

Triplet-Triplet Annihilation for Low Voltage Operation of Organic Light-Emitting Diode

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Abstract

Triplet-triplet annihilation (TTA) can double the energy of excited states. Therefore, it is utilized for reducing the operation voltage of organic light-emitting diodes (OLEDs). We improved the external quantum efficiency of TTA-based upconversion (UC)-OLED through precise device design. Furthermore, the UC-OLED that can emit blue light was demonstrated.

Author Keywords

Organic light emitting diode; driving voltage; triplet-triplet annihilation; upconversion; charge transfer state

1. Introduction

Organic light-emitting diodes (OLEDs) are already commercially available for use in smartphones and large-screen TVs, as they can project high-contrast images. Furthermore, as it is a surface-emitting light source, lightweight, and easy to form films on flexible thin films, it is also expected to become the next generation of lighting. The power consumption of OLED is expressed as multiplying current and voltage. Firstly, concerning current, the efficiency of converting current to light has already been optimized. The efficiency of converting current to light within the device, namely internal quantum yield (IQE) has reached 100%, and the efficiency of the process by which light is extracted from the device surface, namely external quantum yield (EQE) exceeds 20%. These highly efficient emissions have been achieved through the development of phosphorescent and thermally activated delayed fluorescent (TADF) molecules that can produce light from the triplet excited state, which is difficult to emit and is generated at a rate of 75% by charge injection.^[1] On the other hand, the driving voltage of OLEDs remains high. In particular, blue is the most difficult because it has the highest light energy among the three primary colors.^[2] The first reason for the large driving voltage is that organic semiconductor materials used in OLEDs are generally amorphous materials. Amorphous materials have been preferred for OLEDs because it is easy to create a uniform thin film with a low leakage current and less likely to be quenched by aggregation. thin films. However, their charge mobility is low at around 10^{-3} – 10^{-5} cm²/Vs, which causes an increase in voltage.^[3] A second factor causing an increase in voltage is the use of multi-layer device structures with stacked charge transport layers, exciton blocking layers, etc., to suppress the deactivation process.^[4] They lead to increased resistance.

One of the solutions to reduce the driving voltage of OLED is using triplet-triplet annihilation (TTA), a process that produces a single high-energy singlet exciton (S_1) from two triplet excitons (T_1).^{[5][6][7]} Excitation of a low-energy T_1 at low voltage would enable electroluminescent (EL) emission at low voltage through energy gain by TTA, i.e. upconversion (UC). TTA for the low voltage operation of OLEDs has been reported for several

decades, but the device has suffered from low efficiency. We have improved efficiency through precise device design and achieved low-voltage emission in blue OLEDs. This paper summarizes the efforts that have been made to develop UC-OLED.

2. Operation Mechanism of UC-OLED

Reducing the driving voltage of OLEDs by using TTA was first reported by Pandey et al. in 2007.^[8] They used rubrene as the TTA emitter and C₆₀ fullerene as the electron transport layer (Fig. 1a). In the rubrene/C₆₀ OLED device, it was reported that the emission around 560 nm started at 1 V, which corresponds to about half of the rubrene band gap energy of 2.2 eV. However, the mechanism leading to luminescence at applied voltages lower than the equivalent bandgap was unclear, and Auger recombination was proposed as the mechanism. In 2015, Xiang et al. concluded that the mechanism by which the rubrene/C₆₀ OLED devices emit light at low voltages is due to the TTA-UC in the rubrene layer, using transient EL measurements.^[9] The material forming the interface with the TTA emitter, such as C₆₀, plays an important role in the UC-OLED. Since C₆₀ and other materials used in UC-OLED such as Perylenetetracarboxylic Diimide (PTCDI) have a highly electron-accepting ability, while rubrene is used as a donor, forming a donor/acceptor (D/A) interface.

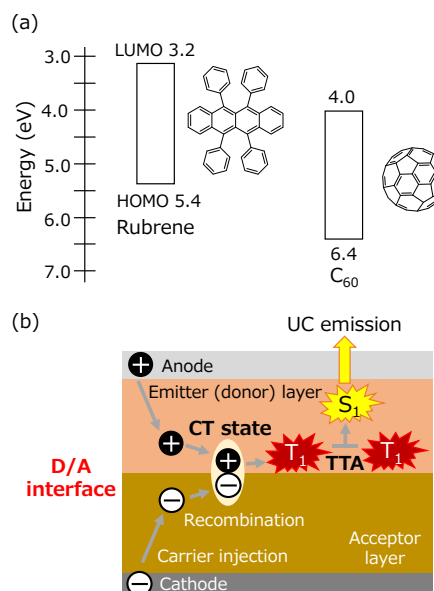


Figure 1. (a) Chemical structures and energy levels of the materials. (b) Schematic of the device structure and the operating mechanism of UC-OLEDs. Reprinted from ref. 6.

