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A high performance deep-blue emitter with an anti-parallel dipole design

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1. Introduction

ABSTRACT

(1)

To increase the fluorescence quantum yield of hybrid local and charge-transfer (HLCT) material, we introduce a symmetric linear D- π -A- π -D structure into molecular design and synthesized a new blue emitter, 2,2'-(2',3',5',6'-tetrafluoro-[1,1':4',1"-terphenyl]-4,4"-diyl)bis(1-(4-(*tert*-butyl)phenyl)-1*H*-phenanthro[9,10-*d*]imidazole) (**4FBTPI**). Organic light-emitting devices employing 4FBTPI as a dopant emitter show good performances, with CIE (Commission Internationale de l'Enclairage) coordinates of (0.15, 0.09), which is very close to NTSC blue light standard (0.14, 0.08), current efficiencies (CE) of 6.03 cd A⁻¹, external quantum efficiencies of 6.94%. This performance is comparable to those of recently reported state-of-the-art deep-blue materials with CIE_y < 0.10.

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Normally, γ and η_{out} are assumed to be 1 and 0.2 respectively for an optimized device fabricated on a glass-substrate without out-coupling enhancement structure [5–9]. The two remaining parameters ϕ_{PL} and η_r are material-dependent and key parameters for evaluating the material performance.

Although it is possible for a conventional fluorescent material to achieve a φ_{PI} higher than 90%, the theoretical maximum of η_r of 25% limits its device efficiency [2]. Recently, materials with chargetransfer (CT) character break the η_r limit of conventional fluorescent emitters, leading to breakthrough in fluorescent OLED [10,11]. The newly emerged thermally activated delayed fluorescent (TADF) materials are mostly constructed with linked strong donors (Ds) and acceptors (As). With spatially separated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distribution, energy offset between the singlet and the triplet excited states $(S_1 \text{ and } T_1)$ becomes small. This enables reverse intersystem crossing (RISC) from T₁ to S₁ at room temperature to harvest the energy of T₁ state for light emission [12,13]. However, due to strong intramolecular charge transfer (ICT) in these TADF materials, their emission spectra are typically board and unfavorable for getting deep-blue emission (e.g. $CIE_v < 0.10$). Moreover, recent research shows the prototypical blue TADF

where, γ is the recombination efficiency of hole and electron, η_{out} is the light out-coupling efficiency, ϕ_{PL} is the photoluminescence quantum yield (PLQY) and η_r is the ratio of radiative exciton.

Blue emitter has been a hot research topic of organic light-

emitting devices (OLEDs) because it is essential for realizing high

performance full-color displays and solid-state lighting [1,2]. Blue

material with a Commission International de L'Eclairage (CIE) co-

ordinate of y < 0.10 is highly desirable because it can improve both

color gamut and energy efficiency of full-color OLEDs [2]. Making

progress in OLED needs both device optimization and material

development [3,4]. External quantum efficiency (EQE) of an OLED is

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 $EQE = \gamma \eta_{out} \phi_{PL} \eta_r$

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determined by the following equation:





PIGMENTS

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emitter DTC-DPS is unstable under excited state because of its weak C-S bond [14]. Alternatively, Ma et al. [8] have developed a series of D-A molecules that have special hybridized local and chargetransfer (HLCT) excited states, in which both the locally excited (LE) and the charge-transfer (CT) states contribute to the excited states. The LE state, with significant HOMO-LUMO overlap, often offers high efficiency fluorescence. On the other hand, while the CT state exciton often has relatively low luminescent efficiency, its weak Coulomb bound facilitates electron flip to raise η_r in fluorescent OLED [8,15–18]. By mixing these two distinct excited states, HLCT materials show impressive devices performances (high η_r and EQE). For instances, with a quasi-equivalent hybridized excited state, TBPMCN [19] achieved a maximum EQE of 7.8% with CIE coordinates of (0.16, 0.16) and η_r of 97% in a non-doped OLED. The extent of LE and CT mixing is inversely proportional to the difference of their energy levels. With closely laid LE and CT energy levels, HLCT material PMSO [20] presents a maximum EQE of 6.8% with CIE_{v} < 0.08 (η_{r} of 47%) in a doped device. However, as mentioned above, φ_{PL} is also an important performance parameter. φ_{PL} of TBPMCN and PMSO thin films are only 0.40 and 0.45 respectively. It is thus interesting to explore approaches for improving the φ_{PL} of HLCT materials.

