

IEICE **TRANSACTIONS**

on Electronics

DOI:10.1587/transele.2024DIS0001

Publicized:2024/07/11

**This advance publication article will be replaced by
the finalized version after proofreading.**

A PUBLICATION OF THE ELECTRONICS SOCIETY



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Origin of Extremely Low Turn-on Voltage in Blue Organic Light-Emitting Diode

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SUMMARY The Origin of the low turn-on voltage in the blue organic light-emitting diode using upconversion is discussed. We have discovered the properties of the intermediate state at the donor/acceptor interface such as the energy levels and the molecular interactions are key in determining the device performance.

key words: *Organic light-emitting diode, Turn-on voltage, Upconversion, Interface*

1. Introduction

Blue light emission is crucial for the development of light-emitting devices due to its high energy compared to the other two primary colors, making it a key source of white light emission [1]. Even though organic light-emitting diodes (OLEDs) are already in use commercially available, such as in smartphone displays and televisions, blue-light emission still faces challenges such as high driving voltage and low stability [2]. For instance, to achieve blue-light emission at a luminance of 100 cd/m², which is similar to a typical smartphone display, a voltage of approximately 4 V is needed [3].

Conventional fluorescent materials are commonly used in commercially available blue OLEDs [4]. Phosphorescent and thermally activated delayed fluorescent materials, which have been the focus of recent research, show high emission efficiencies but are less stable compared to fluorescent materials [5]. This instability is due to the need for phosphorescent and thermally activated delayed fluorescent materials to increase the energy level of the triplet exciton to approximately 3 eV, which is close to the photon energy of blue light. This 3-eV energy level is equivalent to the dissociation energy of the carbon–nitrogen bond in organic molecules [5], causing high-energy triplet excitons with long lifetimes to lead to material degradation. In contrast, fluorescent materials have lower energy levels for triplet excitons, approximately 1.7 eV for anthracene derivatives, which are typical blue-fluorescent materials [6]. Therefore, reducing the driving voltage of OLEDs using blue fluorescent materials is crucial in reducing the energy consumption of OLED displays.

In a previous study, we reported a blue OLED with an extremely low turn-on voltage using an upconversion (UC) process of the excited state [7]. The operating mechanism is illustrated in Fig. 1a. Initially, holes and electrons are injected into the donor (emitter) and acceptor (electron transport) layers, respectively, and they recombine at the donor/acceptor (D/A) interface to form a charge transfer (CT) state. Subsequently, the energy of the CT state is transferred to T₁ of the emitter, resulting in the emission of blue light through the formation of high-energy S₁ by triplet–triplet annihilation (TTA). Because TTA can double the energy of the excited state, the blue emission in the UC-OLED starts from an applied voltage of less than 1.5 V, which is about half the energy of blue light. Because of the utilization of low-energy T₁, the operational stability of UC-OLED is better than that of typical phosphorescent OLEDs [7].

This study delves into the origin of the extremely low turn-on voltage in blue UC-OLEDs. For this, the performance of an OLED device with combinations of two anthracene donors and two naphthalene diimide acceptors was compared, as shown in Fig. 1b. In addition, transient electroluminescence under varying applied voltages and the thickness dependence of the emission layers were investigated.

2. Results and Discussions

Anthracene derivatives were used as emitters (donors) in the UC-OLED. Anthracenes are among the most widely used host materials in blue-fluorescent OLEDs [4]. Anthracene derivatives are also known as TTA emitters because they satisfy the energy requirements for efficient TTA; the energy of T₁ (1.7 eV) is slightly more than half that of S₁ (2.9 eV) [6]. To compare the energy differences between anthracene derivatives, we used two anthracenes: 1,2-ADN and TPA-An-mPhCz [8]. As TPA-An-mPhCz has carbazole and triphenylamine electron-donating groups, the highest occupied molecular orbital (HOMO) energy level of TPA-An-mPhCz is 5.6 eV, which is 0.2 eV shallower than the HOMO level of 1,2-ADN. However, the T₁ levels of these two donors are nearly identical [7].

