission efficiency of Ir(ppy)3 core. The fully-surrounded complexes, (mCP)6Ir and (DAP)6Ir, showed high PLQE even in a neat film, which was comparable to PLQE in a dilute solution. On the other hand, the half-surrounded complexes, (mCP)3Ir and (DAP)3Ir, showed much lower PLQE in a neat film than that in a dilute solution. These complexes are facial isomers, therefore, in (mCP)3Ir and (DAP)3Ir, a some space around pyridyl groups of Ir(ppy)3 core are opened and their three dimensional structure is like a hemisphere, shown in Figure 4, resulting in only partial suppression of concentration-quenching in a neat film of an iridium complex. However, in (mCP)6Ir and (DAP)6Ir, the bulky host dendrons fully surrounded Ir(ppy)3 and effectively prevented the intermolecular interaction between Ir(ppy)3s. There are still small amount of reduction of PLQEs from a solution to a neat film, due to the concentration-quenching even in the fully-substituted complexes. The substituted host dendrons are not enough large to completely suppress the interaction between the core complexes. Adachi et al. reported that an average distance between iridium complexes in a doped film critically influenced on PLQE. Förster type energy transfer between Ir(ppy)3 cores through an overlap of the emission and the absorption causes a decrease of neat film PLQY. If the average distance between iridium complexes is shorter than Förster radius, a strong quenching occurs. The stronger quenching of (mCP)6Ir in the neat film than that of (mCP)3Ir is due to the shorter average distance between the cores derived from a less number of bulky host dendrons of (mCP)6Ir than that of (mCP)3Ir. Substitution of more branched and larger dendrons to the core complexes are desirable to achieve the complete suppression of concentration-quenching.

Solution-processed OLED with (mCP)6Ir showed high efficiencies, 19 lm/W, 32 cd/A, and 12% of external quantum efficiency (EQE) at 100 cd/m², and 11 lm/W, 25 cd/A, 9.1% at 1000 cd/m². The energy levels of the surrounding dendrons intensely affected the charge injection into the emitting layer and the device performance.

4. Solution-processable host materials

Conjugated[13] and nonconjugated[14] polymers have been extensively studied for use as host materials for phosphorescent OLEDs, batch-to-batch variations in molecular weight, polydispersity and purity can lead to different processing properties and performance. Soluble small molecules[15] have the advantage of having no structural defects, and it is easy to obtain better purity from conventional purification methods, such as column chromatography, recrystallization, and train sublimation. We synthesized two small molecules for use as host materials, BCzPPh and BCzPPm (Figure 5). These molecules are designed such that the n-butyl groups afford solubility in common organic solvents, and the meta-linked aromatic moieties lead to suppressed Δ-conjugations and high triplet energy for use in solution-processed phosphorescent OLEDs.
respectively, in the device with BCzPPh. A decline in efficiency was observed as the current density increased. This is likely due to the absence of an electron-blocking layer between the PEDOT:PSS layer and the EML, which leads to unbalanced charge densities under conditions of high current densities. Therefore, a hole-transporting and electron-blocking layer that is insoluble in the EML processing solvent, such as a cross-linked layer\cite{17}, is highly desirable to improve the efficiency and prevent efficiency roll-off.

