Light-Emitting Diodes

Benzimidazobenzothiazole-Based Bipolar Hosts to Harvest Nearly All of the Excitons from Blue Delayed Fluorescence and Phosphorescent Organic Light-Emitting Diodes

Lin-Song Cui, Jong Uk Kim, Hiroko Nomura, Hajime Nakanotani, and Chihaya Adachi*

Abstract: Much effort has been devoted to developing highly efficient organic light-emitting diodes (OLEDs) that function through phosphorescence or thermally activated delayed fluorescence (TADF). However, efficient host materials for blue TADF and phosphorescent guest emitters are limited because of their requirement of high triplet energy levels. Herein, we report the rigid acceptor unit benzimidazobenzo-thiazole (BID-BT), which is suitable for use in bipolar hosts in blue OLEDs. The designed host materials, based on BID-BT, possess high triplet energy and bipolar carrier transport ability. Both blue TADF and phosphorescent OLEDs containing BID-BT-based derivatives exhibit external quantum efficiencies as high as 20 %, indicating that these hosts allow efficient triplet exciton confinement appropriate for blue TADF and phosphorescent guest emitters.

Organic light-emitting diodes (OLEDs) have become important both in commercial displays and lighting applications because of their fine light-emitting characteristics. It is known that singlet and triplet excitons are generated in a ratio of 1:3 by charge recombination in OLEDs.[1] Triplet excitons are typically non-emissive, and lower in energy and longer lived than singlet ones. Therefore, the internal quantum efficiency (IQE) of traditional fluorescent OLEDs is limited to 25 %.[2] Recently, thermally activated delayed fluorescence (TADF) and phosphorescent OLEDs have attracted attention because they can achieve a theoretical maximum IQE of 100 % by harvesting both singlet and triplet excitons for light emission.[3] Singlet excitons in phosphorescent OLEDs with transition metal complexes are easily converted into triplet excitons by rapid intersystem crossing (ISC), and then all the triplet excitons decay radiatively as phosphorescence.[4] In TADF OLEDs, triplet excitons are readily upconverted into singlet ones by reverse ISC owing to extremely small singlet–triplet energy differences, then all the singlet excitons can emit either prompt fluorescence or delayed fluorescence.[5] To date, external quantum efficiencies (EQEs) of over 20 % have been achieved for both TADF and phosphorescent OLEDs.[6]

To avoid unwanted quenching of long-lived triplet excitons in neat films, both TADF and phosphorescent emitters are embedded in a conductive host to form a host–guest system for efficient energy transfer.[7] Host materials are thus are important as emitters to determine overall device performance. An ideal host should possess high triplet energy, appropriate frontier molecular orbital levels, bipolar charge transport ability, and large spectral overlap with doped emitters.[8] To fulfill these requirements, many donor and acceptor building blocks have been developed for host materials.[9] In advanced OLEDs, the holes and electrons are well balanced by using bipolar hosts to enhance emission efficiency and lower efficiency roll-off.[10] However, bipolar hosts usually have low triplet energies because of the strong intramolecular charge transfer between donor and acceptor units. To address this issue, bipolar host design focuses on interrupting the π-conjugation between donor and acceptor units by using saturated (like sp^3-C or Si) or highly twisted π-conjugated spacers.[11,10a] However, such spacers can lead to poor charge mobility in organic conjugated materials.[12] Herein, we report an acceptor unit, benzimidazobenzothiazole (BID-BT), featuring a rigid configuration with benzimidazole as an electron-deficient moiety to aid electron transport, and benzothiazole as the backbone linked by a tertiary nitrogen atom as a bridge. The tertiary nitrogen bridge maintains not only rigidity but also the high triplet energy of the BID-BT ring. We synthesized BID-BT derivatives 2,9-di(9*H*-carbazol-9-yl)benzo[*d*]benzo[4,5]imidazo[2,1-*b*]thiazole (29Cz-BID-BT) and 3,9-di(9*H*-carbazol-9-yl)benzo-[*d*]benzo[4,5]imidazo[2,1-*b*]thiazole (39Cz-BID-BT) as host materials for blue TADF and phosphorescent OLEDs.

The two compounds were prepared by copper-catalyzed Ullmann coupling of halogenated benzimidazo[2,1-*b*]benzo-thiazole with carbazole (Scheme 1). The benzimidazo[2,1-*b*]-benzothiazole backbone was synthesized though cyclization of 2-mercaptobenzimidazole with *o*-nitrophenyl bromide. Compounds were characterized by ^{1}H and ^{13}C NMR spectros-copies, mass spectrometry, and elemental analysis. Synthetic and characterization details are provided in the Supporting Information.