For the acceptor layer of the UC-OLED, we used naphthalene diimide derivatives NDI-HF and NDI-Cy, with fluorene and cyclohexyl side chains, respectively. NDI derivatives have a strong electron acceptability; therefore, they are sometimes used as electron acceptors in organic

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photovoltaics (OPV) [9]. The difference in the side chains between NDI-HF and NDI-Cy results in different lowest unoccupied molecular orbital (LUMO) levels of 3.8 and 3.7 eV, respectively [10].

By using a combination of these two donors and two acceptors, we fabricated a planar heterojunction device with the structure ITO/MoO₃/donor layer/acceptor layer/LiF/MoO₃/Al. Details of the fabrication procedure are described in a previous report [7].

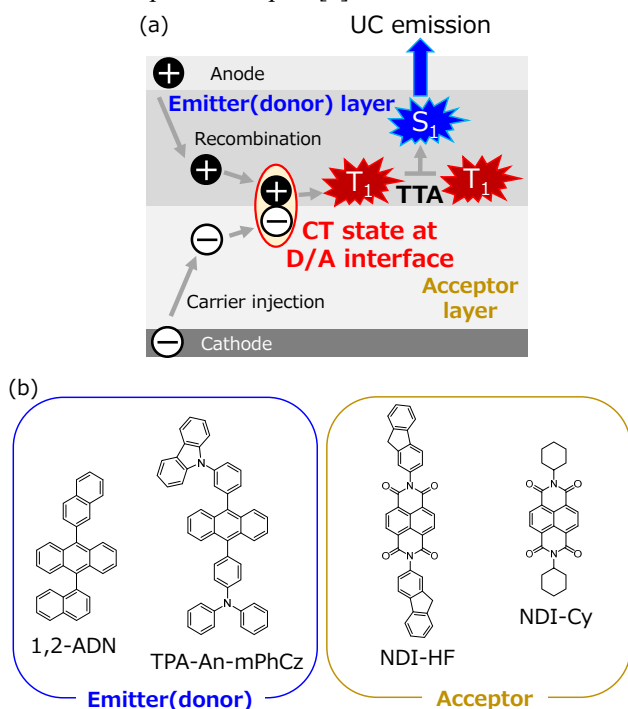


Fig. 1 (a) Schematic of the operating mechanism and the device structure of a UC-OLED. (b) Chemical structures of the emitter (donor) and acceptor materials.

Fig. 2 shows the emission spectra from the UC-OLED using 1,2-ADN and TPA-An-mPhCz as donors and NDI-HF and NDI-Cy as acceptors. All the devices showed blue TTA-UC emission and CT emission, which is an intermediate emission, at wavelengths longer than 650 nm. The wavelength of the CT emission reflects its energy. The CT emission of the device with TPA-An-mPhCz appeared at a longer wavelength than that of the device with 1,2-ADN when the same NDI molecule was used. This result corresponds to a 0.2 eV shallower HOMO level of TPA-An-mPhCz than that of 1,2-ADN. The intensity of the blue TTA-UC emission increased when the D/A combination showed a CT emission at approximately 700 nm. This energy was close to the T_1 of the anthracene derivatives, about 1.7 eV. The results indicate that an appropriate combination of 1,2-ADN/NDI-HF and TPA-An-mPhCz/NDI-Cy, which have similar energies between the CT state and T_1 , shows efficient energy transfer between the two states and TTA-UC emission.

