Molecular-Scale Strategies to Achieve High Efficiency and Low Efficiency Roll-off in Simplified Solution-Processed Organic Light-Emitting Diodes

Young-Hoon Kim, Tae-Hee Han, Changsoo Lee, Yun-Hi Kim, Yang Yang, and Tae-Woo Lee

Solution-processed small-molecule organic light-emitting diodes (OLEDs) are regarded as next-generation flat-panel displays and solid-state lighting sources due to low material loss and a simple device fabrication process. However, they still suffer from low device efficiency and severe efficiency roll-off. Here, molecular-scale strategies are proposed to achieve highly efficient solution-processed small-molecule OLEDs with reduced efficiency roll-off. By combining experiments with ab initio and molecular dynamics simulations, it is shown that an acetylacetonate group in a phosphorescent dopants lowers the dipole moment and molecular interaction energy of dopants, reducing dopant aggregation and increasing charge carrier transport. Furthermore, a charge-balance assistant molecule is incorporated in the mixed-host emitting layer to increase the balance of charge carrier transport and to broaden the exciton recombination zone in the center of the emitting layer. The resulting OLEDs have a current efficiency (CE) of 103.7 cd A\(^{-1}\), which is the highest yet reported in solution-processed OLEDs, and low efficiency roll-off (CE = 99.68 cd A\(^{-1}\) at \(L_{EL} = 100\) cd m\(^{-2}\), and CE = 75.00 cd A\(^{-1}\) at \(L_{EL} = 1000\) cd m\(^{-2}\)) even with the simplified device architecture. It is expected that this strategy will advance the feasibility of commercialization of low-cost high-efficiency OLEDs.

1. Introduction

Organic light-emitting diodes (OLEDs) have various advantages such as light weight, flexibility, compatibility with mass production, and high electroluminescence (EL) efficiency.\(^{[1-5]}\) However, most of efficient OLEDs have had multilayered structure and been fabricated by vacuum thermal deposition, which is expensive, complex, and incompatible with roll-to-roll printing.\(^{[6-11]}\) Minimizing the manufacturing cost of OLEDs is a major challenge for mass production and commercialization of large-size displays and solid-state lighting.\(^{[12-14]}\) Therefore, low-cost solution-processed OLEDs that have simple structure and high EL efficiency must be developed further.

Recently, high EL efficiencies in solution-processed OLEDs have been obtained by using diphenylbis(3-(pyridine-2-yl)phenyl)silane (2PTPS) as an electron transport host in an emitting layer.\(^{[15]}\) 2PTPS has high electron mobility (≈3 × 10\(^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\)) and induces direct charge trapping in the phosphorescent dopants, facilitating balanced charge transport and efficient exciton recombination in the emitting layer. Use of this strategy achieved high current efficiency CE = 101.5 cd A\(^{-1}\) in solution-processed OLEDs based on green-emitting phosphorescent dopants (tris[2-phenylpyridinato-C2,N]iridium(III) (Ir(ppy)\(3\))).\(^{[15]}\) However, the solution-processed OLEDs still undergo severe efficiency roll-off which is a reduction in EL efficiency as luminance increases. Efficiency roll-off reduces the actual efficiency of devices in practical brightness levels of applications such as mobile...
displays (100–400 cd m$^{-2}$), television displays (<1000 cd m$^{-2}$), indoor lighting (<5000 cd m$^{-2}$) and large-area lighting (>5000 cd m$^{-2}$), and leads to high power consumption and excessive heat generation of devices. Therefore, to fulfill industrial standards and extend the range of applications such as traffic lighting, daylight displays or lighting, the efficiency roll-off of solution-processed OLEDs should be reduced.

