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Exciplex-Forming Co-host for Organic Light-Emitting Diodes with Ultimate Efficiency

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Phosphorescent organic light-emitting diodes (OLEDs) with ultimate efficiency in terms of the external quantum efficiency (EQE), driving voltage, and efficiency roll-off are reported, making use of an exciplex-forming co-host. This exciplex-forming co-host system enables efficient singlet and triplet energy transfers from the host exciplex to the phosphorescent dopant because the singlet and triplet energies of the exciplex are almost identical. In addition, the system has low probability of direct trapping of charges at the dopant molecules and no charge-injection barrier from the charge-transport layers to the emitting layer. By combining all these factors, the OLEDs achieve a low turn-on voltage of 2.4 V, a very high EQE of 29.1% and a very high power efficiency of 124 lm W^{-1}. In addition, the OLEDs achieve an extremely low efficiency roll-off. The EQE of the optimized OLED is maintained at more than 27.8%, up to 10 000 cd m^{-2}.

1. Introduction

Recently, highly efficient organic light-emitting diodes (OLEDs) with external quantum efficiency (EQE) of over 29% without any special structures for light extraction have been developed.[1,2] The experimental results raise the question of what the ultimate efficiency limit of an OLED is. There are three factors to consider in an evaluation of the efficiency of an OLED: the EQE, the driving voltage, and the efficiency roll-off. A low driving voltage and a low efficiency roll-off (a high EQE at a high level of luminance) are especially important to reduce the power consumption in solid-state lighting, which requires high luminance and low power consumption.

Theoretical analysis shows that the ultimate limit of the EQE is about 30% for green phosphorescent OLEDs which can be obtained with a fairly thin transparent conducting electrode, emitters with 100% photoluminescence (PL) efficiency, optimized thickness of the organic layers, and an optimized location of the emitting zone in the OLEDs if isotropic emitter orientation is assumed.[3]

Lower efficiency at high luminance in phosphorescent OLEDs has long been an issue in phosphorescent OLEDs, and triplet–triplet annihilation (TTA), triplet–polaron quenching, and loss of charge balance have been proposed as the origins of this issue.[4–6]

The driving voltage of an OLED consists of the voltage that corresponds to the emitting photon energy ($V = E_{\text{photon}}/q$, where V is the voltage, E_{photon} is the photon energy of the emitted light, and q is the unit charge) and the over-potential required to inject and transport electrons and holes from the electrodes to the emitting layer (EML), where the electrons and holes recombine. Therefore, the ultimate low limit of the driving voltage for highly efficient OLEDs must be close to the voltage that corresponds to the photon energy of the light emitted by the OLED.[7] This limit can be obtained by minimizing the over-potential to drive the electrons and holes to the EML.

Among the three factors, the aforementioned experimental results reporting an EQE of 29% suggest that the EQE of the OLEDs has nearly reached its theoretical limit, with the use of innovative device structures and materials.[1,2] Unfortunately, however, this work failed to reach the ultimate limit of either the roll-off or the driving voltage.

Roll-off of the efficiency at high luminance can be reduced by lowering the triplet–polaron quenching and the TTA. One approach to achieve low roll-off is to use a co-host system, which is supposed to have a broad emission zone to reduce the triplet and polaron density without them piling up in a narrow zone in the EML. This method had limited success;[8–10] the roll-off was still high with a ca. 15%–35% reduction of the EQE values at 10 000 cd m^{-2}.

Here we demonstrate an OLED with very high efficiencies, produced by using an exciplex-forming co-host as the EML. The OLED has an ultrahigh EQE of 29.1% and a very low turn-on

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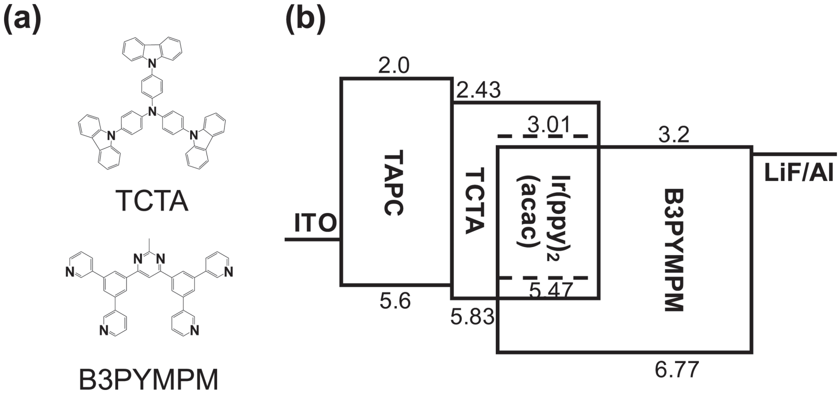

