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lighting-emitting diodes Miao-Miao Xue, Chen-Chao Huang, Yi Yuan, Ye-Xin Zhang, Man-Keung Fung^{*} and Liang-Sheng Liao^{*}

temperature (T_g) is 63 °C.

molecule with a D-A structure is formed.

tricyclic system, as seen in Scheme 1. By combining this new

electron-accepting moiety with a triphenylamine (TPA) group which

possesses outstanding hole-transporting ability, a novel fluorescent

To obtain this novel D-A structure, a new core unit named 2-

bromobenzofuro[2,3-b]pyrazine (2-Br-BFPz) was first synthesized

as a precursor. The 2-Br-BFPz was synthesized by the ring closing

reaction of 5-bromo-3-(2-methoxyphenyl)pyrazin-2-amine prepared

by the Suzuki coupling reaction of (2-methoxyphenyl)boronic acid

and 3,5-dibromopyrazin-2-amine. The D-A fluorescent molecule,

known as TPA-BFPz, was then prepared by the Suzuki coupling

reaction of 2-Br-BFPz with N, N-diphenyl-4-(4,4,5,5-tetramethyl-

1,3,2-dioxaborolan-2-yl)aniline. The synthetic yield of TPA-BFPz was ~60%. Its detailed synthetic route is shown in **Scheme S1** and

the synthetic procedure is described in the electronic supplementary

information (ESI[†]). The thermal properties of TPA-BFPz were

studied using thermal gravimetric analysis (TGA) and differential

scanning calorimetry (DSC), as shown in Fig. S1 and Table S1. It

can be seen that the TPA-BFPz is thermally stable with a 5% weight-

loss temperature (T_d) of up to 350 °C and its glass-transition

A novel electron-acceptor moiety as a building block for

efficient donor-acceptor based fluorescent organic

A new electron-withdrawing moiety (BFPz) is first used as an acceptor in OLED and its corresponding core unit (2-Br-BFPz) was synthesized. Combined with an electron-donating moiety triphenylamine, a novel fluorescent material with a D-A structure named TPA-BFPz was synthesized. Encouragingly, the EQEs of non-doped and doped blue OLEDs reach 3.68% and 4.42%, respectively.

Fluorescent materials have been playing a critical role in organic light-emitting diodes (OLEDs) since Tang's report on tris(8-hydroxyquinoline)-aluminum (Alq₃)-based multilayer devices.^[1-2] In particular with the introduction of the concepts of hybridized local and charge transfer (HLCT) and thermally activated delayed fluorescence (TADF) in recent years, the research based on fluorescent molecules with donor-acceptor (D-A) structure has become a hot topic.^[3-6] A compound with D-A structure means the material is composed of both an electron donor and acceptor moieties. However, electron-acceptor moieties with a strong electron-withdrawing capability are far from adequate.

Therefore, it is crucial to design desirable electron-accepting moieties. As we know dibenzofuran, a classical tricyclic unit, has confined conjugation structures which allow delocalization of both the injected electrons/holes and hence possess outstanding carrier transporting ability.^[7-9] Nevertheless, its electron-withdrawing ability is hardly comparable with other prototypical moieties such as benzimidazole^[10], triazine^[11] and borane derivatives^[12] which have been widely used as electron acceptors in D-A based π -conjugated fluorescent molecules. On the other hand, pyrazine is also known to be an excellent electron-withdrawing molecule.^[13] Therefore, it would be an innovative strategy if a new electron-accepting moiety is synthesized based on a hybrid structure of dibenzofuran and pyrazine. In this way, two nitrogen atoms are embedded into the

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Scheme1. Synthetic strategy of TPA-BFPz.

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Fig. 1. a) UV-Vis and PL spectra of TPA-BFPz; b) PL spectra of TPA-BFPz in different solvents; c) Color of TPA-BFPz in different solvents under UV exposure with a wavelength of 365 nm.