The molecular design of the two hosts was guided by density functional theory (DFT) calculations (B3LYP/6-31g-(d)) to examine their highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and triplet spin density distribution (TSDD). The HOMOs of 29Cz-BID-BT and 39Cz-BID-BT are mainly distributed over the carbazolyl group near the benzimidazo side, while the LUMOs are mostly localized on the rigid BID-BT core (Figure 1). The separated HOMOs and LUMOs resulted

[*] L.-S. Cui, J. U. Kim, H. Nomura, H. Nakanotani, Prof. C. Adachi
Department of Applied Chemistry
Center for Organic Photonics and Electronics Research (OPERA)
Kyushu University
744 Motooka, Nishi, Fukuoka 819-0395 (Japan)
E-mail: adachi@opera.kyushu-u.ac.jp
Homepage: http://www.cstf.kyushu-u.ac.jp/~adachilab/

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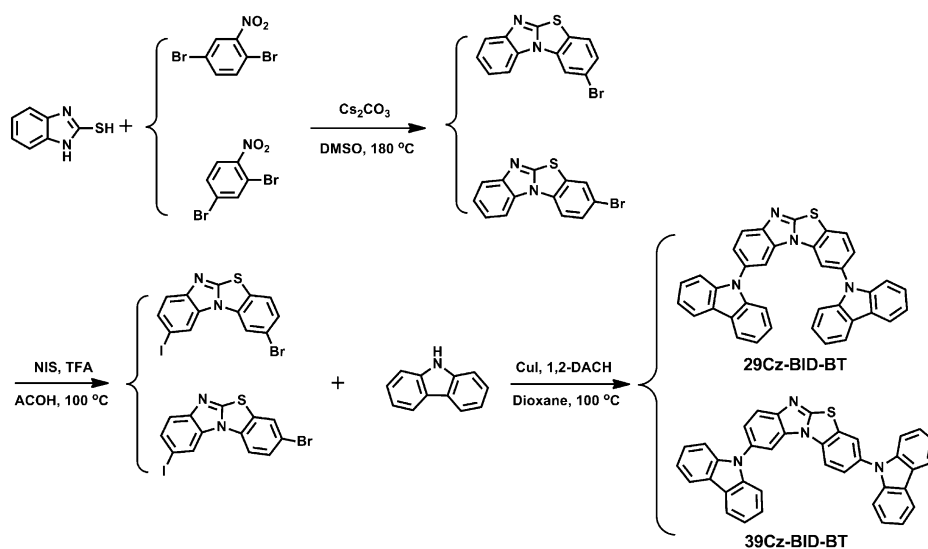
Scheme 1. Synthesis of 29Cz-BID-BT and 39Cz-BID-BT.

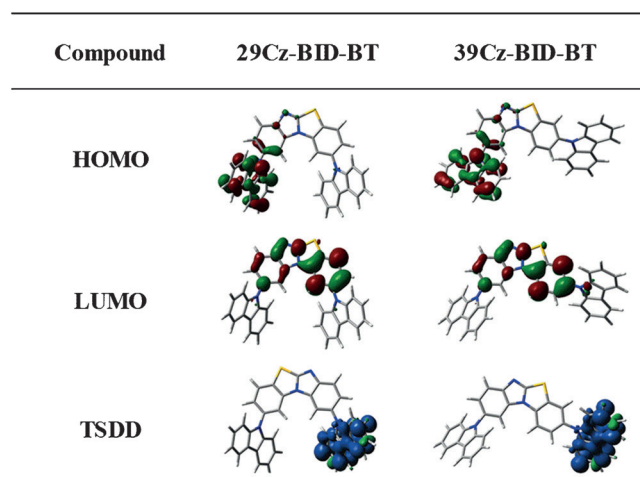| Compound	29Cz-BID-BT	39Cz-BID-BT
HOMO		
LUMO		
TSDD		

Figure 1. Frontier molecular orbitals and spin density distributions of the lowest triplet energy level (T_1) of 29Cz-BID-BT and 39Cz-BID-BT.