Figure 1. a) Molecular structures of TCTA and B3PYMPM. b) Device structure and the energy level of the OLEDs. TAPC = 1,1-bis-(4-bis(4-methyl-phenyl)-amino-phenyl)-cyclohexane. acac = acetylacetonate. ITO = Indium tin oxide.

voltage of 2.4 V. The turn-on voltage is close to the voltage that corresponds to the emitted photon energy. The low driving voltage and high EQE of the OLED allow it to achieve a very high power efficiency of 124 lm W^{-1}. In addition, the roll-off of efficiency of the OLED is extremely low with an EQE of 27.8% at 10 000 cd m^{-2} and 26.0% at 20 000 cd m^{-2}. Plausible origins of the high efficiency, low turn-on voltage, and low roll-off of efficiency of the OLED are discussed based on transient photoluminescence (PL)/electroluminescence (EL) spectra and the recombination mechanism.

2. Results and Discussion

Figure 1 shows a schematic diagram of the device structure for the demonstration of a high efficiency OLED using an exciplex-forming co-host system. 4,4′,4′′-Tris(*N*-carbazolyl)-triphenylamine (TCTA) and bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine (B3PYMPM) were used as the hole-transporting layer (HTL) and electron-transporting layer (ETL), respectively, forming an exciplex easily in an excited state with high PL efficiency.[11] The chemical structure and the energy levels of the molecules are also shown in Figure 1. The device has a very simple structure composed of three transporting materials and one phosphorescent emitting dye. There is only one organic/organic (O/O) junction with a highest occupied molecular orbital (HOMO) level difference of only 0.2 eV for holes and no O/O junction for electrons to reach the EML in the device. Therefore, the over-potential to drive the electrons and holes to the EML after injection can be minimized. Moreover, the energy-level difference between the lowest unoccupied molecular orbital (LUMO) of the ETL and the HOMO of the HTL is only 0.1 eV higher than the triplet energy gap of the dopant. Therefore, a very low turn-on voltage of the OLEDs, as low as the triplet energy gap of the phosphorescent dopant, can be achieved.[12,13]

Figure 2a shows the normalized PL spectra of the TCTA, B3PYMPM and TCTA:B3PYMPM co-deposited films. The molar ratio of TCTA to B3PYMPM in the co-deposited film was 1:1. The TCTA:B3PYMPM film showed a broad and featureless PL spectrum that was red-shifted from the TCTA and B3PYMPM emissions, and the energy of the TCTA:B3PYMPM emission peak was 2.5 eV. This energy is similar to the difference between the HOMO level of the TCTA and the LUMO level of the B3PYMPM, which proves that the TCTA and B3PYMPM molecules form an exciplex upon excitation. Many different structural configurations of the exciplex and indefinite character of the vibrations of the final ground state result in the broad and featureless emission spectrum of the exciplex. In addition, the emission peaks of the TCTA and the B3PYMPM did not appear in the PL spectrum of the TCTA:B3PYMPM film, which indicates that all of the excitons in the TCTA:B3PYMPM film form exciplexes effectively. The PL efficiency of the TCTA:B3PYMPM exciplex was 36 ± 2%.[11] The PL spectrum of the TCTA:B3PYMPM film at a low temperature (35 K) is also presented in Figure 2a. The emission peak of the PL spectrum of the TCTA:B3PYMPM film at the low temperature was very similar to that at room temperature, which indicates that the singlet energy level (S_1) and the triplet energy level (T_1) of the TCTA-B3PYMPM exciplex are very similar. The exciplex is a type of intermolecular donor–acceptor system with a very small orbital overlap between the excited state and the ground state. Therefore, the exciplex is expected to have a very small energy difference between the singlet and triplet excited states.[11,14]

The absorption spectrum of the phosphorescent dopant is compared in Figure 2b with the emission spectrum of the TCTA-B3PYMPM exciplex. Bis(2-phenylpyridine)iridium(III) acetylacetonate [$Ir(ppy)_2(acac)$] (T_1 = 2.4 eV) serves as the emitter, with a lower T_1 level than TCTA, B3PYMPM, or the TCTA-B3PYMPM exciplex (T_1 = 2.76, 2.75, and 2.5 eV, respectively). The overlap between the PL spectrum of the TCTA-B3PYMPM exciplex and the absorption of the $Ir(ppy)_2(acac)$ is quite large; hence, the energy transfer from the exciplex to the $Ir(ppy)_2(acac)$ should be efficient. The Förster transfer radius from the exciplex to the $Ir(ppy)_2(acac)$ calculated from the data was 5.6 nm.[15] The energy transfer from the TCTA-B3PYMPM exciplex to the $Ir(ppy)_2(acac)$ was confirmed from the PL spectra of the $Ir(ppy)_2(acac)$-doped TCTA:B3PYMPM films at various doping concentrations (Figure 2c). The exciplex emission peak appeared at low doping concentrations. However, the exciplex emission peak was eliminated when the concentration of the $Ir(ppy)_2(acac)$ was over 4 wt%, which indicates that the energy transfer from the exciplex to the $Ir(ppy)_2(acac)$ under the photoexcitation is complete when the doping concentration exceeds 4 wt%.