Increasing the relative contribution of the LE component has been shown to be an effective way for raising φ_{PL} in HLCT materials [19,20]. Meanwhile for deep-blue materials, choosing D and A groups wisely are required in order to control ICT for maintaining the deep-blue emission. In this work, we report a new deep-blue material named 2,2'-(2',3',5',6'-tetrafluoro-[1,1':4',1"-terphenyl]-4.4"-divl)bis(1-(4-(tert-butvl)phenvl)-1H-phenanthro[9.10-d]imidazole) (4FBTPI) (Fig. 1a) with HLCT character. Phenanthroimidazole (PI) is an excellent blue-violet fluorophore and bipolar block that can act either as a weak acceptor or weak donor [11,21-23]. Actually, PI is an ideal donor building block for deep-blue emitter considering its weak electron-donating abilities and outstanding photophysical properties. Tetrafluorobenzene with four strong electron withdrawing fluorine atoms was chosen here as the acceptor to link with two PI units. It has been reported that tetrafluorobenzene could cause hypochromatic shift in molecular spectrum and PLQY enhancement, reducing the unwanted red shift and fluorescence quenching from the ICT effects [24,25]. In thin film

state, fluorine atoms could further benefit the film morphology [26]. Inserting a benzene ring between the D and the A unit buffers the push-pull electronic effect and enhances HOMO and LUMO overlap thus increase LE component and raise PLQY in the target molecule. Using a linearly linking, the molecule would process a higher conjugation extent and better electronic communication. which will benefit to CT-LE mixing. For molecules with asymmetric pull-push systems (e.g. D-A and D- π -A), they often suffer from severe emission quenching in condensed aggregated state as those dipole-induced intermolecular interactions inactivate a considerable part of their excitons. In **4FBTPI**, it is a linear D- π -A- π -D electronic structure (Fig. 1b) and the anti-parallel dipoles originated from the two donor ends cancel out. Such a design is aiming at reducing dipole-induced intermolecular interactions and enhancing luminescence of the molecule in solid state [27,28]. Besides, both D and A moieties can give help in electron injunction and transporting hopefully making the target molecule more charge balance compared to common organic emitter with holedominant character, reducing efficiency in device roll-off at high current density [11,29].

4FBTPI shows high PLQYs of 0.99, 0.69 and 0.88 in respectively solution, neat film and doped in a 4,4'-Bis(*N*-carbazolyl)-1,1'-biphenyl (CBP) film. Using 4FBTPI as a dopant emitter in CPB, an OLED delivers a deep-blue emission with CIE coordinates of (0.15, 0.09), a max current efficiency (η_c) of 6.03 cd A⁻¹ and a maximum EQE of 6.94%.

2. Experiment

2.1. Material and methods

The synthesis route of **4FBTPI** is shown in Scheme 1. Mass and ¹H NMR spectra of **4FBTPI** were recorded on a PE SCIEX API-MS spectrometer and a Varian Gemin-400 spectrometer respectively. The glass-transition temperature (T_g) of the compound was determined with differential scanning calorimetry (DSC) under a nitrogen atmosphere by using a TA Instrument DSC2910 and thermogravimetric analysis (TGA) was performed on a TA Instrument TGAQ50. UV—vis absorption and PL spectra were obtained with a Perkin-Elmer Lambda 950 UV—vis Spectrometer and a Perkin-Elmer LS50 fluorescence spectrometer, respectively. Absolute ϕ_{PL} was measured with a LabsphereTM integrating sphere using a monochromatized Xe lamp (NewportTM) as exciting source (at 365 nm). PL lifetime was recorded on an Edinburgh Instruments



Fig. 1. a) Molecular structure and b) design concept of 4FBTPI.

