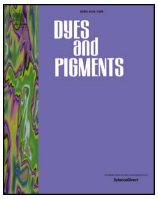
Dyes and Pigments 155 (2018) 51–58

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



Molecular engineering of pyrimidine-containing thermally activated delayed fluorescence emitters for highly efficient deep-blue ($\mathrm{CIE}_y < 0.06$) organic light-emitting diodes

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ARTICLE INFO

Keywords:
Molecular engineering
Pyrimidine
Thermally activated delayed fluorescence
Deep blue OLED

ABSTRACT

The development of efficient and robust, deep-blue, thermally activated delayed fluorescence (TADF) emitters, especially those matching the European Broadcasting Union (EBU) standard with Commission International de L'Eclairage (CIE) coordinates of (0.15, 0.06), is one of the challenging issues in organic light-emitting devices (OLEDs). Through sophisticated molecular engineering, two novel pyrimidine derivatives with D-π-A configuration, 5-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5*H*-benzofuro[3,2-*c*]carbazole (***p*****BFCz-26DPPM**) and 5-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5*H*-benzo [4,5]thieno[3,2-*c*]carbazole (***p*****BTCz-26DPPM**) have been designed and synthesized. There are only negligible differences in the molecular configuration and thermal, electrochemical and photophysical properties for the two compounds. However, TADF properties can be tuned by changing the heteroatom in the donor moiety. Compound ***p*****BFCz-26DPPM** offers a shorter delayed fluorescence lifetime (τ_d) than that of ***p*****BTCz-26DPPM**. The optimized device serving ***p*****BFCz-26DPPM** as dopant presents deep-blue Commission Internationale de l'Eclairage (CIE) coordinates of (0.154, 0.054) and maximum external quantum efficiencies (EQE_{max}) of 6.20%. Remarkably, no-doped device based on ***p*****BFCz–26DPPM** delivers CIE coordinates of (0.153, 0.067) and EQEs as high as 5.80%. These device performances are amongst some of those of the best performing deep blue TADF OLEDs with similar color gamut.

1. Introduction

Organic light-emitting diodes (OLEDs) are deemed to be the most promising candidates for lighting applications and new-generation flexible displays [1–3]. Phosphors containing heavy-metals are able to harvest both singlet and triplet excitons and theoretically approach 100% internal quantum efficiency (IQE), which is superior to fluorescent materials with a limited IQE of 25% [4,5]. However, critical issues for phosphorescence OLEDs regarding high cost, toxicity and stability remain unsolved. As an alternative technology, thermally activated delayed fluorescence (TADF) molecules consisting of pure organic compounds, which can also utilize both eletro-generated S_1 and T_1 excitons *via* efficient reverse intersystem crossing (RISC), has triggered extensive attention [6–9]. In the past few years, TADF-OLEDs have achieved a leap in performances with EQE_{max} values of around 30% for the colors range from pure blue to orange-red [10–16]. In contrast, the development of deep-blue TADF emitters with Commission Internationale de l'Eclairage chromaticity coordinates (CIE) matching closely with the National Television System Committee (NTSC) standard pure blue coordinates of (0.14, 0.08) has remained virtually at a standstill. It is even harder to develop highly efficient OLEDs with stringent EBU standard CIE of (0.15, 0.06). To date, there are only a handful of reports of relatively efficient deep-blue TADF emitters with CIE_y values below 0.08. As shown in Scheme S1, Adachi and co-workers synthesized a 3,6-di-*tert*-butylcarbazole-sulfonyldibenzene hybrid (DTC-DPS) with CIE of (0.15, 0.07) and EQE_{max} of 9.9% [17]. Recently, Lee et al. reported a deep blue TADF emitter ICzCz using carbazole-type ICz as an acceptor by attaching carbazolylcarbazole donor, the corresponding device rendered a CIE of (0.17, 0.04) with EQE_{max} of 2.3% and the maximum brightness was lower than 100 cd m^{-2} [18]. The above research results apparently illustrate that deep blue TADF OLEDs are inferior to other color counterparts. Consequently, the investigation of efficient deep blue TADF emitters still remains a significant challenge.