The OLEDs shown in Figure 1 were fabricated using TCTA-B3PYMPM as co-host of the EML (series A). The device structure of the series A OLEDs is as follows: ITO (100 nm)/1,1-bis-(4-bis(4-methyl-phenyl)-amino-phenyl)-cyclohexane (TAPC) (30 nm)/TCTA (10 nm)/TCTA:B3PYMPM:$Ir(ppy)_2(acac)$ (30 nm)/B3PYMPM (40 nm)/ LiF (0.7 nm)/ Al (100 nm). The molar ratio of TCTA:B3PYMPM of the EML was 1:1 and the doping concentration of the $Ir(ppy)_2(acac)$ varied from 2 wt% to 8 wt%. **Figure 3**a shows the current density–voltage–luminance

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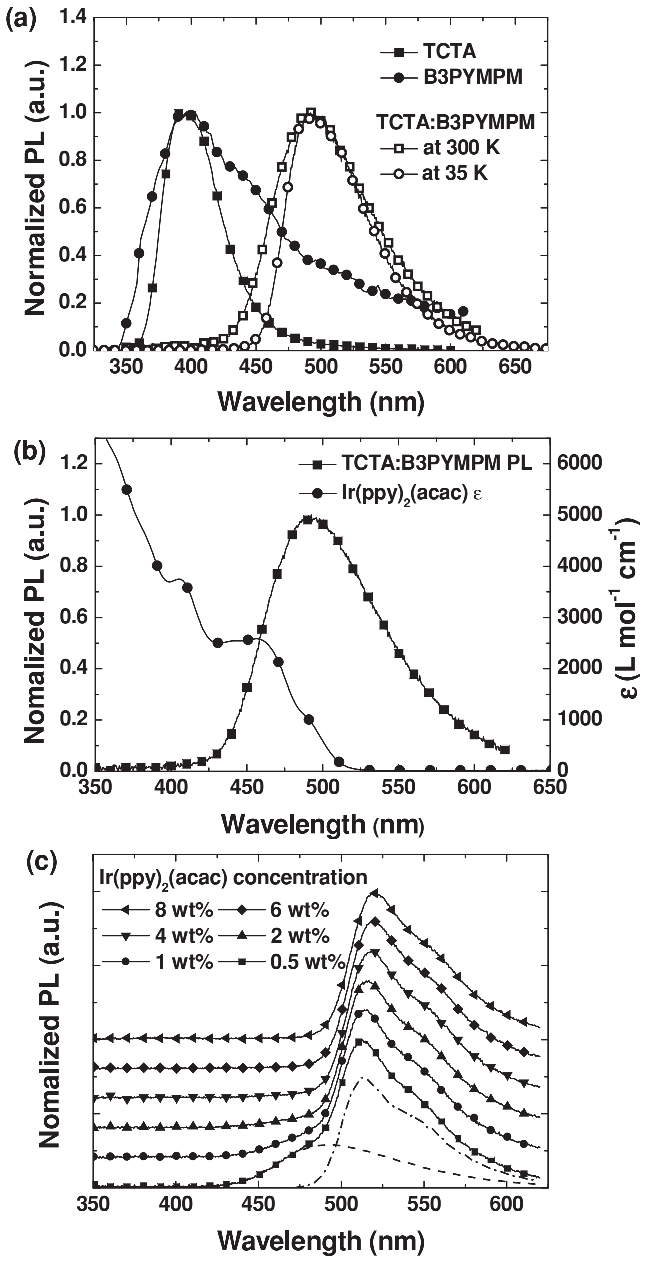

Figure 2. a) Normalized PL spectra of the TCTA, B3PYMPM, and TCTA:B3PYMPM co-deposited films. b) Normalized PL spectrum of the TCTA:B3PYMPM co-deposited film and the extinction coefficient of Ir(ppy)$_2$(acac). c) Normalized PL spectra of the Ir(ppy)$_2$(acac) doped TCTA:B3PYMPM films at various doping concentrations. The PL spectrum of the 0.5 wt% Ir(ppy)$_2$(acac)-doped TCTA:B3PYMPM film is resolved into the TCTA-B3PYMPM exciplex emission (dashed line) and the Ir(ppy)$_2$(acac) emission (dash-dot line).