Scheme 1. Synthesis route of 4FBTPI.

FLS980 spectrophotometer. Cyclic voltammetry (CV) was carried out in nitrogen-purged CH_2Cl_2 (positive scan) at room temperature using a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as the supporting electrolyte. The measurements were carried out at a scan rate of 100 mV s⁻¹ with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode calibrated with ferrocene/ferrocenium (Fc/Fc⁺). For theoretical calculation, geometrical properties were optimized at the B3LYP/6-31 g(d, p) level using the Gaussian 09 program. The excited states are then calculated at the TD-PBE0/6-31 g(d, p) level. The LUMO energy level was estimated by subtracting the optical band gap from the HOMO energy level.

Before device fabrication, pre-cleaned ITO-coated glass substrates with a sheet resistance of 15 Ω square⁻¹ were subjected to UV-ozone treatment for 20 min. All organic films were deposited by thermal evaporation in a deposition chamber with a base vacuum of 5 \times 10⁻⁶ Torr. J-V characteristics were recorded with a Keithley 2400 Sourcemeter. Electroluminescence spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer.

2.2. Preparation of compounds

2.2.1. Synthesis of 2-(4-bromophenyl)-1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-d]imidazole (1) [21]

The 4-bromobenzaldehyde (1.86 g, 10 mmol), 9,10phenanthrenequinone (2.08 g, 10 mmol), 4-(*tert*-butyl)aniline (1.49 g, 10 mmol), and ammonium acetate (4.62 g, 60.0 mmol) were refluxed in an acetic acid solution under an argon atmosphere for 24 h. After cooling to room temperature, an orange-yellow mixture was obtained and poured into methanol under stirring. The raw product was separated by filtration and washed with methanol, and then dried under vacuum. The product was purified by column chromatography (petroleum ether: CH_2Cl_2 , 1:2) on silica gel to give a white powder, with a 92.1% yield.

2.2.2. Synthesis of 1-(4-(tert-butyl)phenyl)-2-(4-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-phenanthro[9,10d]imidazole (2) [30]

A 3-neck 100 mL round bottom flask was charged with a stir bar, 1 (4.04 g, 8 mmol), *bis*(pinacolato)diboron (B2pin2) (2.12 g, 8.4 mmol), anhydrous potassium acetate (KOAc) (2.14 g, 21.6 mmol), dichloro[1,1'-bis(diphenylphosphino)-ferrocene]palladium(II) dichloromethane adduct (Pd(dppf)Cl₂·CH₂Cl₂) (174 mg, 0.214 mmol) and degassed dioxane (40 mL). After the reaction mixture was heated at 85 °C for 16 h, the product was extracted with CH₂Cl₂ and washed with distilled water. The organic extract was dried over MgSO₄, and solvent was removed under reduced pressure to obtain a brown viscous oil. Purification with flash chromatography (petroleum ether: CH₂Cl₂, 1: 4) yielded 3.38 g (76.5%) of tacky white solid.

2.2.3. 2,2'-(2',3',5',6'-tetrafluoro-[1,1':4',1"-terphenyl]-4,4"-diyl) bis(1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-d]imidazole) (4FBTPI)

1,2,4,5-tetrafluoro-3,6-diiodobenzene (0.80 g, 2 mmol), **2** (2.66 g, 4.8 mmol), Pd(PPh₃)₄ (0.23 g, 0.02 mmol), and K₂CO₃ aqueous (2 M, 6 mL) in toluene (60 mL) and ethanol (12 mL) was heated to reflux in an argon atmosphere for 48 h. The solution was cooled to room temperature and extracted with CH₂Cl₂. The extract was dried with anhydrous Na₂SO₄ and concentrated by rotary evaporation. The residue was purified by column chromatography (ethyl acetate: CH₂Cl₂, 1: 100) to obtain the pure product as white powder yield: 53% (0.74 g). ¹H NMR (400 MHz, Methylene Chloride-