In order to probe the interaction between D (TPA) and A (BFPz) in the TPA-BFPz molecule, its photophysical properties were characterized. The UV-Vis spectrum of TPA-BFPz diluted in toluene solution $(1 \times 10^{-5} \text{ mol/L})$ and photoluminescence (PL) spectrum of TPA-BFPz prepared as a film are shown in Fig. 1a. There are two pronounced absorption peaks. The short-wavelength absorption peak at 308 nm can be ascribed to the n- π^* transition of triphenylamine-centered,^[14] and the longer wavelength at 394 nm can be attributed to the charge transfer (CT) transition from D (TPA) to A (BFPz). It can also be seen that the TPA-BFPz (in film) shows a strong emission at 482 nm. Furthermore, the CT characteristic of TPA-BFPz would be quite obvious if different polar solvents were used in the fluorescence measurements. As depicted in Fig. 1b and Table S2, the solvatochromic effect of the PL spectra of TPA-BFPz was observed in different polar solvents. When the solvent polarity was increased gradually from a low-polarity (e.g. hexane) to highpolarity such as N, N-dimethylformamide (DMF), the PL spectra of TPA-BFPz got wider and exhibited a total red-shift as large as 135 nm, i.e., 428 nm in hexane (Hex.), 466 nm in toluene (Tol.) and 563 nm in DMF. But there was an exception that the PL spectra of TPA-BFPz exhibited a blue-shift phenomenon from dichloromethane (DCM) to tetrahydrofuran (THF) while the polarity of THF is larger than that of DCM. That may be because the large electronegativity of oxygen (O) atom in THF molecule may have an short-range effect with α-H in pyrazine part of TPA-BFPz molecule, which may reduce the energy of the ground state and then lead to the blue-shift phenomenon.^[15] For better understanding of the solvent effects on PL behaviors, the UV-Vis absorption spectra of TPA-BFPz measured in different solvents were also shown on Fig. S2. In order to unveil the solvatochromic effect chromatically, the fluorescence of TPA-BFPz dissolved by different polar solvents was observed under a UV lamp (365 nm), as shown in Fig. 1c. It is obvious that all

the materials exhibit strong but diverse fluorescent emissions. The color change from deep blue in hexane to orange yellow in DMF indicates that the TPA-BFPz is a favorable fluorescent material with a strong CT-state characteristic. Meanwhile, it also suggests that TPA-BFPz holds high sensitivity of its fluorescent emission to different types of solvents. Particularly, such solvent effect almost makes it capable of emitting in the entire visible spectrum. With the aim to further investigate its fluorescent properties, the fluorescence quantum yields ($\Phi_{\rm F}$) in solution and in film were tested. As a result, TPA-BFPz exhibited strong fluorescence with $\Phi_{\rm F}$ up to 92% and 78% in DCM solution and in film, respectively. In addition, the transient PL of a neat film of TPA-BFPz was also tested, as depicted in **Fig. S3**. It shows that the TPA-BFPz has a short fluorescent lifetime of 6.9 ns without "delayed fluorescence" phenomenon.

To gain a deeper insight into the relationship between the D (TPA) and A (BFPz) at the molecular level, DFT calculation (B3LYP/6-31 g*) on TPA-BFPz molecule was carried out. As illustrated in **Fig. S4**, due to the electron-donating ability of the TPA unit and electron-accepting ability of BFPz moiety, the highest occupied molecular orbital (HOMO) of TPA-BFPz is mainly distributed in the TPA group and the lowest unoccupied molecular orbital (LUMO) is mainly located in the BFPz moiety, but their molecular orbitals are partly overlapped in the pyrazine part of the BFPz group and benzene ring of the TPA group. Furthermore, the TPA and BFPz groups are twist-linked with a slightly distorted angle (θ_{D-A}) of 21°. The distribution of molecular orbitals and small θ_{D-A} further enhances the radiative-transition rate and fluorescence efficiency.