(*J*–*V*–*L*) characteristics of the series A OLEDs. The driving voltage of the OLEDs was mostly unchanged as the doping concentration increased. The driving voltage at 1 mA cm^{-2} varied by no more than 0.03 V as the doping concentration changed from 2 wt% to 8 wt%, which indicates that the probability of the direct trapping of the charges at the dopant site and the charge transport through the dopants is low in the OLEDs. If charge trapping and transport by the dopants are dominant, the driving voltage of the OLEDs will be increased as the doping concentration increases up to the critical concentration, due to the trapping effect of the dopant, followed by lowering of the driving voltage above the critical concentration.[16] The turn-on voltage of the OLEDs at about 1 cd m^{-2} was 2.4 V, which is as low as the triplet energy gap (2.4 eV) of the phosphorescent dopant, Ir(ppy)$_2$(acac). In addition, the driving voltages of the OLEDs at 1000 cd m^{-2} and 10 000 cd m^{-2} were 3.2 V and about 4.4–4.6 V, respectively. Such low turn-on voltage and over-potentials to drive the high carrier density to the EML of the OLEDs can be achieved because the exciplex-forming co-host system has no charge-injection barrier from the charge-transport layers to the emitting layer.

Figure 3b shows the EQEs and power efficiencies of the series A OLEDs. These OLEDs showed high EQEs and low efficiency roll-offs. The efficiencies of the OLEDs were increased as the concentration of the Ir(ppy)$_2$(acac) increased. The OLED with 8 wt% Ir(ppy)$_2$(acac) achieved a maximum EQE of 26.6%. In addition, the EQE of the OLED was 24.9% at 10 000 cd m^{-2}. The OLED also achieved a high power efficiency of 111.1 lm W^{-1} due to the low driving voltage and the high EQE of the OLED.

The main limitation of the EQE of a phosphorescent OLED is the outcoupling efficiency. The thickness of the ITO layer can also affect the outcoupling efficiency of OLEDs.[3] We fabricated OLEDs with various ITO thicknesses in series B. The device structure of the series B OLEDs was as follows: ITO (*x* nm)/TAPC (*y* nm)/TCTA (10 nm)/TCTA:B3PYMPM:Ir(ppy)$_2$(acac) (30 nm)/B3PYMPM (40 nm)/LiF (0.7 nm)/Al (100 nm). 70-, 100-, and 150-nm-thick ITO layers were selected for this purpose, with the thickness of the TAPC varying accordingly from 60–20 nm to maximize the outcoupling efficiency. The molar ratio of TCTA:B3PYMPM of the EML was 1:1, and the doping concentration of the Ir(ppy)$_2$(acac) in the EML was fixed at 8 wt%. Figure 3c shows the *J*–*V*–*L* characteristics of the series B OLEDs. No OLEDs in this work showed an EL spectrum shift with driving voltage, which indicates that the emission zone does not shift with driving voltage in the OLEDs. The turn-on voltage of all OLEDs was 2.4 V, which is as low as the triplet energy gap of the Ir(ppy)$_2$(acac), and the driving voltage of the OLEDs at 1000 cd m^{-2} was about 3.0–3.2 V. Again, such a low driving voltage can be achieved due to the charge-injection-barrier reduction by the co-host system. The inset of Figure 3c shows the angular distribution of the EL intensity of the series B OLEDs. The EQE and the power efficiency of the series B OLEDs are shown in Figure 3d after calibration using the angular distribution of the emission intensity. Details of the performance of the OLEDs are summarized in **Table 1**. The OLED with the 70-nm-thick ITO showed a very high EQE with a maximum value of 29.1%, which is equal to the highest efficiency reported for conventional bottom-emitting OLEDs to date.[1,2] The low driving voltage and high EQE of this OLED lead to a very high power efficiency of 124.0 lm W^{-1}.

