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A direct evidence for the energy transfer from phosphorescent molecules to quantum dots in a driving light emitting diode

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ABSTRACT

The energy transfer (ET) processes are considered to enhance the emission in the organic/inorganic quantum dots (QDs) hybrid structures. And efficient QDs based light emitting diodes (QLEDs) have been widely reported by employing this hybrid device design. However, such ET processes have so far been only verified in the photoluminescence regime. Therefore, it is insufficient and unconvincing to elaborate the electroluminescence (EL) mechanism in the devices. Here we for the first time demonstrate the ET process between phosphorescent bis(4,6-difluorophenylpyridinato-N,C2)-picolinatoiridium (FIrpic) and QDs in a QLED under the electrical excitation regime by means of transient EL technology. The prolonged EL decay in the transient EL spectrum confirms that the FIrpic molecules with long exciton lifetime, just like an exciton reservoir, can harvest both the leaked electrons from the QDs and holes injected from hole transport layer, which then form excitons and transfer their energy to the QDs.

1. Introduction

Due to their outstanding optical and electronic properties, both semiconductor quantum dots (QDs) and organic phosphorescent molecules have drawn significant research interest in light emitting diodes (LEDs), solar cells, and detectors [1–3]. Large absorption coefficient, high color gamut, and good photo-stability make QDs superior to the counterpart in the display application. And unique properties, including near 100% emission efficiency and long exciton lifetime ($\sim \mu s$) and diffusion lengths ($\sim \mu m$), result in the phosphorescent small molecules to be usually used as the emission units in the organic LEDs [4]. These properties also make them very attractive for the utilization within long-range energy transfer (ET) schemes [5]. Therefore, it is desired to combine the features of QDs and phosphorescent molecules together. Fortunately, the Förster resonance ET provide a feasible scheme for their interactions. Furthermore, it has been proposed that the enhanced performance of QDs based LEDs (QLEDs) containing phosphorescent molecules is due to these ET interactions [6,7]. However, a direct evidence is necessary to support this mechanism.

Generally, the ET processes in the phosphorescent molecules/QDs hybrid structures are investigated and confirmed in a photoluminescence (PL) regime [8], i.e., the excitons are firstly formed in the fluorescent host excited by the high-energy light, then transferring their energy to the phosphorescent guest molecules and finally to the QDs. The exciton lifetime in the phosphorescent molecules is shortened due to their interactions with the QDs in this hybrid donor-acceptor system [6,7]. Recently, the phosphorescent molecules were introduced into the QLEDs, dramatically enhancing the device performance [6,7]. It is believed that the ET from the phosphorescent molecules to QDs is the dominant mechanism leading to the improvement of device performance. However, this ET mechanism is debatable in an electrically driven device because it has been only demonstrated in the PL regime. Moreover, the exciton formation zone is adjacent to the QDs/hole transport layer (HTL) interface in QLEDs as reported in many literatures [9–11], which implies that this interface greatly affects the device performance. In fact, the charge carrier distribution inside the device may be changed with the insertion of phosphorescent molecules, which can also affect the device performance. Thus, besides the ET processes,

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the electrical properties of this interface must be carefully considered after inserting an organic phosphorescent layer. Therefore, it is necessary to distinguish these two effects (charge carrier distribution and ET processes) in the devices or to pinpoint which process is the dominant origin of the performance improvement in QLEDs.

The dynamics of charge carriers in an electrically-driven device was commonly assessed by a time-resolved EL measurement [12,13], also referred to as the transient EL (TrEL) technology in other literatures [14–16]. Many interesting mechanisms such as EL processes [17], charge distribution and storage [13], and exciton quenching [18] were exposed through the TrEL measurements. Due to the very different time scale of exciton lifetimes for Cd-based QDs (tens of ns) and phosphorescent molecules (~μs), it is possible to observe the ET processes (if it is the case) between them through the TrEL behaviour of the devices.

In this work, the influence of the phosphorescent molecules on the charge distribution and ET processes in the devices are systematically explored by depositing bis(4,6-difluorophenylpyridinato-N,C2)-picolinatoiridium (FIrpic) with different thicknesses at QDs/HTL interface. The ET processes between QDs and FIrpic are substantially confirmed by the TrEL results, characterized by a slower EL decay behaviour in the FIrpic-containing devices compared with the control device (without FIrpic layer).

