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

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ABSTRACT

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*-phe-nanthro[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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1. Introduction

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'Eclaire (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 determined by the following equation:

$$EQE = \gamma \eta_{out} \varphi_{PL} \eta_r \qquad (1)$$

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.

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 pa-rameters 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_{PL} higher than 90%, the theoretical maximum of η_r of 25% limits its device efficiency [2]. Recently, materials with charge-transfer (CT) character break the η_r limit of conventional fluores-cent 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 and T_1) becomes small. This enables reverse intersystem crossing (RISC) from T_1 to S_1 at room temper-ature to harvest the energy of T_1 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.* $CIE_y < 0.10$). Moreover, recent research shows the prototypical blue TADF

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 charge-transfer (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 $CIE_y < 0.08$ (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″-diyl)bis(1-(4-(tert-butyl)phenyl)-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 hole-dominant 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 Labsphere™ integrating sphere using a monochromatized Xe lamp (Newport™) as exciting source (at 365 nm). PL lifetime was recorded on an Edinburgh Instruments
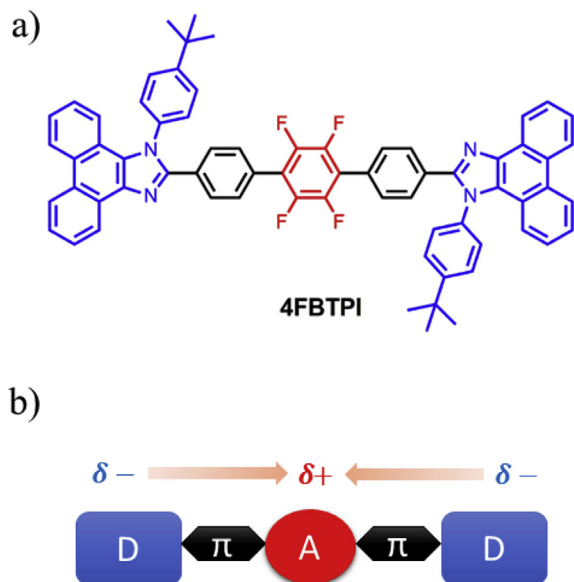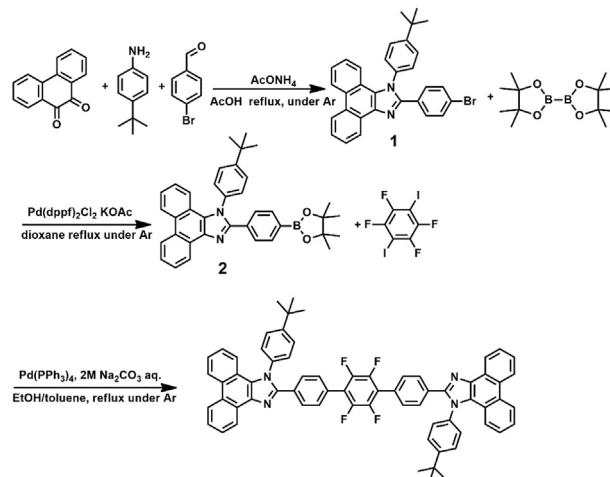

Fig. 1. a) Molecular structure and b) design concept of **4FBTPI**.

Scheme 1. Synthesis route of **4FBTPI**.