The efficiency roll-off in phosphorescent OLEDs basically arises from 1) triplet–triplet annihilation (TTA) and triplet–polaron annihilation (TPA) due to the long lifetime of excited phosphorescent states (approximately microseconds to milliseconds), and 2) charge imbalance and electric-field-induced exciton loss (i.e., exciton dissociation by applied electric field). In solution-processed phosphorescent OLEDs, small organic molecules have low solubility in organic solvents and easily aggregate in the emitting layer, so the efficiency roll-off could be even worse than that in vacuum-deposited counterparts. The molecular aggregates increase the severity of TTA and TPA between dopant molecules because triplet excitons are populated and annihilated. Solution processing cannot easily fabricate multi-layered device structure due to intermixing between layers inducing charge imbalance. Therefore, dopant aggregation and charge imbalance in the emitting layer should be prevented to reduce efficiency roll-off in solution-processed phosphorescent OLEDs.

Here, we demonstrated highly efficient solution-processed phosphorescent OLEDs with low efficiency roll-off by combining two molecular-scale strategies. First, we employed phosphorescent dopant in which one acetylacetone group is attached to the central Iridium. By combining experiments with ab initio and molecular dynamics simulations, we showed that acetylacetone group reduces dipole moment and molecular interaction energy of dopants, preventing aggregation-induced exciton quenching and increasing charge-carrier transport. We also incorporated charge-balance assistant molecule in the mixed-host emitting layer to increase balanced charge carrier transport and broaden exciton recombination zone in the center of the emitting layer by facilitating hole transport and suppressing electron transport. With these comprehensive strategies, we achieved CE = 103.7 cd A$^{-1}$, which is to our best knowledge the highest yet reported in solution-processed phosphorescent OLEDs.

Figure 1. Dipole moment and molecular interaction energy of a) Ir(ppy)$_3$ and b) Ir(ppy)$_2$(acac) calculated by density functional theory (DFT) simulation (gray dot: carbon, white dot: hydrogen, blue dot: iridium (Ir), red dot: oxygen). Molecular distribution of c) Ir(ppy)$_3$ and d) Ir(ppy)$_2$(acac) during spincoating of emitting layer. Operating mechanism of solution-processed OLEDs based on e) high-m (2PTPS:TCTA:Ir(ppy)$_3$) and f) CBP:low-m (2PTPS:TCTA:Ir(ppy)$_2$(acac)) films.
2. Results and Discussion

First, we conducted density functional theory (DFT) simulation to study the effects of acetylacetonate group on phosphorescent dopants (Figure 1a, b, top). We compared Ir(ppy)$_3$ with bis(2-phenylpyridine) (acetylacetonate) iridium(III) (Ir(ppy)$_2$(acac)) in which one acetylacetonate group is attached to the central Iridium. DFT results indicate that acetylacetonate group reduces the dipole moment $m$ of phosphorescent dopant therefore, Ir(ppy)$_2$(acac) has lower $m$ (1.91 D) and molecular interaction energy ($-4.512$ kJ mol$^{-1}$; $-0.047$ eV) than does Ir(ppy)$_3$ ($m = 6.26$ D and molecular interaction energy $= -19.584$ kJ mol$^{-1}$; $-0.204$ eV). Here, a negative value means greater interaction energy between dopant molecules. Reduced $m$ and molecular interaction energy can increase dopant distribution in molecular-scale and decrease interaction between dopants and charge carriers,[27–29] facilitating charge transport.

To study the effects of reduced $m$ and molecular interaction energy by acetylacetonate group on dopant distributions in emitting layer, we simulated distributions of dopants (Ir(ppy)$_3$ or Ir(ppy)$_2$(acac)), tris(4-carbazoyl-9-ylphenyl)amine (TCTA) and 2PTPS in tetrahydrofuran (THF) solvent by molecular dynamics (MD). The number of each dopant, TCTA and 2PTPS was set to be 50. MD simulation reveals that Ir(ppy)$_3$ molecules are more aggregated in TCTA:2PTPS:THF than Ir(ppy)$_2$(acac) molecules (Figure 2a–d). Simulated radial distribution function (RDF) shows

![Figure 2](image.png)

Figure 2. a) 3D molecular distributions of Ir(ppy)$_3$. b) 2D molecular distributions of Ir(ppy)$_3$, TCTA and 2PTPS. c) 3D molecular distributions of Ir(ppy)$_2$(acac). d) 2D molecular distributions of Ir(ppy)$_2$(acac), TCTA and 2PTPS. e) Calculated radial distribution function (RDF) of Ir(ppy)$_3$ and Ir(ppy)$_2$(acac) in TCTA:2PTPS:THF system. Data were calculated by molecular dynamics (MD) simulation.
that Ir(ppy)$_3$ has higher molecular density than does Ir(ppy)$_2$(acac) in a close molecular distance (<0.15 nm) (Figure 2e), confirming that Ir(ppy)$_3$ molecules are more aggregated in TCTA:2PTPS host molecules than Ir(ppy)$_2$(acac) molecules.