d₂) δ 8.78 (dd, *J* = 21.4, 8.4 Hz, 6H), 7.81 (d, *J* = 7.5 Hz, 6H), 7.70 (d, *J* = 8.3 Hz, 6H), 7.58 (d, *J* = 9.2 Hz, 2H), 7.52 (dd, *J* = 11.3, 8.0 Hz, 8H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 1.47 (s, 18H); MS (ESI) *m/z*: [M+H]⁺ calcd for C₆₈H₅₀F₄N₄, 999.15; found, 1000.26 and 500.33.

3. Results and discussion

3.1. Theoretical calculations

To analyze ground state and excited state properties of **4FBTPI**, quantum chemistry calculation was carried out using the Gaussian 09 program. Fig. S1 shows the optimized geometry of its ground state. Across the whole D- π -A- π -D system, twisting angles between building blocks are relatively small. The dihedral angle between the PI unit and the phenyl bridge is 25.4° and that between the acceptor and phenyl bridge is 41.6°. This gives good conjugation, electronic communication and state mixing. As shown in Fig. 2, the "hole" of $S_1 \rightarrow S_0$ transition spreads over the whole skeleton of the molecule, except the benzene ring connected to the N1 position (nitrogen atom in position 1 of PI unit). On the other hand, its "particle" mainly locates at the *p*-tetrafluorophenyl bridge. Obviously, the transition contains both a LE component at the tetrafluorophenyl bridging group and a CT transition from PI units to the terphenyl group. Besides, the very large oscillator strength of $S_1 \rightarrow S_0$ transition ($f_{S_1 \rightarrow S_0} = 2.1897$), which is comparable to some LE molecules [31,32], suggests the LE component has a larger contribution than the CT component in this HLCT state. Such a HLCT state is a reasonable result as we insert a π bridge between D and A groups to weaken electronic push-pull effect and enlarge LE transition range. Other key calculation data including energy diagram and transition of singlet and triplet states are shown in Fig. S2 and Table S1 in the supporting information.

3.2. Photophysical properties

To acquire a better understanding of its excited state property, photophysical properties of the material was investigated by characterizing its UV-Vis absorption and photoluminescence (PL) spectra (Fig. 3) in dilute dichloromethane solution (10^{-5} M) . In the absorption spectrum, typical absorption of π - π * transition of benzene ring and the PI unit at around 260 and 340-370 nm are observed, which are similar to other PI derivatives [11,33], indicating that the tetrafluorobenzene acceptor has relatively little influences on molecular ground state properties. The PL spectrum of 4FBTPI in solution peaks at 448 nm, while the PL spectrum of the film shows a mildly bathchromatically shifted peak at 457 nm. Encouragingly, impressive PLQY data were obtained in both solution and neat film of **4FBTPI** (99% and 69%) (Table 1). In order to gain a deeper blue emission, we doped the material into CBP. With 8 ± 1 wt% of **4FBTPI** as dopant, PL emission of the doped film exhibits a significant hypochromatic shift of 29 nm compared to neat film of **4FBTPI**. Correspondingly, PLQY of the doped film is improved to 88%. Such significant changes may not only origin from eradicating of aggregation effect in solid state, but also influenced by sensitive emitting nature toward circumstance of the CT state and blue shifting effect of tetrafluorobenzene [24].

3.3. Solvatochromic effects

Systematic solvatochromic experiments using ten different aprotic solvents were conducted to further study properties of both ground state and excited state of **4FBTPI**. From its UV–Vis absorption spectra, similar absorption peaks and curves were observed from low polarity hexane to high polarity acetonitrile.



Fig. 2. Natural transition orbitals (NTOs) of $S_1 \rightarrow S_0$ of **4FBTPI**.



Fig. 3. Absorption and PL spectra of 4FBTPI.

Fig. 4. Solvatochromic PL spectra of 4FBTPI.

