

Multiple Resonance Effect-Based Narrowband TADF Emitters

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ABSTRACT

A thermally activated delayed-fluorescence material that exhibits an ultrapure blue emission were synthesized. The emitter consists of five benzene rings connected by two boron and four nitrogen atoms and two diphenylamino substituents. The multiple resonance effect of the boron and nitrogen atoms realizes narrowband emission and fast reverse intersystem crossing.

1 INTRODUCTION

Narrow-band light-emitting diodes (LEDs) are important components in developing energy-saving and high-quality displays that realize a larger colour space than conventional liquid crystal displays. Recently, well-defined LEDs based on gallium nitrides¹, CdS/ZnS quantum dots², and perovskites³ have realized emission bands with a full-width at half-maximum (FWHM) of ~20 nm in the blue region. However, these LEDs suffer from serious problems related to cost, reproducibility, and large-area fabrication. In contrast, organic LEDs (OLEDs) which are employed in displays such as TVs and smart phones, generally exhibit broad emission bands with FWHM >40 nm. Therefore, even the latest commercial OLED displays use colour filters or optical microcavities to enhance the colour purity of the original electroluminescence (EL) spectra, thus permitting significant energy losses in these displays.

2 RESULTS

The broadening of the emission spectra is caused by vibronic coupling between the ground state (S_0) and the singlet excited state (S_1) as well as by structural relaxation at the S_1 state (Fig. 1). As exemplified by perylene, the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of a polycyclic aromatic compound are primarily localized between atoms, thus forming π -bonds. This bonding/anti-bonding character enhances the interactions between the electronic and nuclear vibrational motion between the S_0 and S_1 states as well as the vibrational relaxation at the S_1 state. To suppress emission band broadening, we developed a new polycyclic framework ν -DABNA consisting of five benzene rings connected by two boron and four nitrogen atoms and two diphenylamino groups⁴ (Fig. 1). The multiple resonance effect⁵ of the boron and

nitrogen atoms induces the localization of the HOMO and LUMO on different atoms and minimizes their bonding/anti-bonding character; the resulting non-bonding molecular orbitals (MOs) minimize the vibronic coupling and vibrational relaxation in the material, allowing the realization of an extremely sharp photoluminescence (PL) band with a FWHM of 14 nm. Moreover, the significant localization of the HOMO and LUMO reduces the energy gap (ΔE_{ST}) between the S_1 state and triplet excited state (T_1), promoting reverse intersystem crossing (RISC) from the T_1 to S_1 states as well as thermally activated delayed fluorescence (TADF)⁶.

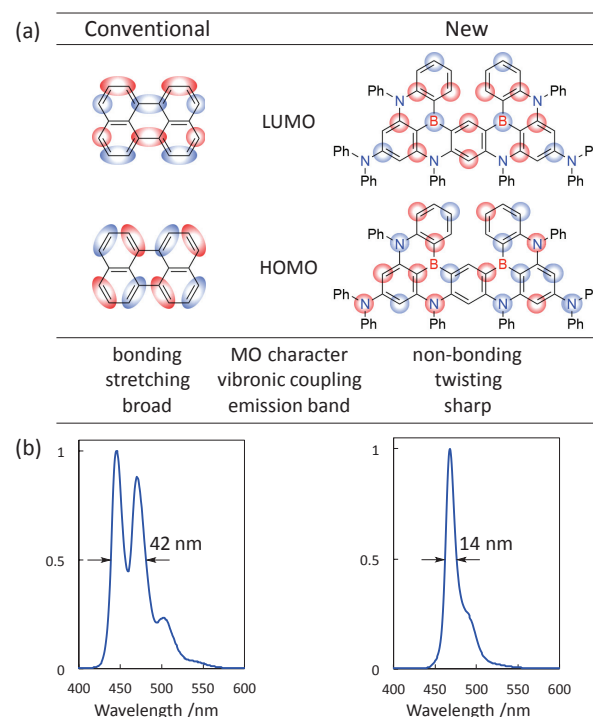


Fig. 1 (a) HOMO and LUMO of a conventional emitter (perylene) and proposed emitter (ν -DABNA). (b) PL spectra of perylene and ν -DABNA in toluene.