The orientation of the emitter was analyzed to clarify whether the EQE value of 29.1% in the OLED corresponds to almost 100% internal quantum efficiency (IQE), because horizontally oriented dipoles give higher outcoupling efficiency than vertically oriented dipoles.[17,18] The distribution of the emitter

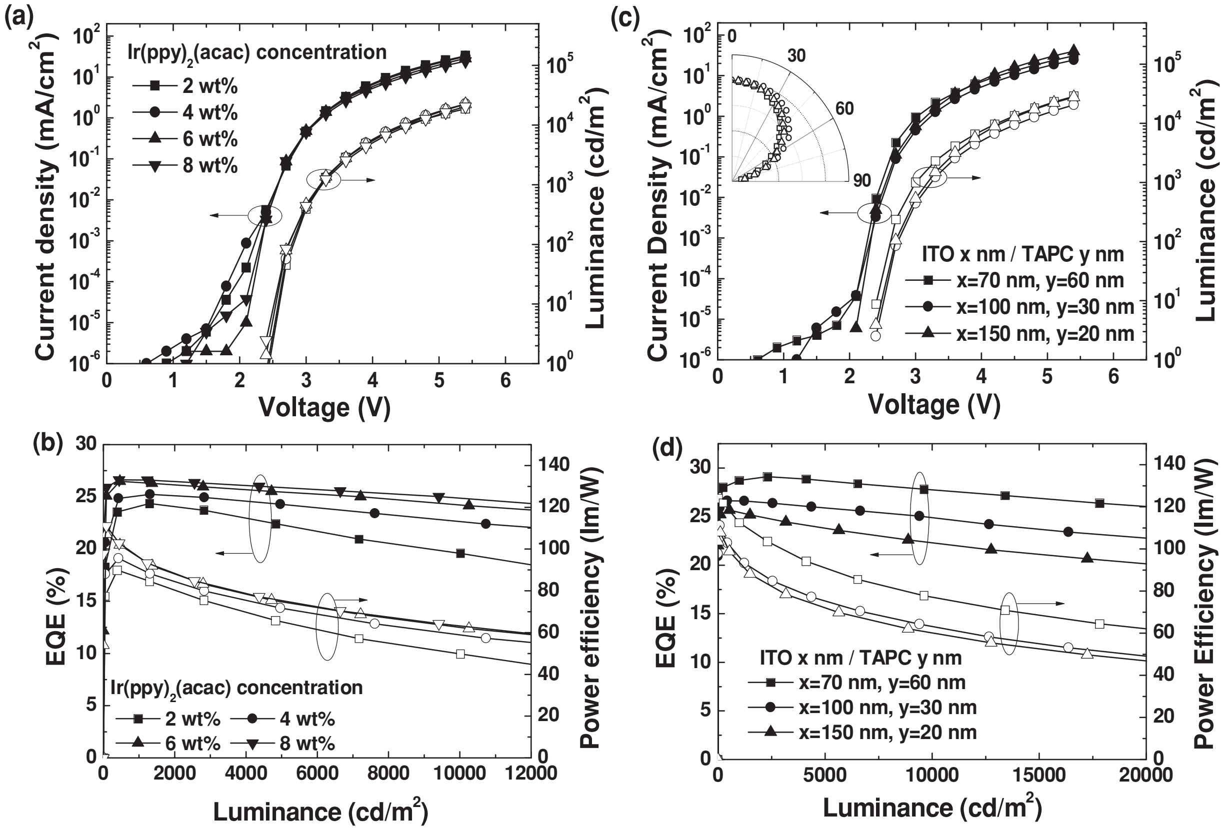

Figure 3. a) Current density–voltage–luminance characteristics of the series A OLEDs. b) EQE and the power efficiency of the series A OLEDs. c) Current density–voltage–luminance characteristics of the series B OLEDs. Inset: Angular distribution of the EL intensity of the series B OLEDs. The solid line represents the Lambertian distribution. d) EQE and power efficiency of the series B OLEDs.

orientation was measured by using the angle-dependent PL measurement[18] (analysis and methodology are described in the Supporting Information). The quantitative analysis of the measurements gives 77% of the horizontally oriented dipoles and 23% of the vertically oriented dipoles, which indicates that the emitters have preferentially oriented along the horizontal direction rather than in an isotropic distribution where emitters would possess 66.7% horizontal dipoles and 33.3% vertical dipoles. The calculated outcoupling efficiency of the device based on the experimentally obtained emitter orientation is 28.3 ± 1.0%, which assumes the emission zone of the OLED using the co-host is uniformly distributed in the entire EML.[8] This value is similar to the EQE of the OLED achieved in this work (29.1%), which indicates that its electrical loss is almost zero.