To study the effects of dopant distribution on film morphology, we fabricate TCTA:2PTPS:Ir(ppy)$_2$(acac) (low-\textit{m}) and TCTA:2PTPS:Ir(ppy)$_3$ (high-\textit{m}) films with different dopant concentrations \([D]\). Low-\textit{m} films with \([D]\approx15\text{ wt\%}\) had low root mean-squared roughness \(r_{\text{rms}} = 0.21\text{ nm}\) with uniform film morphology, whereas high-\textit{m} films with \([D]\approx15\text{ wt\%}\) had \(r_{\text{rms}} = 0.33\text{ nm}\) with some spiking regions (height > 5 nm) (Figure 3). We attribute this to the fact that Ir(ppy)$_2$(acac) has higher solubility (>0.1 wt\%) in THF than does Ir(ppy)$_3$ (<0.03 wt\%) because Ir(ppy)$_2$(acac) has similar \(m\approx1.91\text{ D}\) with THF \(m\approx1.63\text{ D}\) than does Ir(ppy)$_3$ \(m\approx6.26\text{ D}\). \[27,28\]

As \([D]\) increased to 60 wt\%, low-\textit{m} films showed less decreases in steady-state photoluminescence (PL) intensity \(L_{\text{PL}}\) and in relative PL intensities under the continuous excitation, \(L_{\text{PL,rel}} = (L_{\text{PL}}\text{ of film with } [D] = x\text{ wt\%})/(L_{\text{PL}}\text{ of film with } [D] = 1\text{ wt\%})\), than did high-\textit{m} counterparts (Figure 4a–d and Table S1, Supporting Information). These results indicate that acetylacetonate group increases the dopant distribution in molecular scale and also photostability of emitting layer films, which can reduce efficiency roll-off in the OLEDs.\[34\]

To study the effects of dopant distribution on photophysical properties, we measured transient PL of low-\textit{m} and high-\textit{m} films with different \([D]\). In low \([D] <15\text{ wt\%}\), low-\textit{m} films showed longer PL lifetime (e.g., 1.69 \(\mu\text{s}\) at \([D] = 1\text{ wt\%}\)) than did high-\textit{m} films (e.g., 1.364 \(\mu\text{s}\) at \([D] = 1\text{ wt\%}\)) due to aggregation of Ir(ppy)$_3$ molecules and concomitant aggregation-induced exciton quenching (i.e., TTA, TPA) in high-\textit{m} films (Figure 4e,f). However, as \([D]\) increased to 60 wt\%, high-\textit{m} films showed less decrease in PL lifetime (from 1.367 to 0.66 \(\mu\text{s}\)) than did low-\textit{m} films (from 1.69 to 0.62 \(\mu\text{s}\)); we attributed these to electronic energy transfer from less aggregated Ir(ppy)$_3$ molecules to more aggregated adjacent ones.\[35,36\] To systematically analyze the dopant concentration-dependent PL lifetime, PL lifetime of low-\textit{m} and high-\textit{m} films with different \([D]\) were fitted to modified Stern–Volmer equation (Figure 4g,h)\[37\]

\[\frac{\tau_0}{\tau} = 1 + k_s \times [D]\]

(1)

where \(\tau_0\) is the PL lifetime when \([D] = 1\text{ wt\%}\) (lowest dopant concentration), \(\tau\) is the PL lifetime with a certain \([D]\), \(k_s\) is a Stern–Volmer parameter. Low-\textit{m} films were well-fitted by the Stern–Volmer equation resulting \(k_s = 0.295\) while high-\textit{m} films cannot be well-fitted. These results indicate that
Ir(ppy)$_2$(acac) molecules in films well follow the typical intermolecular deactivation (quenching) process in which the presence of adjacent emitting dopants accelerate the decay rate of excited species (PL decay rate), while Ir(ppy)$_3$ molecules have additional factors (formation of needle-like aggregates) which affect PL decay.

