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Application of wide-energy-gap material 3,4-di(9H-carbazol-9-yl) benzonitrile in organic light-emitting diodes

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ABSTRACT

A material with a wide energy gap, 3,4-di(9H-carbazol-9-yl)benzonitrile (2CzBN), was synthesized and applied in organic light-emitting diodes (OLEDs). Pure blue electroluminescence with a peak wavelength of 436 nm and Commission Internationale de l'Èclairage (CIE) coordinate of (0.160, 0.084) were obtained for an OLED containing 2CzBN as an emitter, although its external emission efficiency was limited to around 1% because of the lack of thermally activated delayed fluorescence (TADF) activity. In contrast, a highly efficient TADF-based OLED was obtained when 2CzBN was used as a host instead of an emitter by taking advantage of the high triplet energy (2.92 eV) and unexpected electron transport capability of 2CzBN.

1. Introduction

Organic light-emitting diodes (OLEDs) have been studied extensively with the aim of developing practical display and lighting applications since Tang and VanSlyke reported the first substantial multi-layered electroluminescent (EL) device in 1987 [1]. However, the maximum internal EL quantum efficiency (η_{IQE}) of first-generation OLEDs was limited to 25% because they contained fluorescent emitters that can harvest only singlet excitons [2,3]. Second-generation OLEDs including room-temperature phosphorescent emitters containing heavy metals such as Pt, Os and Ir have been widely developed and nearly 100% η_{IQE} has been achieved by taking advantage of the large spin-orbit coupling of such metals [4,5]. As an alternative to these conventional emission mechanisms, our group has extensively developed highly efficient OLEDs based on thermally activated delayed fluorescence (TADF) [6,7]. In fact, carefully designed TADF emitters can realize η_{IQE} of nearly 100% by utilizing the efficient upconversion process from the lowest triplet state (T_1) to lowest singlet state (S_1). This noteworthy evolution has yielded the next generation of organic luminescent materials.

In the development of OLEDs, highly efficient blue emission has been a goal for both display and lighting applications. One feasible candidate to achieve such OLEDs is TADF emitters, which can be obtained through the freedom in molecular structures [8–12]. To sufficiently utilize the characteristics of TADF emitters in OLEDs, it is crucial to confine triplet excitons on the emitters; to do so, the T_1 energy of the peripheral materials adjacent to the emitters, such as host, electron- and hole-transport layers, must be higher than that of the emitters. Otherwise, the triplet excitons are readily quenched *via* energy transfer to the surrounding materials, resulting in low η_{IQE} [8,12]. Thus, the preparation of materials with a wide gap between their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is of great interest in OLED research. Among various TADF materials, 1,2-bis(carbazol-9-yl)-4,5-dicyanobenzene (2CzPN) is a promising material, demonstrating a relatively wide HOMO–LUMO gap (2.8 eV) and high T_1 energy (2.51 eV) [7,13]. However, the emission color of 2CzPN is sky blue and its T_1 energy is not satisfactory compared with those of recently reported blue TADF emitters [8,10].

In this work, we successively design 3,4-di(9H-carbazol-9-yl)benzonitrile (2CzBN), which has a wider HOMO–LUMO gap (3.26 eV) and higher T_1 energy (2.92 eV) compared with those of 2CzPN. These changes can be ascribed to the presence of a single cyano group. While pure blue emission with a peak EL wavelength (λ_{EL}) of 436 nm and Commission Internationale de l'Èclairage (CIE)

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coordinate of (0.160, 0.084) is achieved in an OLED with 2CzBN as an emitter, η_{IQE} is limited to around 1% because of the lack of TADF activity. We find that highly efficient OLEDs can be obtained using 2CzBN as a host layer by taking advantage of its high triplet energy and suitable carrier transport capability.