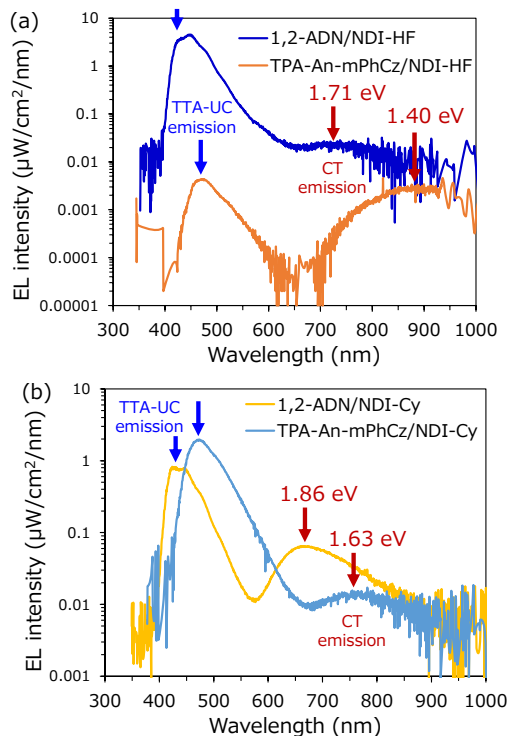


Fig. 2 EL emission spectra of (a) 1,2-ADN or TPA-An-mPhCz/NDI-HF, (b) 1,2-ADN or TPA-An-mPhCz/NDI-Cy devices under a constant current flow (100 mA/cm²).

Figs. 3a and c illustrate the luminance–voltage (L – V) curves of the devices. Blue light emission starts from about 1.5 V in the devices with 1,2-ADN/NDI-HF and TPA-An-mPhCz/NDI-Cy, while it starts at 2.5–3 V in the device with B4PYMPM, which is a typical electron transport material in the OLED field. The extremely low-voltage turn-on is a key feature of UC-OLED. In typical OLEDs, the excited state is first generated in the emission layer through electron and hole injection and recombination. In contrast, charges recombine at the D/A interface to generate a CT state in the UC-OLED. This charge recombination behavior is determined by the CT interaction at the D/A interface. Figs. 3b and d show the highly sensitive incident photon-to-current conversion efficiency (IPCE) spectra. Devices using B4PYMPM showed minimal photocurrent response at wavelengths longer than the HOMO-LUMO transition of anthracene derivatives around 450 nm. In contrast, the device with 1,2-ADN/NDI-HF and TPA-An-mPhCz/NDI-Cy showed a clear photocurrent response up to 700 nm, indicating CT state formation at the D/A interface due to the strong interaction between anthracenes and NDIs. B4PYMPM has a relatively deep LUMO level at 3.7 eV [11]. However, it does not form a CT state at the interface, even with TPA-An-mPhCz, which has a shallow HOMO level. This indicates that not only the energy level but also the structural factors influence the nature of the CT state and the low-voltage turn-on observed in the UC-OLED.