In addition, the EQE of the OLED was 28.7% at 1000 cd m^{-2}, 27.8% at 10 000 cd m^{-2} and 26.0% at 20 000 cd m^{-2}. Over 95% of the maximum EQE is maintained up to 10 000 cd m^{-2} and about 90% at 20 000 cd m^{-2}. This low roll-off of efficiency is remarkable in phosphorescent OLEDs. The extremely low roll-off of the OLEDs indicates that the triplet–polaron quenching and the TTA are very low in our devices. Because the electrical loss is almost zero in our OLEDs, their charge-balance factor must be close to unity. Therefore, the polaron density in the EML is lowered by the extent of formation of excited states in the co-host (exciplex) or dopant (exciton) molecules, which results in low triplet–polaron quenching.

The TTA process of the 8 wt% Ir(ppy)$_2$(acac)-doped TCTA:B3PYMPM co-host system was analyzed using the transient PL decays shown in **Figure 4**. The TTA process is

Table 1. Series B OLED performances.

ITO thickness [nm]	Voltage [V]			EQE [%]			Power efficiency [lm W^{-1}]		
	Turn-on	@1000 cd m^{-2}	@10 000 cd m^{-2}	Max.	@1000 cd m^{-2}	@10 000 cd m^{-2}	Max.	@1000 cd m^{-2}	@10 000 cd m^{-2}
70	2.4	3.0	4.2	29.1	28.7	27.8	124.0	112.5	77.0
100	2.4	3.2	4.6	26.6	26.6	24.9	111.1	96.1	63.2
150	2.4	3.2	4.3	25.7	25.4	22.3	107.8	93.6	60.2

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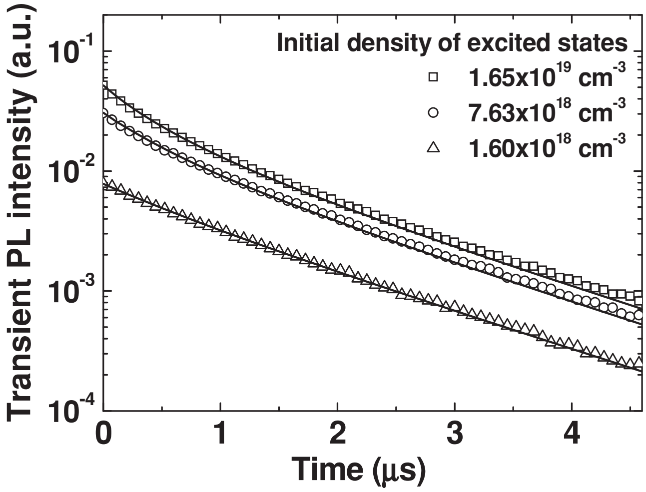

Figure 4. Transient PL decay of a TCTA:B3PYMPM:8%Ir(ppy)$_2$(acac) film at different excitation intensities indicating the density of initial excited states. The excitation wavelength was 355 nm and the detection wavelength was 520 nm. The solid lines represent calculated fits using Equation 1.

quantitatively analyzed using Equation 1 which describes the decay of luminescence after a short optical pulse excitation when the TTA process is included.[4,5]

$$L(t) = \frac{L(0)}{\{1+[n_{\mathrm{ex}}(0)]k_{\mathrm{TT}}\tau/2\}e^{t/\tau} - [n_{\mathrm{ex}}(0)]k_{\mathrm{TT}}\tau/2}, \qquad (1)$$

Here t is the time after excitation, τ is the phosphorescent lifetime, $[n_{\mathrm{ex}}(0)]$ is the density of the triplet excited state at $t = 0$, k_{TT} is the rate constant of the TTA, and L is the luminescence intensity. Here, it is assumed that the luminescence intensity is linearly proportional to the concentration of excited states. The TTA rate constant k_{TT} and the lifetime τ extracted by the calculated fits of the transient PL decay curves are $k_{\mathrm{TT}} = (2.5 \pm 1) \times 10^{-13}$ cm^3 s^{-1} and $\tau = 1.4$ μs, respectively. The TTA rate constant is small enough that it causes negligible roll-off of efficiency (less than 1.5%) up to 25 mA cm^{-2}, which corresponds to the current density emitting 20 000 cd m^{-2} in our devices.

High performance of OLEDs is related to the charge transport and recombination processes in them. In general, there are two mechanisms to form excitons in dopant molecules in a doped EML: direct charge trapping on the dopant or energy transfer from host to dopant. The transport and recombination processes in the devices were investigated using transient EL and the dependence of EL spectra on doping concentration.