2. Experimental section

The devices with a structure of ITO/ZnO (~40 nm)/QDs(~20 nm)/ FIrpic(x nm)/CBP(60 nm)/MoO$_3$(8 nm)/Al(~100 nm) were built with various FIrpic thicknesses for devices B (0.1 nm), C (0.5 nm), and D (1.0 nm). Device A without FIrpic was also fabricated as the reference. The fabrication and measurement procedures are described in detail in the literatures [19,20]. The TrEL measurements are carried out by a home-built system (shown in Fig. 2a) consisting of a photomultiplier tube (Zolix PMTH-S1-CR131), a digital oscilloscope (RIGOL DS4054) and a signal generator (RIGOL DG5102). The devices are driven by a voltage pulse generated by the signal generator and the EL emission is probed by the photomultiplier and is recorded by the digital oscilloscope. The impendence spectroscopy (IS) and photoelectrical (current-voltage-luminance and EL spectrum) measurement procedures have been described in our previous papers [20]. All measurements were performed in air at room temperature.

3. Results and discussion

The QLEDs built in this work are schematically described in Fig. 1a. The transmission electron microscope (TEM) image of QDs is shown in Fig. 1b, indicating an average size of 7.6 nm in diameter. Fig. 1c displays the PL and absorption spectra of the QDs in toluene, as well as the EL spectra of FIrpic and QDs. A large overlap between the FIrpic emission and the QD absorption is observed, which is the prerequisite of the ET from FIrpic to QDs. We know that the electron leakage into the HTL is a universal phenomenon in QLEDs. The leaked electrons form excitons with the holes in the HTL, which results in the parasitic emission from the HTL in the EL spectrum of the QLEDs [21]. The inserted FIrpic layer is expected to be used as the reservoir for both of the electrons and holes, which will then form the excitons and transfer their energy to the adjacent QDs. The energy level alignment for the device shown in Fig. 1d reveals hole accumulation at FIrpic/QDs interface will exist upon inserting the FIrpic at CBP/QDs interface due to the higher HOMO (HOMO = the highest occupied molecular orbital) energy level of FIrpic. Therefore, there may be two effects on the device performance, one is the emission quenching [10] and the other is the resonant ET process from FIrpic molecules to the QDs. It is well known that the TrEL technology can provide detailed information on the carrier dynamics in an electrically driven QLED [22]. Fig. 2b shows the whole TrEL response of the QLEDs with and without FIrpic layers. The green line represents the voltage pulse driving the QLED devices, a 3 V

voltage pulse with a repetition frequency of 1 kHz (40% duty cycle). All the devices present a similar initial luminance overshoot in the turn-on region and is independent on the FIrpic layers. This overshoot phenomenon was also observed in inverted QLEDs reported by Jang group [14]. This may be related to the radiative/nonradiative recombination or/and the QD charging effect induced by the injected charge carriers. However, this overshoot effect is beyond the scope of the present work. Further work is on the way to explore the mechanism of the initial luminance overshoot. As reported previously [22], the detailed charge carriers and light emission (or exciton recombination) dynamics can be found from the initial and delayed parts of the EL response as shown in Fig. 2b and c, respectively. The TrEL response reveals that the QLEDs are beginning with an initial rising EL emission, referred as to EL onset, with a delay time of around a hundred nanoseconds and then followed by a final steady state intensity. This is contributed to the low carrier mobility of the amorphous films. In addition, the devices present a delayed EL emission after turning-off the voltage pulse due to the residual charge carriers within the devices.

It is worth noting that the rising and decay response of the FIrpic-containing QLEDs is very different from that of the control device as shown in Fig. 2b and c. The ET process from FIrpic molecules to QDs will lead to a more delayed EL onset because a part of the excitons is first formed in FIrpic molecules. It is the real case as shown in Fig. 2c that, compared with the reference device A, the EL onset displays a little longer delay time for the device with a thicker FIrpic layer. In other words, the delay time for the EL onset strongly depends on the FIrpic layer thickness. Considering the energy level alignment (Fig. 1d), more holes and electrons will be trapped in the FIrpic molecules for devices with a thicker FIrpic layer, resulting an increasing proportion of excitons formed in FIrpic layer. Consequently, the QLED with thicker FIrpic layer shows a longer delay EL onset as shown in Fig. 2c. This is a strong evidence to prove the ET processes from phosphorescent molecules to the QDs in an electrically driven QLED. It is well known that the EL onset in the LEDs is also related to the injection/transport of charge carriers from the electrodes and charge transport layers. Nevertheless, the electron/hole injection/transport in the QLEDs should not be affected despite the insertion of FIrpic layer, which will be discussed in Fig. 4. Additionally, the emission decay (Fig. 2d) after the voltage pulse turning-off also demonstrates the ET process, which presents a slower decay and prolonged EL emission compared with the device A without the FIrpic layer.