5. Solution-processable and cross-linkable host materials

During the fabrication process of multilayer OLEDs from a solution, it is critical that the underlying layer does not dissolve during the deposition of the next layer from the solution. One approach to solving such a problem is the use of orthogonal solvents in the overcoating process\cite{18}. Usually, the \( \pi \)-conjugated compounds used in OLEDs are sparingly soluble in organic acids and in water. Consequently, such protic polar solvents have been used in the orthogonal solvent approach, although the protic solvents are believed to deteriorate the lifetime of a device. In the solution process, the drying of solvents is a necessary process, and the drying temperature must be lower than the \( T_g \) of all the compounds that compose the device. Accordingly, the choice of materials is limited because of their solubility and thermal stability. The other approach to fabricate multilayer OLEDs is the use of cross-linkable materials, which are coated from the solution and can be subsequently transformed into a covalently cross-linked film upon the application of heat or upon irradiation with ultraviolet light\cite{17,19}. After the compounds have been cross-linked, their films are sparingly soluble in any organic solvent, such as chloroform, toluene, THF, and such solvents can be used as an underlayer in the overcoating process. These insoluble films exhibit high thermal stability, which allows them to withstand the heat used to dry the film during the upper-layer process. Photochemical reaction is one example of a cross-linking method; however, this technique may lead to quenching of excitons because of the photochemical initiator itself or the decomposed residue of the initiator\cite{20}. In contrast, thermally cross-linkable materials\cite{17c,19b-e} are desirable because they do not degrade the light-emitting properties of the materials. Vinylbenzyl ether groups have recently attracted attention as a thermal cross-linking group used in hole-transporting materials for OLEDs\cite{21} and in organic photovoltaic devices\cite{22}. Because free radicals are generated from a Diels–Alder styrene dimer at relatively low temperatures (> 100 °C), no additional initiator is required for the cross-linking reaction\cite{23}.

![Chemical structures of the cross-linkable host materials.](image)

We reported the use of a thermally cross-linkable host material, DV-CBP, that incorporated two vinylbenzyl ether groups as cross-linking groups and CBP as an optoelectroactive backbone for solution-processed multilayer OLEDs. DV-CBP can be thermally cross-linked to form an insoluble emissive layer while preserving the desired light-emitting properties of small-molecule dopants. Using this cross-linking approach, we demonstrated that the well-defined multilayer of a cross-linked emissive layer and an electron-transporting layer from the solution process can decrease driving voltages and improve efficiencies through enhanced electron injection from the cathode through the electron-transporting layer to the emissive layer. V-CBP and DV-CBP exhibited exothermic peaks in DSC measurement between 140 °C and 200 °C, which correspond to the thermal polymerization of the styrene group. The curve of DV-CBP also showed an endothermic peak followed by a narrower exothermic peak as compared with that of V-CBP. This observed thermal behavior of DV-CBP indicates that the polymerization occurs in the partial melting state, which favors a high degree of cross-linking. In the second heating scan, no apparent peaks were observed in the temperature range between 50 °C and 230 °C, which indicated that the resulting polymers exhibited excellent thermal stability against the thermal annealing or drying process after the coating of the upper electron-transporting layer.

The solvent resistance of the thermally cured films was investigated using UV–vis spectroscopy; the results are shown in Figure 7. The thin films were obtained via spin-coating from a 1,2-dichloroethane solution followed by thermal curing at 180 °C for 30 min under a nitrogen atmosphere. The thermally cured film of the
single-styrene-containing compound, V-CBP, was mostly washed away with 1,2-dichloroethane. In contrast, the absorption spectra of the double-styrene-containing compound, DV-CBP, before and after the rinsing process were identical, which indicates that the cross-linked film of DV-CBP is completely resistant to the solvent. When small-molecule dopants such as a blue-fluorescent emitter BDA Vi and an electron-transporting material PBD were embedded into the DV-CBP host matrix, the absorption spectrum did not change after the rinsing with 1,2-dichloroethane. These results indicate that the thermally cured DV-CBP effectively prevents the small-molecule dopants from dissolving during the spin-coating of the subsequent upper layers.

The PLQEs of a fluorescent emitter embedded in DV-CBP as a host matrix were measured using an integrating sphere. Prior to the cross-linking reaction, the DV-CBP host exhibited a PLQE of 76% when doped with blue-fluorescent BDA Vi, which is comparable to that observed using a CBP host (78%). After the thermal cross-linking reaction, the PLQE did not decrease. To investigate the quenching effect of a polymerization initiator AIBN was added into a DV-CBP:BDA Vi film, which was subsequently treated at 120 °C for 60 min under a nitrogen atmosphere. Upon addition of 1 wt% AIBN, the PLQE dramatically decreased to 23% and broad and red-shifted emission spectra were observed. This PL behavior is likely due to the charge-transfer interaction between the emitter and the thermally reacted AIBN or the remaining AIBN itself. The decreased efficiency is also attributable to exciton quenching by a residual amount of radicals.