Recent studies of the transient EL in guest–host systems indicate a transient overshoot or spike after voltage turn-off in many devices.[19,20] The overshoot was attributed to charge trapping on the guest (dopant), which indicates that this method can serve as a tool to identify emitting mechanisms. No overshoot was observed in a system where energy transfer was the dominant excitation mechanism.[19] **Figure 5** shows the transient EL decay of an OLED under different postpulse bias from 0 to –5 V. Voltage pulses lasting for 100 μs that correspond to a current density of 10 mA cm^{-2} were applied to the device to measure transient EL spectra. The transient EL signal showed no overshoot after voltage turn-off, which indicates that energy transfer from host to dopant is the major mechanism that results in light emission rather than direct charge trapping on the dopant. The transient curves after voltage turn-off decayed slowly for about 1 μs, independent of postpulse voltage. A tail observed after 1 μs depended strongly on the postpulse voltage. The initial slow decay has the effect of delaying the exponential decay by about 500 ns even under a high negative postpulse bias of –5 V applied to drive the charges in the reverse direction, as shown by the dotted lines in Figure 5. The delayed decay indicates that excitons are generated on the Ir(ppy)$_2$(acac) molecules after the voltage turn-off has ceased. The independence of the slow decay on the postpulse bias up to ca. 1 μs also suggests that the exciton generation up to this point mainly originates from energy transfer from host exciplexes. If excitons are formed by the recombination of trapped holes or accumulated electrons, the decay characteristics must be influenced by the turn-off voltage. In contrast to the initial decay, the tails depend strongly on the turn-off voltage, which indicates that they originate from the delayed recombination of injected charges remaining after the voltage turn-off with the reverse biases. Higher reverse bias will sweep out the remaining charges from the recombination zone faster than a lower one, reducing the delayed recombination of charges, and resulting in exponential decay when the postbias voltage is –5 V. If holes are predominantly trapped on the dopant because it is energetically favorable compared with being trapped on TCTA and transported via dopants, then holes are predominantly found near the EML/ETL interface. Because the concentration of electrons is highest near the EML/HTL interface, a strong turn-off overshoot of the transient EL decay is expected when holes are mostly trapped on the dopant.

A further piece of evidence for emission resulting from energy transfer from host exciplexes to dopant molecules is the partial emission of the exciplex in the EL spectrum at a doping concentration of 2 wt% (Supporting Information, Figure S2)

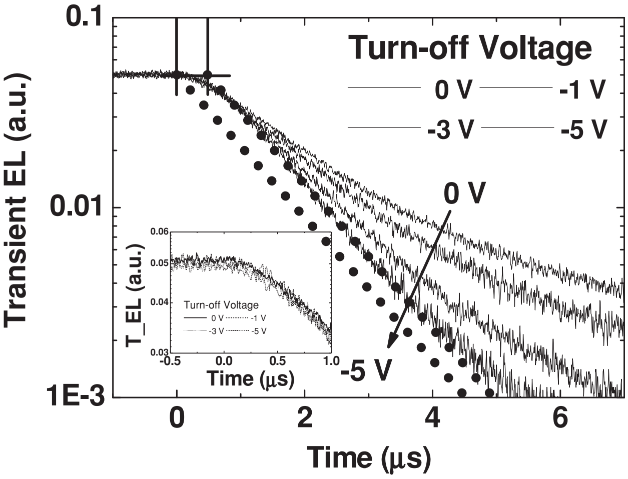

Figure 5. Transient EL decay curves of an OLED with different turn-off voltages. The structure of the device was ITO (70 nm)/TAPC (80 nm)/TCTA (10 nm)/TCTA:B3PYMPM(1:1):8% Ir(ppy)$_2$(acac) (30 nm)/ETL (40 nm)/ LiF (0.7 nm)/Al (100 nm). The inset shows a magnified region of transient EL decay. The *RC* time constant of the experiment is about 45 ns, where *R* is the resistivity and *C* is the capacitance.

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because of incomplete energy transfer from host exciplexes to dopant molecules.

Trap-assisted recombination or charge-carrier storage inside the EML can decrease the efficiency of OLEDs by the presence of additional polarons (exciton–polaron quenching), additional electric field created by the accumulated charges (electric-field-induced exciton dissociation), and by nonradiative recombination of trapped charges (nonradiative quenching). Therefore, the energy-transfer-dominated light emission in these OLEDs with an exciplex-forming co-host is a way to remove trap-induced efficiency reduction in OLEDs and to increase their efficiency.