In general, TADF materials with minimized spatial overlap between the donor (D) and acceptor (A) units can aid in reducing the energy gap

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https://doi.org/10.1016/j.dyepig.2018.03.004
Received 22 January 2018; Received in revised form 2 March 2018; Accepted 2 March 2018

(ΔE_{ST}) between the singlet (E_S) and triplet (E_T) states and thus accelerate the RISC process from its non-radiative T_1 to radiative S_1 states. Unfortunately, a restricted orbital overlap is in favor of a minor ΔE_{ST}, but it is not conducive to a high fluorescence radiative rate (k_F). For alleviating the dilemma of ΔE_{ST} and photoluminescence quantum yield (PLQY) to afford efficient TADF materials, especially for deep blue emitters, the molecular design with judicious selection of donor (D) and acceptor (A) constituents and careful management of the linking topologies are extremely paramount. The D-A system based on the numerous electron-deficient aromatic systems (triazine, benzosulfone, benzonitrile, quinoxaline) exhibited remarkable TADF characteristics [6,19–23]. Lately, a series of outstanding TADF emitters with a D-π-A-π-D configuration through symmetrically linking phenylacridine (Ac) and phenoxazine (PXZ) at the 4,6-diphenyl of the PM moiety have been successively reported [24–27]. In comparison to the ubiquitous triazine acceptor, pyrimidine (PM) has advantages of facile functionalization and less stabilized unoccupied π orbitals, so that the energy gap toward the blue region can be accessed [19,20,28]. Analogously, combining acridine-based donors with pyrimidine-based acceptors through a phenylene π-spacer, Yasuda's group constructed a series of D-π-A TADF emitters. The TADF OLEDs utilizing Ac-PM (Scheme S1) displayed pure blue electroluminescence with external quantum efficiencies up to 11.4% and color coordinates of (0.15, 0.15) [29]. However, the CIE of these devices based on above PM derivatives still lag far behind the EBU standard blue coordinates of (0.15, 0.06) due to their strong intramolecular charge transfer (ICT) behavior. Hence, in order to obtain the deeper emission, it is necessary to construct molecular with D-π-A configuration by coupling PM moiety with the weaker donor than Ac and PXZ.

The donors benzofurocarbazole (BFCz) and benzothienocarbazole (BTCz) were introduced in blue TADF moleculars for improved quantum efficiency and shortened the excited state lifetime [30]. Compared to Ac and PXZ, BFCz and BTCz possess weaker electron-donating ability, which is beneficial for application in deep blue TADF emitter [31]. Besides, 4-phenyl substitution position of the donor units in 2,4,6-triphenylpyrimidine (2,4,6-TPPM) can induce smaller ΔE_{ST} and higher PLQY than its 2-phenyl substituted isomers [32]. Combining all above-mentioned considerations, the sophisticated molecular engineering that constructing D-π-A configuration through substituting 4-phenyl of 2,4,6-TPPM with BFCz and BTCz donors offer potential for achieving deep blue TADF emitter with superior integrated performance (Scheme S1).

Based on this concept, two emitters 5-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5*H*-benzofuro[3,2-*c*]carbazole (***p*BFCz-26DPPM**) and 5-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5*H*-benzo [4,5]thieno[3,2-*c*]carbazole (***p*BTCz-26DPPM**) have been designed and synthesized. Both compounds showed TADF characteristic and moderate photoluminescence quantum yields (PLQY). The concentration-optimized doped TADF device basing on ***p*BFCz-26DPPM** exhibited deep blue emission with CIE of (0.154, 0.054) and external quantum (EQE) of 6.20%. Compared with their doped devices, no-doped device possessed better carrier balance. Then triplet exciton-polaron quenching (TPQ) and singlet–triplet annihilation (STA) weakened. The ***p*BFCz-26DPPM**-based no-doped device realized the 10 folds improved brightness with CIE of (0.153, 0.067), EQE_{max} of 5.80%.

2. Experimental section

The initial reactants, 4-(4-bromophenyl)-2,6-diphenylpyrimidine, benzofurocarbazole (BFCz) and benzothienocarbazole (BTCz), were synthesized according to earlier reports [28,30]. The experimental conditions and instruments used have been referenced in our previous studies and the related solvents were purchased from Aldrich and used as received unless otherwise stated [33].