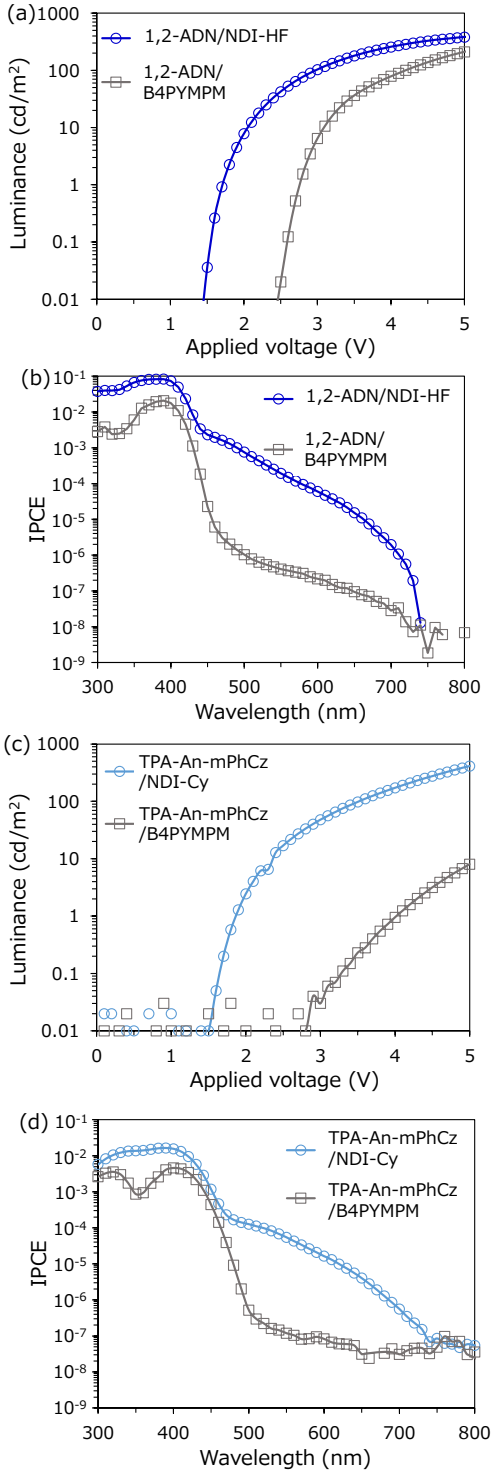


Fig. 3 (a) L - V curves and (b) highly sensitive IPCE spectra for the 1,2-ADN/NDI-HF and 1,2-ADN/B4PYMPPM devices. (c) L - V curves and (d) highly sensitive IPCE spectra for the TPA-An-mPhCz/NDI-Cy and TPA-An-mPhCz/B4PYMPPM devices.

Figs. 4 and 5 show the device using tert-butyl perylene (TbPe) as the fluorescent dopant in the anthracene emission layer to enhance the emission intensity. The doping concentration of TbPe was 0.5 vol%. Fig. 4 shows the transient EL signals of the TbPe-doped device at

varying applied voltages. Only a slow decay component with a lifetime on the order of microseconds is observed, indicating that all the emissions originate from TTA, involving a slow process stemming from T_1 diffusion. Notably, a prompt decay component did not appear even at a voltage exceeding the bandgap of anthracenes, such as 4 V. This result indicates that the direct excitation of S_1 from the injected electrons and holes in the emission layer does not occur even at a voltage larger than the bandgap.

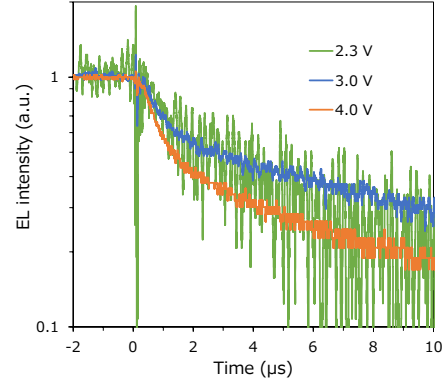


Fig. 4 Decay dynamics of EL emission of the TbPe-doped 1,2-ADN/NDI-HF device under different applied voltage.

Figs. 5a and b show J - V and L - V curves of the 1,2-ADN/NDI-HF device with TbPe-doped layer thicknesses of 25, 50, and 100 nm. The applied electric field was varied at the same applied voltage by changing the film thickness of the emission layer. As shown in Fig. 5a, the threshold voltages of the injection current did not shift with the film thickness, even though the leakage current at a voltage less than 1 V was smaller in the thicker film because of the suppression of leakage at the grain boundary or film edge. In particular, the starting voltage for blue emission in Fig. 5b perfectly coincides with those of the three devices with different emission layer thicknesses. The results indicate that the turn-on voltage of the UC-OLED is determined by the properties of the CT state at the D/A interface rather than by the applied electric field. The starting voltage for blue emission corresponds to other device properties such as organic photovoltaic (OPV) performance. The UC-OLED acts as an OPV because the D/A interface can separate the S_1 generated by photoexcitation to form free charges. The OPV performance of the UC-OLED based on 1,2-ADN/NDI-HF is shown in Fig. 5c. The device showed a short-circuit current density (J_{SC}) of 0.0361 mA/cm², open-circuit voltage (V_{OC}) of 1.32 V, fill factor (FF) of 50.8%, and power conversion efficiency (PCE) of 0.0242% under simulated solar light (AM 1.5, 100 mW/cm²) irradiation. The J_{SC} and PCE values of the device were low because both anthracene and NDI have low absorption in the visible region. However, sufficiently high FF and V_{OC} values indicate that the charge separation efficiency of the UC-OLED is not so low. Importantly, the V_{OC} of 1.32 V was almost the same as the starting voltage of the blue emission in Fig. 5b.