The emission mechanism of UC-OLEDs such as rubrene/ C_{60} is shown in Fig. 1b. The lowest unoccupied molecular orbital (LUMO) level of C_{60} is sufficiently lower than that of rubrene so that electron injection does not occur in the rubrene layer and charge recombination occurs at the D/A interface. When recombination occurs, the formation of a charge-transfer (CT) state as an intermediate at the interface allows selective excitation of low-energy T_1 at low voltages. Subsequently, TTA produces one high-energy S_1 from two low-energy T_1 and finally, EL emission from the device is obtained from S_1 . However, a major problem with the UC-OLED using rubrene/ C_{60} has been a low EQE of less than 0.1%.^[10] Only rubrene emitting yellow light was reported as the TTA emitter for UC-OLEDs in the previous studies.

3. Improvement of EQE in UC-OLED

We fabricated a device in which the rubrene emission layer was doped with 0.5% tetraphenylidibenzoperiflanthene (DBP) as a fluorescent material in a rubrene/acceptor device to improve the emission efficiency of the UC-OLED. The luminance (L)-voltage (V) characteristics of the fabricated UC-OLED devices are shown in Fig. 2a. In the device using rubrene as a donor, and C_{60} or PTCDI as acceptors, emission started at around 1 V, which corresponds to about half the band gap of rubrene, as previously reported. Adding DBP as a fluorescent dopant to this device, luminance increased by a factor of about 10. In the rubrene+DBP/PTCDI device, the emission of 608 nm light, i.e. 2.04 eV, reached 1 cd/m^2 at 0.97 V, while it reached 100 cd/m^2 at 1.33 V. This is the OLED that can reach each luminance with the lowest applied voltage.^{[8][11]} As shown in the photograph in Fig. 2b, bright emission could be obtained by simply connecting a 1.5 V battery to the UC-OLED device.

Here, the EQE of each device was measured at different current densities in order to clarify the effect of DBP doping. The EQE increased with increasing current density in all devices with and without doping (Fig. 2c). This is because TTA is a two-photon process and its efficiency is higher at larger T_1 concentrations.^[12] On the other hand, the EQE decreases in the region of high current densities of around 1,000 mA/cm^2 . This was possibly due to the occurrence of the loss processes such as triplet-charge annihilation.^[13] Comparing the highest EQE of the device when each material was used, the efficiency of rubrene/ C_{60} was very low at 0.075%, as previously reported, while the efficiency improved to 0.215% when PTCDI was used, and further improved by about 10 times to 2.18% when doped with DBP, a fluorescent dopant. Furthermore, increasing the emission layer thickness from 50 nm to 200 nm was found to increase the EQE up to 2.91%.^[6]

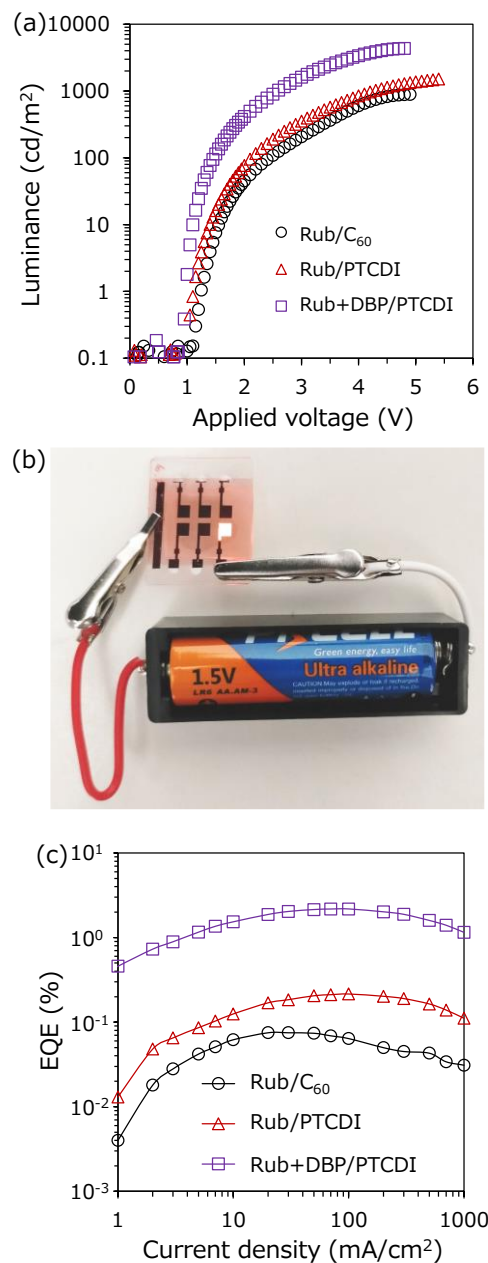


Figure 2. (a) L - V curves of the devices. (b) Photograph of the yellow UC-OLED operated by a 1.5 V battery. (c) EQE of the devices. Reprinted from ref. 6.