To demonstrate the potential of the proposed ultrapure blue emitter, devices with the following

structure were fabricated: indium tin oxide (ITO, 50 nm); N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPD, 40 nm); tris(4-carbazolyl-9-ylphenyl)amine (TCTA, 15 nm); 1,3-bis(N-carbazolyl)benzene (mCP, 15 nm); 1 wt% v-DABNA emitter and 99 wt% DOBNA-OAr (20 nm); diphenyl-4-triphenylsilylphenylphosphine oxide (TSPO1, 30 nm); LiF (1 nm); and Al (100 nm). The EL characteristics and the ionization potentials and electron affinities of these devices are shown in Fig. 2; the device exhibits a pure blue emission at 469 nm with a FWHM of 18 nm, which is smaller than those of both microLEDs and QD-LEDs; the corresponding CIE coordinates are (0.12, 0.11), approaching the (0.14, 0.08) requirements defined by the National Television System Committee. Furthermore, the device shows excellent efficiencies of 34.4% at the maximum (15 cd m⁻²), 32.8% at 100 cd m⁻², and 26.0% at 1000 cd m⁻², which are among the best performance values reported for blue OLEDs. Notably, the efficiency roll-off (1.6% and 8.6% at 100 and 1000 cd m⁻², respectively) is smaller than those in the latest deep-blue OLEDs. We assume that the relatively short TADF lifetime (4.05 μ s) and the large kRISC value (2.0×10^{-5} s⁻¹) suppress the triplet-triplet and singlet-triplet annihilation processes in the device. Further reduction can be achieved by suppression of triplet-polaron quenching with balanced charge injection and transportation. Notably, v-DABNA does not show any thermal degradation at 440 °C, which is in good agreement with the C–N bond dissociation enthalpies that are comparable with those in NPD and mCP. Nevertheless, the emission luminance decreased from 100 to 50 cd m⁻² for 31 h without emission colour change, probably because of the instability of TSPO1, insufficient kRISC value, and the unbalanced charge transportation. Structural modification of v-DABNA and optimization of the device structure using an assist dopant will contribute significantly to practical applications.

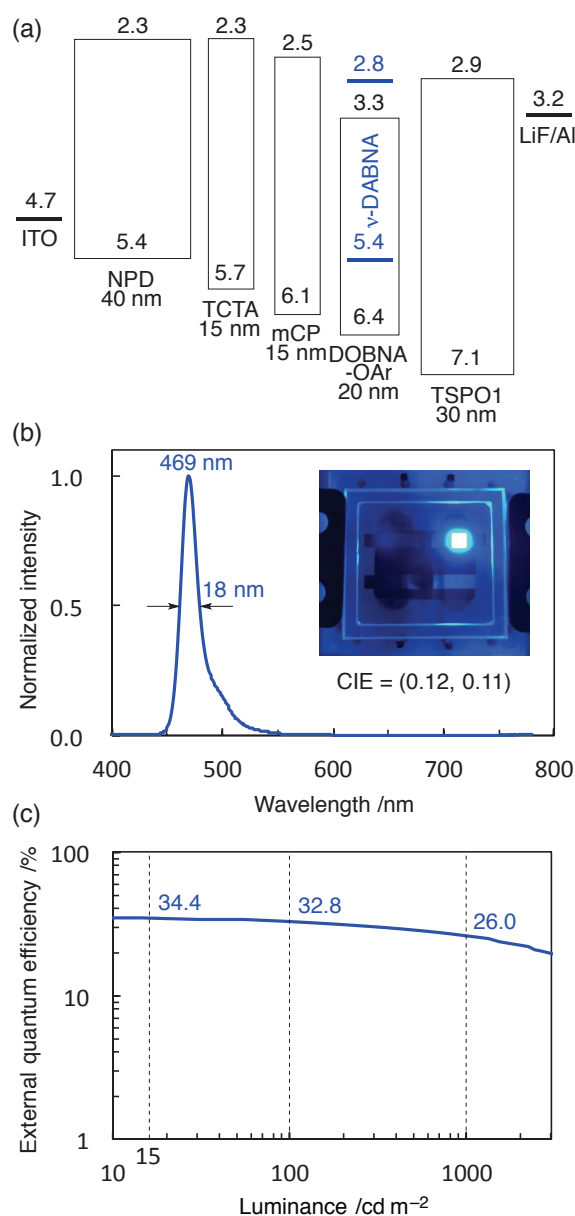


Fig. 2 OLED performance. (a) Device structure and ionization potentials and electron affinities (in eV) for each material. (b) Normalized EL spectra. (c) External quantum efficiency versus luminance characteristics.

3 CONCLUSIONS

We designed a new organoboron-based emitter exhibiting an unprecedentedly sharp emission band with a FWHM of 14 nm using the multiple resonance effect of constituent boron and nitrogen atoms. The proposed emitter showed excellent TADF properties, leading to state-of-the-art OLED performance in the deep blue region. The FWHM of the EL spectrum was only 18 nm, which is smaller than those of the latest microLEDs and QD-LEDs. The described molecular emitter may both significantly improve the performance of displays and provide a new strategy for the development of narrow-

band organic emitters.

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