The EL spectra under different applied voltages for QLEDs with and without FIrpic layer are shown in Fig. 3. The parasitic emission at around 480 nm for device A without FIrpic layer indicates the electron leakage into the CBP layer. With increasing the FIrpic layer thicknesses, the parasitic emission is reduced and finally disappeared (Fig. 3b, c, 3d), which is attributed to the carrier confinement effect of FIrpic layer and the excitons formed in the FIrpic effectively transfer their energy to the QDs. Therefore, there is no contribution from the FIrpic in the EL spectra of devices C and D.

The influence of FIrpic on the device electrical properties is evaluated through impedance spectroscopy measurements. The capacitance-voltage results displayed in Fig. 4a reveal that the FIrpic molecules can trap the holes due to their higher HOMO energy level (hence larger hole-injection barrier from FIrpic to QDs), which is characterized by a larger capacitance after inserting the FIrpic at QDs/CBP interface for devices B, C, and D. Fig. 4b shows the impedance spectroscopy properties of the QLEDs. We can see that the impedance of all the devices is almost identical regardless of the insertion of FIrpic layer. This result indicates that the FIrpic molecules have little effect on the carrier (both electron and hole) transport inside the devices. Further, the identical voltage-current phase curves demonstrate that the inserted FIrpic do not affect both the electron and hole injection. These are also supported by the identical electrical characteristics of the four devices shown in Fig. 4c. Therefore, we could unambiguously conclude that the inserted FIrpic layer only changes the carrier distribution but having no
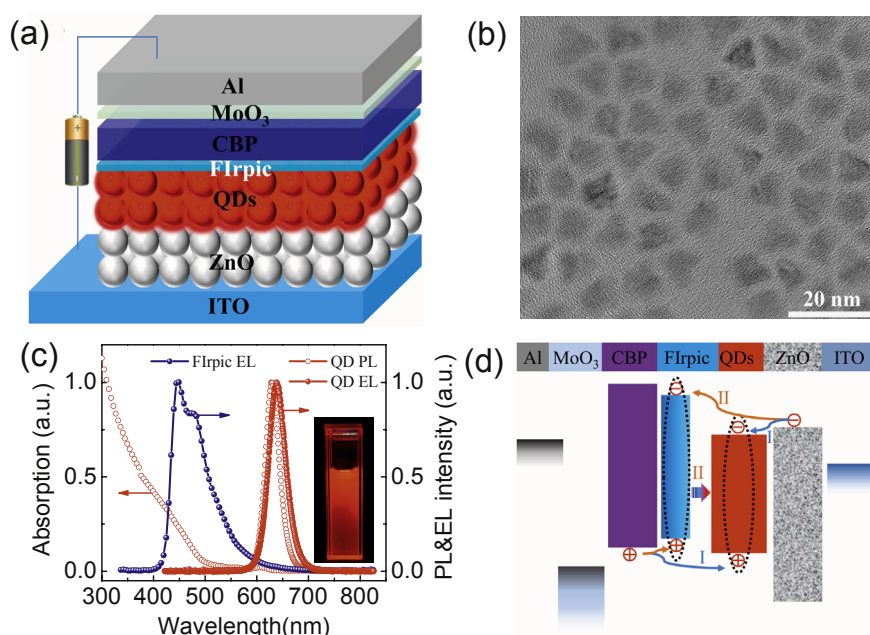
Fig. 1. (a) Schematic device structure. The layer thicknesses are not to scale. (b) TEM image of QDs. (c) Absorption and PL spectra of the QD in toluene, as well as the EL spectra from the QDs and FIrpic. (d) Energy level alignment of the materials used in the devices. The EL emission could be excited by the I direct charge carrier injection or/and II ET process.

effect on the charge carrier injection and transport.