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Summary of the physical data	of 4FBTPI .

Compound	<i>T</i> d ^a [°C]	<i>T</i> g ^b [°C]	HOMO ^c [eV]	LUMO ^d [eV]	λ _{abs} ^e [nm]	λ _{em} [nm]	${ \Phi_{ {f f}}}^{ {f h}}$ %
4FBTPI	498	n.o.	-5.56	-2.44	342, 367	448 ^e /457 ^f /428 ^g	99 ^e /69 ^f /88 ^g

^a Temperature for 5% weight loss.

^b n.o. = not observed.

^c Detected via cyclic voltammetry.

^d Estimated by deducting E_{g} from HOMO levels.

^e Measured in dilute CH_2Cl_2 solution (10⁻⁵ mol L⁻¹).

^f Measured in neat film.

^g Measured in doped film ($8\pm 1 \text{ wt\%}$ in CBP).

^h The fluorescence quantum yield in solution was determined with a calibration standard of 10⁻⁵ mol L⁻¹ cyclohexane solution of 9,10-Diphenylanthracene (0.90); and the solid state quantum yield on quartz plate was determined with an integrating sphere.

While its PL emission (Fig. 4) shows a red-shift of 56 nm from 409 nm in hexane to 464 nm in acetonitrile with widening of full width at half maximum (FWHM) from 53 nm to 83 nm. The PL behavior clearly shows CT character in the excited stated of **4FBTPI**. Moreover, it is interesting that the PL spectrum in hexane only shows a single peak at 409 nm with a shoulder at around 425 nm, which is not a typical LE emission with vibrational structure spectrum nor a structureless CT character spectrum. When the polarity of solvent (in butyl ether) increases slightly, the emission spectrum becomes non-vibrational and keeps this feature until using acetonitrile. The result may indicate that the CT and the LE energy levels are laid very close in **4FBTI** and their mixing state (HLCT) is highly hybridized as the hybrid extent is inversely proportional to energy difference of CT and LE state. As shown in Fig. 5, a linear correlation between Stokes shift and solvent polarity was

found, which is in accordance with the PL spectra behavior of 4FBPTI and other reported highly mixed HLCT materials [19,20]. In these materials, LE and CT energy levels are close and changes in solvent may decrease the CT energy much more obviously than LE energy, so the mixed state will be dominated by the CT ingredient at lower polarity solvent resulting in the observed linear relationship. With the fitting slope, excited state dipole moment (μ_e) of **4FBTPI** is calculated to be 27 D. This result is so close to a CT molecule instead of an HLCT one. However, as we mentioned above, the energy level of CT and LE state lay so close that slight change of the environmental polarity makes the CT character dominate the excited state. Therefore, the LE component cannot be detected and only CT character shown. Similar result is also found in reference 20. 4FBTBI show slightly increased PL lifetimes, as the solvent polarity increases (Table S4), similar effects were also observed in



Fig. 5. Linear correlation fitting with Stokes shifts as a function of solvent polarity for **4FBTPI** in different solvents.

other HLCT molecules [8,19].

3.4. Electroluminescence (EL)

An OLED was fabricated with a configuration of ITO/N,N'-

bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPB) (70 nm)/ 4,4',4"-Tris(carbazol-9-yl)triphenylamine (TCTA) (5 nm)/**4FBTPI** (20 nm)/1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBI) (30 nm)/LiF (1 nm)/Al (100 nm). In the device, NPB is the holetransporting layer, TCTA is the exciton-blocking layer, TPBI is the electron-transporting layer and LiF is the electron injection layer. As show in Fig. S5, blue emission peaking at 460 nm was obtained from the device with a corresponding CIE coordinates of (0.16, 0.18). Turn-on voltage (at 1 cd m^{-2}) was as low as 2.9 V (Fig. 6b). The EL spectrum was well-matched with the PL spectrum of the **4FBTPI** neat film and kept almost the same at 10, 100 and 1000 cd m^{-2} . Moreover, **4FBTPI** gives impressive performance in the device with a maximum current efficiency (CE) of 6.86 cd A^{-1} and a maximum EQE of 4.86% (Fig. 6b). It is worth noting that the device shows only mild efficiency roll-off as luminescence increases and delivers efficiencies of 6.42 cd A^{-1} (CE) and 4.62% (EQE) at 1000 cd m^{-2} . Considering equation (1), η_r was calculated to be 35% at the maximum EQE, which clearly breaks the 25% limit of conventional fluorescent materials.