2. Experimental details

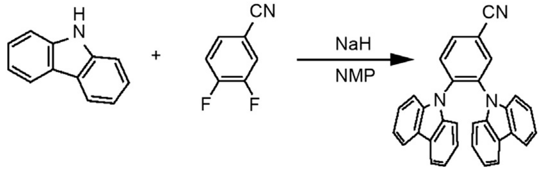
2.1. Synthesis and characterization

All reagents and solvents were purchased from Tokyo Chemical Industry and Wako Pure Chemical Industries, and used as received unless otherwise noted. Reaction was performed under an N_2 atmosphere in dry solvents. We synthesized 2CzBN according to the procedure shown in Scheme 1. Here, nuclear magnetic resonance (NMR) spectra were measured on an Avance III 500 spectrometer (Bruker), and are reported in ppm using tetramethylsilane as an internal standard (TMS = 0 ppm). Fast atom bombardment (FAB) mass spectrum was measured on a JEOL JMS700 MStation. The HOMO energy levels of 2CzBN was determined using an AC-3 ultraviolet photoemission spectrometer (Riken-keiki).

To a suspension of NaH (1.98 g, 60 wt% dispersion in mineral oil, 49.6 mmol, washed with hexane twice) in *N*-methylpyrrolidone (NMP) was added carbazole (9.0 g, 52.9 mmol) at room temperature. The mixture was stirred for 1 h at room temperature. After that, 3,4-difluorobenzonitrile (3.0 g, 21.6 mmol) was added to the solution, and then resulted mixture was heated at 120 °C. After refluxing for 18 h, the resultant suspension was cooled to room temperature and the reaction was quenched by adding water and toluene, then filtrated through celite pad. The product was extracted by toluene three times, and the combined organic layers were washed with brine, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified by column chromatography (NH silica, eluent: hexane/toluene = 2:1, v/v), washed with MeOH, and dried under vacuum to give 2CzBN as white powder (yield = 3.6 g, 38%). Materials are characterized as follows; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.95 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.82–7.75 (m, 4H), 7.18–6.97 (m, 12H); HRMS (FAB) *m/z* 433.1579, (433.1579 calcd for $C_{31}H_{19}N_3$, [M]+). The HOMO energy was estimated to be 6.20 eV by the photoelectron spectrometer.