As reported previously, the ET process will enhance the device performance (including luminance and efficiency) evidently. Fig. 4c shows current density-voltage-luminance (*J-V-L*) properties of the QLEDs with and without FIrpic layer. The current density is a little lower for FIrpic-containing devices than that of device A (without FIrpic) in the low voltage region less than 2 V. This result indicates that the FIrpic reservoir layer can hinder the electron leakage from QDs to anode by confining them within the FIrpic molecules. The turn-on voltages, defining as the voltage while the device luminance reaches 0.1 cd/m^2, are similar for all the devices, around 2.2 V. However, the luminance is enhanced for the devices containing FIrpic layers with the operation voltages ranging from 3 to 7 V as can be seen from Fig. 4c. This is attributed to the ET effect from FIrpic molecules to the QDs. As can be observed from Fig. 1d, the inserted FIrpic actually acts as trap for holes due to its higher HOMO energy level. The holes injected from the CBP HTL could be captured by the FIrpic molecules and then form excitons with the leaked electrons from QD, just like a reservoir for both electrons and holes. Thereby, a resonant ET process from FIrpic to QDs happened in these devices, hence improving the device performance. This is in agreement well with the results discussed in Fig. 2. Fig. 4d shows the current efficiency and external quantum efficiency (*EQE*)
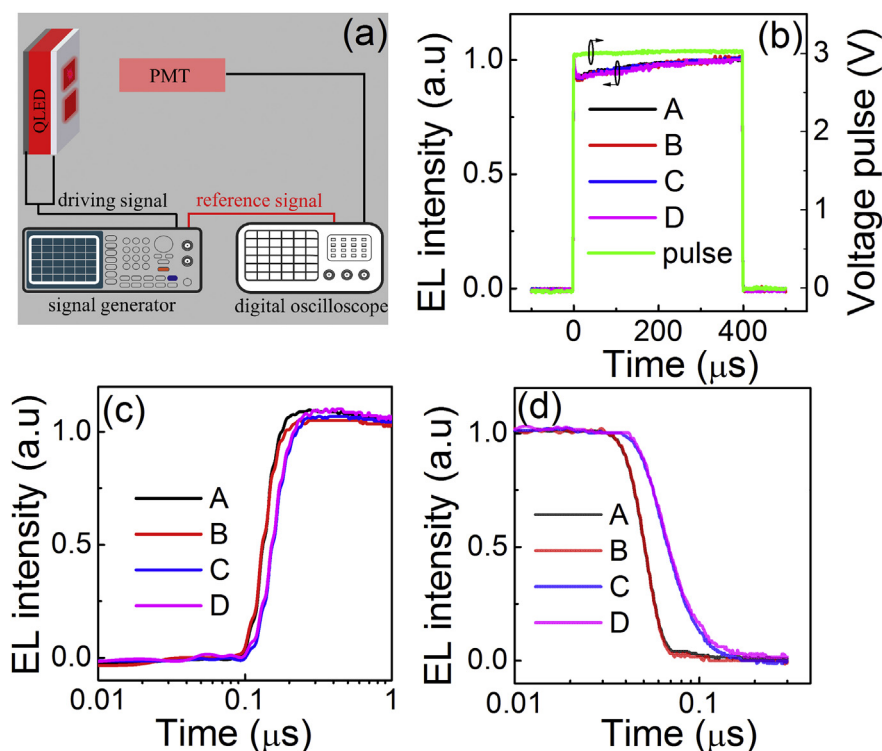
Fig. 2. (a) Schematic diagram for the TrEL measurement system, (b) TrEL response of QLEDs driven by a 3 V voltage pulse with a repetition frequency of 1 kHz (40% µs duty cycle), (c) The initial and (d) decay parts of TrEL response of QLEDs.