Noting a bluer emission and a higher PLQY of **4FBTPI** when doped in CBP, we fabricated a doped OLED with configuration of ITO/MoO₃ (3 nm)/NPB (55 nm)/TCTA (10 nm)/**4FBTPI**: CBP (8 ± 1 wt % 30 nm)/1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) (40 nm)/LiF (1 nm)/Al (100 nm). It is noted that NPB, TCTA and CBP are all arylamine derivatives possessing good hole-transporting



Fig. 6. Performance of non-doped device: a) Current density-voltage-luminescence curves, b) Current efficiency-Luminance-External quantum efficiency curves.



Fig. 7. Performance of doped device: a) current density-voltage-luminescence curves, b) the Current efficiency-Luminance-Extenal quantum efficiency curves.

abilities. To better balance electron and hole currents, TPBI was replaced with TmPyPB [34–36] for increasing the electron mobility of the device and blocking hole more effectively. The EL spectra at different brightness values are shown in Fig. S6. Deep-blue emission with peak at 440 nm and CIE coordinates of (0.15, 0.09) were obtained and the peak position shows little change from 10 to 1000 cd m⁻². Turn-on voltage was determined to be 3.3 V. As shown in Fig. 7 and Table S5, maximum CE and EQE of 6.03 cd A⁻¹ and 6.94% were achieved in the doped device. Performance of **4FBTPI** is comparable to those of the recently reported state-of-art deep-blue materials with CIE_y < 0.10 [20,29,33,37–41]. η_r of the doped device was calculated to be 39%, which is similar to that of the non-doped device indicating the improvement of device performance should be mainly attributed to the increase in PLQY of the doped film.

To better explain the high device efficiency, time-dependent PL and low temperature (77 K) PL measurements were carried out. As illustrated by Fig. 8, only nanosecond scale decay was observed and the larger difference of S₁ and T₁ (ΔE_{ST} was determined to be 0.68 eV, Fig. 9) eliminated the possible contribution of TADF [12,42]. The linear correlation between current density (Fig. S3 and S4) and luminescence reveals long-live T₁ exciton should be not involved in the EL process [20,43]. According to the above discussion on the excited state properties, the high η_r in these two devices is most likely due to the contribution of the ultrafast spin flip of



Fig. 8. Time-dependent PL measurement of 4FBTPI in DCM.



Fig. 9. Low temperature (78 K) fluorescence and phosphorescence of 4FBTPI in DCM.

high-lying CT exciton, "hot" CT channel [5,19].

4. Conclusions

In conclusion, by using PI as a weak donor and tetrafluorobenzene as an acceptor and applying an anti-parallel dipole design strategy, a novel blue-emitting molecule named **4FBTPI** has been designed, synthesized and applied in deep-blue OLEDs. High PLQYs in both solution and solid state were achieved. A non-doped OLED with **4FBTPI** as emitter shows high CE_{max} of 6.86 cd A⁻¹ and EQE_{max} of 4.86% with CIE of (0.16, 0.18). A doped OLED using **4FBTPI** as dopant exhibits deep-blue emission with CIE coordinates of (0.15, 0.09) and high efficiency with a maximum CE of 6.03 cd A⁻¹, EQE of 6.94% and η_r of 39%. The study provides an example of an anti-parallel dipole design of HLCT molecule to endow the material with high PLQY and η_r simultaneously.

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Appendix A. Supplementary data

Supplementary data related to this chapter can be found at http://dx.doi.org/10.1016/j.dyepig.2017.07.008.

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