π–π* transitions of carbazole and BID-BT units, and weak absorption peaks at 325 and 340 nm caused by the n–π* transitions of carbazole and weak intramolecular charge transfer from carbazole to BID-BT. Both compounds exhibited structureless PL spectra with peaks at 360 nm, indicating their excited states possess some charge-transfer character, which is attributed to their separated HOMO and LUMO distributions. The band gap energy (E_g) of 29Cz-BID-BT and 39Cz-BID-BT calculated from the absorption edge of the UV/Vis spectra are 3.46 and 3.45 eV, respectively. The phosphorescence spectra of 29Cz-BID-BT and 39Cz-BID-BT (Figure 2b) reveal their T_1 are 3.02 and 3.04 eV, respectively. Thus, T_1 of both hosts are higher than that of common carbazole-based host 3,3′-bis(carbazol-9-yl)biphenyl, (mCBP; $T_1 = 2.80$ eV). The HOMO levels of neat films of 29Cz-BID-BT and 39Cz-BID-BT measured by
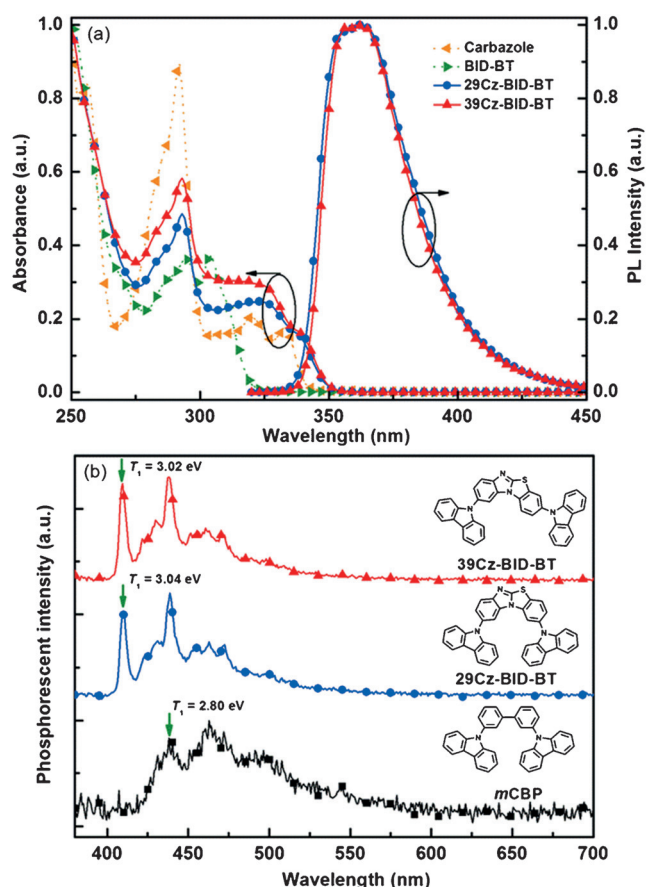
from the strong electron-donating nature of carbazole and electron-withdrawing ability of BID-BT. This implies that HOMOs are determined by carbazole, and LUMOs are determined by the BID-BT core. Thus, these two hosts should display bipolar transport properties in OLEDs. The TSDD simulations revealed the T_1 excited states of 29Cz-BID-BT and 39Cz-BID-BT were completely localized on the carbazole units. Therefore, BID-BT should have a higher T_1 level than carbazole (Supporting Information, Table S1). Time-dependent DFT calculations showed T_1 of 29Cz-BID-BT and 39Cz-BID-BT are > 3.2 eV (Table S1). Cyclic voltammetry revealed that both hosts have distinct oxidation and reduction behaviors (Figure S2), consistent with bipolar charge-transport properties.

Photophysical properties of 29Cz-BID-BT and 39Cz-BID-BT were analyzed using UV/Vis and photoluminescence (PL) spectroscopies. Both compounds showed strong absorption bands at 270–300 nm (Figure 2a), which are attributed to the

Figure 2. a) UV/Vis absorption, and fluorescence spectra of carbazole, BID-BT, 29Cz-BID-BT, and 39Cz-BID-BT (298 K). b) Phosphorescence spectra of mCBP, 29Cz-BID-BT, and 39Cz-BID-BT (77 K).

photoelectron spectroscopy are 6.01 and 6.07 eV, respectively. LUMO levels of 2.55 eV for 29Cz-BID-BT and 2.62 eV for 39Cz-BID-BT were estimated from E_g and HOMO levels.