Solution-processed bilayer OLEDs were fabricated and tested using DV-CBP as a host material for blue-fluorescent BDA Vi with NaF/Al or Ca/Al cathode. A solution-processed multilayer device was also fabricated using TPBi as an electron-transporting layer with the structure of ITO (130 nm)/PEDOT:PSS (40 nm)/DV-CBP:20 wt% PBD:8 wt% BDA Vi (80 nm)/NaF or Ca (4 nm)/Al (100 nm). A solution-processed multilayer device was also fabricated using TPBi as an electron-transporting layer with the structure of ITO (130 nm)/PEDOT:PSS (40 nm)/DV-CBP:20 wt% PBD:8 wt% BDA Vi (40 nm)/TPBi (40 nm)/NaF (4 nm)/Al (100 nm). In this device, all of the organic layers were solution-processed, and the NaF and Al were vacuum-deposited to form a cathode. The multilayer device with TPBi exhibited significantly lower driving voltage than the bilayer device with NaF/Al (3.6 V for the multilayer device vs 7.9 V for the bilayer device at 1.0 cd/m²). The maximum EQE reached 2.3% for the multilayer device, which corresponds to a twofold and fivefold increase compared to the Ca/Al and NaF/Al device, respectively. These results demonstrate that the introduction of a TPBi electron-transporting layer on top of the cross-linked emissive layer drastically improves the device performance by facilitating electron-injection into the emissive layer from TPBi. While the HOMO energy levels of DV-CBP and BDA Vi lie at 6.1 eV and 5.3 eV, respectively, TPBi has a lower-lying HOMO energy level at 6.3 eV. Thus, the high efficiency of the multilayer device arises from the combination of improved electron-injection and hole-blocking, leading to balanced charge carriers in the emissive layer.

6. Solution-processable electron injection materials

Conventional polymer light-emitting devices (PLEDs) employ a highly reactive, low work function metal, such as Cs, Ba, or Ca, as an electron injection layer (EIL) and a cathode to enhance the electron injection to the emitting layer. However, the EIL and the cathode are highly reactive with atmospheric oxygen and moisture, which results in degradation of the device. The high reactivity of the EIL and the cathode makes it difficult to handle these devices in air. To avoid these problems, stable alkali metal fluorides, such as LiF or CsF, are commonly used in the EIL of dry-processed OLEDs. Cs2CO3 has been reported to be an effective EIL material in solution-processed OLEDs because it is soluble in alcohol solvents and can be coated from solution. The solution-processed Cs2CO3 EIL exhibits a high electron injection ability that is comparable to that of alkali metals. However, Cs2CO3 still has some disadvantages; it is hygroscopic and unstable in air, and it requires an ultrathin thickness because it is an insulating...
material. A strong chemical reduction is known to occur between Cs$_2$CO$_3$ and the thermally evaporated Al cathode. Because of this chemical reduction, the thickness of Cs$_2$CO$_3$ must be extremely thin, no thicker than 2 nm, to fully react with the evaporated Al. However, the ultrathin requirement makes it difficult to obtain a uniform thickness and reproducible performance of the device. We previously reported that several lithium phenolate complexes could be used to form an excellent EIL and that the device performance was much less sensitive to the thickness of the coating of these complexes because of their electron-transporting ability. The lithium phenolate complexes also have stability against oxidation and are less hygroscopic. By contrast, nanocrystalline metal oxides such as ZnO have recently been reported to be air-stable electron injection materials in PLEDs. In general, nanocrystalline metal oxide films are fabricated by spray pyrolysis deposition onto ITO substrates using metal oxide precursors. This process requires a high annealing temperature (200 – 450 °C) to obtain highly crystalline states and high mobility in the metal oxides. Because of this requirement for high annealing temperatures, nanocrystalline metal oxides are often used in inverted PLEDs, in which they are deposited onto thermally stable ITO substrates and enhance the electron injection from the ITO into the EML. Non-hydrolytic sol-gel processing of the nanocrystalline metal oxides can avoid high annealing temperatures and deposit controlled nano-sized particles onto a polymer layer at ambient temperature.