To study the effects of dopants on charge transport in emitting layer, we fabricated hole-only devices (indium tin oxide (ITO)/gradient hole injection layer (GraHIL)/[TCTA:2PTPS:X]/TCTA/MoO$_3$/Al) and electron-only devices (ITO/polyethylenimine-ethoxylated (PEIE)/[TCTA:2PTPS:X]/1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBI)/LiF/Al), (where $X = 0, 15\%$ of Ir(ppy)$_3$.

![Figure 4. PL intensity of a) low-m (Ir(ppy)$_2$(acac):TCTA:2PTPS) films and b) high-m (Ir(ppy)$_3$:TCTA:2PTPS) films with different dopant concentration. Relative PL intensity of c) low-m films and d) high-m films with different dopant concentration under the continuous light excitation. Xe lamp with $\lambda = 350$ nm is used for the excitation source. PL decay of e) low-m films and f) high-m films with different dopant concentration. Stern–Volmer plot ($\tau_0/\tau$) of g) low-m films and h) high-m films with different dopant concentration. Red line is fitted curve by Stern–Volmer equation.](image-url)
or Ir(ppy)$_2$(acac)) and measured their hole–current densities and electron–current densities (Figure S1, Supporting Information). Hole–current and electron–current densities were higher in devices with dopants than in devices without dopants due to direct charge injection into dopant molecules that have shallower highest occupied molecular orbital (HOMO) level (≈5.4 eV for Ir(ppy)$_3$, ≈5.6 eV for Ir(ppy)$_2$(acac)) than those of the hosts (≈5.7 eV for TCTA and ≈6.47 eV for 2PTPS).[15] Devices based on low-m showed higher hole–current and electron–current densities than did devices based on high-m. We attribute these that 1) acetylacetonate group, which reduces m of the phosphorescent dopants, induces uniformly distributed Ir(ppy)$_2$(acac) molecules and suppresses the interaction between charge carriers and dopant molecules,[27–29] inducing higher charge carrier mobility in Ir(ppy)$_2$(acac) than that in Ir(ppy)$_3$.[29,30] and 2) deeper HOMO level of Ir(ppy)$_2$(acac) (≈5.6 eV) than that of Ir(ppy)$_3$ (HOMO = 5.4 eV) facilitates efficient direct injection of holes into Ir(ppy)$_2$(acac) from GraHIL (surface work function ≈ 5.9 eV)[7] and hopping of holes between dopants.[15]

Although we prevent dopant-aggregation and increase charge transport in the emitting layer by using phosphorescent dopant molecules with acetylacetonate group, recombination zone forms at the anode side (near the GraHIL) (Figure S2, Supporting Information) due to facilitated electron transport caused by high electron mobility of 2PTPS (=3 × 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$),[15] limiting the device efficiency. To further increase the device efficiency while maintaining low efficiency roll-off, recombination zone should be formed in the center of emitting layer and broadened. We achieved these by adding a charge-balance assistant molecule, which facilitates hole transport and suppresses electron transport, into the mixed-host emitting layer. Here, we incorporated 15 wt% of a charge-balance assistant molecule, 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP), into the mixed-host emitting layer. CBP can facilitate hole transport due to higher hole mobility ($\mu_{\text{hole}}$ = 2 × 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) than that of hole-transporting host TCTA ($\mu_{\text{hole}}$ = 3 × 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$).[15,29] and suppress electron hopping/transport between Ir(ppy)$_2$(acac) molecules because CBP has similar lowest unoccupied molecular orbital (LUMO) level (≈2.8 eV) with Ir(ppy)$_2$(acac) (LUMO level =3.0 eV), inducing electron trapping into CBP as well as into Ir(ppy)$_2$(acac) (Figure 5a).[29,30] These can increase the charge carrier transport balance and broaden the exciton recombination zone in the center of the emitting layer (Figure 5b), which can increase the maximum device efficiency of solution-processed OLEDs.