3. Conclusions

With the use of an exciplex-forming TCTA-B3PYMPM co-host, we successfully developed a phosphorescent OLED with ultimate low driving voltage and high efficiency, and an extremely low efficiency roll-off. The TCTA-B3PYMPM co-host system removes the charge-injection barrier from the charge-transport process to the EML and allows efficient singlet and triplet energy transfer from the exciplex to the dopant because the singlet and triplet energy of the exciplex are virtually identical. Therefore, the OLEDs achieved a low turn-on voltage of 2.4 V, which is as low as the triplet energy gap of the phosphorescent-emitting dopant, a very high EQE of 29.1%, and a very high power efficiency rating of 124.0 lm W^{-1}. The OLEDs also achieved an extremely low roll-off of efficiency, which indicates that TTA and triplet-polaron quenching is low in the exciplex-forming co-host system. The EQE of the optimized OLED remained over 27.8% up to 10 000 cd m^{-2}. This exciplex-forming co-host system represents a new design to produce high-performance OLEDs. An exciplex-forming co-host system composed of an electron-transporting material (ETM) and hole-transporting material (HTM) can be considered a bipolar host with the LUMO level of the ETM and the HOMO level of the HTM as its LUMO and HOMO levels, respectively. Because exciplexes are readily formed by the recombination of electrons and holes in the host, energy transfer from the host to dopant molecules can be used to remove trap-induced efficiency reduction in OLEDs and to increase their efficiency. Moreover, a triplet exciplex has almost the same energy as a singlet one, which is close to the energy difference between the LUMO level of the acceptor host and the HOMO level of the donor host (Δ).[11,14] Therefore, Δ can be as low as the energy of the phosphorescent dopant to harvest both singlet and triplet exciplexes, which allows the production of OLEDs with a turn-on voltage as low as Δ/q.

4. Experimental Section

The OLEDs were fabricated by thermal evaporation onto cleaned glass substrates precoated with 70-, 100-, and 150-nm-thick ITO. Prior to the deposition of the organic layers, the ITO substrates were exposed to UV–ozone flux for 10 minutes following degreasing in acetone and isopropyl alcohol. All layers were grown by thermal evaporation at a base pressure of $<5 \times 10^{-7}$ Torr without breaking the vacuum. The energy levels of the organic materials were obtained from the published literature,[1,21,22]except for $Ir(ppy)_2(acac)$. The HOMO level of the $Ir(ppy)_2(acac)$ was obtained from cyclic voltammetry measurements. The LUMO level of the $Ir(ppy)_2(acac)$ was calculated from the HOMO level and the energy gap, which was obtained from the absorption spectrum. The current density, luminance, and EL spectra were measured using a Keithley 2400 programmable source meter and a SpectraScan PR650 (Photo Research). The angular distribution of the EL intensity was measured using the Keithley 2400 programmable source meter, a rotation stage, and an Ocean Optics S2000 fiber optic spectrometer. The EQE and the power efficiency of the OLEDs were calculated from the current density, luminance, EL spectra, and angular distribution of the EL intensity data. The *J–V–L* characteristics for the analysis of the recombination mechanism were measured using a Keithley 2400 programmable source meter and a Si photodiode (1835C, Newport).

Organic films for the measurement of the PL spectra were fabricated by thermal evaporation on precleaned quartz substrates at a base pressure of $<5 \times 10^{-7}$ Torr. The PL spectra of the organic films were measured by using an integrating sphere. A continuous-wave He/Cd laser (325 nm) was used as an excitation light source and a monochromator-attached photomultiplier tube (PMT) was used as an optical detection system. The low-temperature PL spectrum was measured in a cryostat, and the organic films were cooled down to 35 K. A pulsed Nd–YAG laser (355 nm) was used as the excitation light source and an intensified charge-coupled device (ICCD) was used as the optical detector for the measurements. For the transient PL measurement, a pulsed Nd–YAG laser (355 nm) was used as the excitation light source and a monochromator-attached PMT was used as an optical detection system. Detection wavelength was 520 nm which corresponds to the peak wavelength of the $Ir(ppy)_2(acac)$ emission. The density of the initial excited states was calculated from the laser intensity, absorption coefficient of the film, area of the exciting spot, and film thickness. The laser intensity was controlled by using a neutral density filter. Transient EL measurements were obtained by applying a voltage pulse with a duration of 100 µs using an 8114A pulse generator (Agilent), which corresponds to a current density of 10 mA cm^{-2}, to the device. Different turn–off voltages of –5, –3, –1, and 0 V were used. The repetition rate of the pulses was 10 Hz and the emission was detected using an ACTON spectrometer (SpectraPro-300i) connected to a PMT (PD-438, Acton Research). The detection wavelength was 524 nm, which corresponds to the emission maxima of $Ir(ppy)_2(acac)$. All signals were detected and integrated 1000 times by using an oscilloscope (54642A, Agilent). The voltage applied to the OLEDs was measured over a 1 MΩ resistance parallel to the OLED.

Supporting Information

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

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