As TPA-BFPz possesses outstanding fluorescent properties as mentioned, we further explored it as an emitter for OLED applications. The HOMO energy level of TPA-BFPz was measured by ultraviolet photoelectron spectroscopy (UPS), which is estimated to be 5.62 eV, as shown in Fig. S5. Knowing the band gap of TPA-BFPz as determined from the UV-Vis spectrum in Fig. 1a, the LUMO energy level is calculated to be 2.79 eV. A non-doped OLED with a configuration of ITO/1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HAT-CN, 10 nm)/di-[4-(N,N-ditolyl-amino)phenyl]cyclohexan (TAPC, 40 nm)/TPA-BFPz (20 nm)/1,3,5-tri[(3pyridyl)-phen-3-yl]benzene (TmPyPB, 45 nm)/8hydroxyquinolinolatolithium (Liq, 2 nm)/Al was fabricated. In addition, the energy level diagram for each material used in the devices is summarized in Fig. S6. To our delight, the non-doped device has a low driving voltage of 3.4 V (at a current density of 0.2 mA/cm²) and a maximum current efficiency (CE), power efficiency (PE) and external quantum efficiency (EQE) of 8.0 cd/A, 7.4 lm/W and 3.68%, respectively, with an electroluminescent (EL) peak at 484 nm (Fig. 2, Fig. S7 and Fig. S8). In order to further improve the device performance, we optimized the device structure with a configuration of ITO/HAT-CN (10 nm)/TAPC (40 nm)/bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO):TPA-BFPz (X wt%, 20 nm)/TmPyPB (45 nm)/Liq (2 nm)/Al, in which DPEPO serves as a host material and X represents the doping concentration of TPA-BFPz in DPEPO. As shown in Fig. 2 and Fig. S7, all devices have the same EL peak at 492 nm and driving voltages of less than 3.7 V when driven at 0.2 mA/cm². All the doped devices show a better device performance than the non-doped OLED. But the EL spectra of the doped devices have a redshift about 8 nm compared to that of the non-doped one because DPEPO is a polar Published on 01 December 2016. Downloaded by Athabasca University on 02/12/2016 13:10:50.

molecule. The corresponding device performance is summarized in **Table 1**. As shown in the **Table 1**, the voltages tested at 0.2 mA/cm^2 of devices decreased when the doping concentration of TPA-BFPz in DPEPO increased, which indicated TPA-BFPz might have good electron and hole transporting abilities. When the doping concentration of TPA-BFPz is 30%, the D-A based OLED exhibits maximum efficiencies of 11.5 cd/A, 10.3 lm/W and 4.42%. The superior device performance implies that TPA-BFPz is a favorable D-A molecule and a promising blue fluorescent material in OLED.

Table 1. Summary of electroluminescence data for OLEDs.					
Devices ^a	Voltage [♭]	$CE_{max}^{\ \ c}$	PE _{max} c	EQE _{max} c	
	(∨)	cd/A	lm/W	%	
15%	3.7	11	9.2	4.4	0.19, 0.42
20%	3.6	11	9.4	4.3	0.19, 0.43
25%	3.5	11	9.7	4.27	0.19, 0.44
30%	3.5	11.5	10.3	4.42	0.19, 0.44
50%	3.4	9.5	8.9	3.85	0.18, 0.42
Non-doped	3.4	8	7.4	3.68	0.16, 0.35

a) Doping concentration of TPA-BFPz in DPEPO; b) Driving voltage (at 0.2 mA/cm²); c) CE_{max}, PE_{max}, EQE_{max} = max current efficiency, power efficiency and external quantum efficiency; d) Measured at 5 mA/cm².



In summary, an innovative electron-withdrawing moiety, 2-Br-BFPz, which possesses a highly confined conjugated structure, has been designed and synthesized. We have combined 2-Br-BFPz with the TPA group which is a classical electron-donating unit to form a novel fluorescent material with a D-A structure named TPA-BFPz. Interestingly, the TPA-BFPz exhibits strong fluorescence and has been utilized as a blue fluorescent emitter for OLEDs. The EQEs for non-doped and doped devices reach 3.68% and 4.42%, respectively, which illustrates that the BFPz unit is a promising electronwithdrawing moiety. It is foreseen that the electronwithdrawing unit can be used for designing novel TADF or HLCT materials in the future.

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