The increased charge balance in the emitting layer by incorporation of small amount CBP can be verified by measuring hole–current densities and electron–current densities from hole-only and electron-only devices, respectively (Figure 5c), and capacitance–voltage (C–V) of solution-processed OLEDs as well (Figure 5d). OLEDs based on low-m:CBP showed a maximum capacitance peak at lower voltage (6.45 V) than did OLEDs based on low-m without CBP (maximum capacitance peak at 6.7 V), indicating facilitated charge recombination and increased charge balance.[40,41]

To evaluate our strategies in devices, we fabricated phosphorescent solution-processed OLEDs with simplified structure (ITO/GraHIL/emitting layer/TPBI/LiF/Al). Compared to the OLEDs based on high-m, OLEDs based on low-m had higher current density due to facilitated charge transport by Ir(ppy)$_2$(acac) as discussed above (Figure 5e). Solution-processed OLEDs based on low-m:CBP achieved higher CE = 103.7 cd A$^{-1}$, power efficiency PE = 65.3 lm W$^{-1}$ and maximum luminance $L_{\text{EL,max}}$ = 15 581 cd m$^{-2}$ than did those based on high-m (CE = 101.5 cd A$^{-1}$, PE = 63.7 lm W$^{-1}$, $L_{\text{EL,max}}$ = 3101 cd m$^{-2}$)[15] (Figure 5f–i). To the best of our knowledge, these are the highest CE and PE in solution-processed OLEDs to date. External quantum efficiency (EQE) of OLEDs based on low-m:CBP was calculated to be 26.8% by considering angular emission profile (Figure S3, Supporting Information). Solution-processed OLEDs based on high-m, low-m and low-m:CBP films showed similar out-coupling efficiency (Figure S3, Supporting Information) because both Ir(ppy)$_2$(acac) and Ir(ppy)$_3$ molecules have isotropic (random) orientation in solution-processed films.[42,43] Furthermore, solution-processed OLEDs based on low-m:CBP showed much reduced efficiency roll-off (99.68 cd A$^{-1}$ at $L_{\text{EL}}$ = 100 cd m$^{-2}$, 76.00 cd A$^{-1}$ at $L_{\text{EL}}$ = 1000 cd m$^{-2}$) than those based on high-m (84.76 cd A$^{-1}$ at $L_{\text{EL}}$ = 100 cd m$^{-2}$, 23.19 cd A$^{-1}$ at $L_{\text{EL}}$ = 1000 cd m$^{-2}$) (Table 1; Tables S2 and S3, Supporting Information). The EL spectrum of OLEDs based on low-m:CBP slightly blue-shifted compared to that of OLEDs based on low-m (Figure S4, Supporting Information), confirming increased charge balance and shifted recombination zone from the anode side toward the center of the emitting layer.

3. Conclusion

In conclusion, we have demonstrated highly efficient solution-processed phosphorescent OLEDs with low efficiency roll-off by combining two strategies. First, we used phosphorescent dopant which has one acetylacetonate group attached to the central Iridium. Acetylacetonate group reduces dipole moment and molecular interaction energy of dopants, preventing aggregation-induced exciton quenching and increasing charge-carrier transport. We further improved the charge transport balance and facilitated charge recombination by incorporating a charge-balance assistant molecule. Ultimately, we achieved CE = 103.7 cd A$^{-1}$ and PE = 65.3 lm W$^{-1}$, which are to our best knowledge the highest EL efficiencies in solution-processed OLEDs to date, and dramatically reduced efficiency roll-off in solution-processed small-molecule OLEDs even with simplified structure. We expect that our strategies will contribute to the commercialization of low-cost solution-processed OLEDs in next-generation displays and solid-state lighting.