2.2. Device preparation

First, to investigate the ability of 2CzBN as a blue emitter, an OLED with a structure of indium tin oxide (ITO)/4,4-bis[N-(1-naphthyl)-*N*-phenylamino]-biphenyl (α-NPD) (35 nm)/1,3-bis(9-carbazolyl)benzene (mCP) (10 nm)/10 wt% 2CzBN (emitter):2,8-bis(diphenylphosphoryl)dibenzo[*b*,*d*]thiophene (PPT) (host) (20 nm)/PPT (40 nm)/LiF (0.8 nm)/Al (100 nm) (**device A**) was fabricated (Fig. 1(a)). mCP and PPT were used as hole transport and electron transport layers, respectively, and an emission layer composed of co-deposited 2CzBN:PPT was sandwiched by them because their feasible carrier transport property and high T_1 energy [13,14]. Second, to confirm the performance of 2CzBN as a host, we fabricated the structures ITO/dipyrazino[2,3-f:20,30-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) (10 nm)/9.9′9″-triphenyl-9H,9′H,9”H-3,3′:6′,3″-tercarbazole (Tris-PCz) (25 nm)/mCP (10 nm)/10 wt% 9-(3-(9H-carbazol-9-yl)-9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9H–carbazol-6-yl)-9H–carbazole (3CzTRZ) (emitter):2CzBN (host) (30 nm)/2CzBN (10 nm)/2,7-bis(2,20-bipyridine-5-yl)triphenylene (BPy-TP2) (40 nm)/LiF (0.8 nm)/Al (100 nm) (**device B**), ITO/HAT-CN (10 nm)/Tris-PCz (35 nm)/10 wt% (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) (emitter):2CzBN (host) (30 nm)/2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2 T) (10 nm)/BPy-TP2 (40 nm)/LiF (0.8 nm)/Al (100 nm) (**device C**), and ITO/HAT-CN (10 nm)/Tris-PCz (35 nm)/10 wt% 1,4-dicyano-2,3,5,6-tetrakis(3,6-diphenylcarbazol-9-yl)benzene (4CzTPN-Ph) (emitter):2CzBN (host) (30 nm)/T2 T (10 nm)/BPy-TP2 (40 nm)/LiF (0.8 nm)/Al (100 nm) (**device D**) as shown in Figs. 1(b)-(d). We used 3CzTRZ, 4CzIPN, and 4CzTPN-Ph as dopants because of the typical blue, green, and red emitters showing TADF, respectively, leading to the realization of white OLEDs [7,15]. Because of higher T_1 of 3CzTRZ (2.85 eV) than those of 4CzIPN (2.4 eV) and 4CzTPN-Ph (2.21 eV), the emission layer of **device B** was sandwiched by mCP and 2CzBN to suppress the energy transfer from the emitter [10,16,17]. Electron-only devices (EODs) with the structure ITO/T2T (30 nm)/host layer/T2T (10 nm)/BPy-TP2 (80 nm)/LiF (0.8)/Al (100 nm) were also prepared to evaluate the electron transport properties of various materials. Here, 2CzBN (30 nm) (**device E**), 2CzPN (30 nm) (**device F**), mCP (30 nm) (**device G**), 2CzBN (25 nm)/2CzPN (5 nm) (**device H**), and 2CzPN (25 nm)/2CzBN (5 nm) (**device I**) were used as host layers in the EODs as illustrated in Fig. 1(e). Energy levels of each material are shown in Fig. 1(f), that have been evaluated in previous reports except for 2CzBN [13,15,16]. It is expected that a hole injection from an ITO to a T2T layer is suppressed due to the large injection barrier, resulting in an electron-only transport characteristics. Evaluations of current density (*J*) and luminance (*L*) curves as a function of applied voltage (*V*) (*JVL*) and external quantum efficiency (η_{EQE}) characteristics of the OLEDs and EODs was performed with a Hamamatsu Photonics C9920–12 measurement system.



Scheme 1. Synthesis of 2CzBN.

3. Results and discussion

3.1. Optical properties of 2CzBN films

Fig. 2(a) shows the absorption and photoluminescence (PL) spectra of neat 2CzBN (solid line) and 10 wt% 2CzBN:PPT co-deposited (dashed line) films with a thickness of 100 nm. PL quantum efficiencies of 39% and 37% were obtained for neat and co-deposited films, respectively. The PL emission peaks (λ_{PL}) of the neat (420 nm) and co-deposited (414 nm) films are much shorter than that of a 2CzPN film (473 nm) [7], indicating that 2CzBN has a wider HOMO–LUMO gap than 2CzPN. This feature originates from the presence of a single strongly electron-accepting cyano group in 2CzBN compared with two in 2CzPN. Normalized fluorescence and phosphorescence spectra of a 2CzBN neat film measured at 300 and 50 K are depicted in Fig. 2(b), respectively. From these spectra, T_1 and the gap between S_1 and T_1 (ΔE_{ST}) are estimated to be 2.92 eV from the onset of the PL emission and 0.34 eV from the difference of the onset wavelengths of the fluorescence and phosphorescence spectra, respectively. These results imply that 2CzBN can be used as not only a pure blue emitter in OLEDs but also a host for TADF emitters because it has a high T_1 level, which is essential to confine triplet excitons on emitters. As illustrated in Fig. 2(c), the prompt component is dominant in the transient PL spectra of both neat 2CzBN and 2CzBN:PPT co-deposited films, with lifetimes of 11 and 10 ns, respectively. Conventional TADF molecules typically show a prompt component (several to several tens of nanoseconds) with a transient decay time (several to several hundreds of microseconds) [7,13]. This is because ΔE_{ST} of 2CzBN is larger than those of conventional TADF molecules, suggesting that it lacks TADF activity.

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