4. Low Voltage Operation of Blue OLED

Blue light has the highest energy at approximately 3 eV among the three primary colors. Therefore, Blue OLEDs require high voltages for light emission. Reduction of driving voltages for blue OLED is required to save power consumption of OLED displays. Furthermore, the high energy of the excited state for blue emission leads to a reduction in the device's lifetime. Phosphorescent molecules have been in practical use for red and green OLED, but fluorescent molecules are still mostly used for blue. This is because the blue light energy is comparable to the energy of carbon-nitrogen bond in organic molecules, making it difficult in principle to improve the stability of blue phosphorescent and TADF molecules that produce blue light

from high energy and long-lifetime T_1 .^[14] Therefore, if blue UC-OLEDs could be developed, it would be possible to extract high-energy blue emission from low-energy T_1 , which could lead to lower operation voltage and longer lifetime. However, the UC-OLED has only been reported as a yellow-emitting device using rubrene as the TTA material.

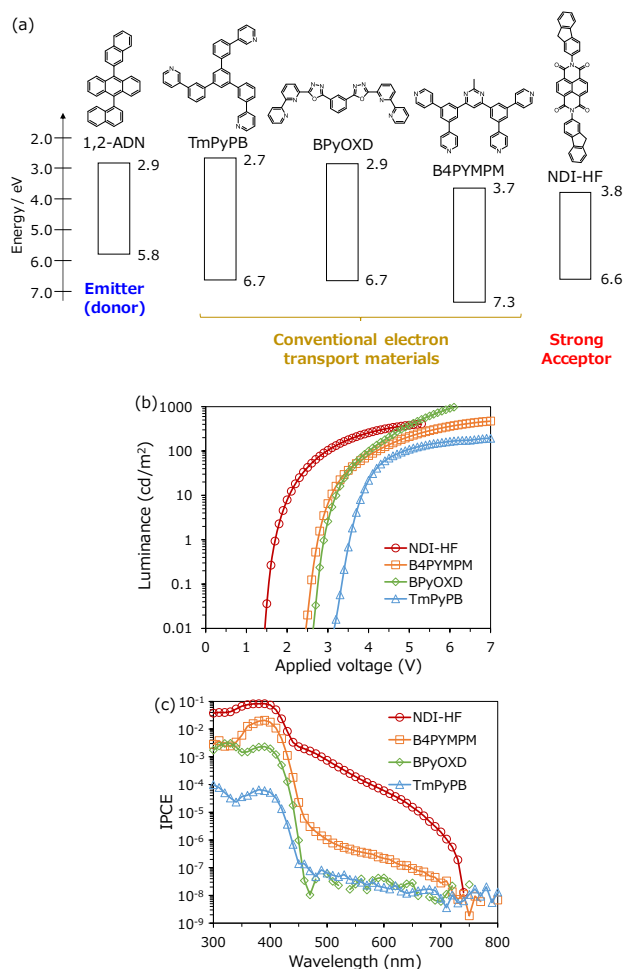


Figure 3. (a) Chemical structures and energy levels of the materials. (b) L - V curves of the devices. (c) Incident photon to current conversion efficiency (IPCE) of the devices. Reprinted from ref. 7.

We therefore fabricated a bilayer device using an anthracene derivative (1,2-ADN), a well-known TTA material. The anthracenes have T_1 energy at approximately 1.7 eV, larger than half of S_1 energy, satisfying the requirement for an efficient TTA emitter. The materials forming the interface with 1,2-ADN, the common electron transport materials TmPyPB, BPyOXD, and B4PYMPM, as well as NDI-HF with strong acceptor properties were used (Fig. 3a). Observation of the emission spectra of these devices showed almost identical emission with a peak at 424 nm (2.92 eV) from 1,2-ADN in all devices. On the other hand, when measuring the L - V characteristics, luminescence was observed from around 3 V when using common electron transport materials, while luminescence started from around 1.5 V when using NDI-HF (Fig. 3b). Highly sensitive photocurrent measurements were performed to clarify the factors behind the difference in the luminescence start voltage (Fig. 3c). While no photocurrent response was observed

in the long wavelength region for devices with common electron transport materials, a signal corresponding to CT absorption was observed around 650 nm only for the 1,2-ADN/NDI-HF devices. This means that the CT state forms only at the 1,2-ADN/NDI-HF interface, and that this CT state formation induced the TTA emission at low voltages.