4. Experimental Section

Fabrication and Characterization of Solution-Processed OLEDs:ITO-patterned glasses were sonicated sequentially in acetone and 2-isopropanol, each for 15 min. Dried ITO-patterned glasses were treated with UV-ozone for 15 min. Then a GraHIL (poly(3,4-ethylendioxythiophene): polystyrene sulfonate and perfluorinated ionomer, 1:1 w/w) was spin-coated at 4500 rpm to give a thickness of 40 nm and baked at 150 °C for 30 min. Substrates were moved to an N$_2$-filled glove box, and the emitting layer, which were composed of hole transport host (TCTA), electron transport host (2PTPS), phosphorescent dopants (Ir(ppy)$_3$ or Ir(ppy)$_2$(acac)) and charge balance host (CBP) and dissolved in THF, was spin-coated to give the thickness of 40 nm. Then TPBI (50 nm), LiF
(1 nm), and Al (100 nm) were deposited sequentially in a high vacuum chamber (<10^{-7} Torr). The current–voltage–luminance characteristics of solution-processed OLEDs were measured using a Keithley 236 source measurement unit and a Minolta CS2000 spectroradiometer.

**DFT Calculations:** Spin-polarized DFT calculations were performed using the generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange correlation functional. All DFT calculations were performed using the Vienna ab initio Simulation Package. Core electrons were treated with the projector augmented wave method. The cut-off energy of plane-wave expansions was set to 400 eV for all DFT calculations. The DFT-D2 method of Grimme was used to treat the van der Waals interactions. For the calculation of the intermolecular
interactions and the single molecules, a Fermi-level smearing scheme with the width of 0.01 eV and 1 × 1 × 1 gamma K-point were adopted. The convergence criteria were 1 × 10^−5 eV for electronic wave functions and 3 × 10^−2 eV Å^−1 for geometries.

**MD Simulations:** The MD simulations were performed using the GROMACS simulation package version 5.0.3.[20] The V-rescale (modified Berendsen thermostat) method was used to maintain the temperature of the system with coupling time of 0.1 ps.[21] For the pressure of the system, the Parrinello–Rahman method was adapted with coupling time of 0.2 ps.[22] The temperature and pressure were set as 300 K and 1 bar. The LINCS algorithm was used for the bond constraints in the system.[23] The cut-off for nonbonded interaction was 2.0 nm. The interaction parameters for the 2PTPS, TCTA, Ir(pppy)3, and Ir(pppy)2(acac) molecules were generated using the SwissParam with CHARMM22 force field.[24] Each Ir atom was treated as a single point charge, as in previous MD studies.[25,26] The interaction parameters Ir(pppy)3 and Ir(pppy)2(acac) were produced by parameterizing the 2-phenylpyridine (ppy) and acetylacetone (acac) molecules. The calculations were performed in a cubic simulation box of 5.0 × 5.0 × 5.0 nm with periodic boundary condition. The molecular ratio of Ir complex (Ir(ppy)3 or Ir(ppy)2(acac)), TCTA and 2PTPS was set as 1:1:1 with a total 5.0 nm with periodic boundary condition. The molecular ratio of Ir complex (Ir(ppy)3 or Ir(ppy)2(acac)), TCTA and 2PTPS was set as 1:1:1 with a total

### Table 1. Device efficiencies of solution-processed OLEDs based on different emitting layers.

<table>
<thead>
<tr>
<th>Emitting layers</th>
<th>Max CE</th>
<th>Max PE</th>
<th>CE, PE@ 100 cd m^−2</th>
<th>CE, PE@ 1000 cd m^−2</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-m</td>
<td>101.50 cd A^−1</td>
<td>84.76 cd A^−1</td>
<td>23.19 cd A^−1</td>
<td>63.70 lm W^−1</td>
</tr>
<tr>
<td>Low-m</td>
<td>82.10 cd A^−1</td>
<td>79.40 cd A^−1</td>
<td>61.92 cd A^−1</td>
<td>51.60 lm W^−1</td>
</tr>
<tr>
<td>Low-m:CBP</td>
<td>103.70 cd A^−1</td>
<td>99.68 cd A^−1</td>
<td>76.00 cd A^−1</td>
<td>65.30 lm W^−1</td>
</tr>
</tbody>
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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

charge balance, charge-balance assistant molecules, density functional theory, dopant aggregation, molecular dynamics

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