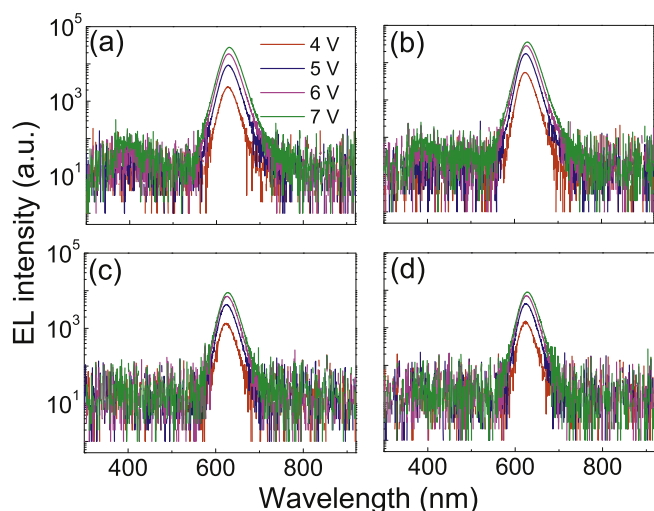**Fig. 3.** EL spectra of QLEDs with and without FIrpic layers.

properties of the QLEDs as a functional of current density (*CE-J-EQE*). The FIrpic-containing devices possess higher *CE* (*EQE*) than the control device A. The optimized *CE* (*EQE*) is achieved for the QLED with 0.5 nm FIrpic layer, and further increasing the thickness of the FIrpic layer causes a reduced device efficiency. This should be due to the concentration quenching reduced by the FIrpic. The phosphorescent FIrpic molecule is deposited directly on the QDs in these QLEDs, thus a thick FIrpic layer will result in aggregation of FIrpic molecules, hence strong interactions between the adjacent molecules will induce the exciton quenching in FIrpic layer and reduce the device performance. It can be seen that the efficiency roll-off, a phenomenon of device efficiency decreasing under high operation current, is slightly more serious for device D than that of other three devices. This is an indirect evidence for the concentration quenching effect of pure FIrpic film and will be discussed in the following text.

Fig. 5a clearly shows the roll-off beheviour of the devices. The *EQE* is normalized according to that of device A (i.e., divided by the peak EQE value of device A). The enhancement factor of the *EQE*, comapred with that of device A, is shown in Fig. 5b as a function of current density, *J*. A large enhancement is achieved within low applied current density (less than 200 mA/cm^2, black grid region in Fig. 5b) for all of

the FIrpic-containing devices. Nevertheless, the enhancement factor is gradually decreased with increasing driven current (larger than 200 mA/cm^2, magenta grid region in Fig. 5b) and a thicker FIrpic layer induces a more serious reduction. This is rational due to the concentration quenching effect of the organic phosphorescent materials. The changes of the current density and luminance of the FIrpic-containing devices relative to the control device are also shown in Fig. 5c and d in detail. *J* (*L*) and J_0 (L_0) are the current density (luminance) of FIrpic-containing QLEDs and control device, respectively. The little change of current density of FIrpic-containing devices compared to the control device further demonstrates that the FIrpic layer has no effect on the carrier transport. In contrary, the device luminance is dramatically enhanced with the insertion of FIrpic layer and a factor of over 20% is obtained with an optimized FIrpic layer (Fig. 5d). Most importantly, the peak values of luminance enhancement are achieved at around 5 V for all of the FIrpic-containing devices, where the *CE* of the devices is at the falling stage. Larger luminance enhancement at higher voltages can be attributed to more carrier leakage or trapping in FIrpic layer. Therefore, a larger proportion of the excitons are formed within FIrpic layer, which means that the device characteristics become strongly dependent on the FIrpic properties under high current (voltage) due to the ET mechanism in these devices.