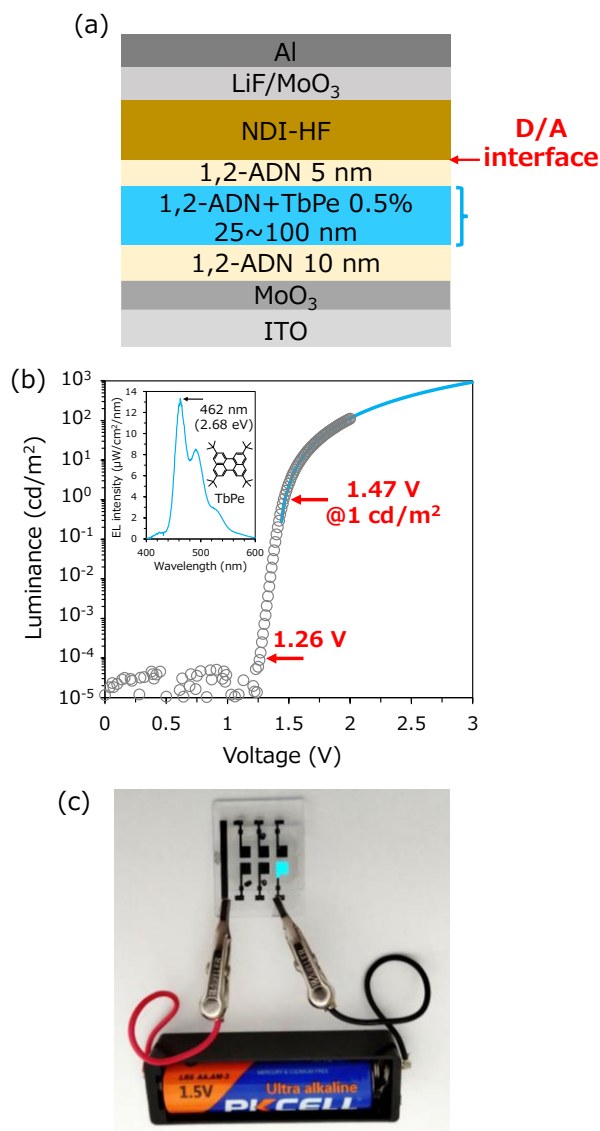


Figure 4. (a) Schematic device structure. (b) L - V curves of the devices. The Inset shows the emission spectrum of the device and the chemical structure of TbPe. (d) Photograph of the blue UC-OLED operated by a 1.5 V battery. Reprinted from ref. 7.

For this 1,2-ADN/NDI-HF combination, the EQE was improved by adding TbPe as a fluorescent dopant. The optimized device structure is shown in Fig. 4a, where the TbPe doped layer is sandwiched by a thin non-doped layer, aiming to suppress the interfacial quenching of the final S_1 at TbPe. In this device, emission from TbPe with a peak at 462 nm (2.68 eV) was observed (Fig. 4b). The L - V characteristics of the optimized device are shown in Fig. 4b, where the blue emission of 2.68 eV can be observed from a very low voltage of 1.26 V. The luminance of 100 cd/m² can be reached at 1.97 V. As shown in

Fig. 4c, this OLED can emit blue light when connected to a single 1.5 V battery. Blue emission at such an ultra-low voltage is not possible even with inorganic LEDs, so the blue UC-OLED was developed at the world's lowest operation voltage, including both organic and inorganic LEDs. The EQE of this device was found to be 3.25%. Furthermore, in order to verify the stability of the blue UC-OLED developed in this study, the decrease in luminance when continuously driven at 1000 cd/m² was compared with a conventional OLED using FirPic.^[15] As a result, it was found that the device's lifetime was 90 times longer than that of the conventional blue phosphorescent device. UC process that utilizes low energy T₁ for blue emission has the advantage of device stability.^[7]

5. Conclusion

Sensitizing TTA using the CT state generated at the D/A interface as an intermediate and appropriately designing a device structure leads to the development of efficient UC-OLED with ultra-low voltage operation. Especially for blue, it is difficult to create highly efficient and stable devices even with other emission mechanisms such as phosphorescence and TADF, so UC-OLEDs could be a potential alternative. The key to the practicality of blue UC-OLEDs in the future will be the realization of blue emission with high color purity and narrow spectral width suitable for display applications and the improvement of EQE. If these can be realized, UC-OLEDs will be developed into an important technology that can reduce the power consumption of OLED displays. Furthermore, controlling conversion processes of excited states near the D/A interface will lead to higher efficiency not only in OLEDs but also in other organic optoelectronic devices such as organic solar cells and the development of novel optical functions such as photon upconversion.

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