Synthesis of 5-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5*H*-benzofuro[3,2-*c*]carbazole (***p*BFCz-26DPPM**): A mixture of 4-(4-bromophenyl)-2,6-diphenylpyrimidine (4.06 g, 10.5 mmol), compound BFCz (2.57 g, 10 mmol), CuI (0.19 g, 1 mmol), K_2CO_3 (6.9 g, 50 mmol), 18-crown-6 (0.264 g, 1 mmol) were dissolved in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU 10 mL) and stirred at 180 °C under a nitrogen atmosphere for 48 h. After cooling to room temperature, the mixture was extracted with CH_2Cl_2 and water. The organic phase was dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent, the residue was purified by column silica gel chromatography (PE: DCM = 10:1) and recrystallized to afford a white product in 64% yield (3.6 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm]: 8.79 (d, J = 7.0 Hz, 2H), 8.67–8.50 (m, 3H), 8.36 (s, 2H), 8.13 (s, 1H), 7.99 (dd, J = 14.3 Hz, 7.8, 2H), 7.85 (d, J = 4.8 Hz, 2H), 7.76 (d, J = 8.1 Hz, 1H), 7.65–7.37 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm]: 165.08, 164.71, 163.78, 156.36, 151.25, 141.08, 140.31, 140.03, 137.99, 137.40, 136.78, 131.00, 130.86, 129.02, 129.00, 128.55, 127.51, 127.36, 125.97, 125.43, 125.04, 122.94, 122.90, 121.34, 121.02, 119.79, 118.14, 116.89, 111.74, 110.30, 109.90, 109.05, 105.55. MS (MALDI-TOF): calculated for $C_{40}H_{25}N_3O$, 563.20; found 562.780, $[M]^+$; Elemental analysis calculated (%) $C_{40}H_{25}N_3O$: C 85.24, H 4.47, N 7.46; found: C 85.27, H 4.50, N 7.41.

Synthesis of 5-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5*H*-benzo[4,5]thieno[3,2-*c*]carbazole (***p*BTCz-26DPPM**): Compound ***p*BTCz-26DPPM** (3.2 g, 55%) was synthesized similarly to ***p*BFCz-26DPPM**. ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm]: 8.85–8.77 (m, 2H), 8.65–8.58 (m, 2H), 8.44–8.33 (m, 3H), 8.29–8.18 (m, 2H), 8.18–8.12 (m, 1H), 8.04–7.98 (m, 1H), 7.91–7.80 (m, 2H), 7.68–7.44 (m, 12H)·^{13}C NMR (100 MHz, $CDCl_3$, δ [ppm]: 165.11, 164.75, 163.80, 140.50, 139.91, 139.70, 138.80, 138.02, 137.43, 136.86, 135.95, 132.96, 130.99, 130.85, 129.35, 129.03, 128.56, 127.52, 127.37, 125.94, 125.42, 124.67, 123.04, 122.81, 121.82, 121.00, 119.46, 117.44, 110.33, 110.06, 107.64. MS (MALDI-TOF): calculated for $C_{40}H_{25}N_3S$, 579.18; found 579.051, $[M]^+$; Elemental analysis calculated (%) $C_{40}H_{25}N_3S$: C 82.87, H 4.35, N 7.25; found: C 82.92, H 4.37, N 7.21.

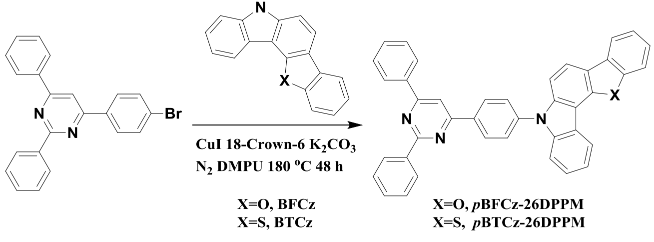
3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes and chemical structures of ***p*BFCz-26DPPM** and ***p*BTCz-26DPPM** are depicted in Scheme 1. The desired molecules, ***p*BFCz-26DPPM** and ***p*BTCz-26DPPM**, were synthesized *via* the Ullmann coupling reaction of 4-(4-bromophenyl)-2,6-diphenylpyrimidine with the corresponding intermediates, while the detailed synthetic procedures were given in the experimental section. The structures of ***p*BFCz-26DPPM** and ***p*BTCz-26DPPM** were confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The target compounds were further purified by repeated temperature-gradient sublimation under vacuum conditions before measurements and device fabrication processes.

3.2. Thermal and electrochemical properties

High decomposition temperatures (T_d, corresponding to 5% weight loss) of 444 °C for ***p*BFCz-26DPPM** and 431 °C for ***p*BTCz-26DPPM** were



Scheme 1. Synthetic route of ***p*BFCz-26DPPM** and ***p*BTCz-26DPPM**.