The transient PL decays of TADF and phosphorescent emitters doped in the two hosts were measured to confirm their ability to confine singlet and triplet excitons. First, 29Cz-BID-BT and 39Cz-BID-BT were doped with blue TADF material 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-diphenyl-9,10-dihydroacridine (DPAC-TRZ). The two doped films exhibited the same prompt and delayed PL emissions at room temperature (Figure 3). The lifetimes of
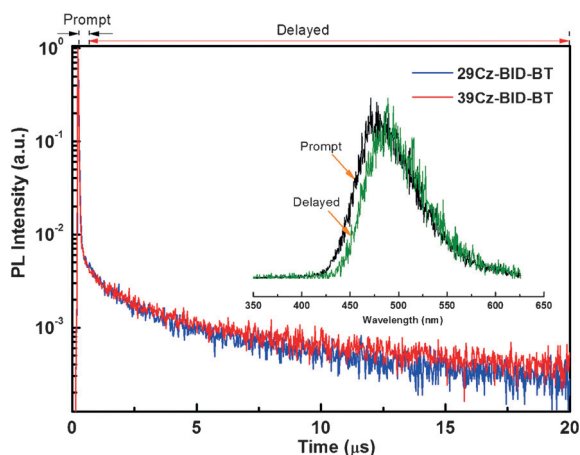

Figure 3. Transient PL decay of 29Cz-BID-BT and 39Cz-BID-BT films doped with 10 wt% DPAC-TRZ. Inset: prompt and delayed PL spectra.

the delayed components of the doped 29Cz-BID-BT and 39Cz-BID-BT films were 7.1 and 8.1 μs, respectively; longer than that of a mCBP:DPAC-TRZ film (3.7 μs; Figure S4). This indicates that mCBP may quench long-lived triplet excitons because of the close T_1 of mCBP (2.80 eV) and DPAC-TRZ (2.85 eV). Next, 29Cz-BID-BT and 39Cz-BID-BT were doped with sky-blue phosphorescent emitter fac-tris[(2,6-diisopropylphenyl)-2-phenyl-1H'-imidazo[e]]-iridium(III) (fac-Ir(iprpmi)$_3$). The two films emitted phosphorescence from the triplet level of fac-Ir(iprpmi)$_3$, with lifetimes of 0.91 and 1.26 μs (Figure S5), similar to reported for fac-Ir(iprpmi)$_3$.[10c] Thus, the hosts readily confined the singlet and triplet excitons of both TADF and phosphorescent emitters. The doped films displayed PL quantum yields > 90% under nitrogen (Figure S6), implying effective energy transfer from the excited states of the hosts to those of the emitters. This is caused by the large overlap between host emission and emitter absorption (Figure S7).

The excellent properties of the two hosts inspired us to investigate their performance in OLEDs. We first fabricated blue TADF devices with the structure ITO/HAT-CN (10 nm)/TAPC (35 nm)/host: 10 wt% DPAC-TRZ (20 nm)/TSPO1 (10 nm)/TPBi (40 nm)/LiF (0.8 nm)/Al (120 nm) (host = 29Cz-BID-BT for device A1, and 39Cz-BID-BT for device A2). In the devices, 1,4,5,8,9,11-hexaazatriphenylene-hexa-carbonitrile (HAT-CN) and LiF served as hole- and electron-injection materials, respectively; 10 wt% DPAC-TRZ doped

in a BID-BT host was used as the emitting layer (EML); 1,1-bis[4-[N,N-di(p-tolyl)amino]phenyl]cyclohexane (TAPC) was used for hole transport and to block electrons; diphenyl-4-triphenylsilylphenylphosphine oxide (TSPO1); and 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) acted as hole-blocking and electron-transporting materials, respectively. The high T_1 of TAPC and TSPO1 confine excitons in the EML. The EL spectra and EQE-current density (J) plots of device A1 and A2 are shown in Figure 4a. The EL spectra
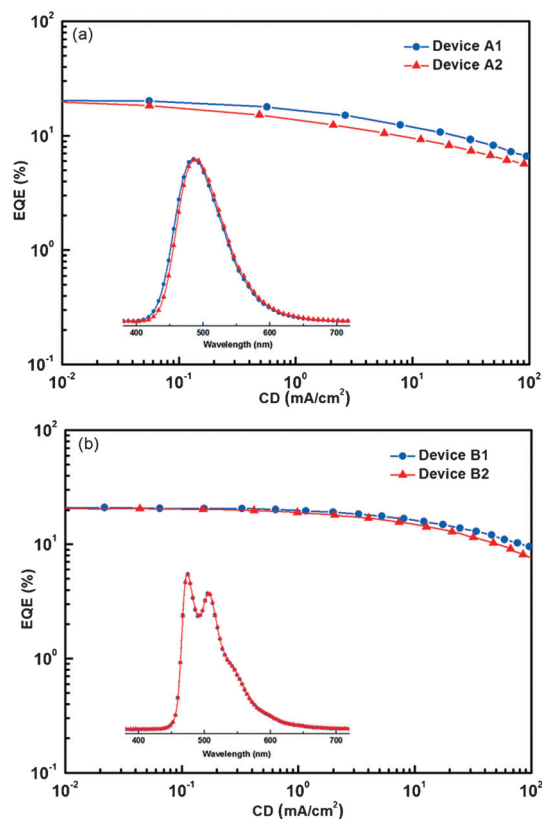