4. Conclusion

In conclusion, we demonstrate for the first time the ET process between FIrpic and QDs by TrEL measurements in an operating QLED, and we believe that it is feasible to extend this technique to the investigation of interactions between other phosphorescent materials and QDs. Moreover, the insertion of a FIrpic layer at QDs/HTL interface boosts the efficiency of the QLEDs without sacrificing the device luminance and turn-on voltage. In fact, considering the energy level alignment and bandgap of both FIrpic and QDs, two effects (hole accumulation and ET) may simultaneously occur in the QLED with one of them playing the dominant role. However, the ET process plays a more primary role in affecting the device performance. It is very significant to harness the phosphorescent materials as the reservoir to harvest the leaked electrons, followed by back-transfer of the exciton energy to the QDs. This demonstration convincingly suggests a clear path towards designing efficient QLEDs. Moreover, this result opens new avenues to explore the interactions between QDs and phosphorescent molecules through complementing a TrEL measurement in an electrically excited QLED
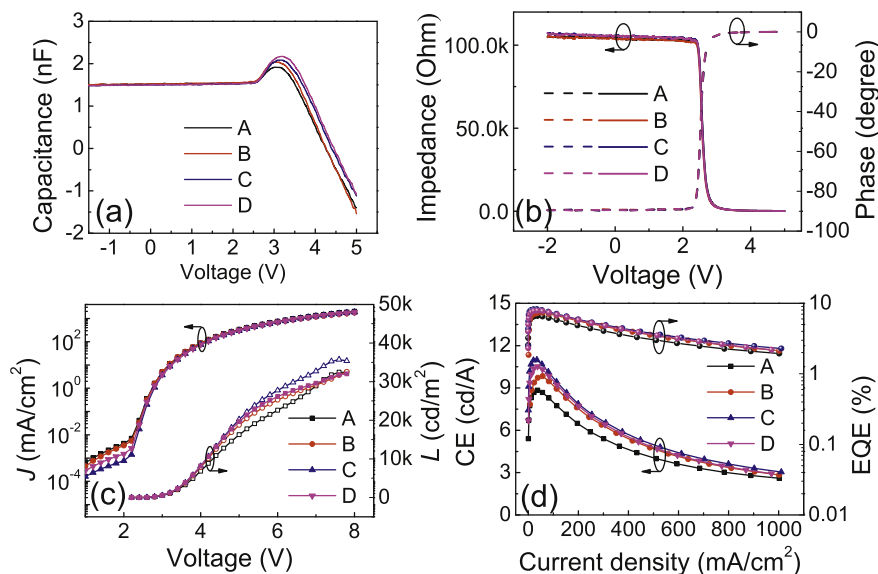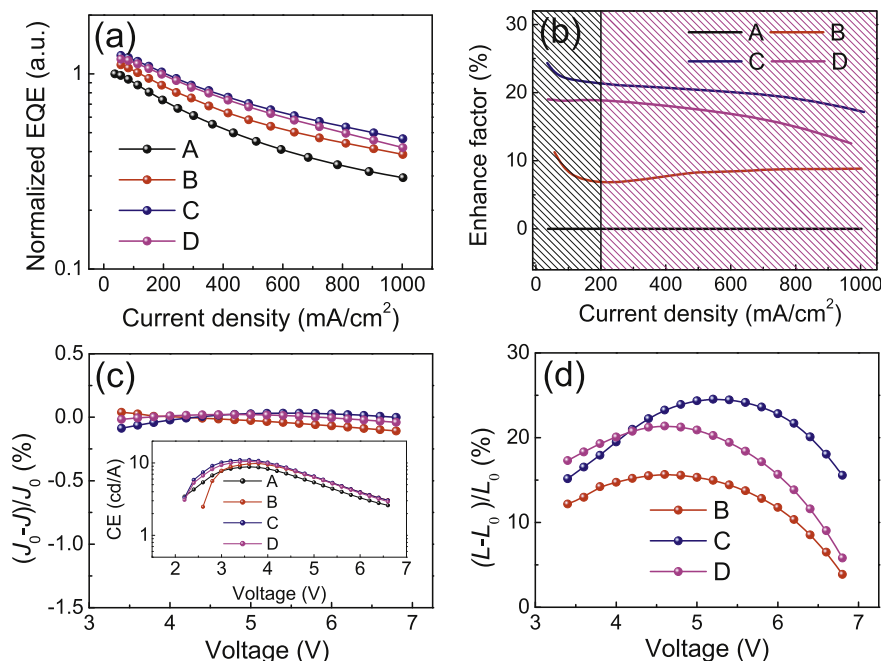

Fig. 4. Photoelectrical properties of devices with and without FIrpic layers. (a) Current density-voltage-luminance (*J-V-L*), (b) *CE-J-EQE*, (c) Capacitance-voltage, and (d) impedance-voltage-current phase properties.

Fig. 5. (a) Normalized *EQE* and (b) *EQE* enhance factor under different current densities compared with the control device. The bias voltages for the current density at 200 and 500 mA/cm^2 are 4.5 and 5.5 V, respectively. Enhancement ratio of (c) current density and (d) luminance as a function of applied voltages. Inset is the *CE-V* properties of devices.

device.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2019.06.045.

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