Figure 8. The chemical structure of Liq and the structure of the device.

We reported the efficient solution-processing of an EIL based on the lithium quinolate complex (Liq); in this EIL, a low driving voltage and improved stability of the PLEDs is achieved. Liq has high solubility in polar solvents, such as alcohols, and it has a smooth surface morphology. Therefore, Liq can be spin-coated onto the emitting polymer; the device prepared with spin-coated Liq as an EIL exhibited a lower turn-on voltage and had a higher efficiency than the devices prepared with spin-coated Cs$_2$CO$_3$ or with thermally evaporated Ca and Liq as an EIL. A smooth film can be formed using a mixture of ZnO nanoparticles and Liq using the solution process without a high-temperature annealing process; the resultant film exhibits better stability in air, and even the thick film (~10 nm) worked efficiently as an EIL in PLEDs.

Figure 9. Current density-voltage (solid symbol) and luminance-voltage (open symbol) characteristics of ITO / PEDOT: PSS / TFB / F8BT / ZnO: Liq (circle), ZnO: Cs$_2$CO$_3$ (triangle) and ZnO (square).

7. Perspectives

In conventional OLEDs, the luminance increases as the current density increases. Over time, the operational lifetime of these devices decreases because of the degradation of the organic material as the charge passes through the organic layer. Thus, it is thought that high luminance and long operating lifetimes cannot be simultaneously achieved in one device. To address this problem, we developed multi Photon-Emission-units (MPE) OLEDs comprising several vertically stacked light-emitting units (LEUs) connected in series by a charge-generation layer (CGL). In the case of two LEUs connected in series, the driving voltage and luminance of the MPE-OLED are the sum of the voltage and luminance, respectively, for the two LEUs, while the current density for two units is the same as that of a single LEU. For this reason, the current efficiency of the MPE-OLED with two LEUs connected in series is twice that of the conventional single-unit OLED. An electric field generates electrons and holes in the CGL that are injected consecutively into the 1st and 2nd LEU and that recombine to generate photons in each LEU. The CGL is composed of electron-accepting materials, such as MoO$_3$, V$_2$O$_5$, and WO$_3$, and electron-donating materials, such as arylamine derivatives. It is important to match the Fermi level of electron-accepting materials and the HOMO level of electron-donating materials. Improvement of electron injection from the CGL into the 1st LEU is also important, and an alkali...
metal-doped electron injection layer (EIL)\textsuperscript{[31-32, 35]} or stack of ultrathin (1 nm) LiF and Al on the electron transporting layer (ETL) of the 1st LEU have been employed to improve the electron injection.\textsuperscript{[36]} With regard to the fabrication process, the MPE-OLEDs have only been produced by thermal evaporation processes, although PLEDs that employ the solution-based processes, such as slot die coating and gravure printing, have lower fabrication costs for a large display or lighting area.\textsuperscript{[36]} In PLEDs, it is difficult to fabricate well-controlled multilayer structures because of the similar solubility of polymer materials in organic solvents.\textsuperscript{[18a, 37]}

Figure 10. Device structure of MPE OLEDs fabricated by the solution-based process.

We present a solution-based process to fabricate stacked OLEDs consisting of two polymer LEUs, connected in series by a charge generation layer (CGL) (Figure 10). We used Cs$_2$CO$_3$-doped ZnO nanoparticles as an EIL on the LE- polymer to improve the electron injection from the cathode. The surface morphology of a spin-coated metal oxide nanoparticle appears to be rough, with many gaps due to agglutination of nanoparticles. We chose poly(4-vinyl pyridine) (PVPy) as a binder to fill the gaps. The surface morphology of a spin-coated metal oxide nanoparticle appears to be rough, with many gaps due to agglutination of nanoparticles. We chose poly(4-vinyl pyridine) (PVPy) as a binder to fill the gaps.

![Cell diagram](image)

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**References**