These values are correlated because both OLED and OPV are diode devices. Further investigation is required to elucidate the relationship between the photophysical processes of these two devices.

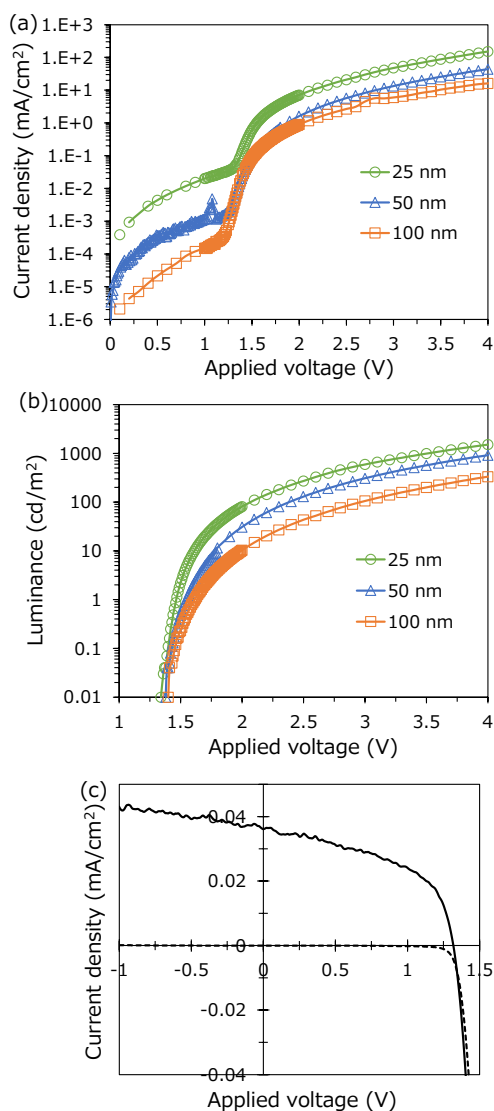


Fig. 5 (a) J - V and (b) L - V curves of the 1,2-ADN/NDI-HF device with the different TbPe-doped layer thicknesses of 25 nm, 50 nm, and 100 nm. (c) The diode characteristic of the TbPe-doped 1,2-ADN/NDI-HF device under dark (broken line) and AM 1.5, 100 mW/cm² irradiation (solid line).

3. Conclusions

In summary, the origin of the ultralow-voltage turn-on for the blue emission of the UC-OLED was discussed. The investigation of material combinations revealed that not only energy levels but also structural factors are important for low-voltage turn-on in UC-OLED. Furthermore, the turn-on voltage does not change with different electric fields, and the emission mechanism remains the same under an applied voltage larger than the bandgap of anthracene, indicating that the properties of the CT state at the D/A interface are key in determining the device performance. Further enhancement of device performance can be

achieved through the appropriate design of the CT state properties at the D/A interface [12].

Acknowledgments

This research was supported in part by JSPS KAKENHI, Grants-in-Aid for Scientific Research (21H05411, 22K14592), JST PRESTO (JPMJPR2101), and The Morino Foundation for Molecular Science. The author would like to thank M. Morimoto at Toyama University for the transient EL measurement, K. Fujimoto and K. Banno at Shizuoka University for the synthesis of NDI derivatives, M. Hiramoto at Institute for Molecular Science, S. Naka at Toyama University, M. Takahashi at Shizuoka University, and Y. Majima at Tokyo Institute of Technology for their valuable comments, K. Tajima and K. Nakano at RIKEN for their assistance with the photoelectron yield measurements.

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