Figure 4. a) External quantum efficiency (EQE) versus current density (J) of device A1 and A2. Inset: electroluminescence spectra. b) EQE against J of device B1 and B2. Inset: electroluminescence spectra.

contained no emissions from host or adjacent layers, indicating that the emissive excitons are confined on the TADF molecules. The Commission International de l'Eclairage (CIE) coordinates of devices have values of (0.16, 0.34). Device A1 and A2 displayed EQEs of 20.8% and 20.4%, respectively, which are the highest reported for blue TADF OLEDs.[6] Device A1 and A2 also exhibited lower efficiency roll-off than that of the equivalent mCBP-based device. This can be ascribed to the well-balanced electron/hole-transport in the EML of device A1 and A2. Next, 29Cz-BID-BT and 39Cz-BID-BT were used as hosts in OLEDs with 15 wt% fac-Ir(iprpmi)$_3$ (device B1 and B2, respectively) to demonstrate their universality. Figure 4b shows the EQE-J plots for device B1 and B2. The maximum EQEs of device B1 and B2 were 21.0% and 20.7%, respectively, which are comparable with

reported values for *fac*-Ir(iprpmi)$_3$-based sky-blue OLEDs.[10c] Device B1 and B2 also displayed low efficiency roll-off; at 30 mA cm^{-2} (~ 10 000 cd m^{-2}), the EQEs of device B1 and B2 were 13.4 % and 12.0 %, respectively.

To examine the bipolar properties of the two hosts, hole- and electron-only devices with the structures ITO/HAT-CN (10 nm)/TAPC (20 nm)/host (60 nm)/TAPC (20 nm)/Al-(100 nm) and ITO/TmPyPB (20 nm)/host (60 nm)/TPBi (20 nm)/LiF (0.8 nm)/Al(100 nm), respectively, were fabricated, using common host *m*CBP as a reference. Figure 5
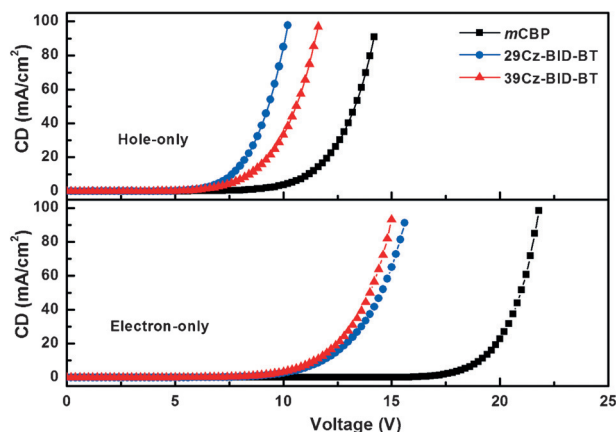

Figure 5. Current density (*J*)-voltage characteristics of hole- and electron-only devices.

shows that the *J* values of hole-only devices with 29Cz-BID-BT and 39Cz-BID-BT are slightly higher than that of *m*CBP, which is attributed to the rigidity of BID-BT. However, the *J* of electron-only devices with 29Cz-BID-BT and 39Cz-BID-BT is much higher than that of *m*CBP because of the electron-withdrawing ability of BID-BT. The differences in *J* between the hole- and electron-only devices with BID-BT hosts are much smaller than that of *m*CBP at the same voltage, explaining the superior bipolar transport and relaxation of roll-off in the OLEDs with the BID-BT hosts than in that with *m*CBP.

In summary, two bipolar hosts with high triplet energy were prepared for use in blue TADF and phosphorescent OLEDs. High EQEs (> 20 %) were realized in both blue TADF and phosphorescent OLEDs using the hosts. Thus, the rigid BID-BT core is effective as an acceptor building block to design bipolar host materials for high-efficiency TADF and phosphorescent OLEDs. Evaluation of the lifetime of devices with BID-BT hosts is in progress.

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